COMPATIBILISATION
OF HETEROGENEOUS POLYMER BLENDS
BY REACTIVE PROCESSING

ISHAK B YAHYA

A Thesis Submitted for the Degree of Doctor
of Philosophy

ASTON UNIVERSITY

September 1994

THE UNIVERSITY OF ASTON IN BIRMINGHAM

COMPATIBILISATION OF HETEROGENEOUS POLYMER BLENDS BY REACTIVE PROCESSING

ISHAK B YAHYA
Doctor of Philosophy
September 1994

SUMMARY

Functionalisation of polystyrene, PS, and ethylene-co-propylene-co-cyclopentadiene terpolymer, EPDM, with acrylic acid, AA, in a melt reactive processing procedure, in the presence of peroxide, trigonox 101, and coagents, Divinyl benzene, DVB (for PS), and trimethylolpropane triacrylate, TRIS (for EPDM), were successfully carried out. The level of grafting of the AA, as determined by infrared analysis, was significantly enhanced by the coagents. The grafting reaction of AA takes place simultaneously with homopolymerisation of the monomers, melt degradation and crosslinking reactions of the polymers. The extent of these competing reactions were inferred from measurements of melt flow index and insoluble gel content. Through a judicious use of both the peroxide and the coagent, particularly TRIS, unwanted side reactions were minimized. Five different processing methods were investigated for both functionalisation experiments; the direct addition of the pre-mixed polymer with peroxide and reactive modifiers was found to give optimum condition for grafting.

The functionalised PS, F-PS, and EPDM, F-EPD, and maleinised polypropylene carrying a potential antioxidant, N-(4-anilinophenyl maleimide), F-PP were melt blended in binary mixtures of F-PS/F-EPD and F-PP/F-EPD in the presence (or absence) of an organic diamines which act as an interlinking agent, e.g, Ethylene Diamine, EDA, and Hexamethylene Diamine, HEMDA. The presence of an interlinking agent, particularly HEMDA shows significant enhancement in the mechanical properties of the blend, suggesting that the copolymer formed has acted as compatibiliser to the otherwise incompatible polymer pairs.

The functionalised and amidised blends, F and A-PS/EPDM (SPD1) and F and A-PP/EPDM (SPD2) were subsequently used as compatibiliser concentrates in the corresponding PS/EPDM and PP/EPDM blends containing various weight propotion of the homopolymers. The SPD1 caused general decreased in tensile strength, albeit increased in drop impact strength particularly in blend containing high PS content (80%). The SPD2 was particularly effective in enhancing impact strength in blends containing low weight ratio of PP (<70%). The SPD2 was also a good thermal antioxidant albeit less effective than commercial antioxidant. In all blends the evidence of compatibility was examined by scanning electron microscopy.

Keyword: *Reactive processing, functionalisation, grafting efficiency, amidisation, blending, compatibilisation, mechanical properties.*

This Thesis is Dedicated to My Parents
and Family

Acknowledgements

Praise be to The Lord of the Universe, the Most Knowledgeable, The Most Merciful whose endless mercy made this work possible.

I wish to acknowledge with gratitude the guidance, advice and encouragement given by Dr. S. Al-Malaika as my supervisor in carrying out this work till completion.

My thanks are also due to Professor G. Scott for useful discussion in the earlier part of this work and Dr. H. H. Sheena for his help and advice. I am grateful to Mr. R. Wheeler in CEAC and Mr. R. Howell in Mechanical Engineering Department for their valuable contribution in fabricating testing instruments and training in the use of SEM, respectively.

My thanks are extended to the Department of Public Service of Malaysia for the award of the scholarship and Standard and Industrial Research Institute of Malaysia (SIRIM) for granting a study leave.

Last but by no means least, I am grateful to my parents, my wife and my children for their immense patience and support throughout this work.

LIST OF CONTENT

CHAPTER 1

CHAPTER 4

LIST OF TABLES

Table Number **Title** **Page number**

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

LIST OF FIGURES

Figures **Titles** **Page Numbers**
Chapter 2

Chapter 3

Chapter 4

Chapter 5

LIST OF SCHEMES

LIST OF ABREVIATIONS

ABREVIATIONS	FULL NAME OR DESCRIPTION
AA	Acrylic acid
Triganox 101 or T101	2,5 di-tert butyl peroxy hexane
DVB	Divinyl benzene
TRIS	2-ethyl 2(hydroxy methyl)1,3 propane diol triacrylate
IA	Interlinking agent
EDA	Ethylene diamine
HEMDA	Hexamethylene diamine
TAIC	Triallylisocyanurate
DCP	Dicumyl peroxide
MA or MAH	Maleic anhydride
DCM	Dichloromethane
DMF	Dimethylformamide
DX	1,4 dioxane
NaOH	Sodium hydroxide
HCl	hydrochloric acid
MR	Molar ratio
PE	polyethylene
PPO	polyphenylene oxide
PVC	polyvinyl chloride
PS	polystyrene
F-PS1	AA functionalised PS by method PM1
PP	polypropylene
F-PP	maleinised PP carrying a potential antioxidant
EPR or EPM	Ethylene-co-propylene
EPDM	ethylene diamine cyclopentadiene terpolymer
F-EPD1	AA functionalised EPDM by method EPM1
A_H-FEPD	Preamidised F-EPD (with HEMDA)
A_E-FEPD	Preamidised F-EPD (with EDA)
F&A-PS/EPDM	Amidised mixture of Functionalised PS and EPDM
OPS	Oxazoline functionalised polystyrene
CPE	Carboxylated polyetylene
LDPE	Linear density polethylene
HDPE	High density polyethylene
NR	Natural rubber
ENR	Epoxydised natural rubber
PET	Polyethylene terephthalate
HBP-b-PS	Hydrogenated block copolymer of PS - polybutadiene
ABS	Acrylonitrile butadiene styrene
HIPS	High impact polystyrene
SEBS	Styrene-co-ethylene-co-Butadine
SEBS-g-MA	Maleic anhydride grafted SEBS
SPD	Solid phase dispersant
SPD_H1	SPD of HEMDA amidised F-PS/F-EPD
SPD_H2	SPD of HEMDA amidised F-PP/F-EPD
MW	Molecular weight
PBT	Polymer blend technology
PAB	Polymer alloy and blend
DSC	Differential scanning calorimetry
Tg	Glass transition temperature
IR	Infra red
FTIR	Fourier transformation infra red
A	Absorbance
C	Concentration
ε	Coefficient of extinction
t	thickness
MFI	Melt flow index
GC	Gel content
Ts or σ	Tensile strength
E	Elongation
Is	Impact strength
SEM	Scanning Electron Microscopy
PM1	Functionalisation of PS with AA by method 1
EPM1	Functionalisation of EPDM with AA by method 1

CHAPTER 1

1.0 INTRODUCTION

1.1 General

Polymer blend technology has been widely adopted in industry to produce new material useful in applications such as components for industry and construction The main advantage of this approach is the wide possibilities of creating new material with acceptable physico-mechanical properties using the existing general purpose polymers, without going all the way of developing new polymers or copolymers with properties meeting the requirement of their end use. The latter approach besides incurring great investment (for material development and construction of manufacturing plant) and long time to reach maturity (suitable to be introduced commercially), offer no guarantee of success(1) .The PBT to generate polymer alloy and blend (PAB) is such an attractive alternative that has been predicted that use 'use of PAB will dominate the thermoplastic market in commodity and engineering resin application' (2).

Through intimate mixing of appropriate weight proportion of two or more polymers, the properties of the end product can be designed and tailor made.

There are a number of reasons for blending; those pertinent to engineering polymer blend are a) generation of unique material, b) extending the performance of expensive resin and c)quick modification of performance. Those inherent to commodity resin blend are b-c ,and d) high performance at a reasonable price. Utracki has reviewed selected examples of blending for property enhancement such as impact, stiffness, flame retardancy, chemical sand solvent resistance, barrier properties and processability from the recent patent literature (up to 1987)(3). Selected properties (tensile strength & elongation, impact strength, flexural modules) of engineering PAB available commercially were also reviewed. A typical polycabonate (PC) for example has good tensile strength (56MPa) but is quite poor in impact strength (640 J/m). Blending with SEBS enhanced both properties (61MPa, 910 J/m) (3). A PA-6,6 (83MPa, 53J/m) when blended with an elastomer enhanced the impact strength significantly (1030 J/m) although it suffered a slight reduction in tensile strength (62MPa). PVC is a well known hard brittle polymer and difficult to be processed in a conventional processing machine. The situation is alleviated by compounding with , various fillers and additives which would improve the strength of the modified polymer, render it tougher and processable in a normal extruder. New management of the municipal plastic waste comprising mixtures of polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), acrylic etc. involves melt blending in specialised equipment resulting in new usable material which can be remoulded to form low cost utility items such as plant pots ,rubbish bins, fences etc.

Most PAB are manufactured as short runs, to suit certain applications by small and medium sized plastics manufacturers. They are prepared (^{4,5}) by:

-mechanical mixing in extruders, compounders, intensive mixers, motionless mixers, cryogenic grinders.

- dissolving the ingredients in common a solvent.

-latex blending.

- dissolving or dispersing one polymer in the monomer of another, then polymerising

On an industrial scale, polyblend and polyalloys are mainly prepared by the first methods (^{6}) . Commercial grade PAB can be devided into two groups (3), i.e. engineering blend and commodity resin blend. The growth in engineering PAB is particularly impressive , with high temperature resistant and/or electrically conductive resins lead the way. In 1987, it was reported that about 60% of commercial engineering grade PAB was in the USA . Over 20% are sold to automobile, aerospace and business machine/appliance industries. A concise review on the type, use and properties of commercial PAB up to 1987 are available (3,6,7)

Since 1947 until nowadays research in polymer blends has attracted many scientist, technologies and engineers alike; many new discoveries in term of new polymer alloys as well as techniques have been made. But this area of technology besides offering simplicity and straight forwardness in method also carries many more unsolved scientific and technical problems .

One of the major problems is incompatibility. Most polymer pairs do not form a miscible blend when melt mixed, resulted in a sharp interface with a low level of adhesion. The blends are characterised by a large particles dispersed phase (as seen under a high magnifying microscope such as transmission and electron microscopes), smooth surface, without evidence of physical contact at the interface. The blends normally exhibit inferior mechanical properties.

1.2 Compatibility in polymer blends

In a thermodynamic sense, the term compatibility is used to be synonymous with miscibility, complying to the negative Gibb's free energy requirement (see section 1.2.1). In blend between two polymers, the term is used *to characterise the extent of component to resist gross phase segregation or giving desirable blend properties, although they are not compatible in thermodynamic sense* (8).

1.2.1 Thermodynamic of polymer blends

The thermodynamic rule governing the miscibility behaviour between two polymers is best understood through the Gibb's free energy of mixing, ΔG_m (9). Complete miscibility exists only if

$$\Delta G_m < 0 \qquad (1.1)$$

and

$$\frac{\delta^2 \Delta G_m}{\delta n2} > 0 \qquad (1.2)$$

Where n is mole fraction of the solute. Free energy of mixing consists of entropic and enthalpic contribution and can be described by the equation

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1.3)$$

where ΔH_m = molar enthalpy of mixing;

ΔS_m = molar entropy of mixing

The ΔH_m and ΔS_m together determine whether the components are compatible.

Since mixing involves an increase in the disorder of the system, the entropy of mixing is generally positive. If ΔH_m is negative, in which mixing is exothermic, the components will be miscible. If ΔH_m is positive, as may be the case, to counterbalance the effect of the entropy of mixing, the deciding factor would be the relative magnitude of the two terms.

The mixing of a polymer with another polymer in a blend involves entropy of mixing and consists of two terms, the configurational entropy and the local pair interaction entropy. The molar configurational entropy of mixing ΔS_m^* arising from the number of ways the polymer and solvent molecules in the solution arrange themselves, and is given by

$$\Delta S_m^* = -R(n_1 f_1 + n_2 f_2) \qquad (1.4)$$

where n_1 and n_2 are mole fractions of solvent and solute, and f_1 and f_2 are volume fractions.

If the molar volume of the two components are equal, equation. 1.4 reduces to the equation for an ideal solution:

$$\Delta S_m^* = -R((n_1 Ln_1 + n_2 \ln n_2) \qquad (1.5)$$

The local pair interaction entropy arises from interactions between neighbouring units which are different from those in the pure component and is more difficult to quantify. The possible interaction between segments of a polymer chain with a segment of a second polymer give an effect which contributes to the molar entropy of mixing and is proportional to the molar volume of the polymer. In view of the size of the molecule, this contribution could therefore be appreciable.

The molar enthalpy of mixing, which is also mainly due to segmental interaction of the neighbouring units, increases with the molar volume of the polymer. A dimensionless parameter k_{12} was used by Flory$^{(10)}$ to represent the enthalpy and contribution due to local pair interaction, and obtain the following expression for ΔG_m:

$$\Delta G_m = RT((n_1 \ln f_1 + n_2 \ln f_2 + k_{12} n_1 f_2) \qquad (1.6)$$

Configurational entropy does not increase with the size of the molecule, but interaction entropy and molar enthalpy increase with the chain length of the molecule, in proportion to the molar volume. As a result the interaction entropy effect tends to dominate the configurational entropy effect in the mixing of polymers. Complete compatibility is only possible when the k_{12} is either very small or negative.

Only a few polymer pairs form miscible blends to the molecular scale, those include poly(phenylene oxide)/polystyrene (PPO/PS) and polyvinylchloride/polylactone (PVC/PCL). Such miscible systems is characterised by the presence of single phase, exhibit a single-glass transition temperature, Tg, located in between the Tg of the two components and homogeneity at a 5-10nm scale (11)

They behave like a single-component polymer, transparent in appearance and because there is no phase boundary , can be moulded without streaking. Their heat distortion temperature varies smoothly with composition and therefore is easy to predict and control. The mechanical properties are mostly additive or exhibit a maximum, even though the impact strength may be reduced.

The majority of polymer blends however are not miscible in a thermodynamic sense as well as in a performance related sense, and always result in material with inferior mechanical properties as compared to the individual components and easily undergo coalescence and phase segregation leading to catastrophic failure. This is because of the existence of unfavourably high interfacial tension at the components interphase which prevent good dispersion of the dispersed phase into small particles and thus prevent strong adhesion between the interphase 12). Because of the multiphase nature of the blend, opacity is the rule, and injection moulded parts may show swirl and other pattern surface imperfections and relatively poor weldlines.

In many situations however, complete miscibility is not desirable as it inhibits total disappearance of component integrity, but a total immiscibility is also an obvious disadvantage. A partial miscibility, in many applications would be more desirable over the both extreme situations as the structure and properties of the components (within the individual domain) are preserved and the properties of the blend is a sum of properties of the individual polymer. Furthermore, complete molecular state of homogeneity is not often preferred since it is often required that the identities of individual polymers prevail in their discrete micro domains(13)

What is required is *technological compatibilisation* as defined more clearly by Coran and Patel (14)

"Technological compatibilisation is the result of a process or technique for improving the ultimate properties by making polymers in a blend *less incompatible;* it is not the application of a technique which induces 'thermodynamic compatibility' which would cause the polymers to exist in a single molecularly blended homogeneous phase".

1.2.1 Indication and test of compatibility

Level of miscibility is assessed based on aforementioned characteristics (i.e. TG, optical transparency, degree of dispersion of dispersed phase). Optical transparency (15) is a rough indication, provided the difference in component refractive indices is sufficiently far apart (not less than 0.01) and the phase size is not below 100nm . Measurement of Tg by differential scanning calorimetry (DSC) or dynamic mechanical thermal analysis may give a reliable indication so long as the phase domain is not smaller than 10nm and the component Tg is sufficiently far apart. Then any existing degree of miscibility is shown by the position of the Tg approaching each other, nearer at greater miscibility.(16).The use of radiation techniques , x-ray and neutron sources have been reported(15, 17). These methods offer advantages as the sample can be tested while in equilibrium, under a steady state condition. Microscopic methods (scanning electron or transmission electron microscopies,) have become important tools for qualitatively correlating the surface morphology with the degree of dispersibility and thus the degree of compatibility(18)

1.3 Compatibilisation of heterogeneous (immiscible) polymer blends

The science and technology of imparting a certain extent of miscibility to the heterogeneous blends have been work out with great enthusiasm by scientists and technologists alike, both from academia and industry. Ever since, many methods have been developed based on either mechanical or chemical means. Using more efficient mechanical blending machines have been a norm among manufacturers, but chemical means as complementary method have become increasingly more important in recent years. Mixture of two polymers are compatible when the following characteristics are available (19).

1. identical structure segment,
2. difference in solubility parameter (d) is less than 1
3. possess functional groups capable of specific interaction.

It is marked by a very close match in cohesive energy density or in specific interaction, which produces a favourable enthalpy of mixing. Miscibility is further strengthened with the ability to cocrystallise (20).

However, as well known, most polymer pairs do not form compatible blends, in a thermodynamic sense as well as in performance related sense, and therefore always results in a material with inferior mechanical properties as compared to the properties of component and can easily undergone phase segregation. This is because of the existence of unfavourably high interfacial tension at the interphase which reduce the adhesion between the blend component and contribute to the inherent difficulty to impart a predetermined degree of dispersion to the mixture.

Although the mechanical properties of heterogeneous blends can be improved by maximising mixing efficiency through the use of efficient internal mixer or extruder, the blends produced are still immiscible in nature with high probability of phase segregation. The most effective way of improving their properties is by improving the situation at the interface i.e. by compatibilising them through the use of block or graft copolymers, pre-synthesised (see section 1.3.1) and then added later to the blend mixture, or *in situ* formed during mixing (21). The continuous reactive processing, particularly extrusion technology, using a twin screw extruder has become increasingly important. This technique is used to compatibilise polymer blends through reaction during compounding.

Reviews on synthesis and use of copolymers as compatibilisers are available (22,23,19) The copolymers pre-requisitely containing segments miscible with or capable of specific interaction through forces such as coulombic, dipole, dipole interaction etc. with the blend component.

Molau (24, 25) was among the earliest to study in detail the morphology of ternary blends of polymer A and B with AB block copolymers.

It was shown that block or graft copolymers added to concentrated solutions of immiscible polymers could slow down the phase segregation or demixing process by two or more orders of magnitude. Further study by Inoue et al(26, 27) reported that

under microscopic examination, when one or both of the homopolymers were mixed with their copolymer, the domain size of the latter increased , showing evidence of the homopolymer being incorporated into the copolymer domain, followed by a simultaneous decrease in the size of the domain of the homopolymer.

This provides direct evidence that a block copolymer may acts as an emulsifier which "solubilises" the two immiscible homopolymers into the domains of the corresponding block segments. The block copolymer restrains phase segregation and coalescence of homopolymers back into their microscopic domains, and therefore facilitates mixing of the two immiscible homopolymers. The state of thermodynamic immisciblility remains unchanged, and the compatibility achieved is only in a technological sense as mentioned before. It was found out, and then became universally agreed that solubilisation only occurred when the molecular weight of the homopolymer is less or comparable to the molecular weight of the corresponding segments in the block copolymer. In a reverse situation, the homopolymer forms a separate phase and is not solubilised into the copolymer domain. This conclusion however was derived from observation on solution cast mixtures, and was not clearly verified for melt blended systems.

Further work by Heikens et al (28) in PS/PE system (which would also be applicable to other systems) found that a block copolymer is more effective than graft copolymer as compatibiling agent (as in the latter, multiple branches will restrict the penetration into similar homopolymer phases) and two block copolymers were found to be more effective than three block polymers, and a tapered two block copolymer (in which some mixed sequences existed at the block centre) is more effective than a pure two block copolymer of the same MW.

The diffuse part was suggested to act more as a solubilising agent rather than as an anchoring agent. Excessively high MW (in excess of 100,000) of segments may be less effective due to inter- and intermolecular interaction which caused chain entanglement, which reduces accessability of such segment to homopolymer.

In HDPE/PS blends, better results were obtained with two block copolymers compared to S-EB-S , which converted the blend from a cheesy to a ductile material but gave a lower modulus and yield strength.

The copolymer can be arbitrarily divided into four types, A-B, A-B-A, A-B-C and $(A-B)_nX$. A represents a homopolymer segment consisting of A, and similarly for B and C.

$(A\text{-}B)_nX$ are radial block polymers with n diblock sequences attached to a central unit, X. If the copolymers were to be added separately into blends of A and B , many methods such as homopolymerisation, free radical, anionic, cationic, condensation and Ziegler are used to prepare the block copolymer, but in principle, only anionic (used in the preparation of A-B, A-B-A and $(A\text{-}B)_nx$ types) and a condensation mechanism produce high yields of block copolymer. A concise review of the methods is available (29). The anionic polymerisation is considered the most versatile method of preparation as with non polar monomers used, the absence of termination or transfer process enable , in principle, the production of near monodisperse blocks (of well defined morphology). In practice however, due to inclusion of impurities such as moisture, oxygen and carbon dioxide, many copolymer obtained contained impurities(30)

The compatibiliser or solid phase dispersant (SPD) can be formed ***in situ*** by a reactive compatibilisation procedure (21) whereby functionalised polymer (A-x) having a reactive functional group x and the other functionalised polymer (B-y)having a functional group y which can react with x , and thus

(A-x) +(B-y) ------------> A-x-co-y-B
A copolymer (SPD)

The copolymer formed will potentially able to compatibilise mixture of polymers A and B. Another type of copolymer formation reaction is from polymer of A-x type,, in which the x group capables of reacting with a readily available group in polymer B, resulting in an A-g-x-co-B copolymer which can potentially compatibilise a mixture of polymers A and B. Inert (non polar ,non reactive) polymer can be functionalised by a variety of vinyl monomers carrying a functional group as described in section 1.3.1. The SPD acts as an organic surfactant, concentrated at the interface of the two incompatible polymer phases, where it reduces the interfacial tension and promotes adhesion between the phases and also controls the particle size of the dispersed phase in a blend. The position of the copolymer (at interphase) was demonstrated in PS/PE, 80:20 as well as PE/PS 80:20 addition of a triblock copolymer of poly (styrene-b-isoprene-b-butadiene) (31).

1.3.1 Functionalisation of inert Polymers

Grafting of MAH onto PS and polyolefins can be traced back as early as to 1961. Most are however, described in patents.(whereby the detailed method of preparation, composition and analysis were not disclosed). For grafting to PS and its copolymer , few examples can be quoted:

MA was grafted to a copolymer of styrene-divinylbenzene (99:1) by soaking the copolymer in a mixture of MA and ethylene dichloride. Stirring with the anhydride and

aluminium chloride, followed by destruction of the catalyst and soaking in alkali solution, produced cation-exchange resins(32)
MA and an alkyl vinyl ether was grafted to PS slurried in benzoyl peroxide or azobisisibutyronitrile. PS was first chlorinated and then freshly used, stirred with a mixture of the two monomers, washed and soaked in aqueous alkali. (33)

MA was also grafted to polyolefins as shown in the following exemplification's. It was grafted to chlorinated EPR (Cl 1.5%) by heating the mixture at 180°C in o-dichlorobenzene. Treating the chlorinated grafts with dimethylaminopropylamine or tris-(hydroxymethyl) aminoethane resulted in a product used as a detergent lubricant additive(34).

Small amounts of anhydride grafted to polyolefins or chlorinated polyolefins, changed the polymer into waxy products. The relatively polar polymer produced, facilitated the production of emulsions and improved adhesion to polar textiles, metals, and plastic films. PE was degraded in an extruder at 420°C, and treated with 10%MA in a Dowtherm heated autoclave for 90min at 220°C to affect grafting(35)

Grafting to PP by heating in refluxing chlorobenzene using benzoyl peroxide or t-butyl peroxybenzoate as a catalyst. The product was precipitated with acetone . The grafted level varied from 0.4 to 3.3% in accordance with the amount charged(36)

MA was grafted to an EP copolymer in bulk at 200 C (88) or in refluxing chlorobenzene in the presence of di-t-butyl peroxide (37).
The incorporation of MA produced large increases in tensile strength, elongation and hardness as shown in table 1.1(38)

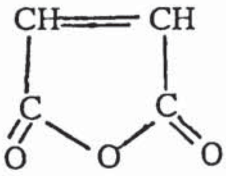
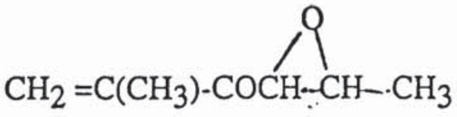
Table 1.1 Properties of PP-g-MA

Material	Tensile Strength (MPa)	Elongation (%)	Harness
Atactic PP	5.4	110	10-15
Graft (4.5% anhydride)	19.5	400	50-55

Functionalising inert , non polar polymers was recognised as a means of enhancing certain properties such as to improve adhesion to metal , plastics and glass surfaces (39), inorganic fillers(40) and glass fibre (40,41) and more commonly for producing a copolymer to be used as SPD as described earlier on

In a more recent development, reactive modifiers which contains at least one centre of unsaturation , can undergo an addition reaction with polymer radicals were used to functionalise inert polymers during extrusion (42). Examples of such modifiers are given in table 1.2

Table 1.2: Monomeric reactive modifiers used in functionalisation of polymers

Reactive Agent	Structure	Polymer	References
1. Acrylic acid	$CH_2=CH_2\text{-}COOH$	PP, PE	41,44
		EPR, EVA	44
2. Methacrylic Acid	$CH_2=C(CH_3)\text{-}COCH_3$	PE, PP, EPR, NR	44
3. Maleic anhydride		PP	41,4
		EPR	39
		HPB	46
		PS	52
		PE	45.
		LDPE, LLDPE	4
4. Dibutyl Maleate (DBM)	$CH\text{—}COO(CH_2)_3CH_3$ $\Vert$ $CH\text{—}COO(CH_2)_3CH_3$	EPR	50
5. Methyl Methacrylate	$CH_2 = C(CH_3)\text{-}COCH_3$	EPDM, EPR	4
		PB	
6. Butyl Acrylate	$CH_2 = CH\text{-}CO(CH_2)_3CH_3$	PE, PP	4
7. Glycidyl Methacrylate	 $CH_2 =C(CH_3)\text{-}CO\underbrace{CH\text{-}CH}_{}\text{-}CH_3$	PE,PP	5

In an extruder, under the condition of temperature and shear experienced, small quantity of macro-radicals are form, followed by addition reaction of the reactive modifiers to polymer. In most cases, peroxides were added to enhance the reaction. The otherwise clean main grafting reaction however is in competition with other reactions such as degradation-crosslinking of polymer, homopolymerisation of modifier, crosslinking of the grafted polymer and radical scavenging by free oxygen and stabilisers often present in the polymer (41).

1.3.1.1 Functionalisation of polymers with maleic anhydride and acrylic acid

The most commonly used monomer of all is maleic anhydride (MAH) (39,41,46,47,49,52,57). Reactions were done in solution, using solvent and employing peroxide such, examples xylene and benzoyl peroxide for PP(47), xylene and dibenzoyl peroxide for EPR(57) or in bulk (or melt) with dicumyl peroxide for PE(45). A reaction mechanism for solution grating to EPR was also proposed (50), and started with the formation of a polymer macroradical (P·) due to hydrogen atom abstraction from the EPR by radical originated from thermal decomposition of the peroxide. Addition of P· to an MAH double bond, generated a new radical P·'which is terminated by recombination or disproportionation, resulted in MAH grafted EPR. Grafting of MAH to polyolefins in general and particularly in LPDE in the melt, in the presence of a peroxide results in considerable crosslinking. This problem could be abated by the addition of sufficient amounts of dimethylformamide (45).

Contrary to MAH, reports on grafting of AA to polymers were not easily available in open literature, but mostly described in patents. A brief account is given in a review by Brown and Orlando(44). The grafting reaction is performed in extruders by adding the monomer in a stream of molten polymer.

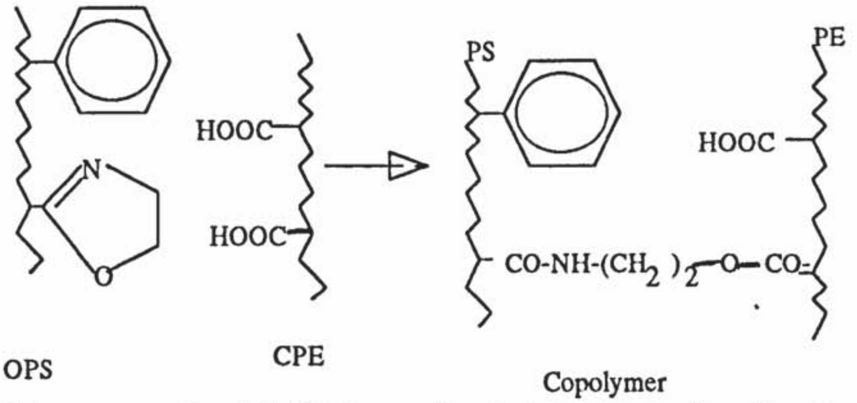
1.3.2 General Routes for Compatibilising Polymer Blends

The incorporation of a copolymeric compatibiliser or solid phase dispersant (**SPD**) to affect compatibility can be carried out via two routes:

1. Addition of a third component (SPD), block or graft copolymers and a variety of low molecular weight reactive chemicals, capable of specific interaction and/or chemical reactions with the blend constituents. The block or graft copolymer should posses a segment which is miscible with at least one of the blend components

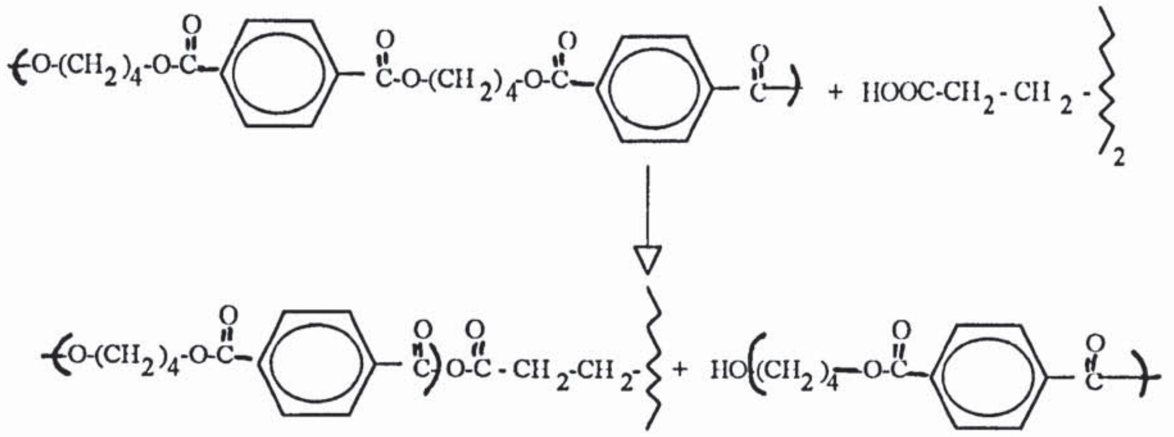
2. By blending of the polymer mixture(e.g A&B) in the presence of functionalised polymers (similar or different from the component of the blend), e.g. A-x & B-y in which the functional group x and y are and capable of enhanced specific interactions and/or chemical reactions, resultting in a copolymer A-g-x-co-y-g-B which can act as an SPD.

In this section only blends compatibilised by direct addition of a compatibiliser or by in situ compatibilisation via reactive processing , will be reviewed. This is followed by a more detailed account on specific blends related to compatibilisation of polystyrene and polypropylene with ethylene propylene diene terpolymer (EPDM).
In the Polystyrene/polyolefin blend system, Saleem and Baker (53) melt blended a PS/PE mixture in the presence of oxazoline functionalised PS, the details of which will be discussed in section 1.4.. Scheme 1.1 represents the reaction involved in this system



Scheme reaction 1.1: Melt reaction between oxazoline functionalised PS (OPS) and carboxylated PE

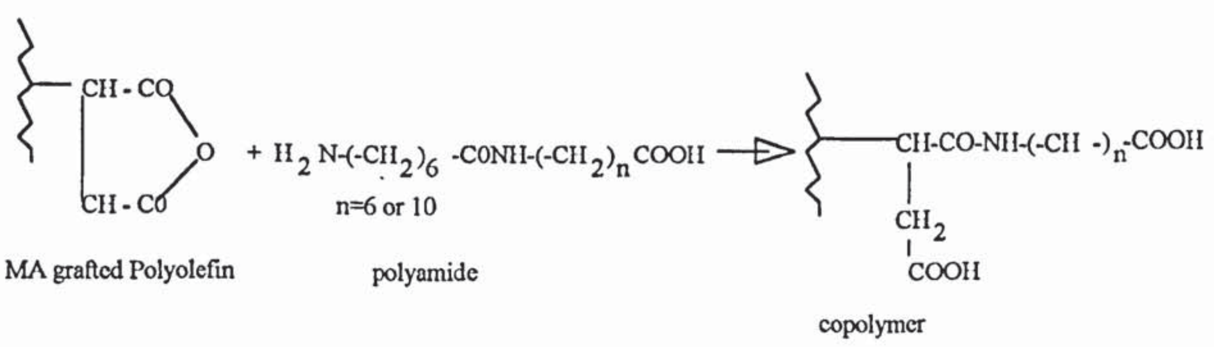
Blends between PP and PET (used as geotextiles) compatibilised by the addition of acrylic acid grafted PP (PP-g-acrylic acid), resulted in compatibilised blends (showing reduction in dispersed phase size) with no significant improvement in mechanical as well as permeability properties. It was suggested that the lack of improvement was due to a small concentration of acrylic acid and therefore warrant further investigation(54). The reaction leading to the formation of a copolymer is presented in **reaction scheme 1.2**



Scheme reaction 1.2: Melt reaction between PET and AA grafted PP

Blends of PE and natural rubber (NR) with PE or PP, containing maleic anhydride functionalised PE (PEm), sulphonated EPDM, , epoxidised natural rubber (ENR), in the presence or absence of a catalyst (DCP) were studied by Choudhury and Bhowmick (55). Blends of NR/ENR/PEm/PE showed greatest improvement in tensile strength (45%higher than the control NR/PE). The NR/S-EPDM/PEm/PE also showed the same improvement. Adhesive strength was improved in both blends.

The use of functionalised polymer with a terminated group which can readily react with functional group in the second polymer, was fully utilised especially in the blends between polyamide polymers and polyolefins for the the purpose of impact modification. The inert polymer (e.g. polyolefins were pre-functionalised with unsaturated carboxylic acid, the most commonly used being maleic anhydride (MA). Reaction between the anhydride and amino group resulted in the in situ formation of copolymer (polyamide - g-polyolefin) which acted as a compatibiliser. Pioneered by Ide and Hasegawa (56), polyamide modification in this way ,since then, has been widely studied (56-62) , taking advantage of the presence of amine and carboxyl ends groups. The essential reaction involved can be represented as in follows:



Using a similar approach, in another work by Cimmino et al (57), a blend between polyamide 6 and ethylene-co-propylene (EPM) were compatibilised by the addition of MA-functionalised EPM (EPM-g-succinic acid). They obtained blends of improved impact properties at low temperature (-20°) when the rubber is partly or entirely EPM-g- succinic acid.

Xanthos and Dagli (58) studied blend of PA6 /PP in the presence of AA functionalised PP (PP-g-AA) and MA functionalised PP (PP-g-MA). It was found out that the reaction between $-NH_2$/-COOH in the former occurred more readily than the amino/anhydride group of the latter, but the size of the dispersed phase in the latter is finer as compared to that in former blend. The improvement obtained was presumed to be due the compatibilisation activity of the copolymer formed in situ during the melt blending.
Gelles et. al.(59) functionalised block copolymer of PS-poly(ethylene-co-butylene) with MA which when blended with Nylon-6 resulted in blends with improvement in impact properties higher than if conventional styrenic block copolymer (without functionalisation with MA) was used.

A different approach of functionalising PE was examined by Curto et al. (60). They photo-oxidised PE with UV light to introduce carboxylic group and then melt blended it with a polyamide (N6). Some improvement in tensile strength was achieved, thought to be a result of a reaction between the carboxylic group and amine group of nylon-6.
In the work of Miettinen et al (61), the effect of addition of MAH functionalised SEBS in a PP/PA-6 blends were investigated. At 10% SEBS-g-MA concentration, the Izod Is has increased several orders of magnitude over the basic blend of PP/PA-6 of 80:20 composition ratio. Another similar polymer mixture (21) compatibilised by addition of MA- grafted ethylene-co-propylene, resulting in an increase in impact and tensile strength. At a typical optimum formulation, the Izod impact strength obtained was 36kg-cm/cm together with a tensile strength 250MPa.
Blends of PA6 and ethylene-co-MA were investigated by MacKnight et al. (62)Blends of small particle size of dispersed phase and improved ultimate tensile properties were obtained, which was considered attributable to the formation of a copolymer (PA6-g-MA-co-ethylene).
The in situ formation of copolymer SPD by transesterification is often used to compatibilise polyester mixtures . Mondragon and Nazabel(63) melt blended mixtures of polycarbonate/phenoxy at 230°C, and achieved an interchain exchange after 40-60min processing.

The blend shows remarkable improvement in Young's Modulus and particularly the yield stress. The elongation at break was however decreased.

In a similar study, in polycarbonate/polyarylacrylate blends, both based on bisphenol A, a transesterification reaction occurred without the use of a catalyst (64). A similar study with a blend of PC and polyarylate was reported (65). Modest improvement in flexural modulus, flexural yield strength, Izod and dart drop impact strength were obtained. Tensile strength however , decreased at higher polyarylate content.

Blends were also functionalised by the addition of low molecular weight reactive compounds, as illustrated in the following examples. Teh and Rudin (66), used a crosslinking co-agent, triallyl isocyanurate to enhance the crosslinking reaction between PS and PE to generate a PS-TAIC-PE copolymer which would act as a compatibiliser. A significant improvement in impact strength was achieved at a ratio of TAIC/ dicumyl peroxide (TAIC/DCP) of 0.3 to 0.5 (from 1.1KJ/m^2 to 1.6KJ/m^2). The tensile strength in all blends was however, lower than that of PS alone . Elongation at break increased, but fortunately (as indicated by the increase in Young's modulus with the increase in the TAIC/DCP level) was not due to the softening effect.

Xanthos et al (67) used a chlorinated paraffin and a dimaleimide to act as compatibiliser for a PP/plasticised PVC blends. It was suggested that processing induced free radical reaction which was responsible for the formation of polar PP. A polar interaction between the activated PP and PVC had compatibilised the blends. Another technique which has good potential to be used for inter- and intra- polymer (s) grafting (provided one has amino group and the other has carboxylic group) was introduced through the work of Shaul et al (68). Organic phosphites such as triphenyl phosphite was used to induce self reaction between amino and carboxylic end groups of polyamide(s) resulted in a polymer of higher MW, or a copolymer. The reaction proceed through an diaryloxy or dialkyloxy phosphine intermediate which broke up to produce an amide bond and disubstituted phosphite reaction by products.

In another instance (69), a catalyst, p-toluensulphonic acid was used to catalyse ester-amide interchange reaction between PET and PA. Results of ^{1}H and ^{13}CNMR analysis showed that the interchange reaction proceeded well under the catalytic action
of the catalyst and can be accomplished during a single pass through an extruder (2-4 min residence time).

1.4 Compatibilisation of PS Blends

PS is an essential commodity plastics widely used in many applications, particularly in packaging and other domestic uses. A general purpose grade of PS is a linear, completely amorphous and readily available at low price. The relatively low resistance to crazing and brittle fracture, susceptibility to water (at high temperature) and mediocre oil and chemical resistance limits its application .The main purpose of blending with other polymers is to overcome these limitations, to improve its other properties such as mechanical properties (tensile and impact properties) and to look into the possibility of discovering of a novel material, while at all times will maintain its high modulus. Although the best route for improving impact properties is by styrene copolymerisation around a finely dispersed rubber phase such as in the production of HIPS (70), blending of the glassy polymer with elastomers as a second blend component, especially in the light of recent development in blending technology would represent a more versatile approach.(71). This would allow the production of a continuum of different compositions by simply processing various proportions of the base polymers.

PS is not miscible with a majority of other polymers , blending of which will yield a polymer of inferior mechanical properties. The main aim of blending is to achieve partial miscibility, or ' technological compatibilsation' as proposed by Coran and Patel quoted previously (14), interfacial condition which is as elucidated before, is more preferable than complete miscibility. An older approach is by addition of block or graft copolymer which contains segments capable of specific interaction and/ or chemical reaction with the blend component, locating at the interphase and thereby lowering the interfacial tension, and promoting dispersibility of the dispersed phase and greater adhesion. Extensive work of PS blend with polyethylene has been done in the past encouraged by the early work of Locke and Paul (72). They found that improvement of the incompatible PS/LDPE blend can be affected by the addition of graft copolymer of PS-PE. The improvement of mechanical properties and reduced phased size in the PS/LDPE blends was later confirmed through the work of Heikens et al (73, 74-76). Maximum improvement was achieved when the PE component was replaced entirely with the copolymer(51). The morphological observation showed a reduction in domain size and this was thought to be due to the to interfacial action of the copolymer and was related to the appearance of irregularities on the surface of the dispersed phase (75, 76). Increase in adhesion between the blend component was confirmed by a peel test measurement (77). In PS/amorphous ethylene propylene rubber blends similar compatibilisation was achieved through the addition of PS-g-EP copolymer (78).

Different copolymer structures (graft, diblock) gave a different compatibilising effect. Extensive investigations by Heikens et al in PS/PE systems using graft and diblock copolymers in order to compare the effectiveness of the two structures, found higher effectiveness of the diblock over the graft, and among the former, the tapered diblock structure which had a random PS/PE segment at the centre was the most effective; with the uneven tapered diblock coming the second. Further work by the same group showed that only a mall amount (less than 1%) of the tapered diblock copolymer was required to bring about a great increase in adhesion. These studies also showed that compatibilisation does not always bring beneficial changes. Greater interphase adhesion was accompanied by a reduction in modulus of blend below that of the PS, depending on the amount of softer phase included. Excessive reduction in the dispersed phase size does not always result in toughening of the blend ,as was also found in the work of Saleem and Baker (53).

The effect of triblock copolymer consisting of a polystyrene end block and a hydrogenated polybutadiene midblock, equivalent to an ethylene-butene-1 copolymer (SEBS) was also investigated (79,80,) This copolymer was commmercialised by Shell Chemical Co. as Kraton G. The potential compatibilising activity for the PS/HDPE was indentified by Paul(79). The SEBS has affected considerable improvement in blend ductility, but at the expense of tensile and modulus, both which were reduced. The peel test measurement proven that the increase in adhesion was as direct effect of the SEBS addition. A similar copolymer was used by Scott et. al (81) along with other copolymers (EPDM, ABS, SBS, ACS, HIPS and PU) to examine their potential as compatibiliser or SPD in PS/LDPE blends, and found that the highest increase in tensile and impact properties was caused by the SEBS (at a high concentration of 20%). In other work by Scott (82), copolymers of PS and LDPE were generated by processing the mixture of homopolymers with a peroxide. The presumed formed copolymer which when subsequently added with PS / LDPE blends gave a fair improvement in blend properties.

A further more extensive research work on PS/PE blends were continued by Fayt et al (83, 84-88). Hydrogenated Polybutadiene-polystyrene diblock copolymer (HBP-b-PS) of well controlled molecular characteristics were prepared having pure and tapered diblock structure and were used in many PS/PE blends. In all blends involved , diblock copolymers, showed a significant increase in tensile properties. This effect was believed to be superior to other form of copolymers (graft, tri- & multiblock and star shaped copolymers)[66] and was thought to be due to a greater anchoring capability of the diblocks over the rest resulting in higher dispersion and adhesion.

In reactive blending systems, Saleem and Baker (89,90) evaluated compatibilising effects in PS/PE blends in which the homopolymers were completely or partially substituted by oxazoline functionalised PS,OPS (containing 1% oxazoline) and carboxylic acid functionalised PE, CPE (containing 6% acrylic acid; commercial grade). The blends showed favourable changes of torque, phase structure and thermal properties which were attributed to the compatibilising effect of the OPS-co-CPE formed. The increase in torque, infra red and scanning calorimetry studies provided evidence of a reaction between the functionalities. The elongation of reactive OPS/CPE blends were higher than in PS/PE blends. In their subsequent work (91), comparisons were made between the two methods of with regard to processing and compatibilisation in the PS/PE blends. In the first method, mixtures of PS/PS , were processed in the presence of a small quantity of OPS and CPE. In another blend system, a prereacted optimum 60:40w/w blend of OPS/CPE was added as SPD in a PS/PE blend. In the first technique, blends of improved tensile strength (0-25% PE) were obtained but without improvement in elongation, and this was attributed to the smaller than optimum domain size which do not yield stable crazes. In the second blend the compatibiliser was found compatible and has improved tensile strength especially in 80:20 blends.

1.4.1 Blend of PS with EPDM Rubber

The ability of rubber to improve the impact strength of brittle, glassy polymer depends on rubber particle size, degree of crosslinking, and mechanical compatibility of the rubber phase with the matrix . Improvements can usually be achieved by grafting of the matrix polymer onto the rubber backbone. This has been the concept adopted in the production of HIPS and ABS [92,93].

The presence of high concentrations of unsaturated polybutadiene rubber in HIPS however, caused high susceptibility to photo oxidation with eventual reduction in mechanical properties of the blend. Replacing the unsaturated rubber with saturated copolymer rubber was an attempt to overcome this problem. Unfortunately, the blend obtained by direct blending of rubber with PS has inferior mechanical properties than those obtained with butadiene rubbers. The problem was partially alleviated by introducing in situ formed copolymer which acted as a compatibiliser based on the principle previously discussed. In earlier work by Natta et al (94), in a process called compounding, a mixture of styrene monomer and EPR was treated with a peroxide to induce grafting, polymerisation and crosslinking to take place resulting in a mixture consisting of PS, EPR, PS-g-EPR, crosslinked and grafted copolymer. This mixture blended with PS, resulting in blends of improved impact strength higher than that of the PS/EPR blend.

Compared to EPR, another rubber ethylene propylene diene copolymer (EPDM) has excellent resistance to weather, ozone and oxidation (95). However, just as is the case with EPR, blends of EPDM with PS are not compatible, hence resulting in inferior mechanical properties (96).In the work of Shaw and Singh (97), styrene graft EPDM (EPDM-g- Styrene) was used to blend with PS (in the presence of tert-butyl p-cresol). A consistent improvement in impact strength was obtained over the uncompatibilised blend up to 10% rubber content (11KJ/m^2 as against 4KJ/m^2) in uncompatibilised blend. The reasons given for improvement are:

i. Improved adhesion between the PS and the rubber phase.

ii. Increase rubber phase volume due to very high grafting percentage and grafting efficiency.

iii. The gel content in the matrix

In their subsequent work 98) the rubbery component was replaced completely by modified EPDM .The rubber was grafted with styrene-co- methyl methacrylate by solution synthesis in the presence of dibutyl peroxide. Blends of PS with the grafted copolymer showed that the tensile strength of both the blend and PS/EPDM blends generally decrease (compared to that of PS) with an increase in rubber content, but above 5% , the effect was less than in PS/EPDM blends. A rubber content up to 4% caused a sharp increase in impact strength. Above this level the impact strength decreased sharply. Improvement of impact strength was presumed to be due to low copolymer occlusion within the rubber phase, which resulted in a more flexible rubber particle of higher craze initiation and crack termination efficiency which enhanced energy absorption during impact (99).

In another study (100) a polyblend of EPDM-g-(styrene-co-maleic anhydride) was used, resulting in a similar improvement in impact strength. Comparing the effect of the three modified rubbers, in tensile strength, PS/EPDM-g-Styrene>PS/EPDM-g-SMAH>PS/EPDM-g-SMMA>PS/EPDM. For impact strength, PS/EPDM-g-Styrene>PS/ EPDM-g-SMAH> PS/EPDM-g-SMMA>PS/EPDM. In PS/EPDM-g-Styrene is compatible at all compositions (up to 10% rubber content).

1.5 Compatibilisation of PP/EPDM Blend

Blends of PP/EPM have been exploited commercially since the middle 1940's and are mostly described in the patent literature. Compositions consisting of a high proportion of EPM (40/60-85/15, EPM to PP) are useful for automotive parts for industrial components. The Tg of the blend suggested consist of two separate phases, indicating immiscibility of the two polymers. Polypropylene is a low impact resistant polymer and this limits its application in areas where higher impact resilience is required(101). The impact strength of PP can be favourably influenced by physical blending, or solution copolymerisation with elastomers ,e.g. EPM, EPDM, styrene-butadiene, or isoprene, styrene block copolymer (SBS) or SIS elastomers ,butyl rubber etc. , in order to broaden the area of application of PP, e.g. used in low low temperature applications. In commercial terms this will strengthen its competitiveness against HDPE, ABS or HIPS .

Resistance of rubber impact modified polymer is governed by the development of craze and this is very much dependent on the particle size of the rubber. Its function is not only to initiate craze but also to prevent, or at least delay the formation of cracks of critical length which will lead to material break (102). Pronounced crazing was found to develop when the rubber diameter is 0.5mm. When the particle is smaller than 0.5mm no crazes appeared to develop around individual rubber particles .The higher the diameter, the greater is the propensity to form crazes. When the diameter less than 0.5mm , the mechanism is dominated by shear yielding, with very little crazing (103). The level of crystallinity of PP and the copolymer rubber plays an important role. Increasing crystallinity in polyolefin phase would increase the tensile strength and lower the ultimate elongation. Speri and Patrick (104) showed a direct relationship between the increase in notched Izod impact strength of the EPDM modified PP with the increase in rubber content. Improvement in the impact strength is accompanied by a reduction in tensile strength, modulus and heat distortion temperature as compared to the unmodified PP.

Impact strength was very much dependant on the rubber particle size (and increases very rapidly as the dispersed phase particle size approaches 0.5mm), and on the stress whitening, suggesting that craze formation is responsible for a large amount of energy which can be absorbed in this system.

RESEARCH OBJECTIVE AND STRATEGY

Polypropylene (PP) and polystyrene (PS) are two commercially available polymers of low impact strength, see section 1.4&1.5. Impact improvement by blending with a copolymer elastomer is being widely examined, especially in the area of compatibilising with graft or block copolymers which are capable of promoting beneficial interfacial situation leading to the enhancement of mechanical properties. In this research , the concept of incorporating the SPD which contains segments of homopolymer of blend component is applied. The non-polar polymers (PS, EPDM and PP) were firstly functionalised using melt reactive procedures in an internal mixer, with monounsaturated monomers, i.e. acrylic acid (AA), **I**, for PS and EPDM; diphenylanilinomaleimide, **II**, for

PP; in the presence of a peroxide, triganox 101, **III**, or dicumyl peroxide (DCP), and coagent divinyl benzene (DVB), **IV**, for PS, and trimethylolpropane triacrylate (TRIS), **V**, for EPDM and PP. The T101 is a novel peroxide, capable of decomposing to give 4 alkoxy radicals (RO·) and is therefore potentially capable of delivering it's catalytical activity much more than other peroxides such as a dicumylperoxide or dibenzylperoxide. The use of DVB and TRIS as coagent utilises the recent technology developed at Aston University which is based on the use the polyreactive coagents, in a melt processing procedure to promote the grafting of vinyl containing antioxidants to the polymer which gives a fully bound (non migratory) antioxidant system (102). In this work, the resulting AA functionalised PS (F-PS) and EPDM (F-EPD) samples were consequently melt blended in the presence and absence of an *'interlinking agent'*, (IA) which are organic diamines, ethylene diamine (EDA), **VI**, and hexamethylene diamine (HEMDA), **VII**, to promote interlinking (coupling) reactions between the carboxylic group of the grafted AA with the amine group of the IA, which gave a copolymer macromolecule capable of acting as SPDs, hence compatibilising the polymer pairs.

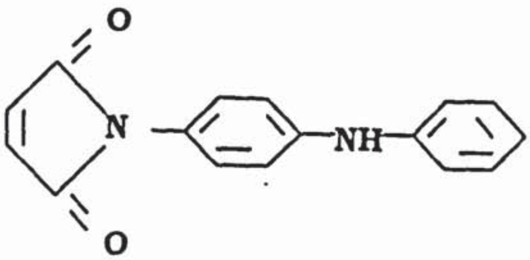
The use of diamines as IA in systems such as this a novel approach, which has not been described elsewhere. The blends obtained could stand as compatibilised blends of homopolymers in their own right, but also potentially could be used as masterbatch SPDs, taking advantage of the already 'built in' copolymer, to be used in compatibilising similar binary mixtures or different polymer pairs bearing similar (but not identical) molecular structures. Thus, blends of PS/EPDM of various weight proportions containing a range of functionalised and amidised PS/EPDM of various weight proportions containing a range of functionalised and amidised PS/EPDM as SPD were made and their physical and mechanical properties were examined.

In the latter part of this research, diphenylanilinomaleimide functionalised polypropylene (F-PP) which also carried a potential thermal antioxidant grafted via the MAH, F-PP has been integrated. The F-PP was blended with the F-EPD in the presence and absence of the IA and the resulting blends were also studied with regards to its compatibilising capabiliity in the PP/EPDM binary mixtures

I $CH_2=CH\text{-}COOH$

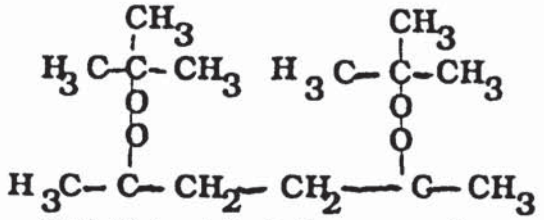
Acrylic acid

II



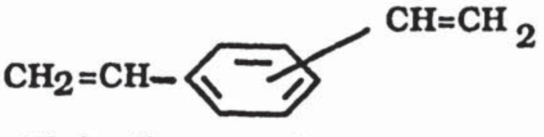
N-(4- anilinophenyl maleimide); solid

III



2,5 di-tert butyl peroxy hexane (or Triganox 101); liquid

IV



Divinylbenzene (MW=130); liquid

V $[CH_2=CH\text{-}(C{=}O)\text{-}O\text{-}CH_2]_3\text{-}C\text{-}CH_2CH_3$

Trimethylolpropane triacrylate (MW=296); liquid

VI $H_2N\text{-}(CH_2)_2\text{-}NH_2$

Ethylene diamine, liquid

VII $H_2N\text{-}(CH_2)_6\text{-}NH_2$

Hexamethylene diamine

The scope of work undertaken is summarised as follows:

1. Functionalisation of PS and EPDM in the presence of peroxide (T101) and enhanced by coagents , DVB for PS and TRIS for EPDM. Effect of the coagents are the main objective of this part of the work. Grafting level and effect of processing conditions and chemical compositions/concentrations were examined by infra red spectroscopy. Effects in terms of crosslinking and degradation were quantified by measurements of melt flow index and insoluble gel content.

2. Blending of F-PS/F-EPD and F-PP/F-EPD in the presence and absence of organic diamine interlinking agents (EDA, HEMDA) were carried out together with optimisation of processing conditions and interlinking agent concentration. Physical, mechanical and morphological properties of the blends were examined. The use of the diamines as interlinking agent is considered novel in this part of the work.

3. A study of the effectiveness of the functionalised and amidised PS/EPDM and PP/EPDM as an SPD in PS/EPDM and PP/EPDM blend systems were carried out . The physical, mechanical, morphological and thermal properties of the straight and compatibilised blends were measured and evaluated.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIAL

Polymers:

POLYSTYRENE

Commercial grade general purpose polystyrene, PS, (Huntsman 311, in a pellet crystalline form; I, table 1) , low flow, improved strength for extrusion; MFR=3.0 (5kg load, 200°C). IR spectrum of thin film pressed from unprocessed and processed PS are shown in figures 2.1a and 2.1b respectively.

ETHYLENE PROPYLENE DIENE TERPOLYMER

Commercial grade, EPDM (Keltan 1720, DSM; II, table 1) containing 55% ethylene , 4.5% dicyclopentadiene monomer; the rest was propylene monomer. Specific gravity 0.86, Mooney viscosity at 125°C is 63. IR spectrum of pressed thin film of unprocessed and processed polymer are shown in figures 2.2a and 2.2b respectively.

POLYPROPYLENE

Commercial grade, PP (Propathene ICI, HF-26; III, table 1), powder, supplied by ICI (Plastics Division) Ltd. IR spectrum of thin films (unprocessed and processed) are shown in figures 2.3a and 2.3b respectively.

Agents:

ACRYLIC ACID

AA, Ex- Aldrich, liquid; IV, table 1; MW = 72, stabilised , 98% purity. IR spectrum (pure) is shown in figure 2.4.

Coagents:

DIVINYL BENZENE

DVB, ex Aldrich, liquid; V, table 1; MW= 130.19, stabilised, 55% mixed isomers, technical grade. IR spectrum is shown in figure 2.5

TRIMETHYLOLPROPANE TRIACRYLATE

TRIS , ex Ancomer, liquid; VI, table 1; MW=296.32; IUPAC nomenclature: 2-ethyl 2(hydroxy methyl) 1,3 propanediol triacrylate. IR spectrum is shown in figure 2.6.

Free Radical Initiator (FRI)

TRIGANOX 101

Noury initiator, T101, ex Akzo Chemie, liquid; VII, table 1; MW=290.4; $t_{1/2}$ at 180° C = 73.7sec. IR spectrum is shown in figure 2.7

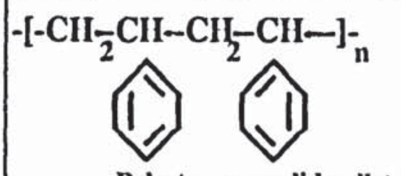
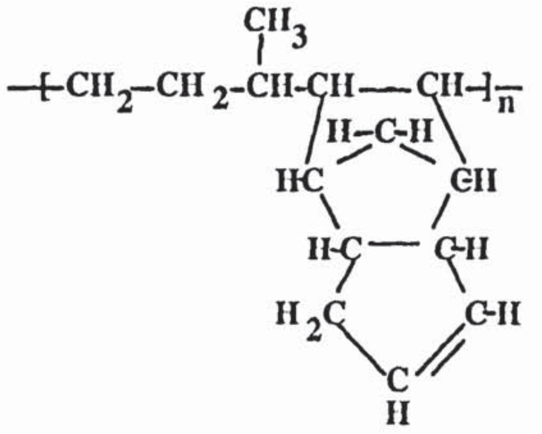
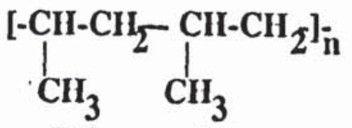
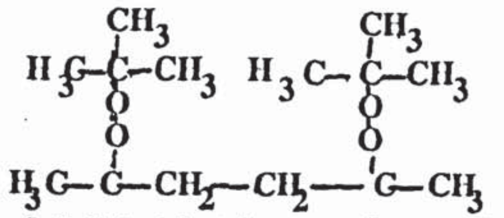
Interlinking Agents:

Hexamethylene diamine, HEMDA (ex Aldrich), solid, MW = 116; Ethylene diamine, EDA (ex Aldrich), liquid, MW = 60. IR spectra are shown in figures 2.8 and 2.9 respectively.

Solvents

Dichloromethane, dimethylformamide,, methanol and ehtyl acetate are technical grade , used without purification; 1,4 dioxane was ex BDH (99% purity) also used without purification.

Table 2.1: Chemical structure and codes for polymers, peroxide, agents and coagents used in work described in this thesis.

Structure number	Chemical structure, name and molecular weight (MW)	Abreviation
I	 Polystyrene; solid pellet; MFR=3.0 (5Kg load, 200 C)	PS
II	 Ethylene propylene dicyclopentadiene terpolymer; rubber block (55% ethylene, 40.5% Propylene and 4.5% dicyclopentadiene)	EPDM
III	 $[\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}\underset{CH_3}{CH}\text{-}CH_2]_n$ Polypropylene	PP
IV	$CH_2=CH\text{-}COOH$ Acrylic acid	AA
V	 Divinylbenzene (MW=130); liquid	DVB
VI	$[CH_2=CH\text{-}(C=O)\text{-}O\text{-}CH_2\text{-}]_3\text{-}C\text{-}CH_2\text{-}CH_3$ Trimethylolpropane triacrylate (MW=296); liquid	TRIS
VII	 2,5 di-tert butyl peroxy hexane (or Triganox 101); liquid	T101
VIII&IX	$H_2N\text{-}(CH_2)_2\text{-}NH_2$ Ethylene diamine, liquid $H_2N\text{-}(CH_2)_6\text{-}NH_2$ Hexamethylene diamine, solid	EDA, HEMDA

2.2 POLYMER PROCESSING AND MOULDING

2.2.1 General Processing Method In an Internal Mixer

EPDM was cut into small cubes before use, while PS, PP were used directly as supplied. All polymer processing were carried out in a HAMPDEN-RAPRA torquerheometer (an internal mixer), see figure 2.10, coupled to a motor drive of a Brabender Plasticorder which displayed changes in torque values during the processing operation. Processing temperature (160°-200°C), time (5-40min) and rotor speed (40-110rpm) were all varied and the torque values were recorded every 15 seconds (sec) during processing. The processing commenced after the polymer was placed in the mixing chamber and the ram was in a closed position. During processing the shearing and mixing of the polymer took place through the rotation of the two rotors in the chamber in opposite direction to each other. At the end of the processing the polymer was removed, and immediately immersed in cold water to stop any further reactions.

2.3 Functionalisation of PS and EPDM in an Internal Mixer using Reactive Processing Procedure.

In a typical processing operation, the processing machine is used to homogenise and convey polymer melt in a typical physical process where minimum changes are involved. In a reactive processing operation on the other hand , chemical reactions are deliberately promoted in the polymer melt and the processing machine is used as a chemical reactor. Reactions such as grafting, chemical crosslinking and chain scission may occur, resulting in chemically modified polymers. In this work the main reaction targeted for the functionalisation of PS and EPDM is the grafting of monomeric acrylic acid (AA) to the polymer backbone. Further reactions carried out in the polymer melt include the interlinking of the AA functionalised polymers (PP, EPDM, PS) by a second reactive monomer, a diamine in order to produce a solid phase dispersant (**SPD**) which is subsequently used to compatibilise blends or to *in situ* compatibilise the functionalised polymer component of blends. The concentration of the grafted AA was determined, after an exhaustive extraction procedure by using carbonyl group (>C=O) absorbance(from of the AA . Three main variables were considered during a typical processing operation: composition of reactants, processing conditions (temperature, speed and time) and methods of addition of polymers and reactive modifiers. In order to find the most suitable processing method for functionalisation of PS and EPDM, which leads to the highest concentration of grafted

AA, five different processing methods were examined for each polymer (i.e. PS and EPDM).

2.3.1 General Reactive Processing method for Polymer Compositions in Torquerheometer.

Reactive processing of polymer(s) (one or more polymers) in the internal mixer involved, generally, the addition of the polymer(s), peroxide as (free radical initiator), reactive modifiers (agent and co-agents) to the mixer either all together or in a given addition sequences and the polymer was processed under closed mixing conditions (ram down). Details of each individual reactive processing procedure for functionalisation and reactive blending of polymer(s) will be given in the appropriate results chapters (chapters 3&4).

2.4 Preparation of Films ,Sheets and Slabs by Compression Moulding

Thin films (0.1-0.2mm) for infra red analysis, sheets (1-2mm) for tensile measurements or slabs (6.0-6.5mm) for impact test specimen (see section 2.7.2.2) were prepared by compression moulding using a Daniel Press with electrically heated platens. A rectangular shaped stainless steel mould containing 4 cavities with each cavity has a dimension of length: 15cm, width: 3cm and thickness: 0.6cm was used for preparation of thick slab, see figure 2.11. Each cavity has a capacity to hold about 28g of polymer samples (cut in small pieces) . The filled mould was placed in between two heat resistant grade of cellophane film (which acted as releasing agent) and then in turn placed in between two stainless steel plates. The polymer was preheated for 6min (no pressure) and then the pressure was increased over a period of 1-2min up to the maximum value (85kg/cm^2), followed by a period of 1-2min of continued heating under the full pressure. Immediately thereafter the press was cooled down to below 100^{o}C, using running water while maintaining full pressure in order to cool the polymer sample. Films were moulded in a similar manner from 3-5g polymer using cellophane film and stainless steel plate , except in this case, a shorter preheated period of 3min was used. For the preparation of a sheet of specified thickness (instead of a film), a spacer of known thickness was placed in between the cellophane film.

2.5 EVALUATION OF THE EXTENT OF FUNCTIONALISATION (GRAFTING EFFICIENCY) DURING REACTIVE PROCESSING

2.5.1 Development of Analytical Procedure to Remove 'free' Additive (AA and Homopolymerised AA) from functionalised PS (F-PS).

The F-PS is expected to contain AA grafted PS as well as free AA and polyAA. The total concentration of AA/polyAA in free and grafted forms, and the concentration of the grafted AA were monitored by infra red spectroscopy of thin F-PS films.. The measurement of concentration of grafted AA was only carried out after removal of the free AA/polyAA from the F-PS. A suitable separation procedure was developed for solutions of reactively processed PS. Three different methods using different solvents [Dichloromethane (DCM), dimethylformamide (DMF) and 1,4 dioxane (DX) were investigated. A simple experiment to determine solubility of PS, AA and polyAA in the the three solvents was carried out by adding separately 0.3g material to the solvents and the solubility was examined after 48 hours of immersion at room temperature. Similarly, the solubility of AA and polyAA in water was assessed. The miscibility of the solvents with watewas assessed by mixing the solvents in water at a range of proportions (one hour, room temperature). It was found that the DCM acted as a good solvent for PS but did not dissolve free AA/polyAA. The DMF dissolved PS and AA/polyAA; the DX acted as good solvent for PS and AA but partially dissolved polyAA. As for water, the DCM was not miscible; the DMF and DX were both miscible in a wide range of proportions. The AA, polyAA, DMF and DX were also dissolved in aqueous sodium hydroxide solution (2N NaOH), which was used in the separation procedure.
The potential separation method was assessed as follows:

About 3.0g of the F-PS sample, cut in small pieces, was dissolved in 150-200ml of a solvents (DCM, DMF or DX). About 300ml of 2N NaOH was vigorously stirred using a mechanical stirrer and the F-PS solution was added in a small stream till finished. The F-PS precipitated out and was filtered off, washed successively with dilute 0.5N NaOH solution, 1:1 water:diluted HCl , water and finally methanol. It was sucked to dryness and transferred to a vacuum oven (50-55°C) for complete dryness. The dry fibrous and fluffy material of 'separated' F-PS was converted into a film by compression moulding, see section 2.4. The thickness of the film was measured and the IR spectrum was recorded.

The solution of the F-PS is expected to contain AA- grafted PS, unbound AA, polyAA, copolymer of AA with co-agent (e.g. DVB). In DCM the F-PS was not completely clear in appearance. The cloudy effect was probably due to the undissolved homopolymers such as poly AA and polyDVB. When it was mixed and vigorously stirred with the NaOH solution the residual AA and polyAA were expected to dissolve into the NaOH, leaving the DCM layer free from the residual monomer and homopolymer. Therefore the recovered PS should also be freed from the unbound AA/polyAA.

In the case of DCM-NaOH method, the resulted liquid mixture (in a separating funnel) has taken very long time (more than 24 hrs) to adequately separate into two layers before the aqueous layer could be drained off. The DCM layer, (white and milky) expected to contain F-PS free from unbound AA/polyAA was saturated with water which had to be removed later. Various solid drying agents such as anhydrous calcium chloride, anhydrous magnesium sulphate and anhydrous sodium sulphate were tried, but none of these could satisfactorily remove all the water. This method was therefore temporarily abandoned and the experiment was continued with a second alternative method.

The solution of F-PS in DMF was clear in appearance and this understandably should be the case as both the PS and AA and most of the polyAA are soluble in this solvent. However a small fraction of polyAA of higher molecular weight may still remain undissolved. The mixing with the NaOH solution resulted into two separated layers: a PS layer (which floated on the top of the liquid) and an aqueous layer containing NaOH, DMF and all the AA/polyAA. The insoluble fraction of polyAA as well as the DMF-soluble polyAA is expected to become saponified by the NaOH, and hence dissolves into the aqueous layer. The PS layer which also contained AA functionalised PS should be at this stage almost free from the AA/polyAA. The solution of F-PS in DX was clear in appearance as in the case of the DMF and similarly the treatment with the NaOH solution has resulted into similar behaviour as in the case of the DMF.

In the DMF-NaOH method, the PS was separated out during gradual mixing with the NaOH solution and floated at the top as white fibrous matter. The filtration and first drying stage was carried out easily. Subsequent washing with the diluted NaOH should have sufficed the removal of final trace of polyAA in the recovered PS. By mixing the fibrous PS with 1:1water diluted HCl the grafted sodium acrylate should be converted back into the original acidic form. The final washing with methanol should remove water and trace of DMF and the subsequent drying under vacuum should affect complete removal of both solvents.

Similar observation was obtained in the case of the DX-NaOH method. However this method was chosen over the DMF-NaOH method based on consideration that the boiling point of the DMF is higher (153°C) than the DX (101°C) and therefore the former is more difficult to remove by vacuum evaporation. Furthermore, the DMF also contained a carbonyl group and hence any trace of it left in the F-PS would contribute an error in measurement of IR absorbance which is used in determining the concentration of the grafted AA to PS. A schematic representation of the DX-NaOH method is given in chapter3 (Scheme 3.3)

2.5.2 Analytical Procedure to Remove 'Free' Additives' (AA and Homopolymerised AA) From functionalised EPDM (F-EPD) and Assessment of Grafting.

A Soxhlet extraction method using methanol as a solvent was used to remove the unbound AA/polyAA in the functionalised EPDM (F-EPD) film. Methanol was found to be a good solvent for AA and polyAA at least up to 2000 weight average molecular weight. This was verified by adding 0.3g commercial polyAA of average MW of 2000 into 150ml of methanol and left aside for four hours at room temperature. All the polymer was found to dissolve, leaving a clear supernatant solution. A 24 hour total extraction period was found sufficient to remove the unbound AA/polyAA from the F-EPD specimen. In most cases, the film specimens were found wrinkled after the extraction and therefore required repressing into fresh thin films before the IR spectrum could be scanned. The concentration of the grafted AA was measured as described in section 2.5.4.

2.5.3 Determination of wavenumber of the waveband of carbonyl group of AA in F-EPD and F-PS

Carbonyl group of acrylic acid (from IR) was used to calculate the extent of grafting of AA in the functionalised polymers. For this purpose, a number of polymer sample controls were processed (see table 2.2) and examined by IR to establish the carbonyl group position and any interference from other absorptions (e.g. from reactive agents). Figures 2.12 and 2.13 compare IR spectra of different compositions of each of the two polymers (PS and EPDM) .The carbonyl peak used for calculation was taken at 1733cm^{-1}for F-PS and 1712cm^{-1}for F-EPD. The carbonyl group of the free unsaturated AA gives absorbance at 1703 (see figure 2.10). When become saturated by grafting, as shown by spectrum d, the

wavenumber is expected to shift to higher value; it appears at 1709cm^{-1}. This peak is well away from the peak due to grafted TRIS (1744cm^{-1}), see figure 2.13, and therefore imposes no interference to the analysis. The vibration of
-C=C- of AA at 1636cm^{-1}also disappears when grafting occurs.

Table 2.2: Determination of IR carbonyl absorption wavenumber of grafted AA in PS and EPDM: Composition of polymers with agents and coagents. Processing conditions: 180°C, 60rpm, 10min .

Polymer	Designation	Composition of polymer agent and coagent					
		PS (%)	EPDM (%)	AA (%)	T101 (MR)	DVB (%)	TRIS (%)
PS	PSa	100	-	0	0	0	-
	PSb	94	-	6	-	0	-
	PSIc	97	-	0	-	3	-
	PSd	94	-	6	0.04	0	-
	PSe	93	-	6	0.04	3	
EPDM	Ra	-	100	0	0	-	0
	Rb	-	99.5	0	0	-	0.5
	Rc	-	100	-	0.005	-	0.5
	Rd	-	97.0	3	0.005	-	-
	Re	-	96.5	3	0.005	-	0.5

2.5.4 Calibration curve for AA and Assessment of It's Grafting Efficiency in PS and EPDM

An IR calibration curve for AA was developed to be used for quantitative measurement of the concentration of grafted AA in the both polymers. Solutions of AA in methanol at several different concentrations were prepared and IR spectra in the region of 1600cm^{-1}to 1800cm^{-1} were scanned using a Perkin Elmer FTIR spectrometer Model 1711, interfaced to a computerised data station. The peak height of the carbonyl absorbance (A) was measured as illustrated in **figure 2.14.** A curve of AA concentration against the peak height (absorbance) , measured using the baseline method ([106]) was constructed and Coefficient of Extinction was calculated based on the Lambert-Beers equation **$A=\varepsilon Ct$** where A is absorbance, C is the concentration (g/liter) ,t is thickness of the cell (cm) and ε is the coefficient of extinction ($l.g^{-1}.cm^{-1}$). After establishing the value of ε , the value of C for a solution of unknown concentration can be calculated ,where A and t are known. The calibration curve was used for determination of concentration of grafted AA both in the F-PS and the F-EPDM, using polymer specimen in the form of thin film of known thickness. A a calibration curve for AA was see **table 2.3** and **figure 2.15** (the value of ε was found to be **11.77 $l.g^{-1}cm^{-1}$**).

Table 2.3: Calibration curve of AA in methanol: Effect of AA concentrations (0-12.0 $g.l^{-1}$) on IR absorbance peak height at $1704cm^{-1}$.

Concentration of AA in methanol ($g.l^{-1}$)	**Absorbance peak height**
0.0	0.00
4.0	1.19
8.0	2.24
12.0	3.41

The concentration of retained AA (bound and unbound) in F-PS and F-EPDM was determined from the calibration curve by measuring the peak height of the carbonyl absorbance band of the AA at $1733cm^{-1}$and $1712cm^{-1}$, respectively.

2.6 POLYMER STABILITY TEST

2.6.1 Measurements of Melt Flow Index

The melt flow index (MFI) is a measure of melt viscosity, and is related to the molecular weight of the polymer. A low MFI indicates high melt viscosity and correspondingly high molecular weight. When compared to MFI of an untreated polymer, a lower MFI is normally associated with the occurrence of crosslinking during processing, whereas a high MFI value is associated with occurrence of chain scission or oxidation during processing. The MFI was determined by using a Devonport Melt Flow Indexer having a die diameter of 2.1mm. The apparatus was heated and maintained at $190^{o}C+0.5^{o}C$ (for PS) or $230^{o}C+0.5^{o}C$ (for EPDM). The barrel was charged with 4.0-5.0g polymer (cut into small pieces) tapered down with charging tool to exclude the air, and was left for 4 minutes (min) for the temperature of the sample to reach equilibrium. A load of 2.16kg was used to extrude the melt through the die. The extrudate was cut with a sharp device every interval of 60sec. A minimum of 10 extrudates were weighed individually and their average weight was determined.

The MFI was calculated using the following equation:

$$\text{MFI (g/10min)} = \frac{\text{Average weight of individual cut (g)}}{\text{Cutting time interval (min)}} \times 10$$

2.6.2 Measurements of Insoluble Gel

The insoluble gel (gel content) is a measure of the insoluble fraction of a modified polymer after being exhaustively extracted with a solvent which dissolves the original polymer. A known weight of finely cut (or in film form) polymer was placed into a known weight aluminium oxide thimble. The thimble and its content was placed into a Soxhlet extraction apparatus assembly and the extraction was carried out for 24hr using appropriate solvent; xylene for EPDM/F-EPD and diethyl acetate for PS/F-PS. The thimble was dried in vacuum oven at 50^{o}C, cooled down to room temperature and reweighed. The net weight of the residue was calculated and the gel content was computed by the following relationship :

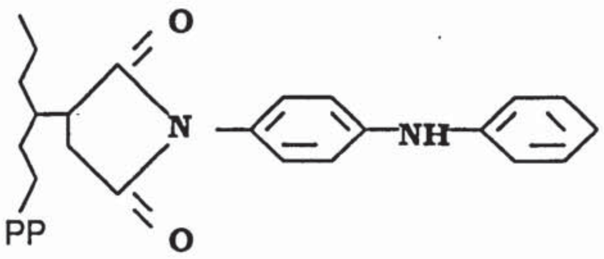
$$\text{Gel content} = \frac{W_1}{W_0} \times 100$$

where W_1 is the residual weight of the extracted polymer (the insoluble) and W_0 is the original weight of the polymer before extraction.

2.6.3 Thermal Ageing of Polymer Films

Blends of PP/EPDM/SPD2 were prepared. The SPD2 was a compatibiliser , a blend of EDA (XIII, table 2.1) or HEMDA (IX, table 2.1) amidised F-PP/REPDM, 60/40. The F-PP, see structure X below, was a PP reactively processed with a peroxide (dicumyl peroxide at 2%),TRIS (0.25%) and a thermal stabiliser, N-(4-anilinophenyl) maleimide , PM, (1%), in a Busko Kneader at 190^{o}C, 90 rotation per minute and dwelling time of approximately 4min. The modified PP was then diluted 1:1w/w with virgin PP using the same processing conditions. The concentration of bound PM obtained was approximately 70%(i.e. approximately 0.175% of the original added). The PM was expected to provide certain degree of protection for the polymer from thermal degradation.

Film specimen of the blends (3cmx1cmx0.1cm) were placed inside a single cell Wallace oven maintained at 140°C and an airflow of 2.0 $cm^3 min^{-1}$until the specimen was embrittled. Embrittlement time was recorded and compared with other thermally stabilised blend samples.



N-(4- anilinophenyl maleimide) grafted PP; solid
Structure X

2.7 EXPERIMENTAL TECHNIQUES

2.7.1 Specroscopic Techniques

Fourier Transform Infrared (FT-IR) Spectroscopy was carried out on a Perkin Elmer 1710 infra red spectrometer equipped with data station. Measurements were mainly carried out for thin (0.008-0.1mm thickness) polymer films or solutions. All solvents used were spectroscopic grade.

Atomic absorption spectroscopy was carried out on a Perkin Elmer 330 spectrophotometer to determine concentration of trace iron in the F-PS samples prepared as a function of T101 concentrations, see chapter 3, section 3.2.1.3.1, as follows: The polymers (small cut pieces) were digested, in Kjeldahl flasks, with mixture of concentrated H_2SO_4:HNO_3, 1:1 at approximately 130°C until clear solutions were achieved. Each of the solutions were transferred into volumetric flasks, and made up to the mark by addition of distilled water. A blank solution was prepared from equal amount of the acidic mixture used in the digestion and distilled water. A standard calibration curve (concentration of Fe^{+3} against absorption) were prepared by measuring absorptions of calibration solutions of known concentrations of ferric nitrate in 0.5N nitric acid solutions.

2.7.2 Mechanical Properties Testings

2.7.2.1 Tensile Measurements

Tensile strength was measured on a Testometric MACRO 500 Tensile Tester, using a crosshead speed of 2cm/min for the PS/EPDM blends and 5cm/min for the PP/EPDM blends. The testing machine was interphased with an Apple computer, which was in turn connected to a printer. A Testometric software was used to manipulate the raw data. Dumb bell shaped test pieces , see figure 2.15, used have the following dimension :

length: 50mm
width: 4mm
thickness: 0.3-1.0mm
gauge length: 30mm

From the stress-strain curves the ultimate tensile strength (UTS) and elongation at break were automatically computed using the following equation:

$$\text{UTS (N/mm)} = \frac{\text{Force at break (N)}}{\text{Thickness (mm) x width (mm)}}$$

$$\varepsilon\,(\%) = \frac{\text{Length at break- original length}}{\text{original length}} \times 100$$

The original unit of N/mm^2 was re-expressed in MPa using relationship 1N/mm^2=1MPa. In case Young's modulus is used, it is defined as the ratio of applied tensile stress to the resulting strain, parallel to the tension expressed in MPa/cm.

2.7.2.2 Impact Strength Measurements

Impact strength (**Is**) is a measure of resistant of a material against and impact force. Two types of impact tests were used, dart drop impact test and Charpy impact test. For the former, the test was carried out using a laboratory tester consisted of a long copper tube fitted vertically to a top thick metal slab (figure 2.16). The top assembly was placed on top of a flat thick bottom slab. The specimen under test, of known thickness was placed in between the slabs right beneath the hole of the tube, and then a ball bearing (approximately 8mm diameter) was slowly lowered down to settle on the specimen. A solid cylindrical metal of known mass (the dart) was introduced into the tube, held with a spatula at a known height. The dart was dropped and the effect on the specimen was examined. A combination of weight of the dart and the height of falling was systematically determined to provide potential energy which would just break the film. An average of 5 readings was taken for each sample measured. The impact strength was calculated using the following equation:

$$\mathbf{Is} = \frac{\mathbf{m(g) \times g\ (cm.sec^{-1}) \times h(cm)}}{\mathbf{t(mm)}}\ \mathbf{(ergs/mm)}$$

where m=mass of the dart (e.g. 45g,70g & 110g)
g= acceleration due to gravity (32 cm.sec^{-2})
h= initial height
t= thickness of specimen

The Charpy test was carried out using a commercial Charpy impact tester, the Hounsfield Plastics Impact Tester (figure 2.17a). The notched specimen was a rectangular bar with dimensions of 44.8mm length, 6.5mm width, 6.0 mm thick and the root of the notch of 4.7mm, cut from the slab prepared earlier, see section 2.5. A Hounsfield notch cutting device was used to cut a notch at the middle of the rectangular bar (figure 2.17b) . The specimen was fitted horizontally into the cylindrical holder and the midpoint position adjusted to touch the tip of the cutting tool. The holder and therefore the specimen was moved in semicircular movements to affect the cutting, a small bit at a time. Deeper cutting was achieved by cautiously sliding the cutting tool forward towards the specimen. The final root thickness (4.7mm) was ascertained by sliding a special thickness gauge through the notch. The notched specimen was placed horizontally on a holder having a gap of 37.5mm with the notch facing away from the striker. The specimen was struck with a known capacity striker at the notch point, see figure 2.17a.

If the specimen broke, the striking energy consumed is automatically indicated on a dial attached to the instrument. If it is not broken, a striker of higher capacity was used.

The impact strength is calculated using the following relationship:

$$\mathbf{Is} = \frac{\mathbf{Impact\ energy\ (ft.lb)}}{\mathbf{root\ thickness\ of\ specimen\ (in)}} \mathbf{\times\ 187\ \ (Joule/m)}$$

The value in ft-lb.in^{-1}is convertable to joule/meter (J/m) by multiplying with 187 (107).

2.7.3 MICROSCOPIC TECHNIQUE

2.7.3.1 Scanning Electron Microscopy

The morphology of the blends is the physical structure of the matrix and disperse phase as observed under an electron microscope such as a scanning electron microscope (SEM). The surface condition of the broken impact test specimen indicates the level of compatibility between the dispersed phase and continuous matrix. A relative display of rough surface, especially when full with work of microfibrils, as compared to the control, indicates certain extent of compatibility has occurred between the two phases. Thin specimens were cut from the fractured surface of the impact test specimen, see previous section 2.5.2.2, mounted on a metal disc using a double layer adhesive tape and subjecting to vacuum coating with gold for 20min to obtain a gold layer of 200μm thickness. The specimen was then examined under a Cambridge Scanning microscope at appropriate magnification and photographed.

2.8 EXPERIMENTAL ERROR

Experimental errors are estimated to indicate confidence level of the data obtained. It arises as a result of errors during the processings and measurements. In Chapter 3, the experimental error for the grafting concentrations of AA to PS in the F-PS and the EPDM in the F-EPDM is estimated to be 5%. This comprises 3% during the processing, 1% durimg the compression moulding (for making film) and 1% during the infra red analysis. In the chapter 4, a 4% ~~confidence level~~ experimental error for the values of the tensile and impact properties is estimated, comprises errors of 1% during the processing, 2% during the compression moulding and 1% during the measurement. A lesser 3% of error is estimated for the processings and measurements in the Chapter 5.

Figure 2.1a: IR spectrum of virgin PS pellets pressed into a film (0.1mm thick)

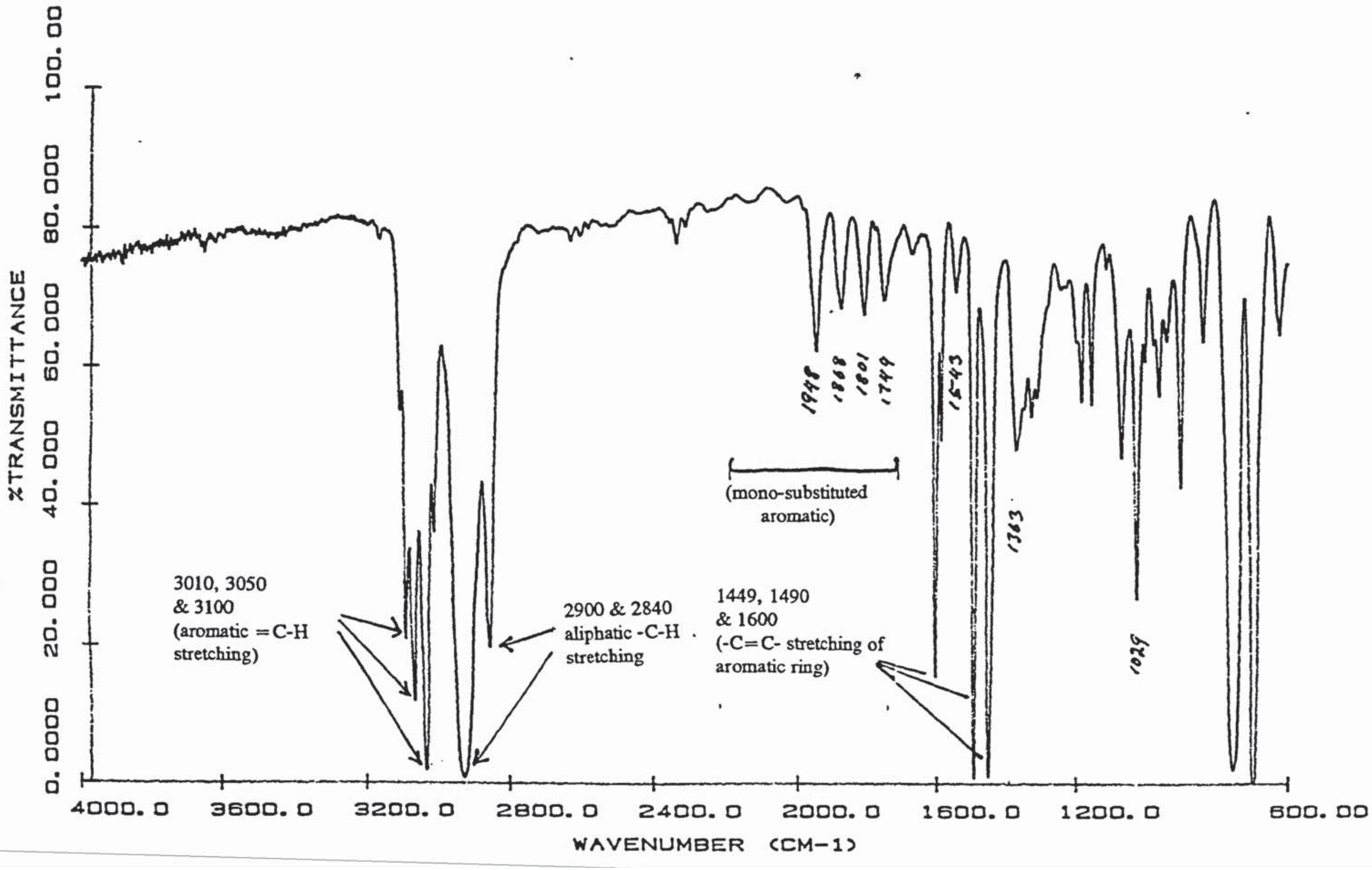
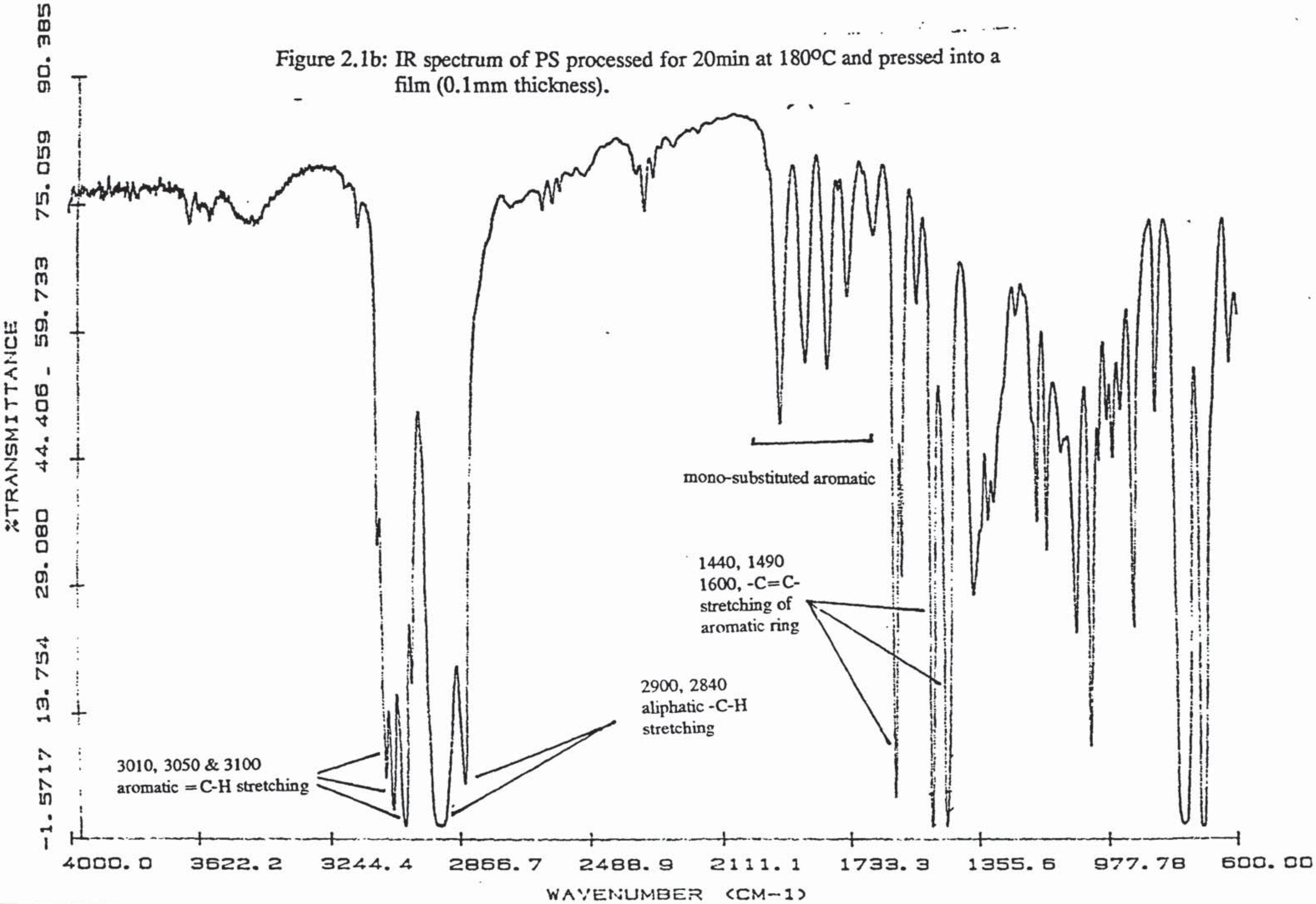


Figure 2.1b: IR spectrum of PS processed for 20min at 180°C and pressed into a film (0.1mm thickness).



Fibure 2.2a: IR spectrum of fresh EPDM, film (0.1mm thick)

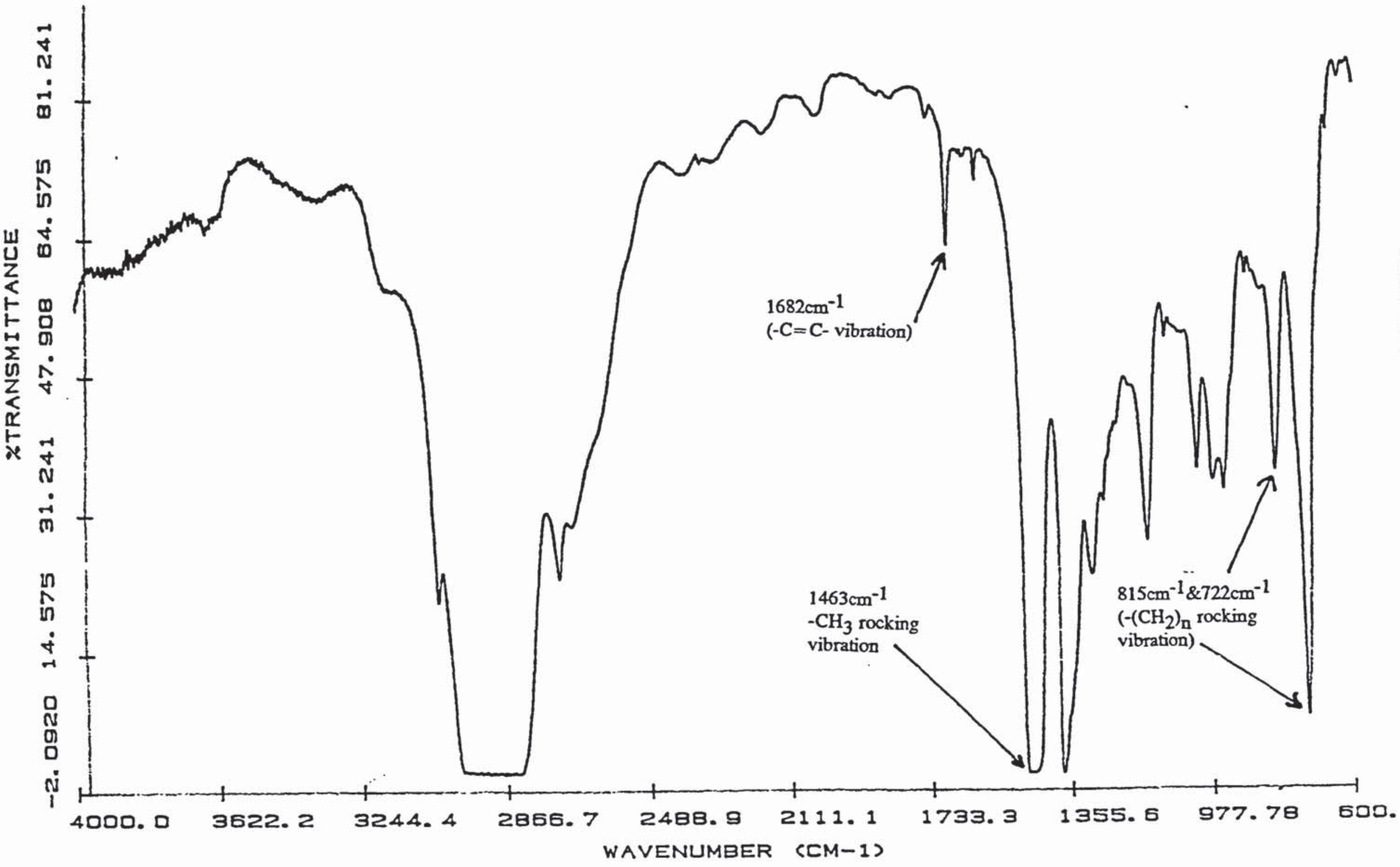


Figure 2.2b: IR spectrum of EPDM processed alone for 20min, film (0.1mm thick).

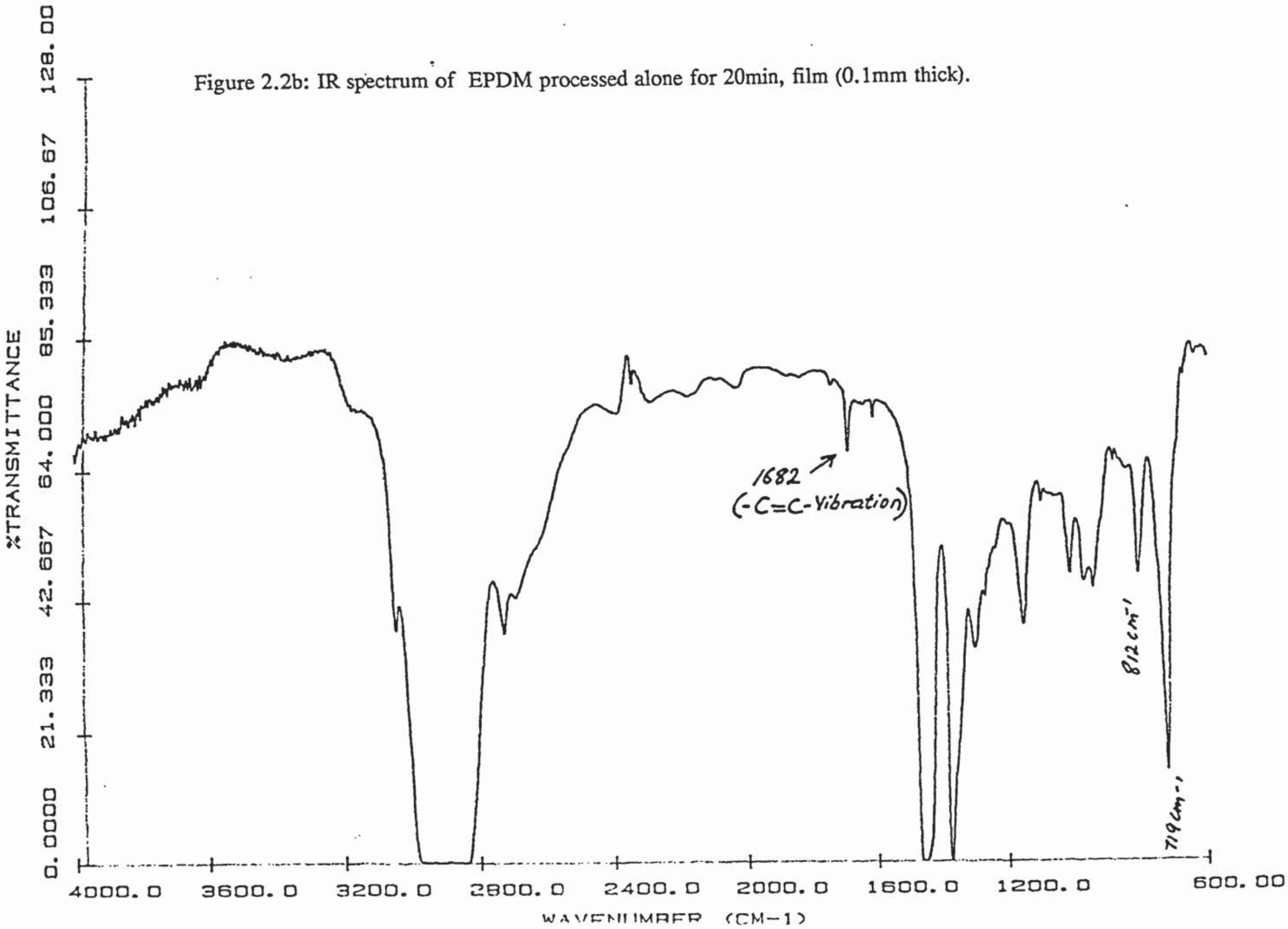


Figure 2.3a: IR spectrum of virgin PP powder pressed into film (0.1mm thickness)

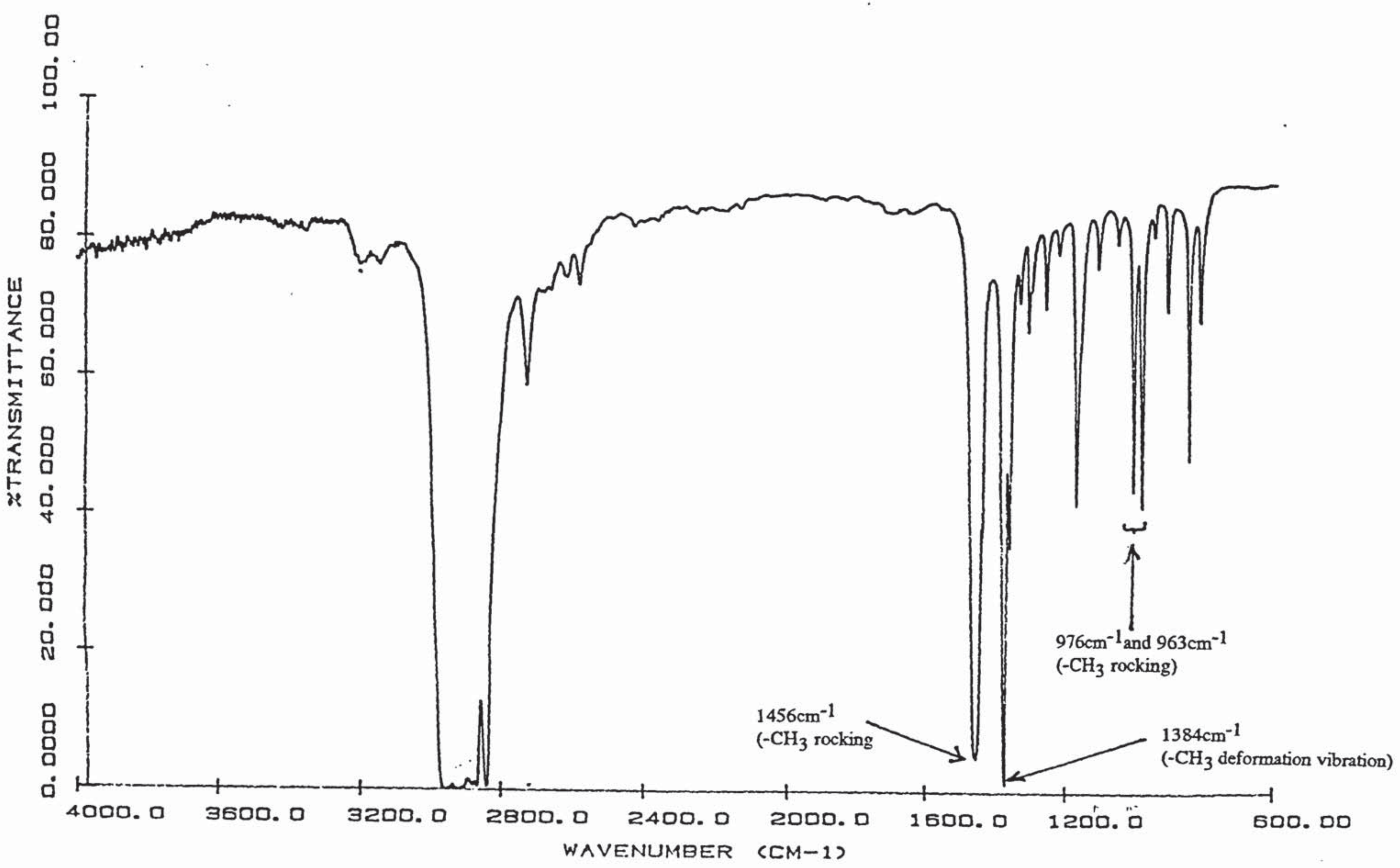
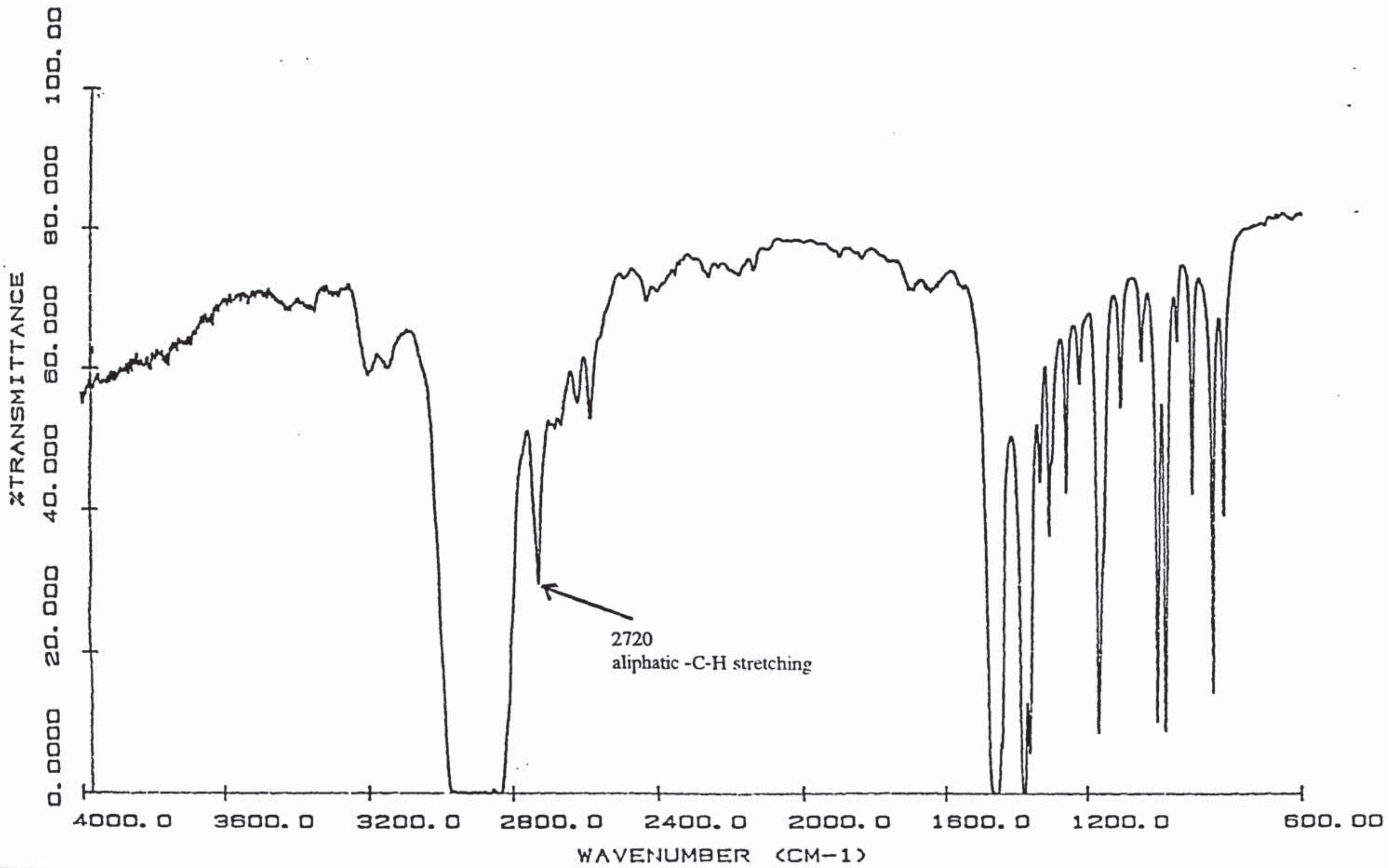


Figure 2.3b: IR spectrum of PP processed alone for 20min and pressed into film (0.1mm thickness)



2720
aliphatic -C-H stretching

Figure 2.4: IR spectrum of acrylic acid (AA) as thin liquid film (in between KBr discs)

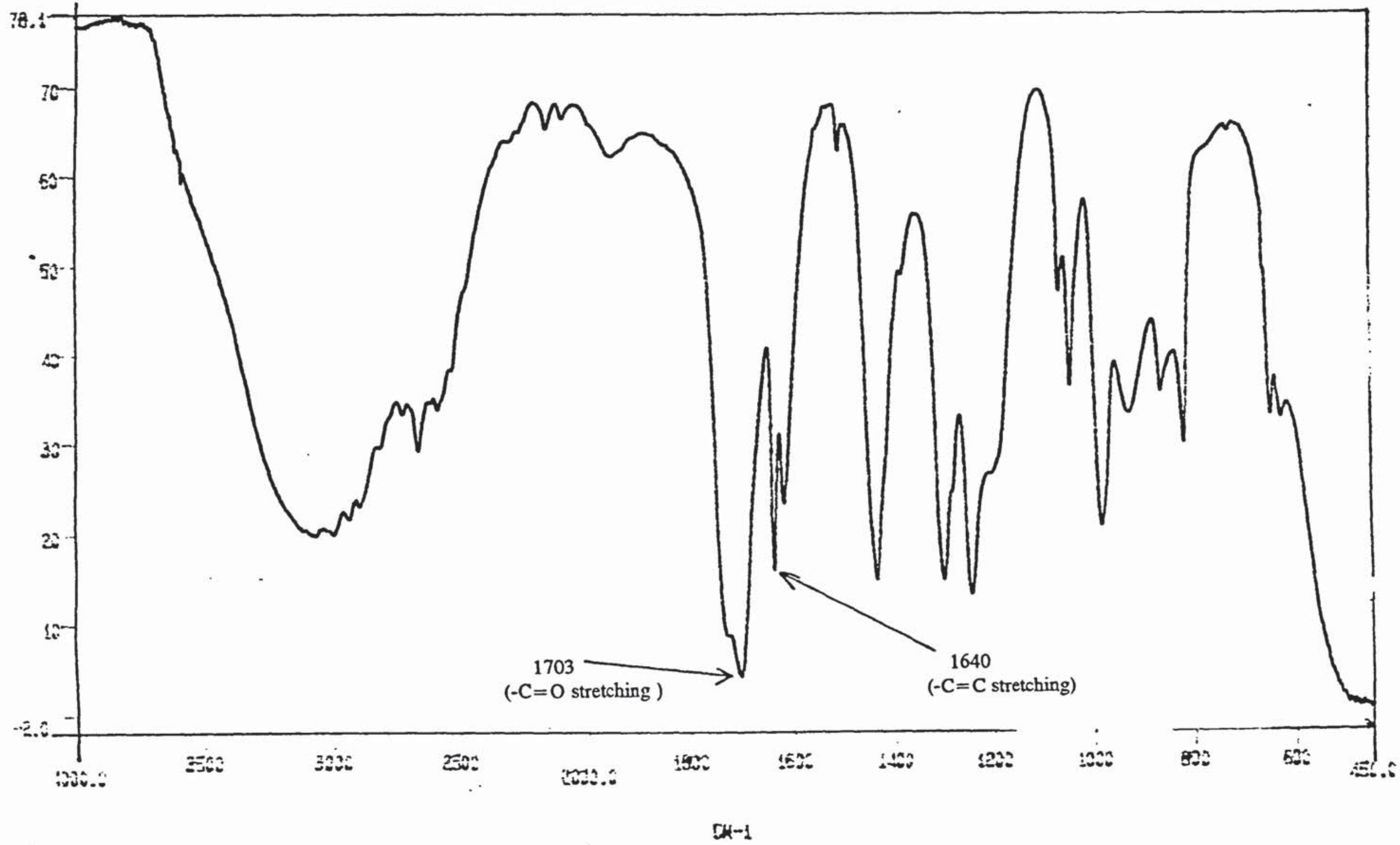


Figure 2.5: IR Spectrum of divinyl benzene (DVB) as thin liquid Film (in between KBr-discs)

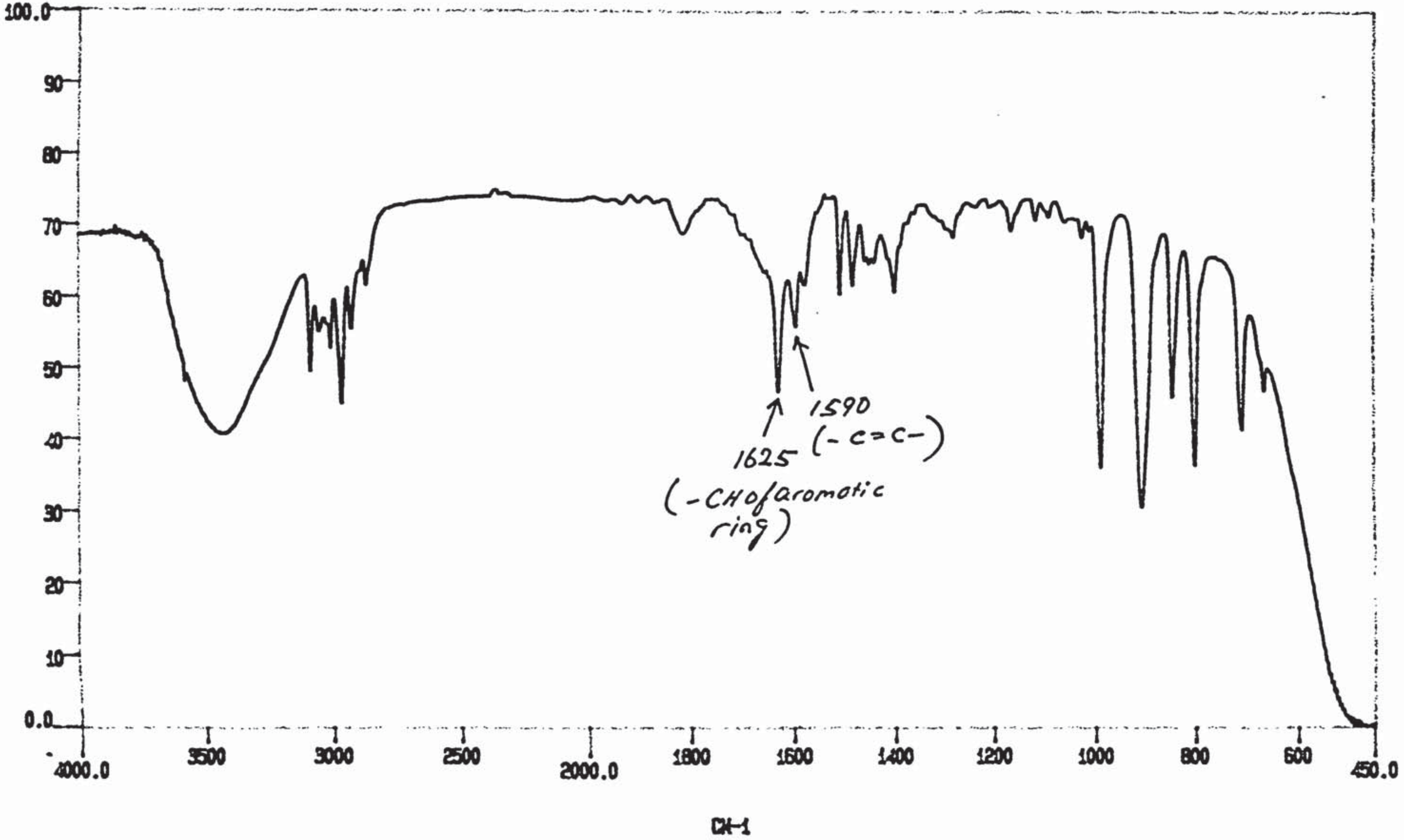


Figure 2.6: IR spectrum of pure TRIS as thin liquid film (in between KBr discs)

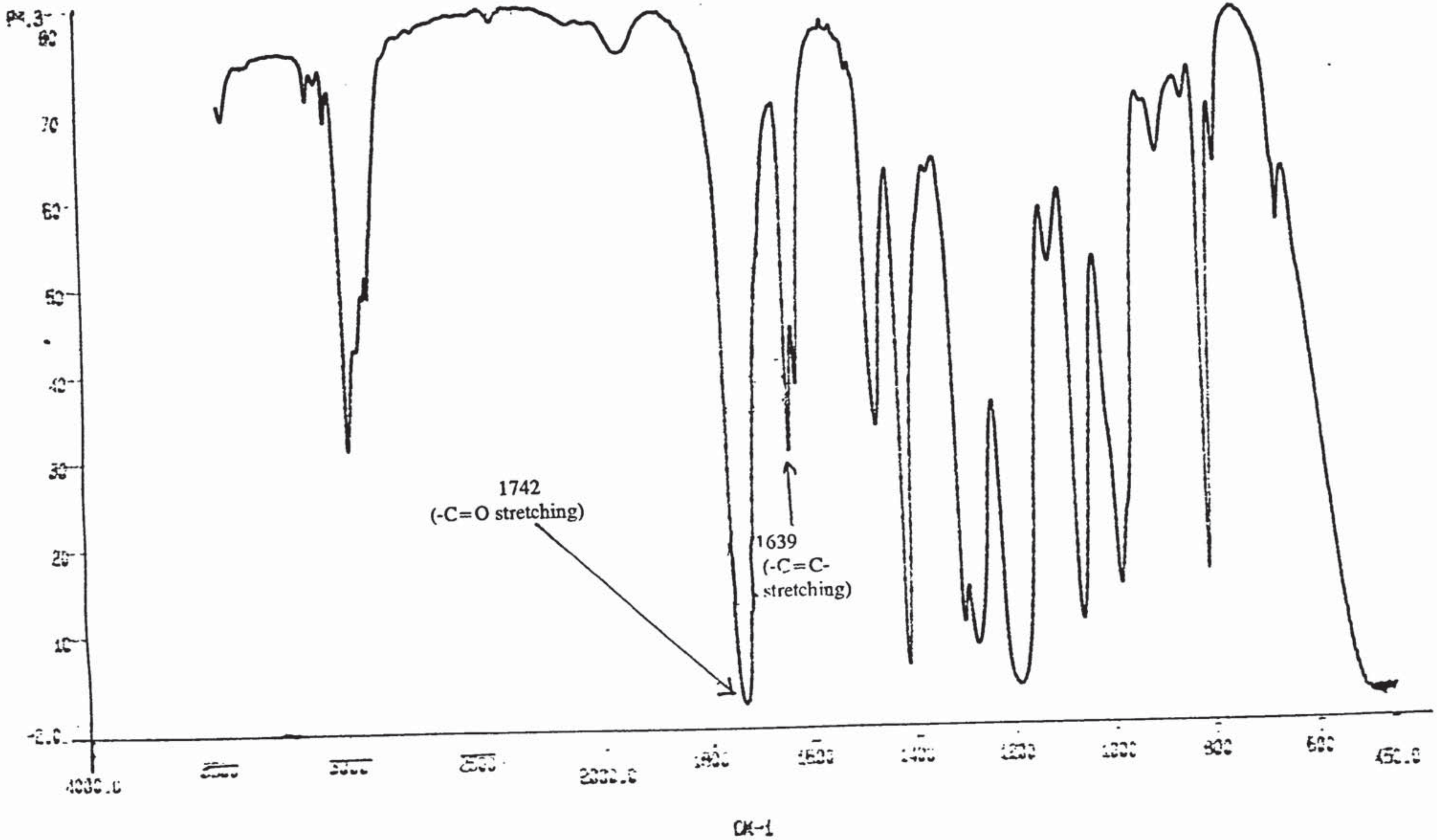


Figure 2.8: IR spectrum of HEMDA (in nujol, in between KBr disk)

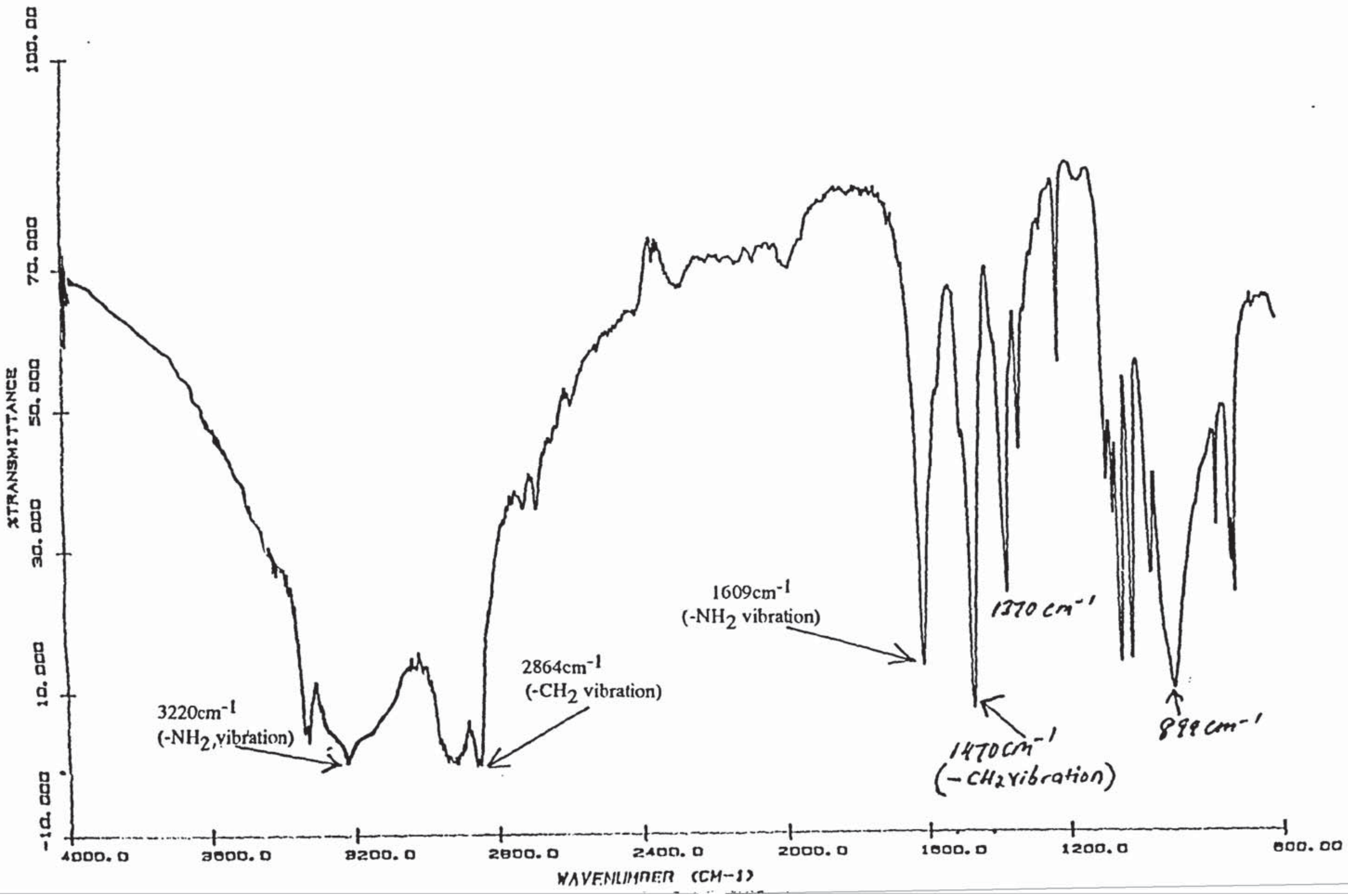
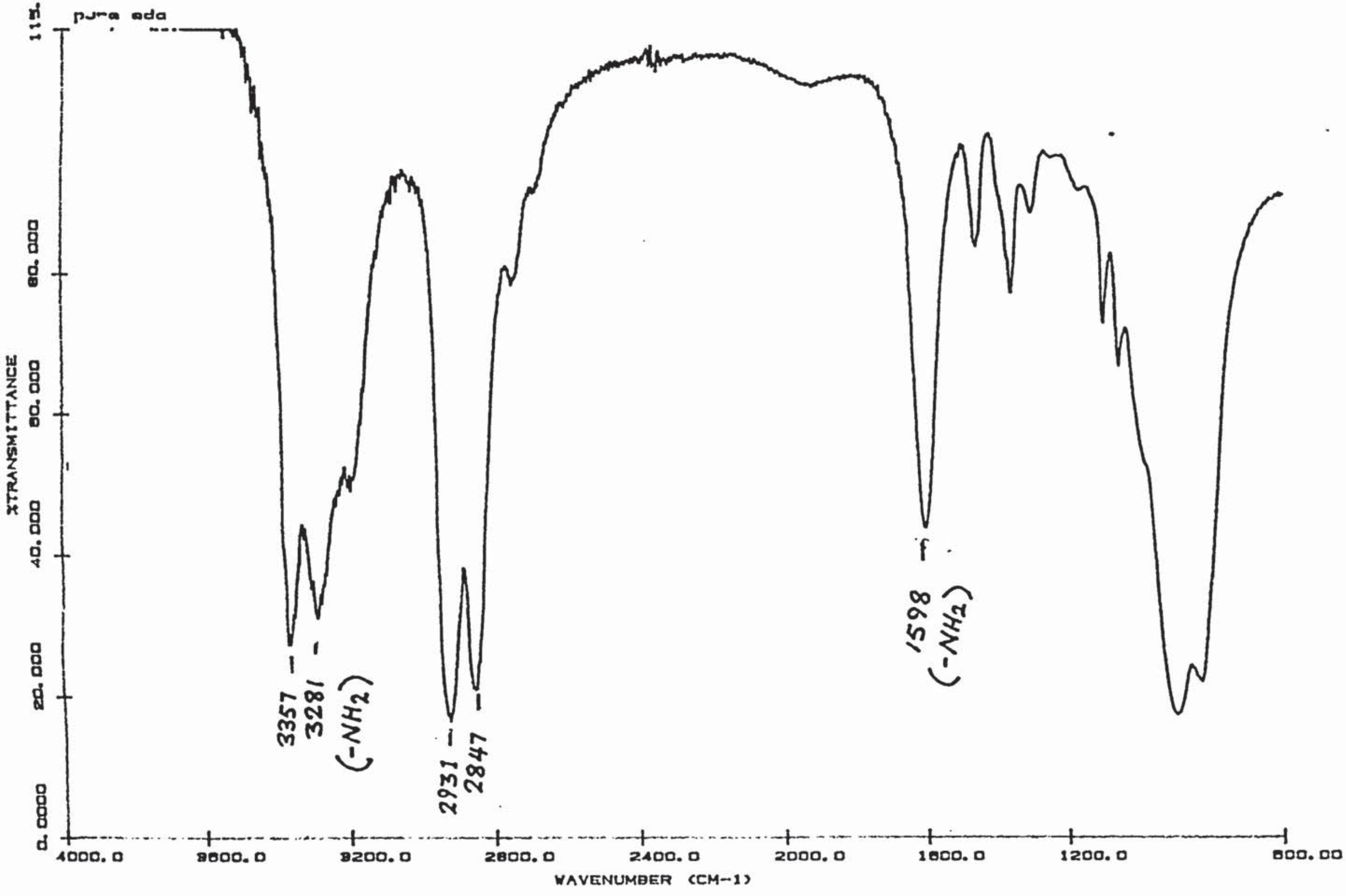


Figure 2.9: IR spectrum of liquid EDA film in between KBr disk



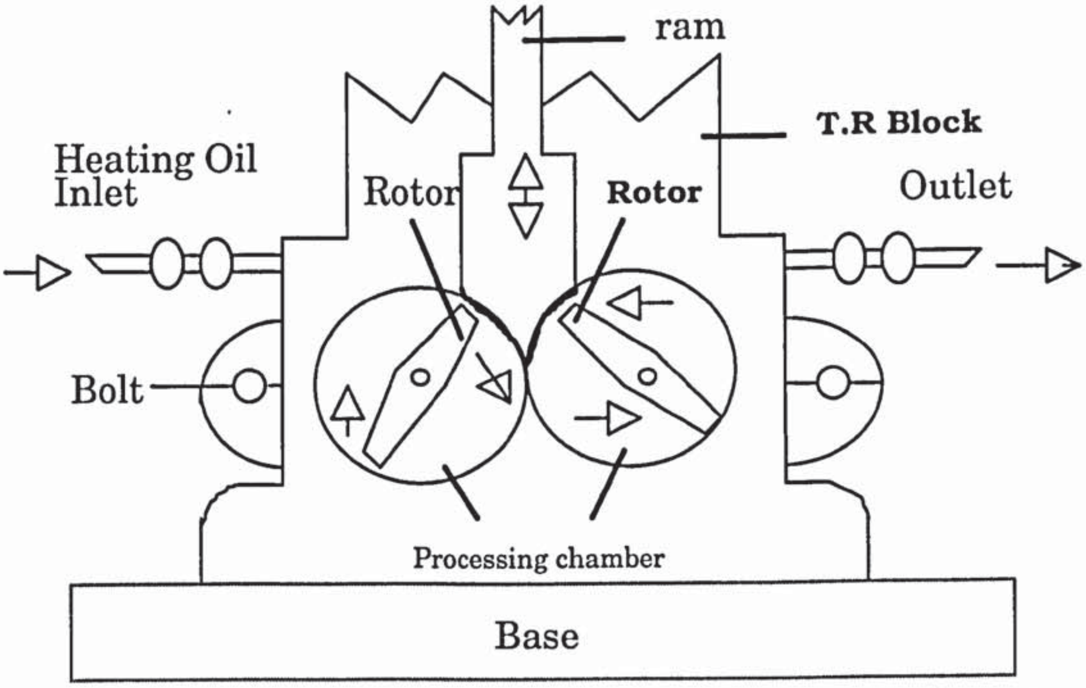


Figure 2.10: Processing chamber of a HAMPDEN RAPRA torquerheometer (an internal mixer)

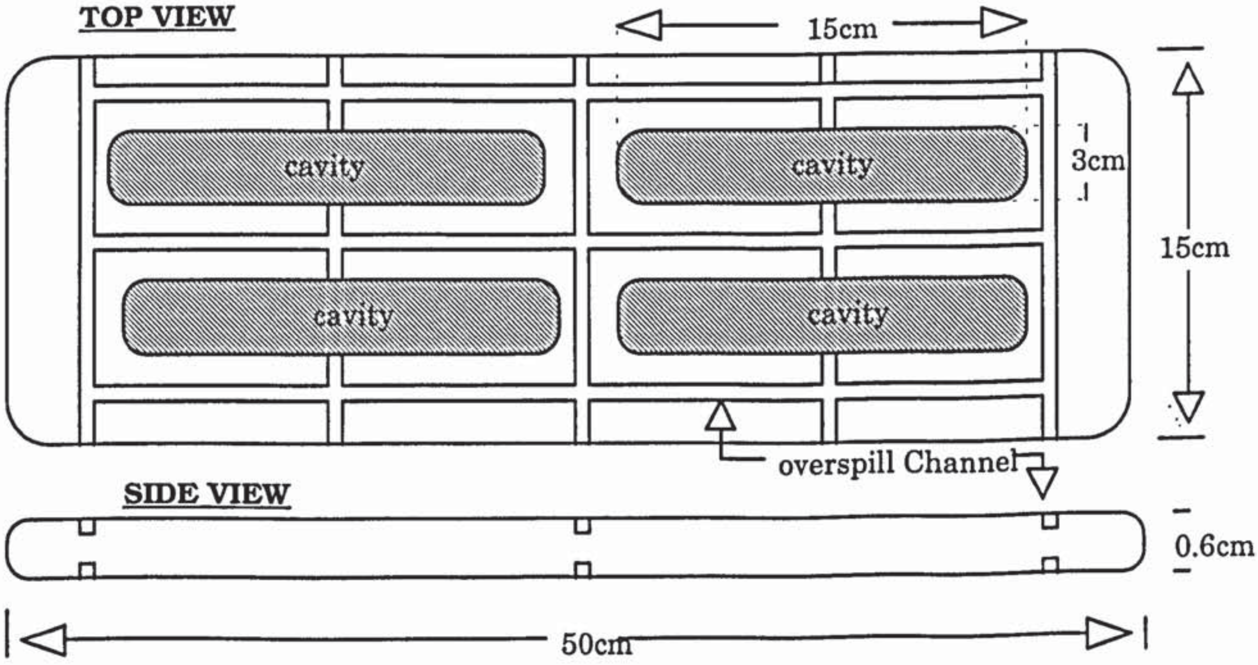
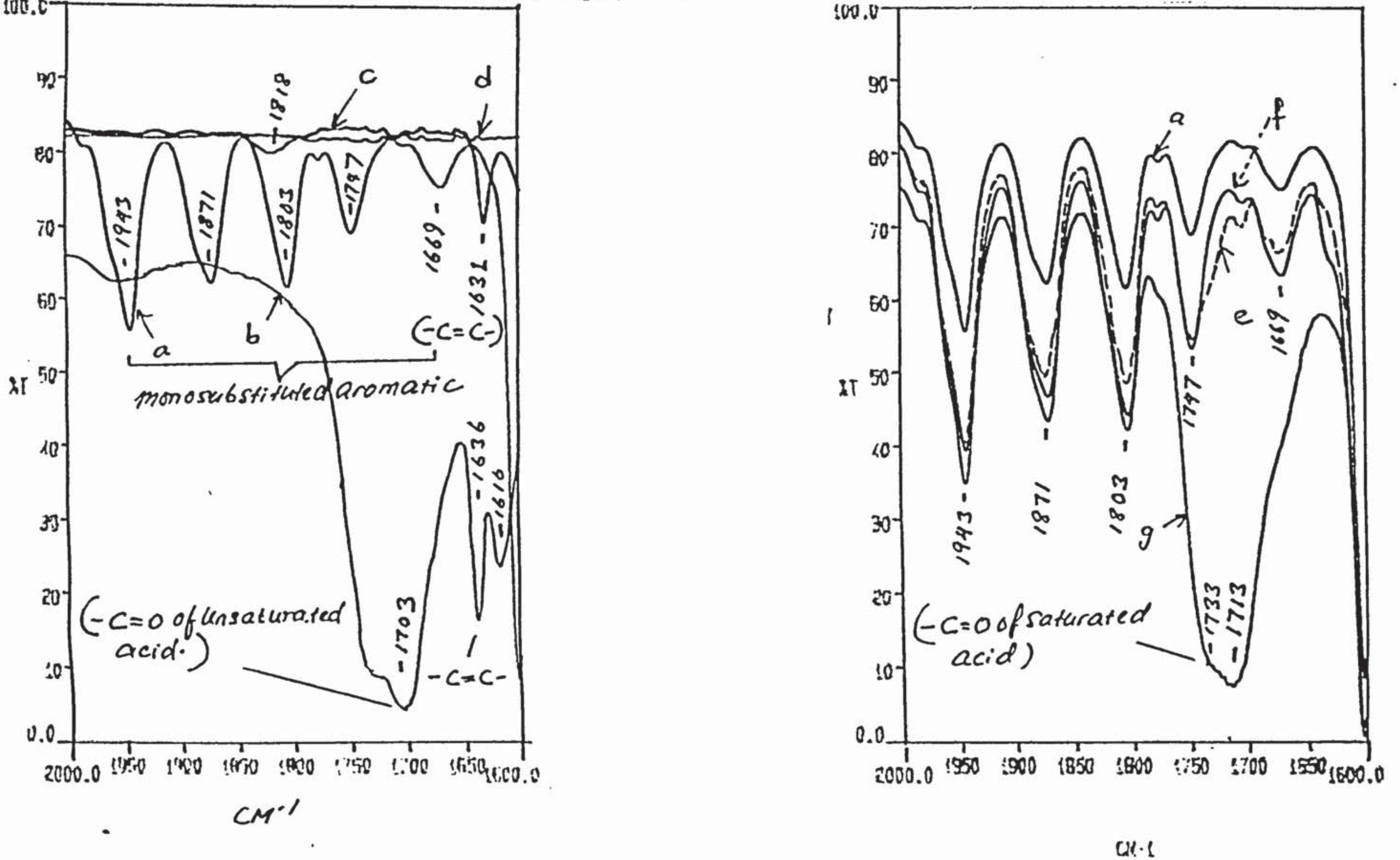
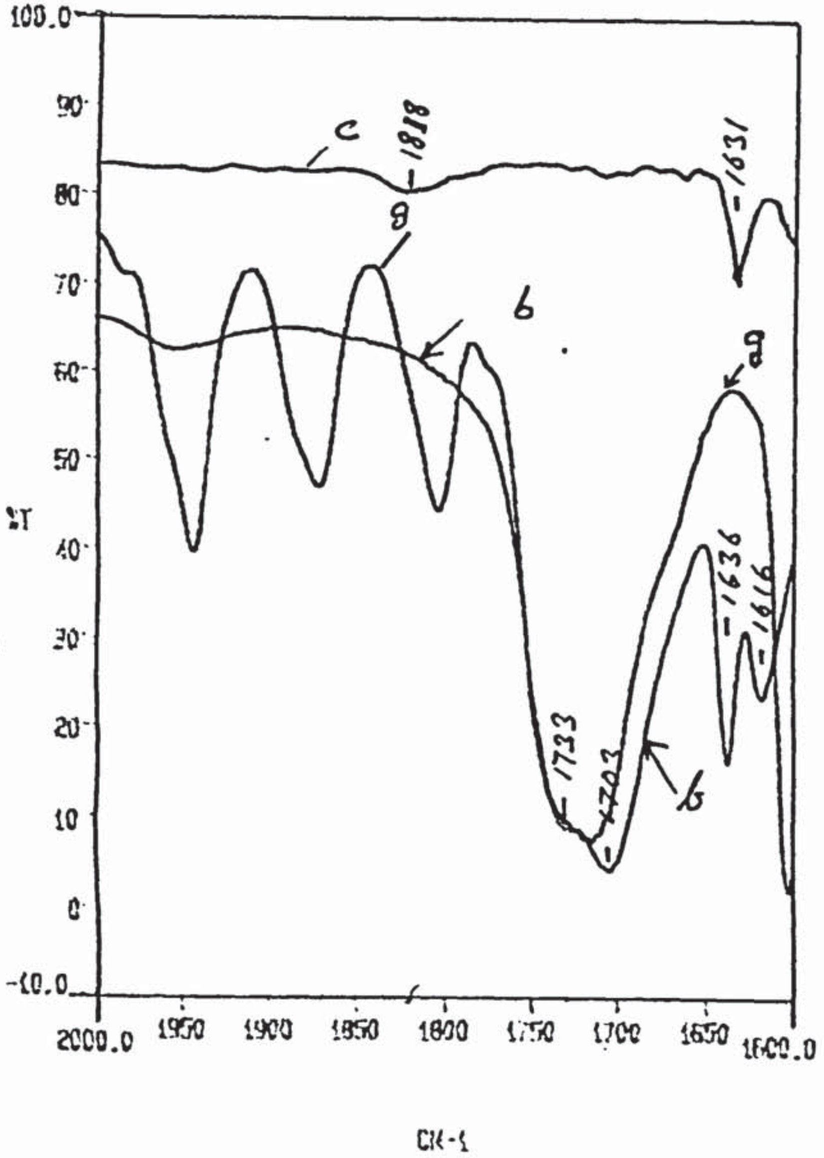


Figure 2.11: Compression moulding mould for preparation of slabs

Figure 2.12: IR spectra of agent, coagent, peroxide, modified PS and functionalised PS (F-PS1) with and without DVB. The letters represent: a. PS, b. AA, c. DVB, d. T101, e. PSb, f. PSc, g. PSd and h. PSe. Samples b,c&d were liquid films in between KBr discs, a,e,f,g &h were films(0.1mm thickness). Composition for PSc to PSe are given in table 2.2; processing conditions were 180^{0}C, 60rpm, 10min.



continue figure 2.12



continue figure 2.12

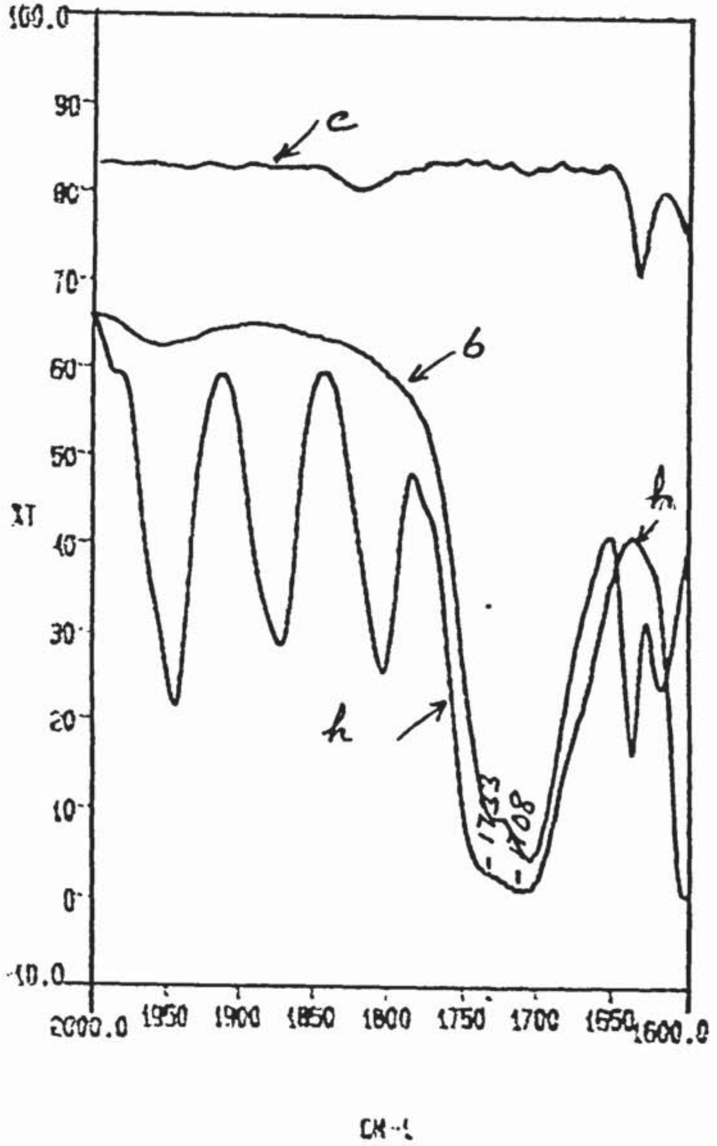


Figure 2.13: IR spectra of agent, coagent, peroxide, modified EPDM and functionalised EPDM (F-EPD) with and without TRIS. The letters represent : a. AA, b. T101, c. TRIS, Ra. EPDM, Rb. EPDM+TRIS, Rc.EPDM+TRIS+T10 1, Rd. F-EPD without TRIS, Re. full F-EPD. Compositions of Ra to Re are in table 2.2; processing conditions were 180ºC,60rpm,12min. Samples a,b&c were thin film of pure liquid in between KBr disk; while Ra to Re were thin polymer films (0.1mm thickness).

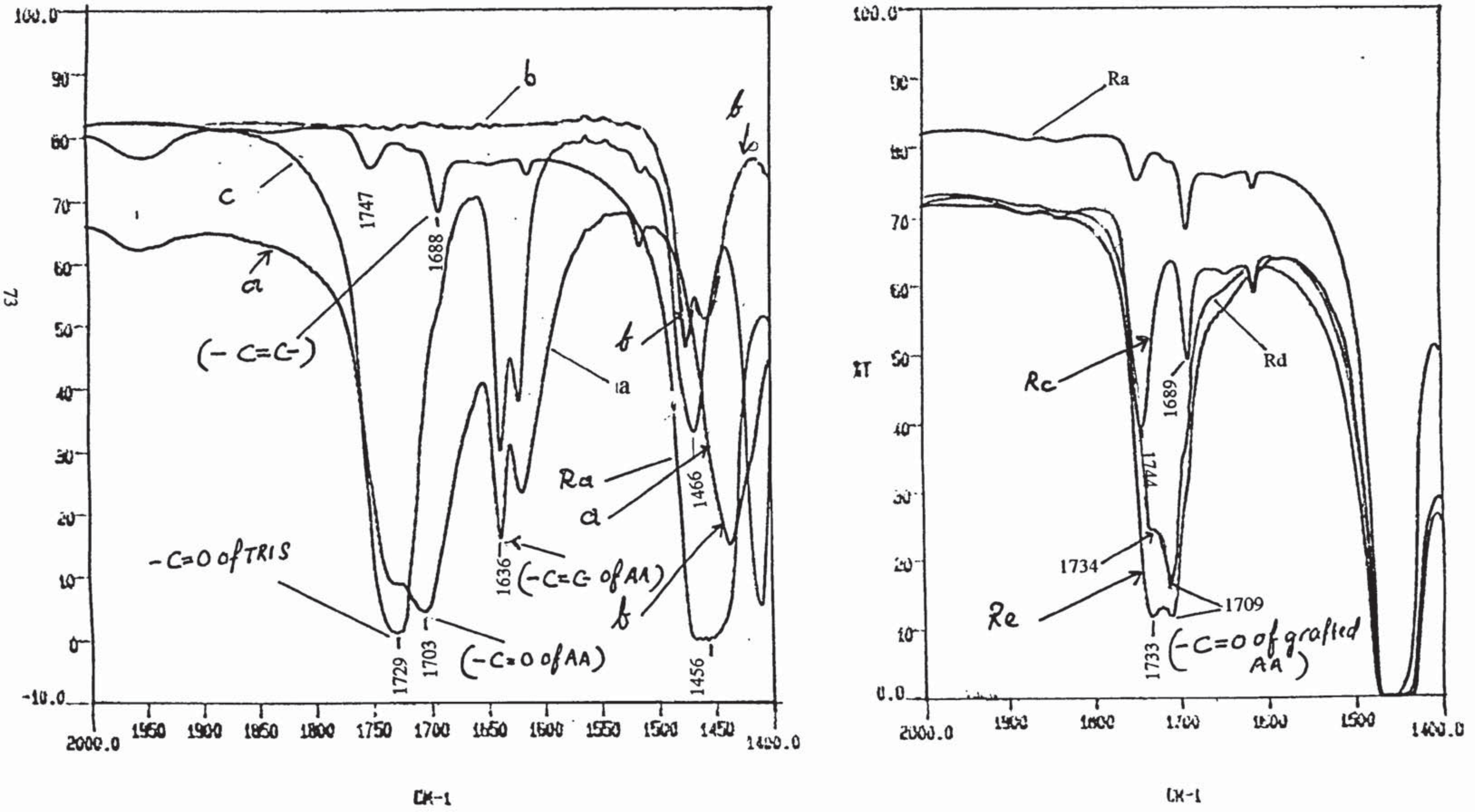


Figure 2.13 continue.....

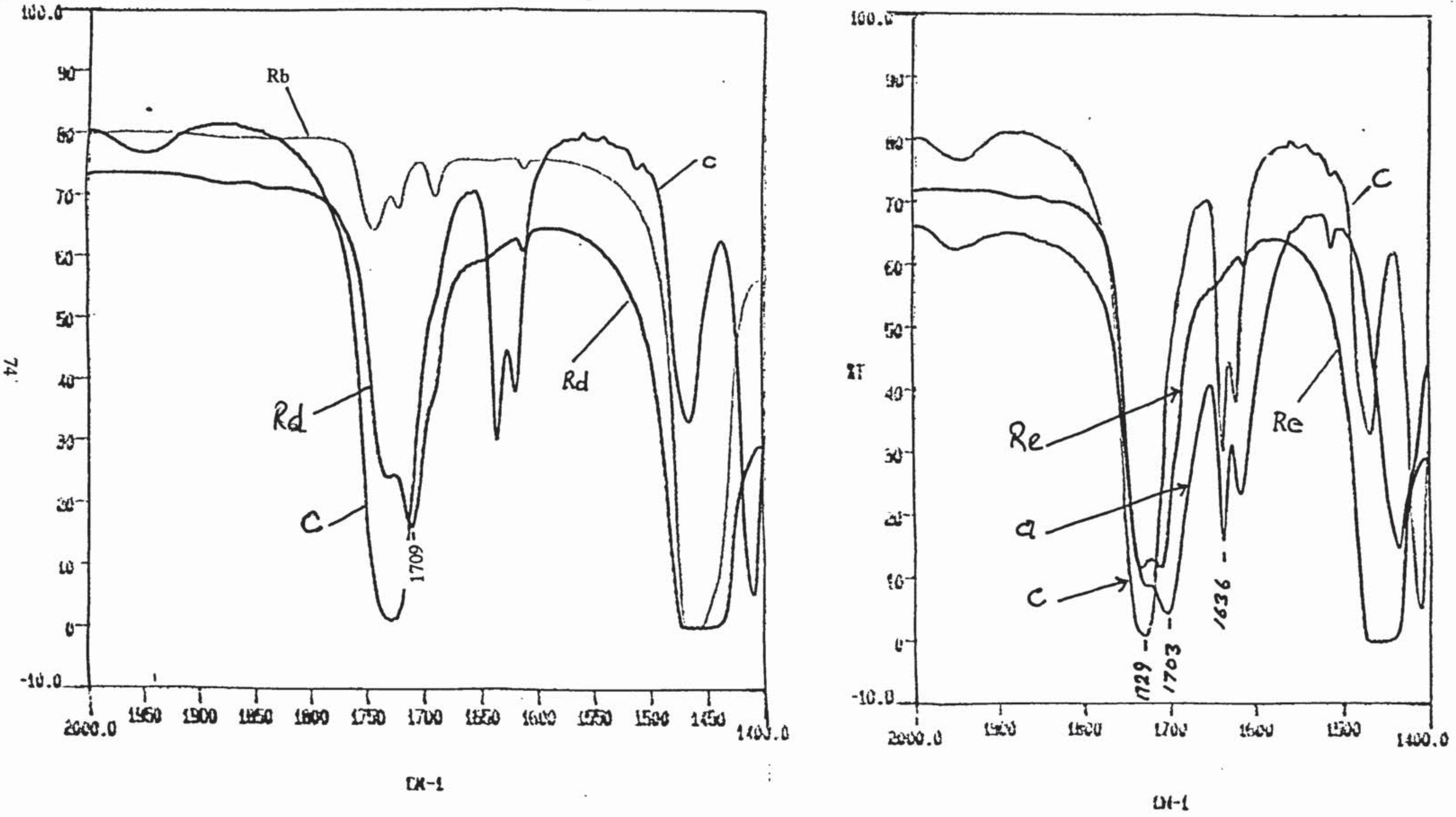
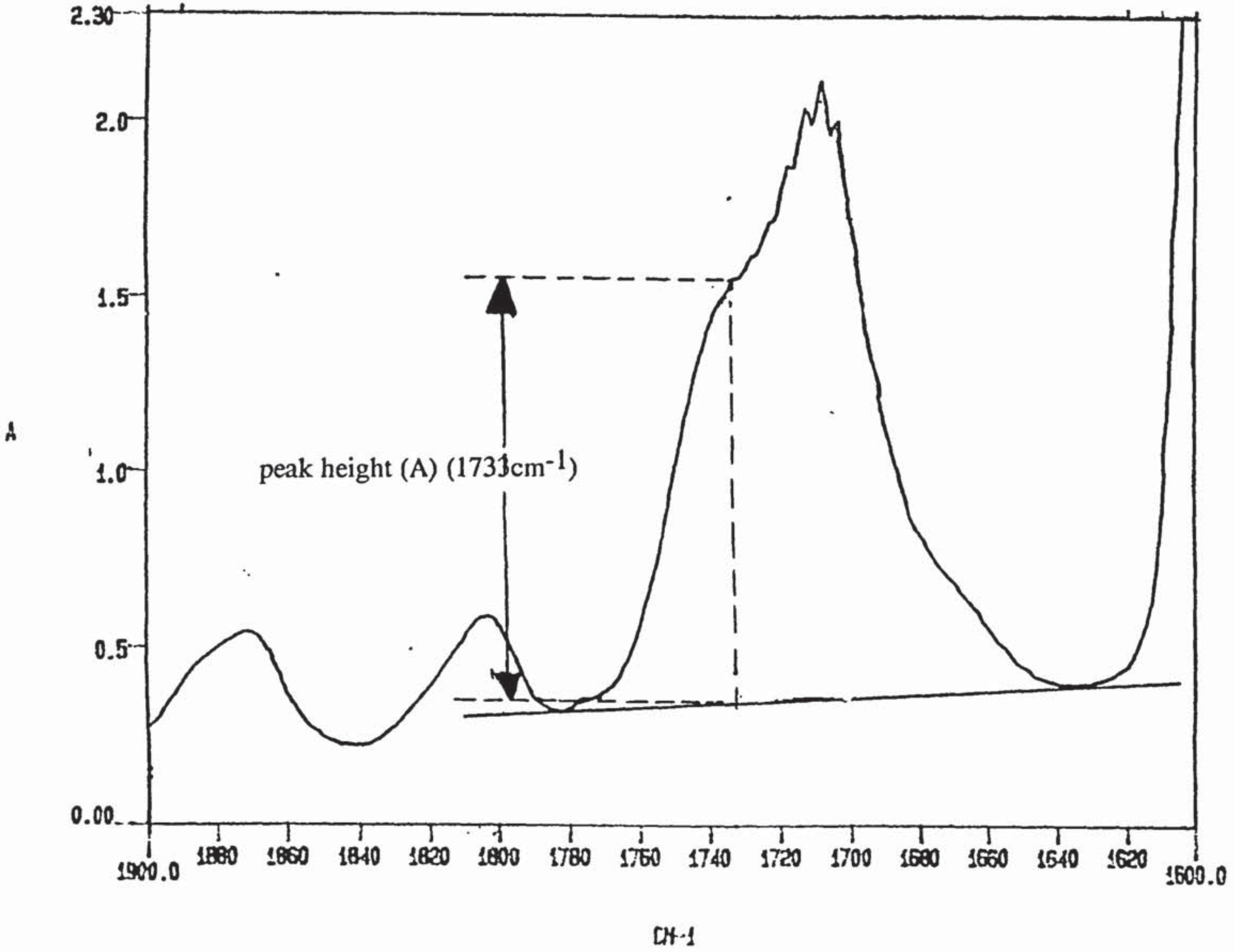


Figure 2.14: Measurement of peak height (at 1733cm^{-1}) of a typical IR spectrum of a thin polymer film (0.1mm thickness), using baseline method



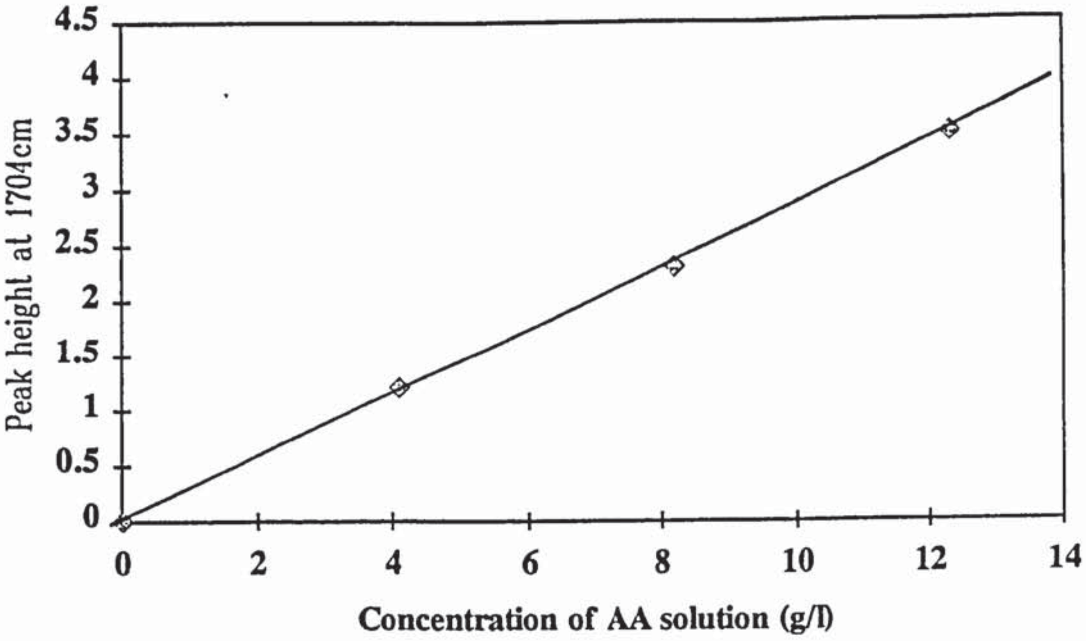


Figure 2.14b: IR calibration curve: Effect of AA concentrations in solutions of AA in methanol (0-12.3%) to IR absorbance peak height (baseline method) at 1704cm^{-1}, measured in a Perkin Elmer 1710 FTIR spectrometer.

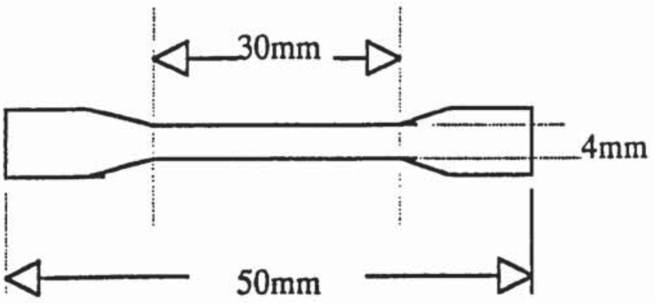


Figure 2.15: Dumb bell shaped specimen

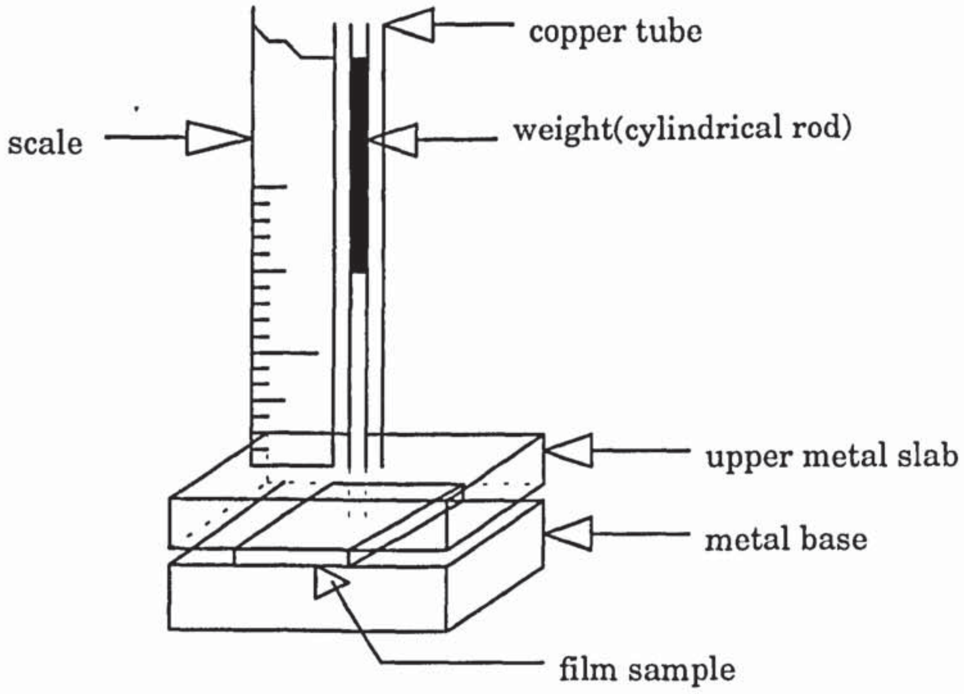
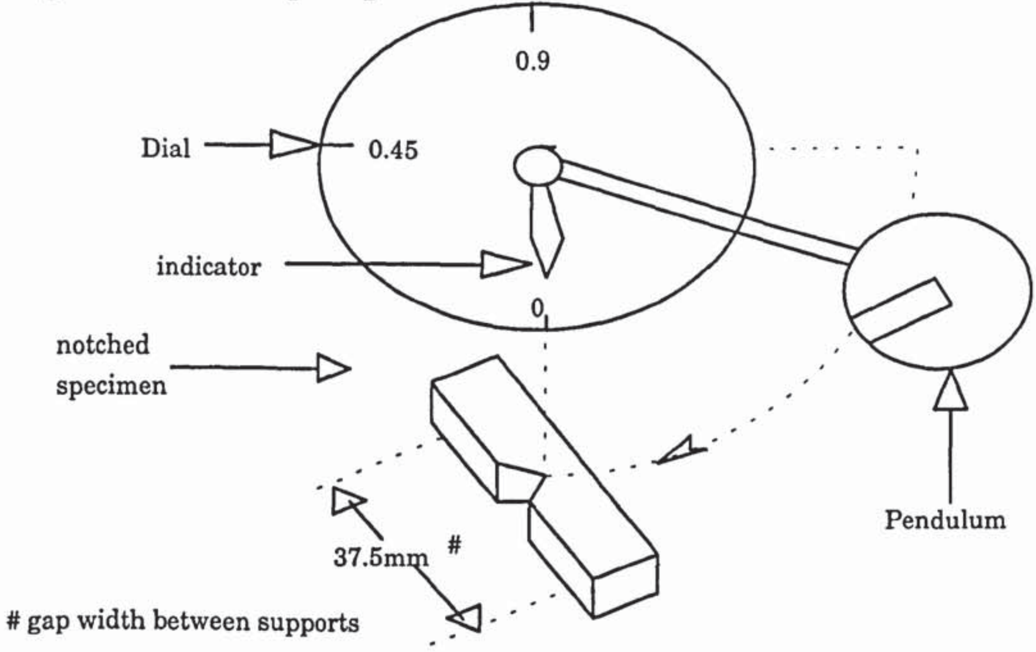
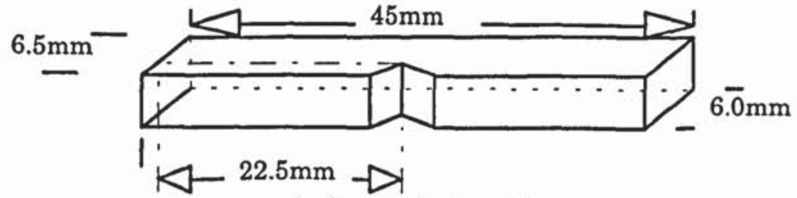


Figure 2.16: Drop impact test tester





An impact test specimen

Figure 2.17a: A diagrammatic layout of a Charpy impact tester

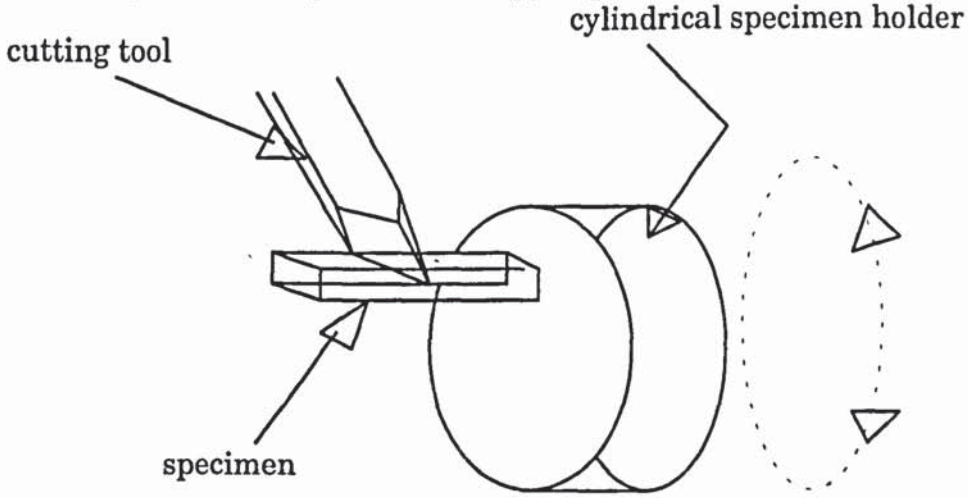


Figure 2.17b: Cutting a notch at an impact bar specimen using a Hounsfield notch cutting device.

CHAPTER 3

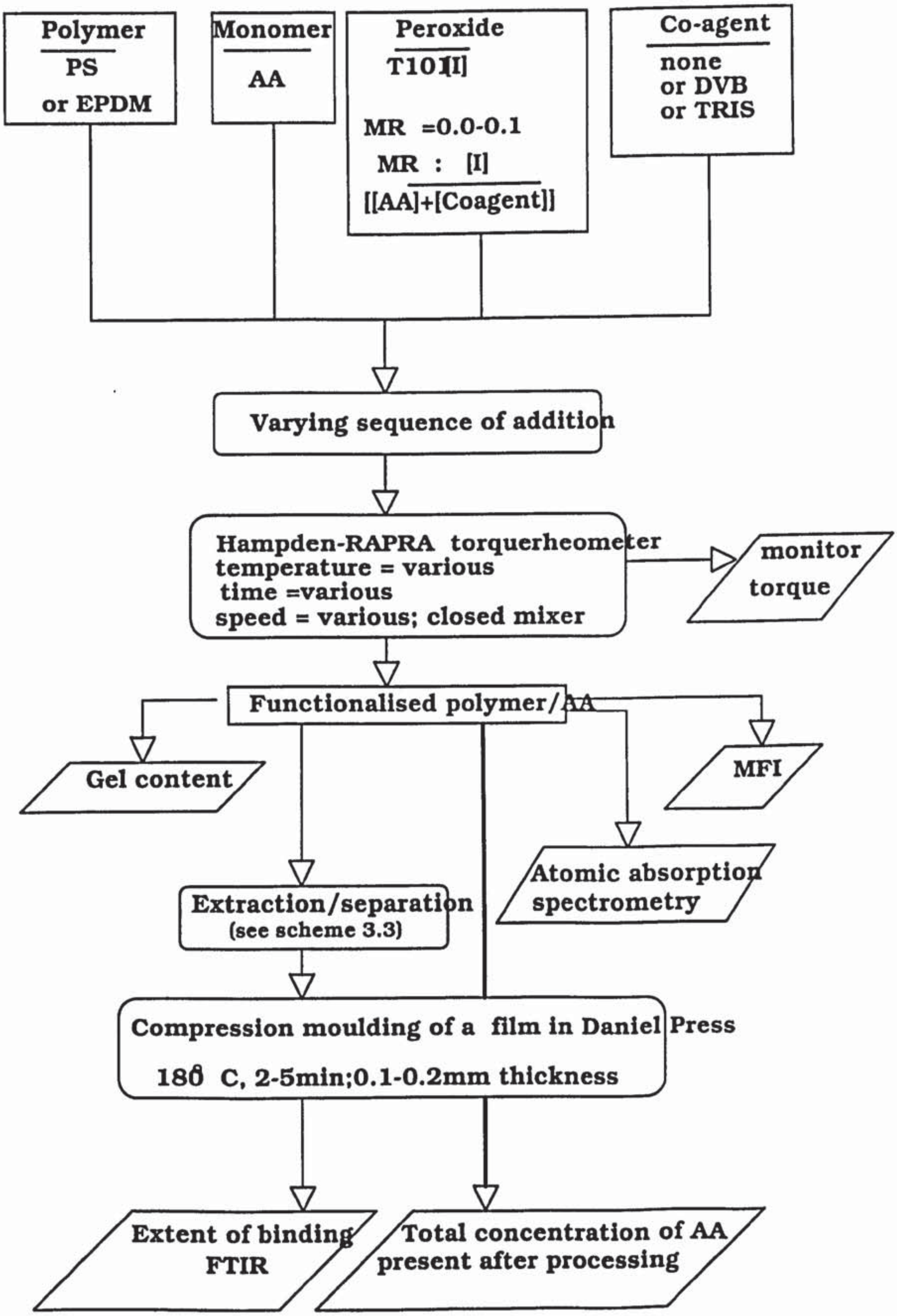
FUNCTIONALISATION OF PS AND EPDM WITH ACRYLIC ACID BY REACTIVE PROCESSING AND PHYSICAL PROPERTIES CHARACTERISATION

3.1 OBJECT AND METHODOLOGY

A novel approach to functionalisation of polymers has recently been developed at Aston University (^{108}), with the main object of enhancing grafting efficiency of wide range of monomers. This is based on the reaction of vinyl monomers (referred to as **'agents'**) in the polymer melt in the presence of a small concentration of a comonomer containing two or more reactive functions (referred to as **'coagent'**). The chemical modification of the polymer takes place during the melt processing operation in extruders or internal mixers, whereby both chemical composition and processing parameters are optimised; this is referred to as 'reactive processing'.

The main object of the work described in this chapter is to investigate the extent of functionalisation of PS and EPDM by acrylic acid (**I**), AA, (agent), using the co-agent technology, with the overall aim of subsequent blending of the functionalised polymers to achieve compatibilised blends of PS and EPDM. The coagents used for EPDM and PS were a trifunctional molecule Tris (**III**), and a difunctional molecule, DVB (**IV**), respectively, see **table 3.1a**. The effect of these coagents on the grafting efficiency of AA in the two polymers were examined. Reactive processing parameters and chemical composition in both cases, were optimised to affect an enhanced grafting efficiency of AA to the polymers.

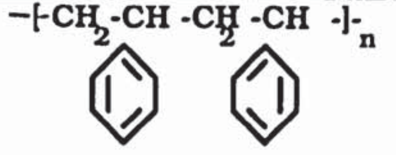
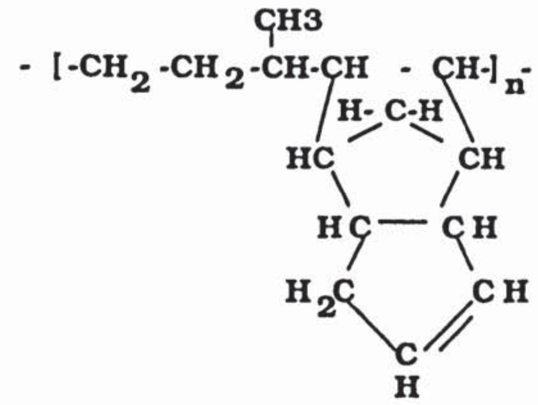
The general experimental procedure used to produce the functionalised polymers (PS or EPDM) using an internal mixer (torquerheometer) and the tests carried out on these polymers are shown in **scheme 3.1** and all samples processed are given in table 3.2. In general, the polymer was processed with AA (**I**) in presence or absence of various concentrations of peroxide, T101 (**II**), and a coagent (**III** or **IV**). The method of addition of the different compounding ingredients, the processing parameters and the chemical composition were varied and different reactive processing procedures were developed in order to achieve the highest level of grafting reaction of AA.



Scheme 3.1: Flowchart of general procedures for functionalisation of PS and EPDM and the subsequent analysis

The grafting efficiency, in the presence and absence of a coagent was compared. The functionalised polymers were then tested for physical appearance, grafting efficiency, melt stability by measuring melt flow index, (MFI), and the extent of insoluble fraction (gel content) which may be present.

Table 3.1a: Chemical structure and codes for polymers, peroxide, agents & coagents used in work described in this chapter.

Structure number	Chemical structure, name and molecular weight (MW)	Abreviatio
I	$CH_2{=}CH\text{-}COOH$ **Acrylic acid (MW=72); liquid**	AA
II	$(CH_3)_3COOC(CH_3)_2\text{-}CH_2\text{-}CH_2\text{-}C(CH_3)_2OOC(CH_3)_3$ **2,5-dimethyl 2,5-ditertiarybutylperoxy hexane (MW=291); liquid**	**T101**
III	$[CH_2{=}CH\text{-}(C{=}O)\text{-}O\text{-}CH_2\text{-}]_3\text{-}C\text{-}CH_2\text{-}CH_3$ **Trimethylolpropane triacrylate (MW=296); liquid**	**TMPTA** **(Tris)**
IV	 **Divinylbenzene (MW=130); liquid**	**DVB**
V	 **Polystyrene; solid pellet; MFR=3.0 (5Kg load, 200 C)**	**PS**
VI	 **Ethylene propylene dicyclopentadiene terpolymer; rubber block (55% ethylene, 40.5% Propylene and 4.5% dicyclopentadiene)**	EPDM

The composition of polymers with reactive agents/coagents are given in **table 3.2.**

Table 3.2: Composition of mixtures of polymers, PS and EPDM with peroxide T101, agent (AA), and coagent (DVB in case of PS; TRIS in case of EPDM) used in work described in this chapter. All controls were processed via methods PM1 for PS and EPM1 for EPDM.

Polymer functionalised	Processing method/ scheme no.	Product label	Concentration of polymer, peroxide, agent and coagent					
			PS (%)	EPDM (%)	T101 (MR)	AA (%)	DVB (%)	TRIS (%)
PS	Controls/3.2	PSC0	100	-	-	-	-	-
		PSC1	94	-	-	6	-	-
		PSC2	94	-	0.04	6	-	-
		PSC3	91	-	0	6	3	-
		PSC4	97	-	0.04	0	3	-
	PM1/3.2	F-PS1	91	-	0.04	6	3	-
	PM2/3.3	F-PS2	9	-	0.04	6	3	-
	PM3/3.4	F-PS3	91	-	0.04	6	3	-
	PM4/3.5	F-PS4	91	-	0.04	6	3	-
	PM5/3.2	F-PS5	91	-	0.04	6	3	-
EPDM	Control/3.9	F-EPD(C)	-	94	0.008	6	-	0
	EPM1/3.9	F-EPD1	-	93	0.008	6	-	0.6
	EPM2/3.10	F-EPD2	-	93	0.008	6	-	0.6
	EPM3/3.11	F-EPD3	-	93	0.008	6	-	0.6
	EPM4/3.12	F-EPD4	-	93	0.008	6	-	0.6
	EPM5/3.13	F-EPD5	-	93	0.008	6	-	0.6
Effect of processing conditions								
For processing PS (constant time, 10min; varying temperature and speed)			91	-	0.04	6	3	-
For Processing EPDM (varying temperature, speed and time)			-	93	0.006	6	-	0.6
Effect of chemical compositions								
For processing PS								
T101			91	-	0-0.04	6	3	-
DVB			91	-	0.04	6	0-4.0	-
For processing EPDM								
T101			-	93	0.005-0.008	6	-	0.6
TRIS			-	93	0.005	6	-	0-2

3.2 RESULTS

3.2.1 FUNCTIONALISATION OF PS BY ACRYLIC ACID

3.2.1.1 Effect of Processing Parameters and Methodology

The effect of five different processing methods on grafting efficiency of AA to PS was investigated. The major variable in these methods is the sequences of addition of agents (AA & T101) and the coagent (DVB) to PS. The aim was to develop a method which affects a high grafting effeciency of AA to the polymer. The processing was carried out in a torquerheometer using the same conditions in all methods (oil temperature 180°C, ram speed 60 rotation per minute (rpm) and a total time of 10min, except for the fifth method (method 5) whereby instead of a fixed oil temperature of 180°C, a temperature gradient (160°-180°C in 2.5min) was used. In all the methods, the melt temperature was measured using a precision thermocouple which was connected directly into the melt . In most of the cases the actual processing temprature was lower than the fixed oil temperature, varying in the range of 25-30°C degrees depending on the ambient temperature.

Method I

This processing method , **PM1**, is described in scheme 3.2. A mixture of PS with AA(6%), DVB (3%), and peroxide T101(0.04MR) [molar ratio, MR defined as the ratio of moles of T101 to the total number of moles of all other reactive components which could potentially consume the free radical initiator in the reaction mixture], was tumble mixed at room temperature and then introduced into the pre-heated mixer of the torque rheometer while the ram was in a lifted position. The ram was closed and the processing commenced and continued for 10min at 180°C and 60rpm. The resulted functionalised PS (F-PS1) was immediately quenched in cold water to prevent oxidation and heat degradation. About 3.0g of the F-PS1 was subjected to a rigorous separation procedure (see scheme 3.3) to remove unbound AA and polyAA. The resulted F-PS, in loose fibrous form, was compression moulded (180°C, 2min) to produce a film (0.1-0.2mm thick) which was used for measurement of the concentration of grafted AA by FTIR, see section 2.5.4 in chapter 2.

Method 2

In the second method, **PM2,** see scheme 3.4, the effect of pre-processing the coagent DVB with PS in the first 2min and a later addition of a mixture of AA / T101 was investigated. In this method, in the absence of the peroxide T101, a uniform mixing between DVB and PS is expected to be achieved without a substantial chemical reaction (no peroxide used at this stage). The subsequent addition of the peroxide (added as mixture with AA) to the internally mixed PS/DVB should lead to promotion of the grafting reaction of the coagent, DVB, to the PS ; this reaction is expected to compete with the grafting reaction of the AA to PS. In the presence of peroxide (T101), any remaining unsaturation of the grafted DVB can then react with the AA functionality, resulting in grafting of AA to PS via the DVB molecule. An enhanced grafting efficiency is expected via this method.

Method 3

In method 3, **PM3,** (see scheme 3.5), the effect of pre-processing the coagent DVB with the PS on the grafting efficiency of the AA to PS was further investigated using a modified approach to PM2. A small fraction of the total peroxide (25%of the total amount) was used initially with the PS/DVB mixture, which was processed for 1.7 minute (as in PM2), before the addition of AA and the remaining fraction of T101. During this initial processing period, an intimate mixing is expected, and the small amount of peroxide initially added is expected to lead to certain extent of grafting reaction between the DVB and PS. Subsequently, the addition of the major part of the peroxide should lead to higher extent of grafting of the DVB with concomittant grafting of AA on the PS backbone (via the grafted DVB). This method is expected to lead to even higher grafting efficiency than both methods PM1 and PM2.

Method 4

In this method, **PM4,** (see scheme 3.6), a modified approach to PM1 was examined. Here, the reactive agents/coagent mixtures were injected into the PS melt after 1.7min of processing PS alone. This was an attempt to compensate for the effect of the smooth surface of the PS pellets which may not be able to retain the other additives when used in the pre-mix mode (i.e. by PM1 method), resulting in some loss of the liquid additives during the transfer into the mixer. Furthermore, a further loss due to evaporation was noticed during the transfer of the first mixture into the mixer, in the three previous methods. A direct addition of the additives into the PS melt using syringe with a long needle which reaches to the melt, while the rotor of the mixer was in rotating position should minimise such losses, hence improving the amount of the additives being retained and subsequently could result in a higher concentration of AA being grafted to PS .

Method 5

Method 5, **PM5**, is another modified version of method PM1 (see scheme 3.7). The aim here was to further minimise the loss of the additives during the direct transfer into the mixer and this was achieved by adding all ingredients at lower temperature. In this method the premixed mixture of PS , AA, T101and DVB was processed first for 1.7min at 160°C. This was followed by a gradual increase in temperature up to 180°C which took 2.5min. Once the temperature reached 180°C, the processing was continued for a further 5 minutes.During the gradual increase in temperature , the reactive agents are expected to mix uniformly with the PS, and hence a reduced loss of additives may be achieved leading to higher grafting efficiency. This method should affect the highest retention of the reactive agents as compared to the four previous methods.

The results of analysis from all methods, see table 3.3, are reported in terms of concentration of retained AA (in gram per 100g) of the functionalised polymer (Stage B), concentration of grafted AA (in gram/per 100g) of the processed polymer (stage C), percentage concentration of retained AA per 6g (as 100%) of originally added AA (Stage D), percentage concentration of grafted AA per 6g (as 100%) of originally added AA (Stage E) and the grafting efficiency which is the ratio of the values of C to B (or E to D), stage F. The guiding principle for the calculations are given in **scheme 3.8.** Similar method of calculations were applied in other sections pertaining to concentration of AA in PS. Similar method of calculations on binding efficiency in functionalised EPDM (F-EPDM) was used in the subsequent relevant sections of the chapter. Table 3.3 shows that the concentration of the retained AA/polyAA in F-PS5 (prepared by method PM5) has acquired highest amount of the grafted [AA] when compared to the other four methods and therefore this method was considered to be the best. Methods PM1, PM3 and PM4, within experimental error are as good as each other and method PM2 is the worst. Incorporation of DVB has clearly increased the level of binding of AA. Although the grafting efficiency achieved in samples processed using all methods were high, nearly 100%, the absolute concentration of AA grafted is highest when method 5 was used.

Table 3.3: Comparison of effect of the five processing methods PM1,PM2,PM3 ,PM4 and PM5 on efficiency of grafting of AA to PS.Total amount of reactive modifiers used in all methods: AA 6%, T101 0.04MR, DVB 3% [schemes 3.2 to 3.6]; processing conditions: 180°C, 60rpm, 10min. in PM1 to PM4; 160°-180°C, 60rpm, 10min in PM5.The notations A,B,D,E and F are defined in scheme 3.8.

Processing Methods		Actual [AA] after processing (N.B: Initial added amount of AA = 6g/100g PS); # stage A				
		Based on weight of functionalised polymer (Actual remaining)		Based on inital [AA] added		% grafting efficiency
		Before extraction by method of scheme 3.3 g/100g # Stage B	After extraction by method of scheme 3.3 g/100g # Stage C	B -x100(%) A (total AA remaining) # Stage D	C -x100 A (% grafted AA) # Stage E	E -x100 B Based on actual after extraction (%) #Stage F
PM1(C1)	PS +AA------------------> F-PSC1	0.11	0.11	2	2	100
PM1(C2)	PS+AA+T101 ---------> F-PSC2	0.80	0.40	13	7	50
PM1	PS+AA+DVB+T101 ---> F-PS1	0.70	0.65	12	11	93
PM2	PS+DVB | }------------------>F-PS2 AA+T101	0.51	0.48	8	8	100
PM3	PS+DVB+T101 |} ----> F-PS3 AA+T101	0.60	0.57	10	10	100
PM4	PS | } -----> F-PS4 AA+DVB+T101	0.64	0.61	11	10	95
PM5	PS+AA+T101+DVB----> F-PS5	1.01	0.95	17	16	94

Processing via methods 2, 3 and 4 involved opening the mixer in order to add certain components of the reactive system, while methods 1 and 5 involved direct addition of additives at the beginning of the processing. Figure 3.1a shows that the torque curves of polymers processed by the different methods are very similar except for the height of the initial torque peak corresponding to the melting of the polymer processed , which is highest when all additives are added after 1.7min as in method PM4 . Figure 3.1b confirms this and also shows lowering in the height of the initial tq peak when the polymer was processed by methods 1 and 5 where additives are introduced initially with the polymer. It is important to note that both methods lead to a clear second torque peak which is delayed when a temperature programme is used for processing by method 5. The occurrence of a second peak when a co-agent is used for polymer modification have been observed previously with different polymers by Al-Malaika et al ([109]) and it was shown to be associated with crosslinking and grafting reactions. It is important to note that in all cases (methods 1 to 5), the torque at the end of processing, levels off and is similar to that of the unmodified polymer (see figure 3.1).

The IR spectra of thin films of the F-PS samples, in the wavenumber range of interest (1600-2000cm^{-1}), see figure 3.1c&d, has shown strong wavebands in this region. The >C=O absorbance in the range 1700-1800cm^{-1} must be a composite absorbance band due to stretching vibrations of various carbonyl groups such grafted AA (to PS), homopolymer of AA and copolymer of AA/DVB. Since the interest was mainly in the saturated grafted AA , the wavenumber used was 1710 cm^{-1}, see section 2.5.3. At 1710cm^{-1}, the height of the absorbance peak , see figure 3.1d&e, was proportional to the concentration of saturated AA, present in the graft , the unbound AA and in combination thereof.

The gel content, see scheme 3.9 part a, and the melt flow index (MFI), see **table 3.3** were measured and presented. A very small amount of gel was found in a mixture processed with DVB by methods 1 and 4 indicating some crosslinking reaction. From the MFI values of the samples, it was shown that the AA and T101 have caused chain scission and degradation to PS, reflected by a high MFI value whereas MFI values when the DVB is used are, in general, lower.

The colour of the F-PS samples obtained was white with a comparatively narrow range degree of opacity when the samples were in the shape of a disc (2-3mm thickness), but were almost invariably transparent when in the form of films (0.2mm thickness). The transparency (disc form) was much reduced when samples were compared to PS processed alone or PS processed with DVB and T101but without AA, using the same processing condition (180°C, 60rpm,10min). The opacity of the processed PS without the DVB (i.e.

PS with AA and T101i.e. PSC2) was, however, higher than the one processed in the presence of the coagent. The white colour and the opacity were probably due to the presence of various macromolecules which existed as a dispersed phase, immiscible in the PS matrix.

Table 3.4: The Gel content (see sch.3.9a) and melt flow index (MFI of the F-PS films prepared by methods PM1 to PM5 . The MFI values were measured at 190°C,using weight 2.16Kg and die of 2.1mm diameter.

Composition of mixtures	Processing methods	sample code	Gel content (%)	Mel flow index (g/10min)
PS	PM1	PSC0	0	0.32
PS+AA	PM1	PSC1	0	1.64
PS+AA+DVB	PM1	PSC2	0	1.48
PS+AA+T101	PM1	PSC3	0	3.22
PS+T101+DVB	PM1	PSC4	2	1.87
PS+T101+AA+DVB	PM1	F-PS1	5	2.23
PS+T101+AA+DVB	PM2	F-PS2	0	2.22
PS+T101+AA(6%+DVB	PM3	F-PS3	0	2.51
PS+T101+AA+DVB	PM4	F-PS4	1	2.76
PS+T101+AA+DVB	PM5	F-PS5	0	3.20

In the molten state, the substances tended to stick strongly to the rotors as well as to the inner wall of the mixer rendering it quite difficult to be removed, whereas a molten mass of PS (processed alone), was relatively easily removed from the mixer. This characteristic of the F-PS molten mass is believed to be due to the presence of polar components in the form of unbound polyAA and grafted AA to PS which increases the adhesivity between the polymer and the metal surface of the mixer.

3.2.1.2 Optimisation of processing conditions

Processing temperature and speed, were varied at a fixed processing time of 10min. Mixtures of PS with AA(6%), T101(0.04MR) and DVB (3%) were processed using method PM1, see scheme 3.2. The temperature was varied between 160°-200°C (at 60rpm and 10min), while for the speed, a range of 45-100rpm (200°C and 10min) was used. The F-PS samples obtained were analysed by infra red and the results are reported in **table 3.5**; the IR spectra are shown in **figure 3.1e** and **3.1f.** Both temperature and speed have affected the retained and grafted [AA] in the processed PS samples. The temperature and speed of 200°C and 100rpm respectively were considered better than the rest and will be used together with 10min time for further processing.

Table 3.5: Effect of processing temperature and speed on retained and grafted [AA] to PS in F-PS samples prepared from mixtures of PS, AA(6%), T101(0.04MR), DVB(3%); at variable temperature (160^{0}-200^{0}), speed (45-100rpm) and time 10min using PM1 method. For the different stages see scheme 3.8.

	Actual AA concentration remaining after processing (NB: initial added amount of AA=6g/100g PS;#stage A) # stage A				
	Based on weight of functionalised polymer		Based on actual [AA] added		grafting efficiency(%)
Processing conditions	Total (AA) remaining after processing g/100g Stage B	grafted [AA] g/100g Stage C	% total AA (after processing) $\frac{B}{A} \times 100$ (%) Stage D	% grafted AA $\frac{C}{A} \times 100$(%) Stage E	$\frac{C}{B} \times 100$ (%) Stage F
Temperature ^{o}C					
160	1.03	1.01	18	17	98
180	0.70	0.65	12	11	93
190	1.07	1.04	18	17	97
200	**1.28**	**1.27**	**21**	**21**	**100**
60rpm,10min					
speed (rpm)					
45	1.21	1.17	20	20	100
60	1.28	1.27	21	21	100
75	1.07	1.02	18	17	96
90	1.14	1.11	19	19	100
100	**1.35**	**1.32**	**23**	**22**	**98**
200^{0}C,10min					

3.2.1.3 Effect of Chemical Composition

(a) Effect of Peroxide Concentration on Appearance, AA Grafting Efficiency and Crosslinking/Degradation Reactions

The work on functionalisation of PS with AA was started by carrying out experiments to qualitatively assess the possibility of grafting versus homopolymerisation of AA in a PS melt, in a torquerheometer, using processing method PM1, see **scheme 3.10**. The results on visual appearance of the F-PS1 discs (2-3mm thickness) are given in **table 3.6.**

Table 3.6: Effect of [T101] on physical appearance of F-PS1 samples prepared from mixture of PS with AA(6%), T101(0.0-0.1MR), DVB(0%,2%) at 180°C, 60rpm,10min; PM1 method.

Sample number	Concentration of agent/co-agent			Colour observation in F-PS1 discs (2-3mm thick)
	AA (%)	DVB (%)	T101 (MR)	
1	0	0	0.0	colourless-transparent
2	6	0	0.0	dark brown-transparent
3	6	0	0.005	light brown-semi tansparent
4	6	0	0.01	brownish-opaque
5	6	2	0.01	brownish-semi transparent
6	6	0	0.02	white-opaque
7	6	0	0.03	white-opaque
8	6	0	0.05	white-opaque
9	6	0	0.10	white-opaque

The brown colour of discs obtained from the mixtures containing no or very small concentration of peroxide was suspected to be the due to attack of the metal lining of the mixer cavity by the AA during processing. Atomic absorption spectrophotometry (AAS) experiments, see **scheme 3.10** were carried out on discs number 2 to 5 to obtain more information. The results of AA analysis are given in **table 3.7.** The white colour was suspected to be due to AA homopolymer evenly distributed in the PS matrix. The incompatibility of polyAA with PS has caused the whiteness and opacity. The opacity was increasing in intensity with increase in T101concentration.

Table 3.7: Iron concentration in samples 2-5 of table 3.4, obtained by atomic absorption spectrophotometric analysis.

sample number	Concentration of agent/peroxide		$[Fe^{+3}]$ in F-PS (%)	Colour of polymer samples
	AA (%)	T101 (MR)		
2	6	0.0	0.12	dark brown, transparent
3	6	0.005	0.01	light brown, semi-transparent
4	6	0.01	0.02	brownish,opaque
6	6	0.02	0.07	white opaque

A high iron concentration in sample no.2, has proven that the brown colouration was indeed due to ferric iron. Addition of 0.005MR T101 .has resulted in 12 times reduction in the iron concentration, probably as a result of maximum conversion of AA into oligomeric form which reduces the acid strength . At higher [T101] however, the $[Fe^{+3}]$ increased again.

A quantitative assessment of the effect of peroxide concentrations on the total retention of AA/polyAA and extent of grafting of AA to PS was carried out in order to obtain an optimum concentration of peroxide T101 which affects maximum binding of AA to PS. The grafting efficiency of AA processed at variable peroxide concentration (0.0-0.04MR of T101, using PM1method) ,see **scheme 3.10**, is shown in **table 3.8**. The variation of torque with time during processing of these samples and changes in their IR (>C=O) are shown in **figure 3.2a&b**,. In the absence of peroxide but presence of the coagent (PSC3), the amount of AA retained in the polymer after processing was found to be only 2%(stage B). This very small concentration of AA, however remained in the polymer after extraction (stage C). Increasing concentration of peroxide (in presence of DVB) has lead to a much higher retention level of AA in the polymer, up to 22%

(b) Effect of coagent concentrations on the concentration of grafted AA on PS

A series of experiments were carried out to quantitatively assess the effect of the coagent (DVB) concentration (0-4.0%) on the retention level of AA/polyAA and extent of binding of AA to PS (via processing method PM1), see **scheme 3.11**. Results of these experiments are given in **table 3.8** and **figure 3.2c** .

Table 3.8 illustrates the important role that the coagent, DVB, plays in the grafting of AA to the polymer backbone. In the absence of co-agent ,DVB, plays in the grafting of AA to the polymer backbone. In the absence of DVB (PSC2), the total amount of AA retained in the polymer after processing was found to be 14%, but only half of this became grafted (after exhausted extraction). However the use of DVB has led to retention of up to 22%, of AA which became almost 100% grafted to the polymer.

Further, the amount of AA retained and grafted is shown to be proportional to the coagent concentration and is maximum at 3%. Very small amount (<1%) of crosslinking gel was observed in all cases, except at 2.5% DVB concentration when the sample was completely soluble.

Table 3.8: Effect of peroxide (T101) and coagent (DVB) concentrations on the concentration of the grafted AA to PS in F-PS samples. In case of T101, processing mixture was PS, AA (6%), T101 (0.00-0.04MR), DVB (3%). In case of DVB, processing mixtures was PS, AA(6%), T101(0.04MR), DVB(0-3.6%). Processing conditions and method in both cases were 200°C, 100rpm, 10min; Method PM1, scheme 3.2)

[T101] & [DVB]	Actual AA concentration after processing (NB: initial added amount of AA = 6g/100gPS; #stage A]					
	Based on weight of functionalised polymer		Based on initial [AA] added		% grafting efficiency	
	Total [AA] (remaining after processing) g/100g Stage B	grafted [AA] g/100g Stage C	% total AA (after processing) B -x100(%) A Stage D	% grafted AA C -x100(%) A Stage E	C -x100 B Stage F	
PM1 [PS+AA(6%)+ DVB(3%)] Control 1(PSC3)	0.11	0.11	2	2	100	
PM1 [PS+AA(6%)+T101(XMR)+DVB(3%)] <u>[T101]MR</u>						
0.01	1.05	0.98	18	16	93	
0.02	1.20	1.05	20	18	88	
0.03	1.16	1.15	19	19	100	
0.04	1.31	1.30	22	22	100	
PM1[PS+AA(6%)+T101(0.04MR)] (no coagent) Control 2 (PSC2)	0.84	0.42	14	7	50	
PM1 [PS+AA(6%)+T101(0.04MR)+DVB(X%)] <u>DVB (%)</u>						Insoluble gel (%)
0.5	1.04	0.70	15	10	67	0.2
1.0	0.93	0.75	16	13	81	0.6
1.5	0.85	0.85	15	15	100	1.0
2.0	0.98	0.98	18	18	100	0.2
2.5	1.14	1.14	20	20	100	0.0
3.0	1.31	1.30	22	22	99	0.2
3.6	1.11	1.05	19	18	95	0.9

3.2.2 FUNCTIONALISATION OF EPDM BY ACRYLIC ACID

3.2.2.1 Effect of Processing Parameter and Methodology

Functionalisation of EPDM was carried out in a similar way to that discussed for the PS in the previous section. Different processing methods (EPM1to 5) were used to examine the effect of varying the sequence of addition of the reactive agents, see schemes 3.12-16 in order to optimise the grafting of AA to EPDM. Processing conditions were kept constant at 180°C, 60rpm, 12min in methods EPM1 to EPM4, while in method 5 (EPM5) a contineous variable temperature of 130°-180°C was used at 60rpm and total period of time of 12min.

3.2.2.1.1 Effect of Processing Methods , Processing Conditions and Chemical Composition on Grafting Efficiency of AA to EPDM.

3.2.2.1.1.1 Effect of processing methods

Method 1

The general experimental procedure used for this method, referred to as EPM1 is described in **scheme 3.12.** The results of infra red analysis of the amount of bound/unbound AA are shown in **Table 3.9**. The colour and degraded fraction ; gel content (see scheme 3.9 part b) ; and the IR spectrum of EPDM and F-EPD samples are shown in **table 3.10,** and **figure 3.3.**

Method 2

The process method 2, EPM2 is described in **scheme 3.13** and all the relevant results are shown in tables 3.9 & 3.10, figures 3.3.

Method 3

Scheme 3.14 describes processing by method 3, EPM3. All relevant results are shown in tables 3.9 & 3.10, figures 3.3

Method 4

The procedure used for method 4, EPM4 is described in **scheme 3.15**, and all the relevant results are shown in tables 3.9 & 3.10, figures 3.3.

Method 5

Finally, the procedure for method 5, RM5 is described in **scheme 3.16**, and all relevant results are shown in tables 3.9 & 3.10, figures 3.3

Table 3.9 shows that the different processing methods have pronounced effect on the binding efficiency with EPM5 method leading to the highest retention of AA as well as high grafting efficiency. The results demonstrate the higher effectiveness of the methods involving premixing of polymer and reactive agents over the methods which involve using sequential addition of the liquid reactive agents. Comparing the grafting efficiency achieved in F-EPDM1 and F-EPDMC (control, without the co-agent) indicates the effectiveness of the co-agent TRIS in enhancing the grafting reaction. The colour of all proceesed samples varied from light pale yellow, to brownish yellow, with white 'crumbled' envelopes present as defects intermeshed with the 'fleshy clean' proportion of the samples (examined in their original shaped as samples came out of the mixer). The white defects (w_d) were cut off from pre-weighed polymer (w_p) samples and their retention amount, calculate as percentage relative to the initial weight of the processed polymer $\{(w_d/w_p)x100\}$, was determined, see table 3.10. This amount was taken very qualitatively to reflect the extent of crosslinking/degradation reactions which are in direct competition with the targeted grafting reaction of AA to EPDM. Very high insoluble gel contents were found in all methods except in EPM2, see table 3.10, indicating the presence of high degree of crosslinking in the F-EPDM samples, rendering them unsuitable for future use in blending, see chapter 4. This situation warrant investigation on the effect of lower [T101] in order to obtain F-EPDM samples of balanced properties (between grafting efficiency and gel content), suitable to be used in the future blending work.

Table 3.9: Comparison of effect of the *five* processing methods EPM1, EPM2, EPM3 EPM4 and EPM5 [Scheme 3.12-3.16] on the grafting efficiency of AA to PS. Total amount of reactive modifiers in all methods were AA(6%), T101 (0.008MR), TRIS (0.6%); processing conditioons were 180^0C, 60rpm ,12min. The notions A,B,C,D,E, and F are described in scheme 3.8.

	Processing Methods and processed samples	Actual AA concentrations after processing (N.B.: Initial added amount of AA=6g/100g EPDM) #Stage A				
		Based on weight of functionalised EPDM (Actual remaining)		Based on initial [AA] added		% grafting efficiency
		Total [AA] (remaining after processing) (g/100g) #Stage B	Grafted [AA] (g/100g) #Stage C	% total [AA] (after processing) B/Ax100(%) #Stage D	% grafted [AA] C/Ax100(%) #Stage E	C/Bx100(%) #Stage F
EPM1	EPDM+AA+TRIS+T101--->F-EPD1	1.11	0.89	19	15	80
EPMC	EPDM+AA+T101------------->F-EPDC	0.64	0.41	11	7	64
EPM2	EPDM+TRIS ¦ }-------------------->F-EPD2 AA+T101	0.41	0.40	7	7	100
EPM3	EPDM+TRIS+T101 ¦ }------------>F-EPD3 AA+T101	0.68	0.68	11	11	100
EPM4	EPDM ¦ }------------>F-EPD4 AA+TRIS+T101	0.48	0.40	8	7	83
EPM5	EPDM+AA+TRIS+T101---->F-EPD5	1.20	1.02	20	17	85

Table 3.10: The colour and approximate crosslinked/degraded fraction of EPDM1, EPDM2, EPDM3, EPDM4 and EPDM5 samples obtained by processing mixtures of EPDM with AA, T101 and TRIS by methods EPM1 to EPM5.

Processing methods	**colour of undegraded fraction**	**Approximate crosslinking/degraded fraction (%)**	**Insoluble gel content (%)**
EPM1	brownish yellow	20	83
EPM2	light brownish yellow	20	22
EPM3	light pale yellow	40-60	87
EPM4	brownish yellow	10	79
EPM5	light brownish yellow	10	-

3.3.1 Effect of Processing Conditions

The effect of processing temperature, rotor speed and time were investigated by processing mixtures of EPDM with AA(6%), T101(0.005MR) and TRIS(0.6%) at variable parameters in question using method EPM1, see **scheme 3.17**. The results from IR analysis of the concentration of grafted AA/polyAA are given in **table 3.11** and the IR spectra are shown in figures 3.3b&c. The three processing parameters have significant effects on the binding concentration of AA ot EPDM, see table 3.11 and figure 3.3b,c&d. Table 3.11 has shown that processing conditions of 160°C for 10min at a speed of 45rpm have resulted in considerable increase in retention of AA and binding over the other conditions examined.

These conditions were therefore considered optimum and will be used in all work described in following section.

3.3.2. Effect of Chemical Composition

(a) Effect of peroxide concentration on the grafting efficiency of AA

The effect of proxide T101 concentration on the extent of grafting of AA to EPDM was investigated by processing mixtures containing variable concentration of T101 (0.0-0.006MR), using method EPM1,see **scheme 3.18**. The results on retained AA (bound and unbound) are presented in **table 3.12a**.Variation of torque with time, gel content and IR spectra are shown in **figure 3.4, table 3.12b** and **figure 3.5**. The peroxide has a prominant effect on the level of grafted AA to EPDM. Addition of 0.005MR, see table 3.11, has resulted in 90% increase (in VP5) (in binding

Table 3.11: Effect processing conditions (temperature, rotor speed and time) on retained AA/polyAA and grafted AA to EPDM of F-EPD1s prepared from mixtures of EPDM, AA(6%), T101(0.005MR), TRIS (0.5%) at 140°-200°C, 45-100rpm, 5-20min by EPM1 method.

	Actual AA concentration after processing (N.B.: Initial added amount of AA= 6g/100g PS)				
	Based on weight of of functionalised EPDM		Based on initial [AA] added		Grafting efficiency
Processing conditions	Total [AA] (remaining after processing) g/100g Stage B	Grafted [AA] g/100g Stage C	% total [AA] (after processing) B/Ax100(%) Stage D	% grafted [AA] C/Ax100(%) Stage E	C/Bx100(%) Stage F
Temperature (°C)					
140	0.6	0.4	9.2	6.7	75
160	2.2	1.8	36.5	30.3	83
180	1.6	1.3	25.8	22.0	85
200	0.7	0.6	11.3	10.0	88
100rpm, 11min					
Time (min)					
5	1.8	1.5	30	25	83
7	2.2	1.8	37	30	81
10	2.4	2.1	40	35	88
15	2.1	1.7	35	28	81
17	2.0	1.6	33	27	81
20	2.0	1.5	33	25	76
160°C, 100rpm					
Speed (rpm)					
45	2.5	2.4	41	36	87
60	1.8	1.5	30	25	82
80	1.3	1.1	22	18	85
100	2.4	2.1	39	35	89
160°C, 7min					

Table 3.12a: The effect of [T101] and [TRIS] on the grafted [AA] to EPDM in F-EPD1 samples processed at 160^0 C, 45rpm, 10min using in both cases AA(6%),T101(0.008MR), TRIS(0- 2.0%) in case of TRIS; of EPDM with AA(6%), TRIS(0.5), T101 (0.005-0.008MR) in case of T101. Composition with asterisk was without the TRIS, a control.

		Actual AA concentration after processing (N.B: Initial added amount of AA = 6g/100g EPDM; #stage A)				
	sample code	Based on weight of functionalised EPDM		Based on initial [AA] added		Grafting efficiency (%)
Concentration of agent and Coagent		Total [AA] (remaining after processing) g/100g #Stage B	Grafted [AA] g/100g #Stage C	% total [AA] (after processing) B/Ax100(%) #Stage D	% grafted [AA] C/Ax100(%) #Stage E	E/Dx100(%) # Stage F
RM1C [EPDM+AA(6%)]	VP0(C)	0.75	0.60	2.5	10	80
RM1[EPDM+AA(6%)+T101 (0.005-0.008MR) +TRIS(0.6%)]						
[T101]MR						
0.005						
0.006	VP5	0.15	0.12	22.5	18.8	84
0.007	VP6	0.17	0.15	26.0	22.8	88
0.008	VP7	0.15	0.12	23.0	18.3	80
	VP8	0.16	0.11	24.5	16.8	69
RM1[EPDM+AA(6%)+T101 (0.005MR)+TRIS (0-2%)]						
[TRIS] %						
0.0	VTR1	0.55	0.44	9	7.3	81
0.05	VTR2	1.5	1.20	20	20	80
0.1	VTR3	1.2	1.10	21	18	90
0.2	VTR4	1.2	1.16	23	19	90
0.3	VTR5	1.4	1.32	24	22	96
0.5	VTR6	1.6	1.45	27	24	89
0.6	VTR7	1.26	1.24	21	21	100
0.7	VTR8	1.31	1.14	22	19	86
1.0	VTR9	1.32	1.04	22	17	77
1.2	VTR10	1.40	1.05	23	18	68
1.5	VTR11	1.47	1.04	25	17	66
2.0	VTR12	1.62	1.10	27	18	

concentration as compared to the binding achieved as a result in mechanoscission in mixture of EPDM with AA [VP0(C)]. Maximum retention and grafting was achieved at 0.006MR. The insoluble gel of the F-EPD samples are much lower at [T101] lower than 0.008MR, see table 3.11b . At 0.005MR the gel is reasonably low and the F-EPD was processable.

Table 3.12b: Effect of [T101] on insoluble gel of the the F-EPD samples [EPDM+AA(6%)+T101(0-0.008MR)+TRIS(0.5%)] after 24hrs extraction with xylene, see scheme 3.9 partb.

Peroxide T101 concentration (MR)	Insoluble gel content (%)
0.00	0
0.003	32
0.004	35
0.005	43
0.006	63
0.008	83

b) Effect of coagent concentration on the grafting efficiency of AA

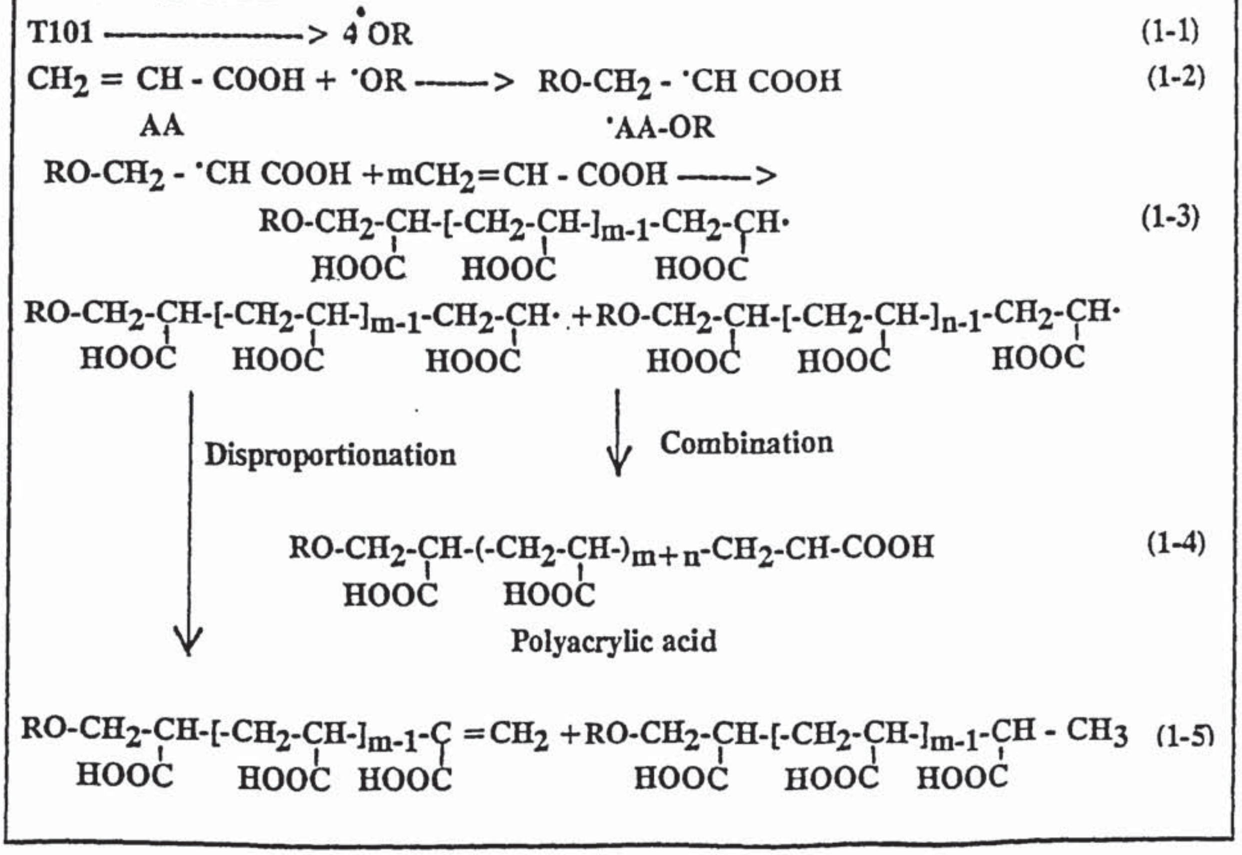
Similarly effect of coagent TRIS concentration was investigated by varying the concentration of the coagent in the reaction mixtures, as described in detailed in **Scheme 3.18** , The results on retained AA (bound and unbound) are presented in table 3.12:, torque against time in **figure 3.6**, IR spectra in **figure 33e.** It is clear that the coagent TRIS has strong influence on the binding concentration. Maximum effect was achieved, however, at very low concentration . Addition of 0.05% TRIS has resulted in almost 130% increasing retention of AA and its in binding concentration, However, no significant change in the binding concentration was affected by increasing TRIS to higher concentration. The maximum binding however, was achieved at 0.5% [TRIS] and this concentration will be used in future work. The incorporation of TRIS has variable effect on torque, see **figure 3.6.** In the concentration range of 0-0.4%, the effect on the maximum torque was small. Increasing to 0.5% and above has caused increase in the peak, perhaps due to greater extent of crosslinking and grafting.

3 .4 DISCUSSION

3.4.1 Effect of Chemical Composition, Methods and Processing on Grafting Efficiency of AA to PS

The use of a peroxide to initiate the formation of radicals is essential for the functionalisation of AA to PS. Although it was shown previously (39) that the effect of shear alone (formation of radical via mechano-scission) does lead to some grafting of functionalised agents onto hydrocarbon polymers, results from table 3.3 and figure 3.7 show clearly that the amount of AA retained in the polymer in the absence of peroxide is very small, while the use of increasing concentration of a peroxide increases the level of retention of AA considerably; addition of only 0.04MR T101 leads to an increase of more than an order of magnitude of the amount of AA retained (see figure 3.7, stage D). In the absence of the co-agent, the peroxide concentration affected the physical appearance of the F-PS samples (see table 3.6, page 72). The progressively cloudier appearance observed with increasing [T101] suggests a corresponding increase in intensity of reactions resulting in products which were not compatible with PS, probably consisted of homopolymer of AA, see reaction scheme 1.

Reaction scheme 1



$$T101 \longrightarrow 4\,{}^{\bullet}OR \qquad (1\text{-}1)$$

$$\underset{AA}{CH_2 = CH - COOH} + {}^{\cdot}OR \longrightarrow \underset{{}^{\cdot}AA\text{-}OR}{RO\text{-}CH_2 - {}^{\cdot}CH\,COOH} \qquad (1\text{-}2)$$

$$RO\text{-}CH_2 - {}^{\cdot}CH\,COOH + mCH_2{=}CH - COOH \longrightarrow RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}[\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}]_{m-1}\text{-}CH_2\text{-}\underset{HOOC}{CH}{\cdot} \qquad (1\text{-}3)$$

$$RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}[\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}]_{m-1}\text{-}CH_2\text{-}\underset{HOOC}{CH}{\cdot} + RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}[\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}]_{n-1}\text{-}CH_2\text{-}\underset{HOOC}{CH}{\cdot}$$

Disproportionation

Combination

$$RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}(\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-})_{m+n}\text{-}CH_2\text{-}CH\text{-}COOH \qquad (1\text{-}4)$$

Polyacrylic acid

$$RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}[\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}]_{m-1}\text{-}\underset{HOOC}{C}{=}CH_2 + RO\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}[\text{-}CH_2\text{-}\underset{HOOC}{CH}\text{-}]_{m-1}\text{-}\underset{HOOC}{CH} - CH_3 \qquad (1\text{-}5)$$

The use of DVB has led to changing the appearance of the samples from opaque to semi-transparent, (see samples 4 and 5 in table 3.5), most likely due to an increasing level of the grafted AA to PS (via DVB) at the expense of the extent of homopolymerisation hence decreasing the incompatibility level in the polymer system. The AA when present alone, did attack the metal surface lining of the mixer, see table 3.6 , resulting in formation of a trace amount of ferric acrylate, see **reaction scheme 2**, which has imparted the brown colour to the polymer samples. The PS sample processed with 0.005MR T101 (no.3) was found to contain tenfold lower concentration of iron than the one processed without peroxide. The addition of small concentration of peroxide has most probably promoted the speed of the homopolymerisation reaction with concomitant grafting reactions of AA hence reducing the chance of conversion into iron acrylate.

Rreaction scheme 2

$$\underset{\text{AA}}{6CH_2 = CH\text{-}\ COOH} \dashrightarrow CH_2 = CH\text{-}\ COO^- + 6H^+ \qquad \text{(R5)}$$

$$2\ Fe\ + 6H^+ \dashrightarrow 3\ H_2\ + 2Fe^{3+} \qquad \text{(R6)}$$

$$2Fe^{+3} + 6\ CH_2 = CH\text{-}\ COO^- \dashrightarrow \underset{\text{ferric acrylate (brown)}}{2\ (CH_2 = CH - COO)_3Fe} \qquad \text{(R7)}$$

Highest level of retention of AA was obtained by using methods 1 and 5 (see **figure 3.7**) which involved direct addition of all additives compared to sequential addition of the different additives, used by methods 2 to 4, which the latter method involved short time opening of the mixer , which momentarily exposed the polymer to the atmosphere, and may have contributed to some physical loss of the liquid additives. The initial low temperature used in the temperature programme employed by method 5 offered additional mixing advantage and lowering the probability of physical loss which led to enhanced efficiency of mixing of the additives with polymer and this must have contributed to the highest level of retention of AA observed in this method, see figure 3.7.

In all processing methods used, the effect of the co-agent, DVB, on the level of retention and grafting efficiency of AA in PS melt was remarkable. The grafting efficiency at peroxide concentration of 0.04MR was 100% in the presence of DVB compared to only 50% in its absence (see figure 3.7). Higher concentration of DVB gives rise to both higher level of retention of AA in the polymer after processing (Stage

D) and higher level of grafting (Stage E), see figure 3.8. The presence of co-agent DVB also affects the shape of the torque peak. Figure 3.1 shows that the use of DVB is responsible for the appearance of a second torque peak (absent when PS is processed in absence of DVB). The torque peak levels off (to the same level of polymer control or processed with AA) ,in all cases, at the end of the processing operation (after 10min). This suggests that the polymer may initially be involved in some crosslinking reactions involving DVB and AA (responsible for the torque maximum) but the crosslinked polymer undergoes some preferential chain scission leading to a drop in torque values at the end of the processing. Figure 3.11 and table 3.12 show the changes in torque (expressed as the different between the maximum of the second tq peak to the final torque) for the functionalised PS samples processed by different methods in the presence of the co-agents. The significant increase in torque peak obtained suggests greater extent of interaction between the agent/ co-agent and polymer. Multifunctional co-agents, such as DVB and TRIS, have been shown in previous work at Aston (109,110,111) to lead to a torque peak when processed with mono-functional agents, e.g. antioxidant, and this was attributed to the initial interaction between agent/co-agent and polymer which lead to some crosslinking, but the torque peak was shown to reduce to the level of the unmodified polymer at the end of processing suggesting some rearrangement of the crosslinked graft to form soluble polymer(110) . Similarly, in this work ,table 3.4 shows that there is no gel in the finally processed PS by all methods, except for method 1 which leads lead to very small amount of gel (~ 5%) . The effect of increasing peroxide concentration on the torque peak is shown to mainly decrease the time required to reach the torque peak maximum, see figures 3.2 (see also table 3.14) and this corresponds to a highest level of retention of AA and grafting efficiency (see also table 3.8).

Table 3.13: Effect of [T101] on time to reach maximum torque, maximum torque and final torque for mixture of PS with AA (6%), T101(0.0-0.04MR) and DVB(3%); processed at 200°C,100rpm, 10min; PM1 method.

[T101] MR	Time to reach maximum torque (min)	Height of Maximum torque (Nm)	Final torque (Nm)
0	2	6.4	6
0.01	4.5	13	13
0.02	3.25	13.2	11
0.03	2.5	12	9
0.04	2.3	13	8.5

Examining the effect of different additives on the melt stability of PS processed by method 1, see figure 3.12, reveals that the effect of peroxide (sample PSC-4) on the AA modified PS (PSC-2) is to increase the MFI, i.e. decrease molecular weight (MW). Peroxides are known ([112]) to lead to chain scission in PS. Addition of DVB (F-PS1) to the AA-peroxide-polymer decreases the MFI suggesting some crosslinking reaction between DVB-AA-polymer which is expected from the use of a multifunctional co-agent ([110,111]). This is further confirmed by the fact that addition of DVB (PSC-3) to on an AA-Modified PS containing no peroxide (PSC-2) leads to a lowering of the MFI, indicating some crosslinking via the DVB·. Reaction of PS melt with DVB in the presence of peroxide (PSC-5) leads to a small amount of gel (~1%) in the final polymer. However the addition of AA to this DVB-ROOR-modified PS (F-PS1) leads to higher gel formation (~5%) and to a higher MFI value (lower MW) suggesting that the grafting between DVB-AA and PS is most likely taking place at the expense of the DVB-PS crosslinking reaction hence leading to the high retention and grafting of AA onto PS, see figure 3.7 which shows clearly that the use of DVB leads to grafting of all the retained AA while a sample processed in its absence , looses half of the total retained AA after extraction. This is a very significant improvement to the grafting efficiency of the monofunctional modifier AA, and a strong evidence of the effectiveness of the DVB as a coagent.

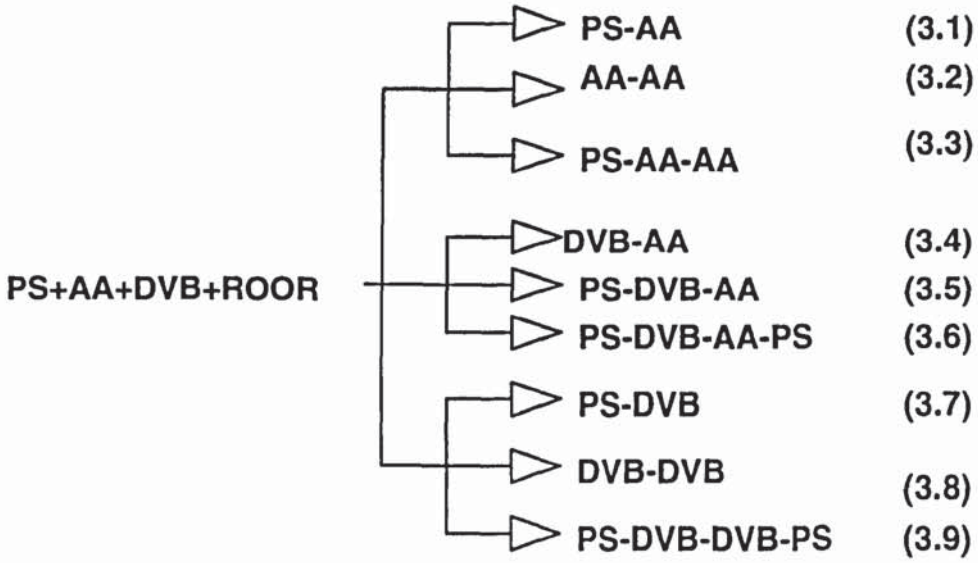
Optimisation of processing conditions in a fixed composition of PS containing 6%AA, 0.04MR T101and 3%DVB has led to high level of retention of AA and grafting efficiency (see table 3.4). Optimum processing conditions which lead to most effective AA functionalisation on PS were **200°C, 10min and 100rpm.**

3.4.2 Nature of the reactions involved in the reactive processing of PS with AA in presence and absence of coagent DVB.

The possible reactions which can take place during the reactive processing of PS with AA are given in the **reaction scheme 3.3.** Since two functional monomers were involved in all the processing methods used, a complete presentation of reactions involved must be more complicated than what is described in this very simplified scheme. The effect of T101under the high melt conditions used in all processing methods is to generate the free radicals in the polymer and the reactive modifiers. Once radicals are produced in the polymer melt, various reactions can take place, including homopolymerisation, copolymerisation, grafting and crosslinking, as summarised below (see scheme 3.3):

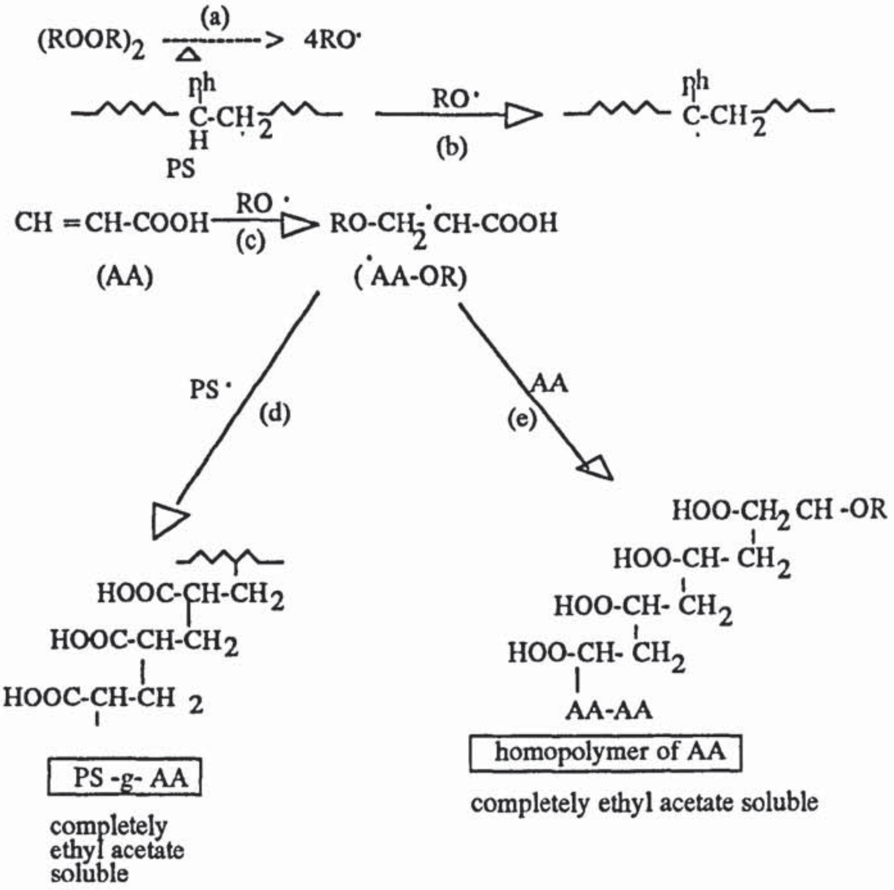
1. AA may graft to PS with or without coagent (see reaction 3.1 and 3.5)

2. AA can oligomerise or homopolymerise and then this may become grafted to PS backbone (see reaction 3.2 and 3.3).
3. AA can copolymerise with DVB (coagent), and this can be followed by grafting on the PS backbone (see reaction 3.4 and 3.5). This may then form crosslinking with PS (see reaction 3.6)
4. The co-agent can graft onto PS (see reaction 3.7) or undergo homopolymerisation and then may terminated by crosslinking (see reaction 3.8 and 3.9).

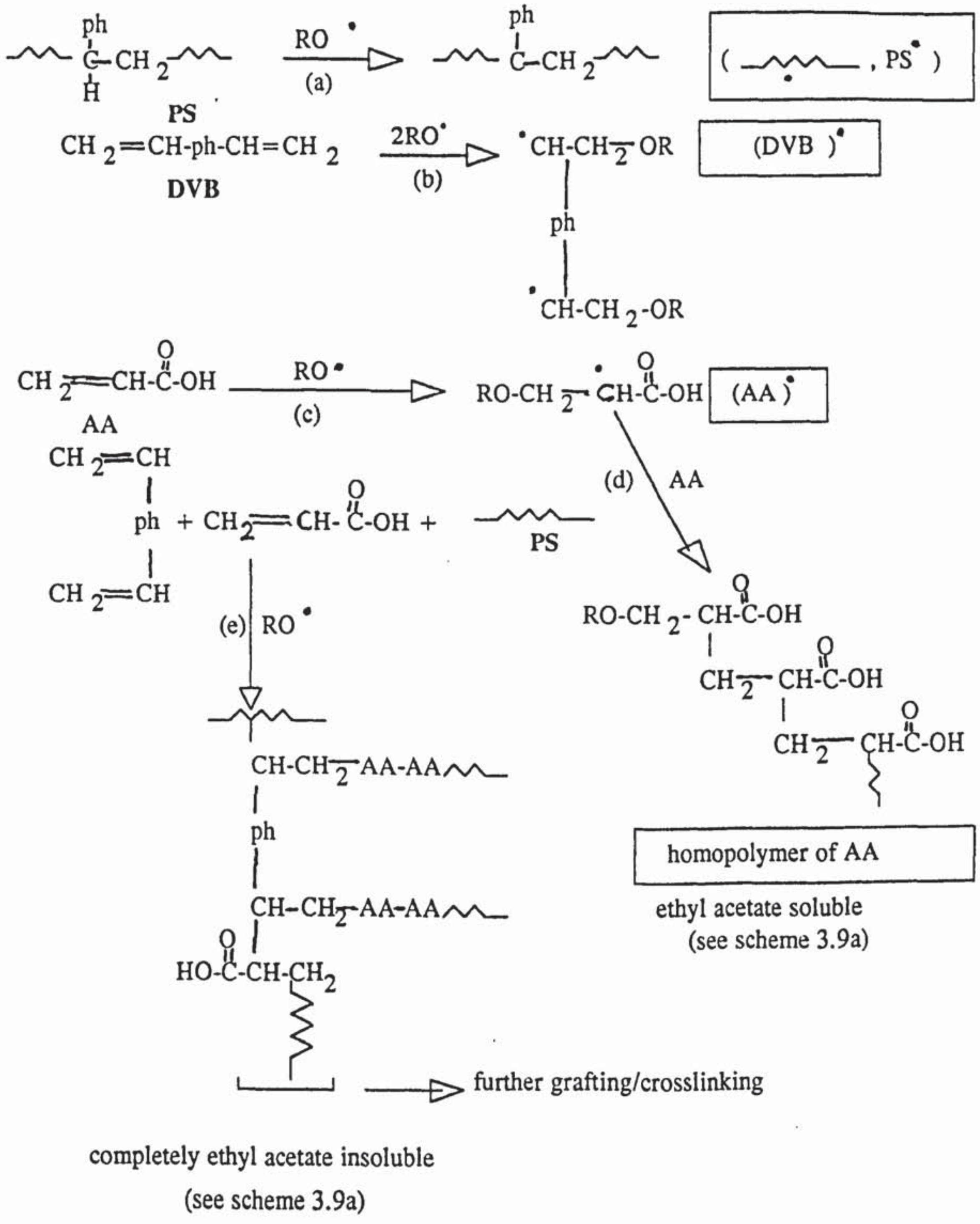


Reaction Scheme 3.3: general reaction scheme showing the possible end products of homopolymerisation, copolymerisation and crosslinking reactions for mixture of PS with AA, T101 and DVB processed at 180°C, 60rpm, 10min.

More detailed reactions pathways leading to important products are shown in schemes reaction scheme 3.4 (without DVB) and 3.5 (with DVB); (66).



Reaction scheme 3.4: Suggested reaction mechanism which occur during reactive processing of PS with AA in the absence of co-agent but in the presence of peroxide



Reaction scheme 3.5: Suggested reaction mechanism for melt reaction of PS with AA processed in the presence of DVB and peroxide.

3.4.3 Effect of Processing, method, Conditions and Chemical Composition on Grafting Efficiency of AA to EPDM

Acrylic acid functionalisation of EPDM was carried out by an approach very similar to that described for PS in the previous section. However, the co-agent used in this case was the trifunctional TRIS. Similar to functionalisation of PS, five different processing methods were used for EPDM. Figure 3.11 shows clearly, that again, the direct addition of methods 1&5 lead to the highest level of retention of AA in the polymer and a high efficiency of grafting which again leads to the conclusion that the main part of the retained AA becomes grafted onto the polymer. Optimisation of the processing conditions and chemical composition (see figures 3.12-3.14) lead to doubling the amount of the retained AA in the polymer (~40%) with very high grafting efficiency (~88%), see figures 3.13.

The addition of TRIS again leads to formation of a torque peak maximum, see figure 3.6 and table 3.14 which can be taken as indicative of different chemical reactions taking place during the reactive processing involving the multifunctional TRIS. Table 3.14 shows that the peroxide concentration only shifts the time to the occurrence of the peak maximum. The importance of the use of TRIS in both increasing the concentration of retained AA and improving the grafting reaction cannot be overemphasised.

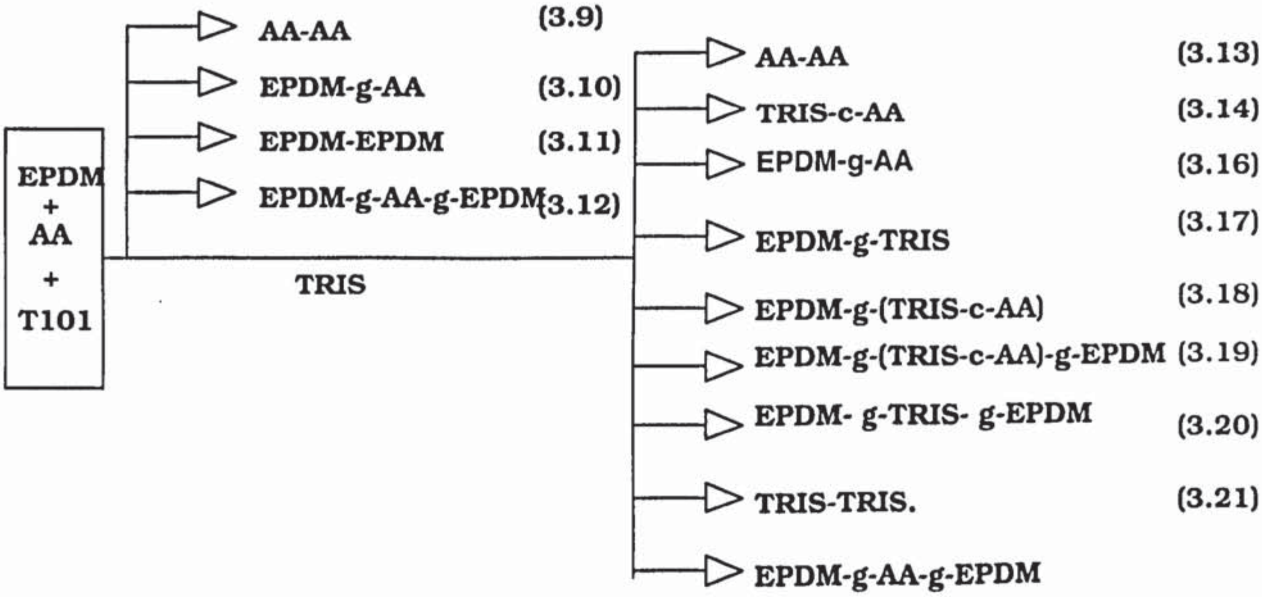
Table 3.14: The effects of [T101]and [TRIS] on second maximum torque and final torque of torque-time curves of mixtures of EPDM, AA(6%), T101(0.006-0.008MR), TRIS (0%, 0.6%), processed at 180^{o}C, 60rpm, 11min.

[T101] (MR)	[TRIS] (%)	Time at peak (min)	peak value (Nm)	Final torque value (Nm)
0.006	0.6	5.0	52	45.5
0.007	0.6	5.5	57	49
0.008	0.6	6.0	56	53
0.007C	0.0	9.0	58	57

The probable products formed from reactions which can take place in the melt is shown in simplified **General Reaction Scheme 3.6.** as discussed below:

In the absence of TRIS:

1. The AA· may homopolymerise or oligomerise and then terminated by combination or disproportionation or grafted to EPDM (see reactions 3.9 and 3.10).
2. The AA· may react with EPDM via the polymer unsaturation and then terminate by reacting with EPDM· resulting in crosslinking (see reaction 3.12).
3. EPDM· may be terminated by combination, resulting in crosslinking (see reaction 3.11).

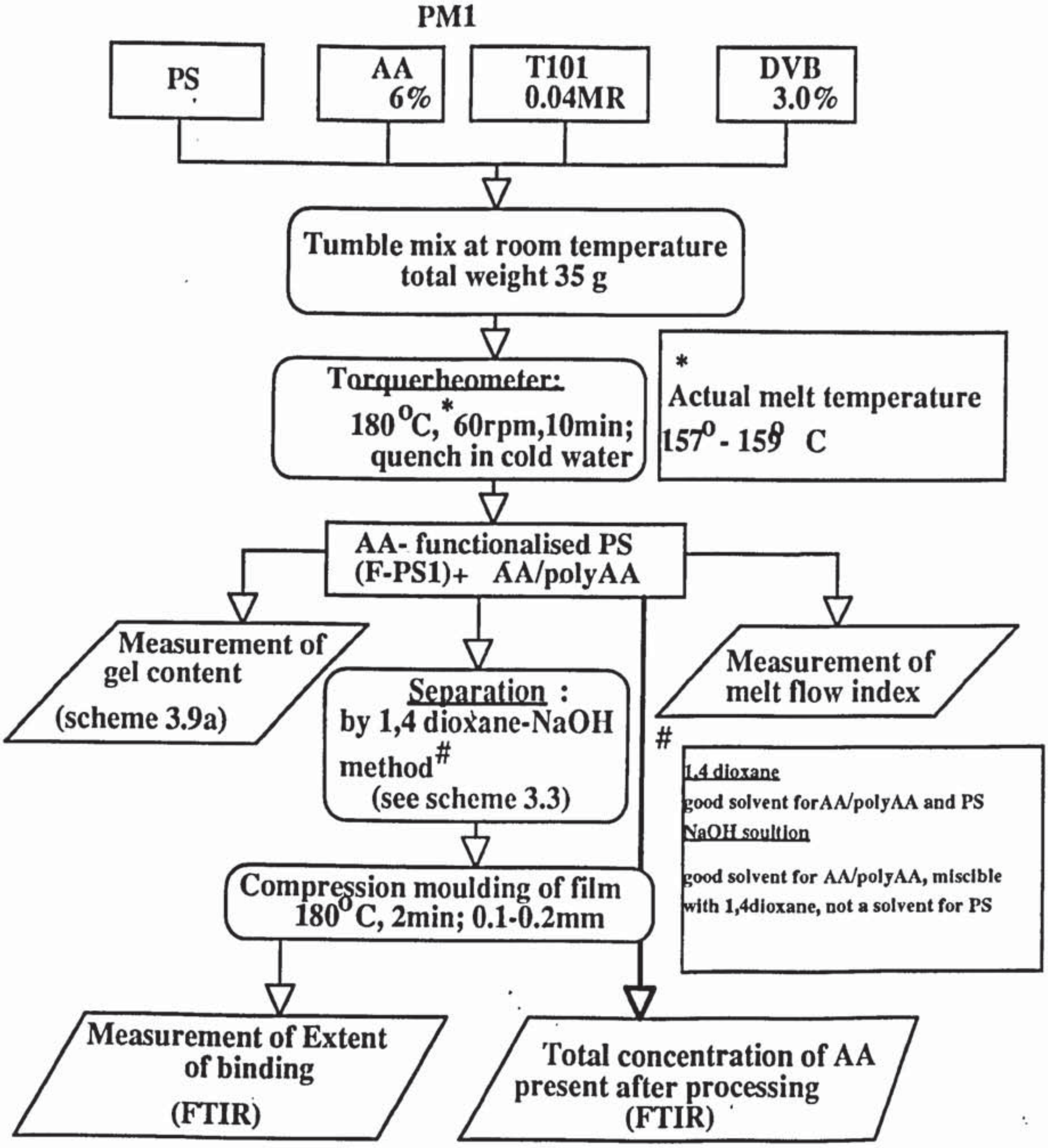


Reaction scheme 3.6: Simplified possible reaction pathway during reactive processing of EPDM with AA in presence and absence of a co-agent

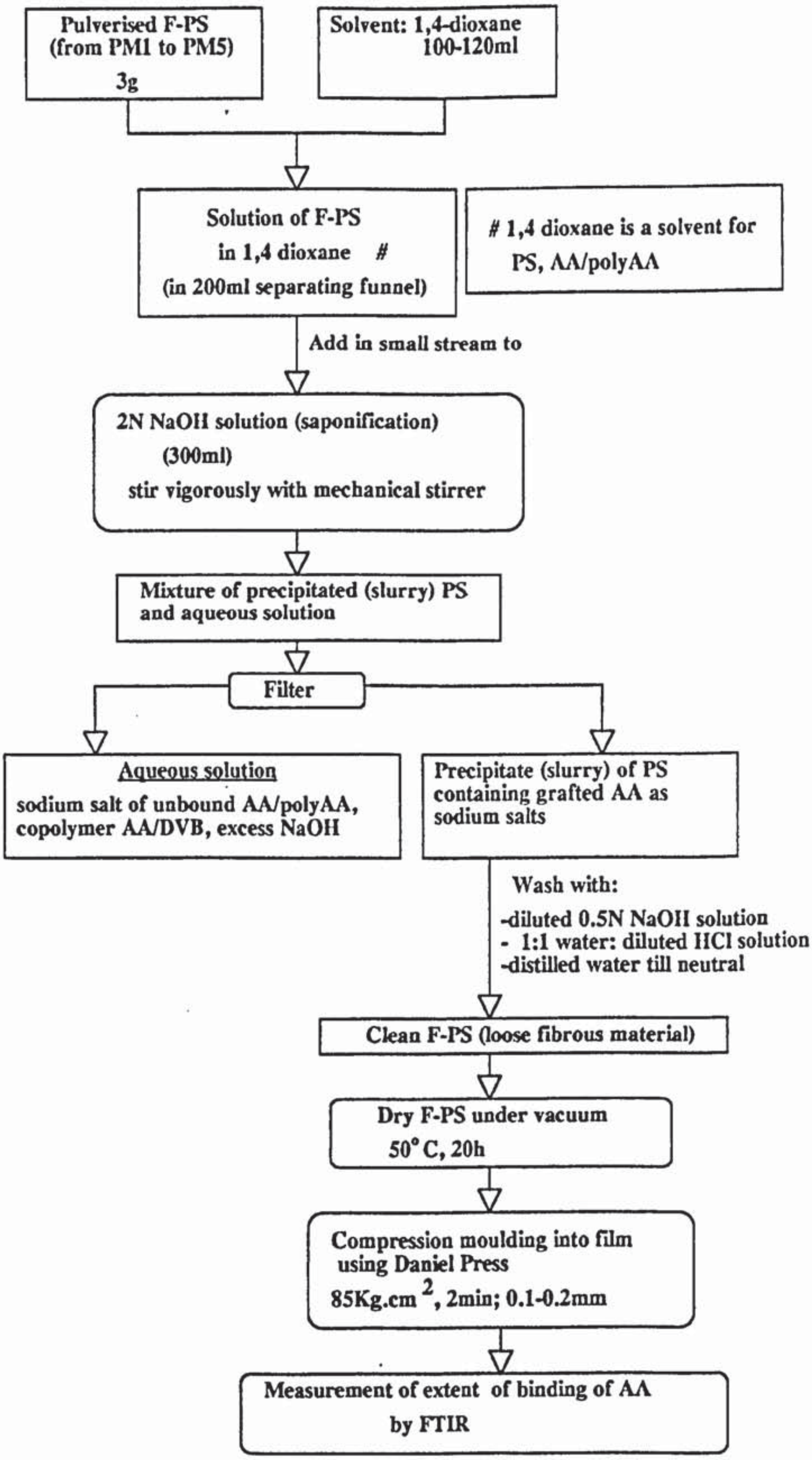
In the presence of TRIS:

4. The AA· and TRIS· may homopolymerise or oligomerise and then terminate by combination or disproportionation (see reactions 3.13 and 3.19) , or grafting to EPDM (see reactions 3.16 and 3.17).
5. The AA· may copolymerise with TRIS, follow by termination via disproportionation or grafting to EPDM backbone (see reactions 3.14 and 3.18).
6. The AA· may copolymerise with TRIS, follow by grafting and crosslinking with EPDM (see reaction 3.19).
7. The AA· and TRIS· may react with EPDM and EPDM· resulting in crosslinking (see reactions 3.20 and 3.21).

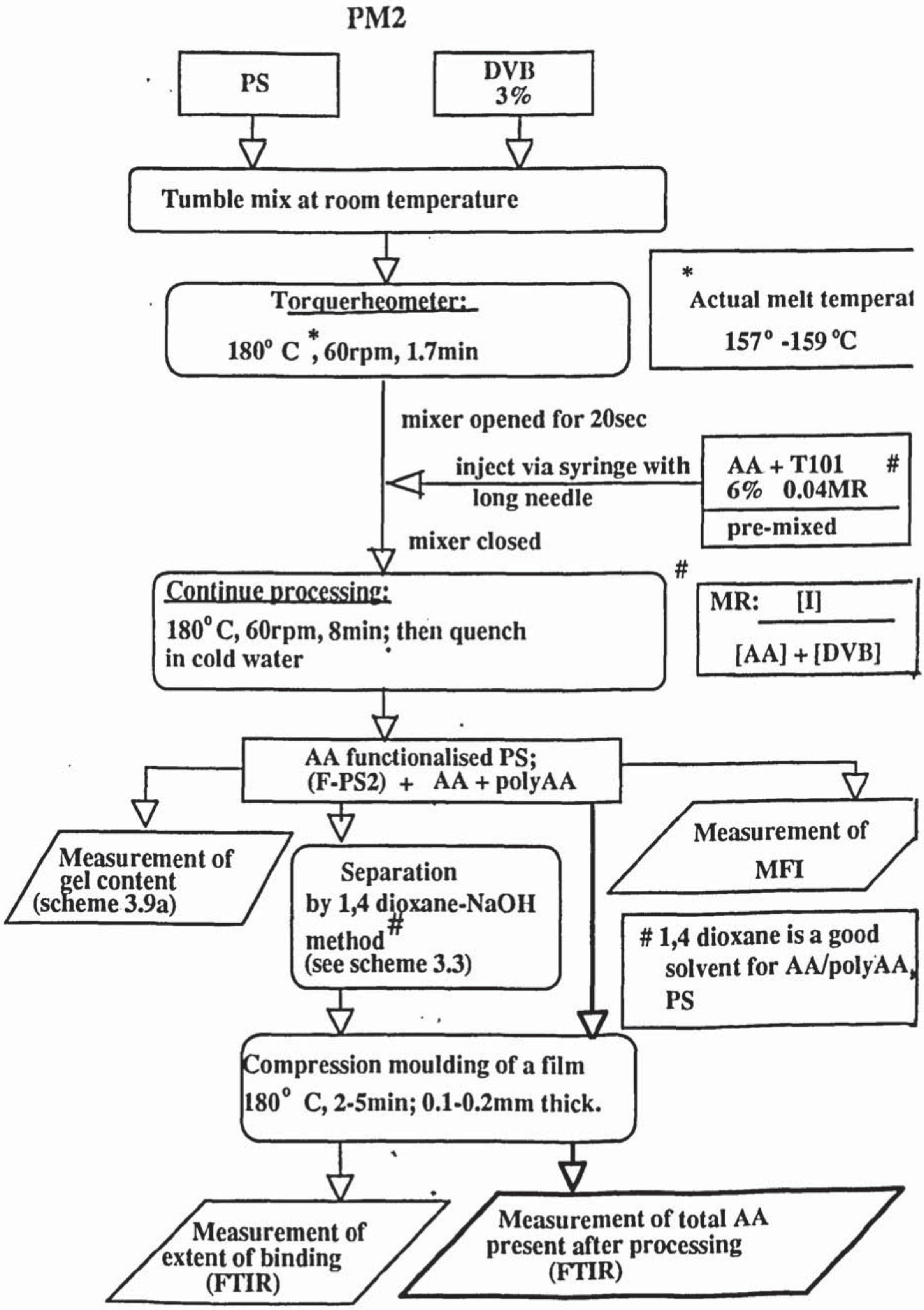
All reaction products which involve AA being grafting to EPDM, as homo- or copolymer with TRIS; and also the crosslinked macromolecules which contains AA, would result in variable degrees of functionalisation to the EPDM. Reaction scheme 3.7 shows more details the nature of the important reaction involved.



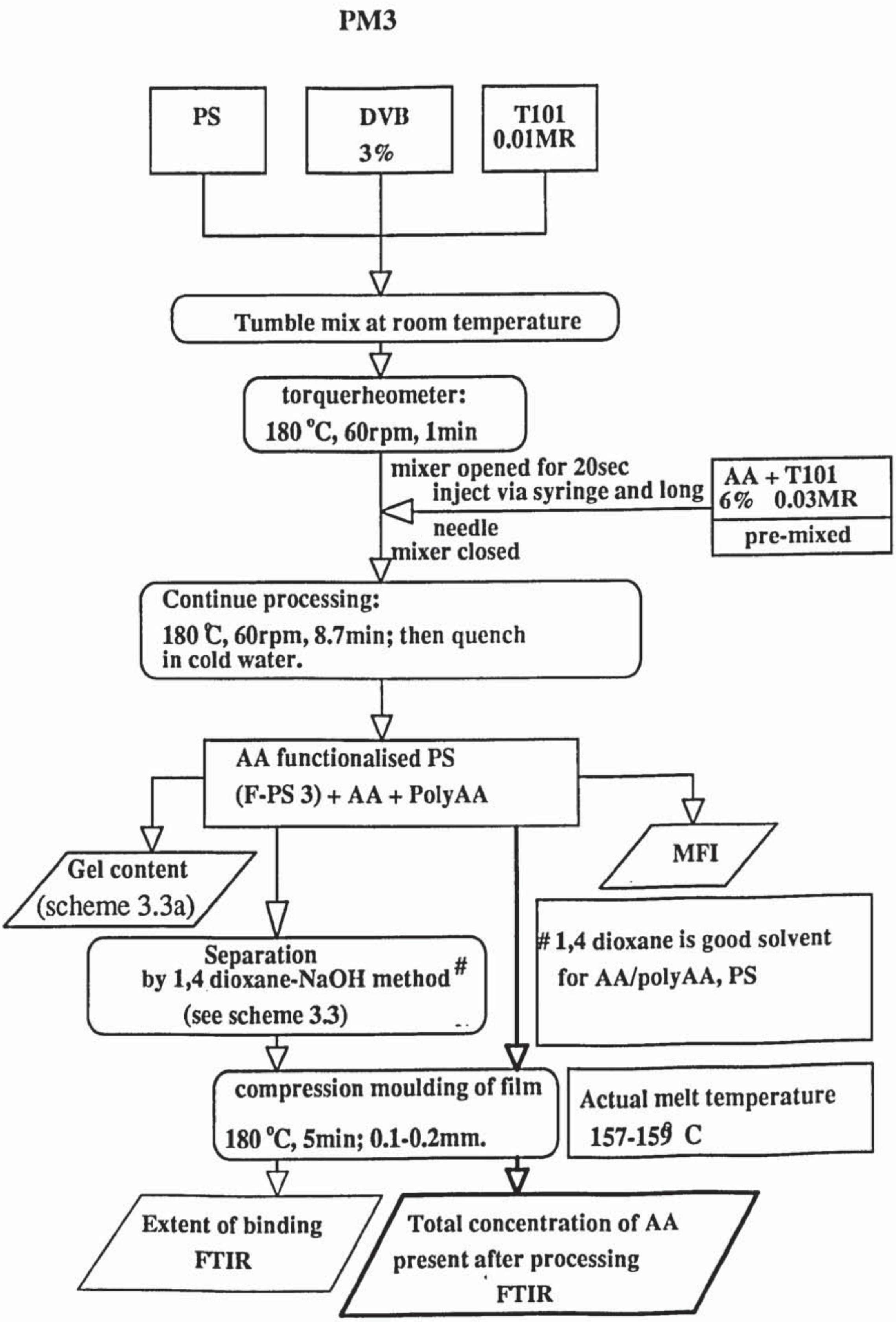
Scheme 3.2: Flowchart for the procedure used for functionalisation of PS by method PM1 and the subsequent treatment and analysis of the F-PS1.



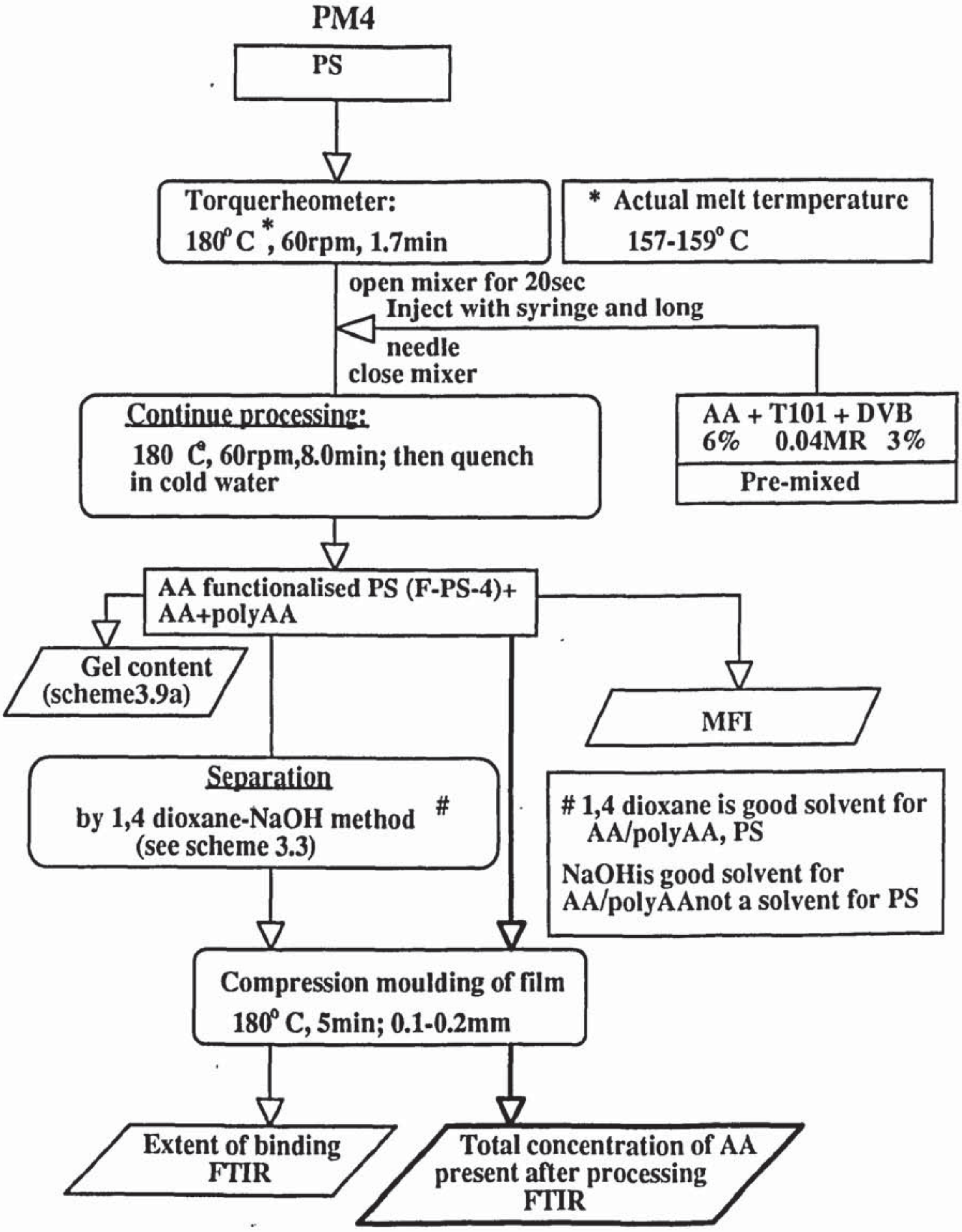
Scheme 3.3: Separation of unbound AA/polyAA from F-PS and determination of concentration of grafted AA to PS by FTIR spectroscopy



Scheme 3.4: Flowchart for functionalisation of PS by method PM2
and the subsequent treatment and analysis of the F-PS2

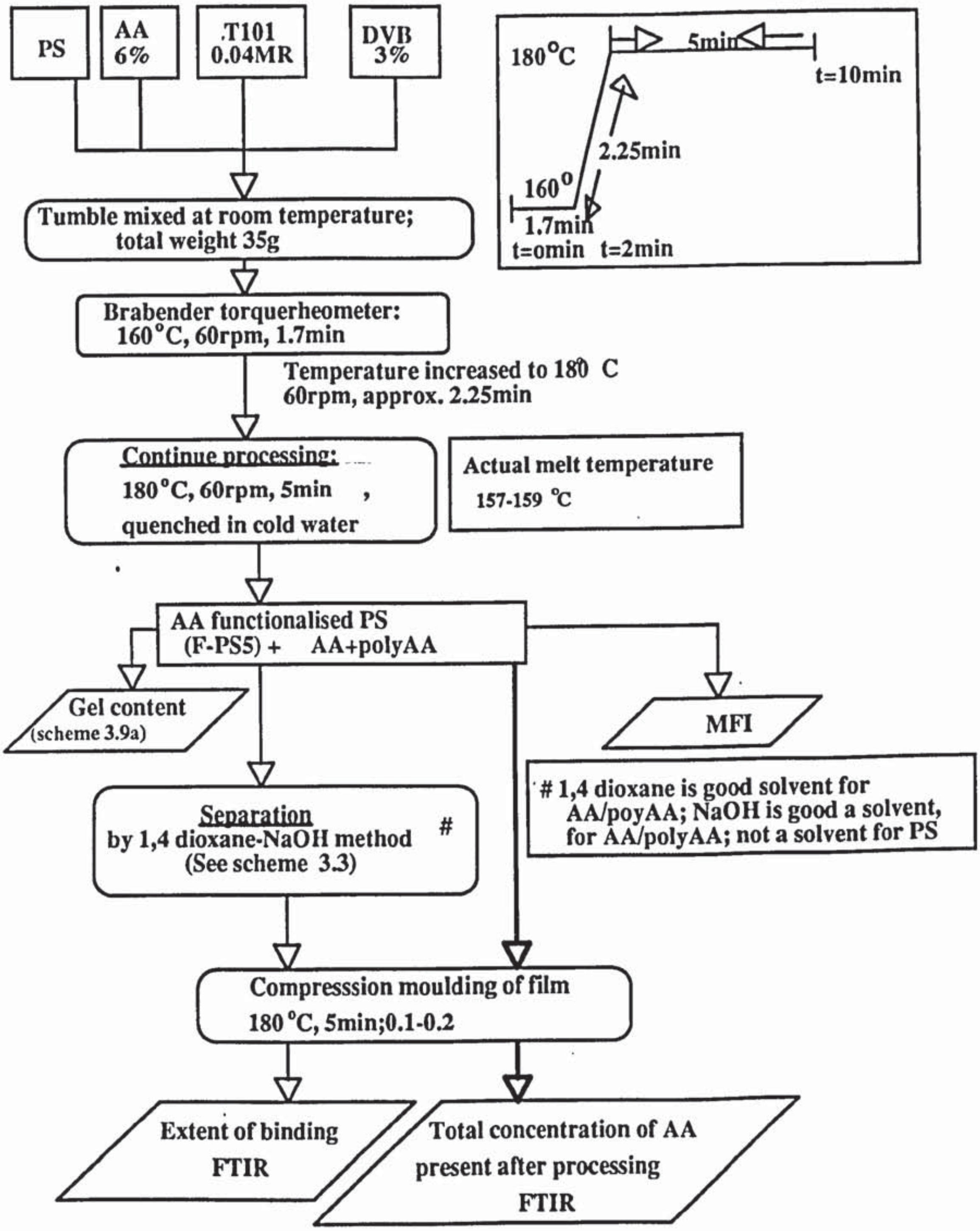


Scheme 3.5: Flowchart of procedure used for functionalisation of PS by method PM3 and subsequent treatment and analysis of F-PS3 sample.

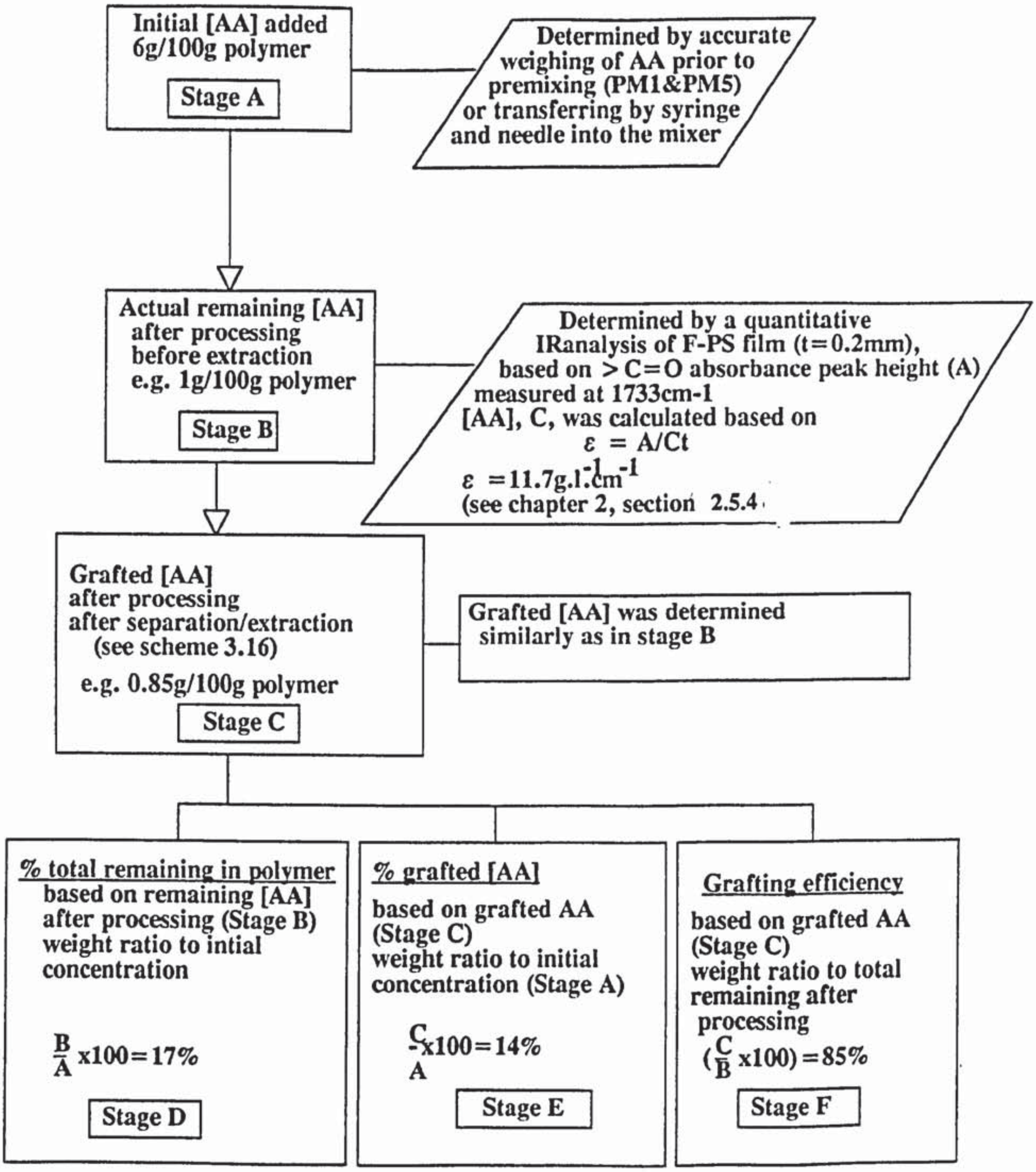


Scheme 3.6: Flowchart for procedure used for functionalisation of PS by method PM4 and subsequent treatment and analysis of the F- PS4

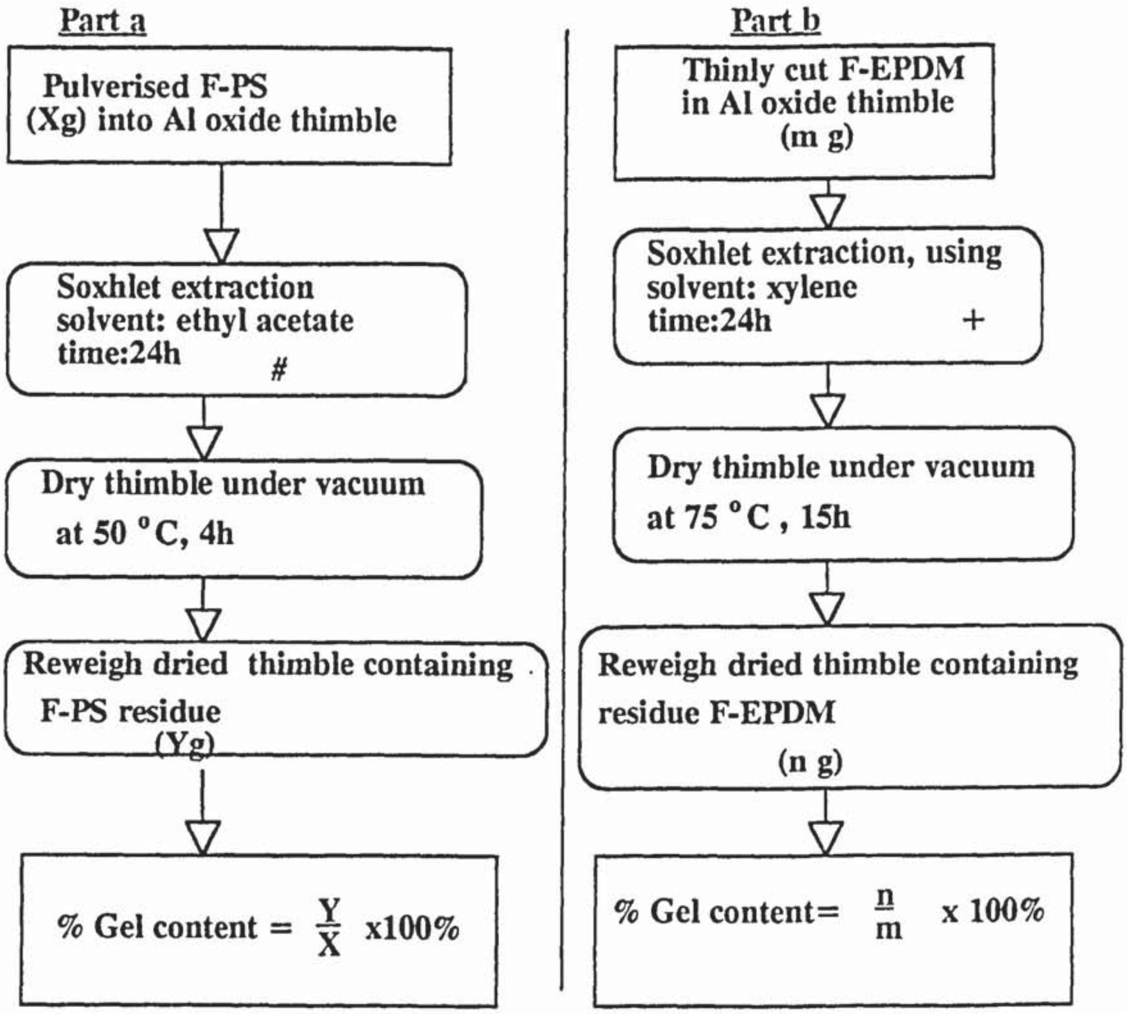
PM5



Scheme 3.7: Flowchart for procedure used for functionalisation of PS by method PM5 and subsequent treatment and analysis of the F-PS5.



Scheme 3.8: Schematic representation of definitions of stages A to F and method of calculation of the concentration of AA in functionalised polymer.

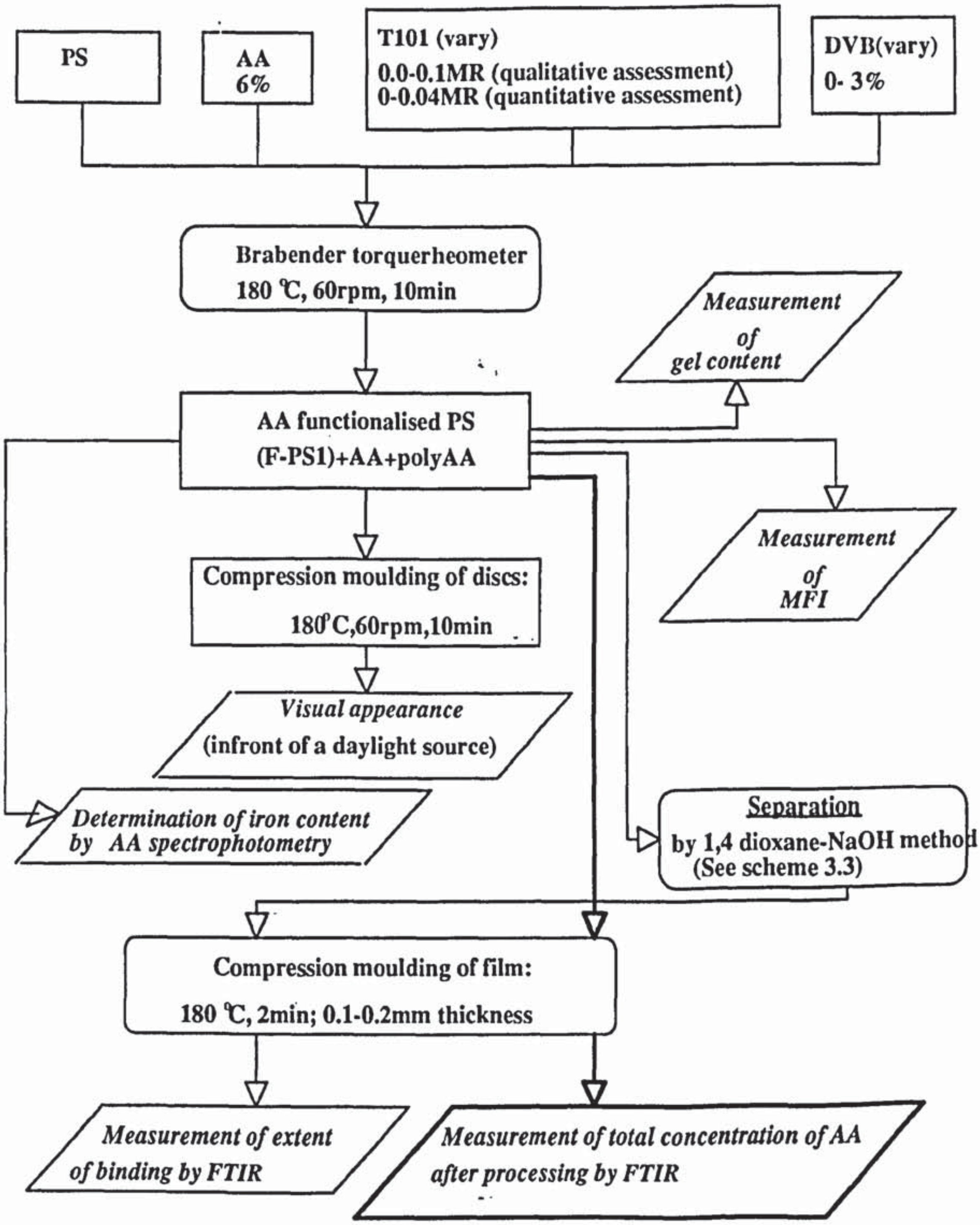


#Ps is very soluble in ethyl acetate at reflux temperature

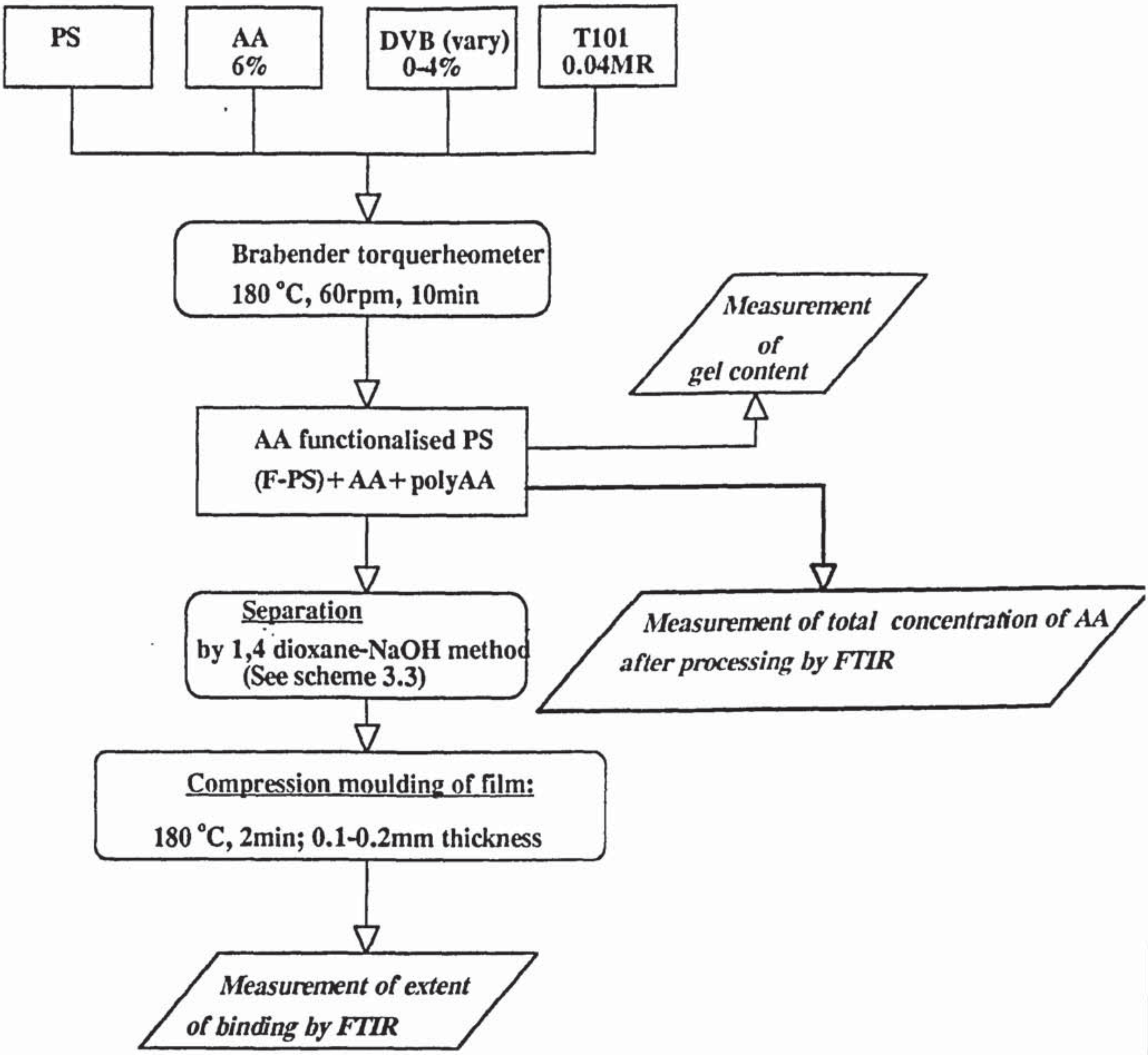
+EPDM is soluble in xylene at reflux temperature

Scheme 3.9(a&b): Flowchart for determination of gel content for F-PS (in part a) and F-EPDM (in part b)

PM1

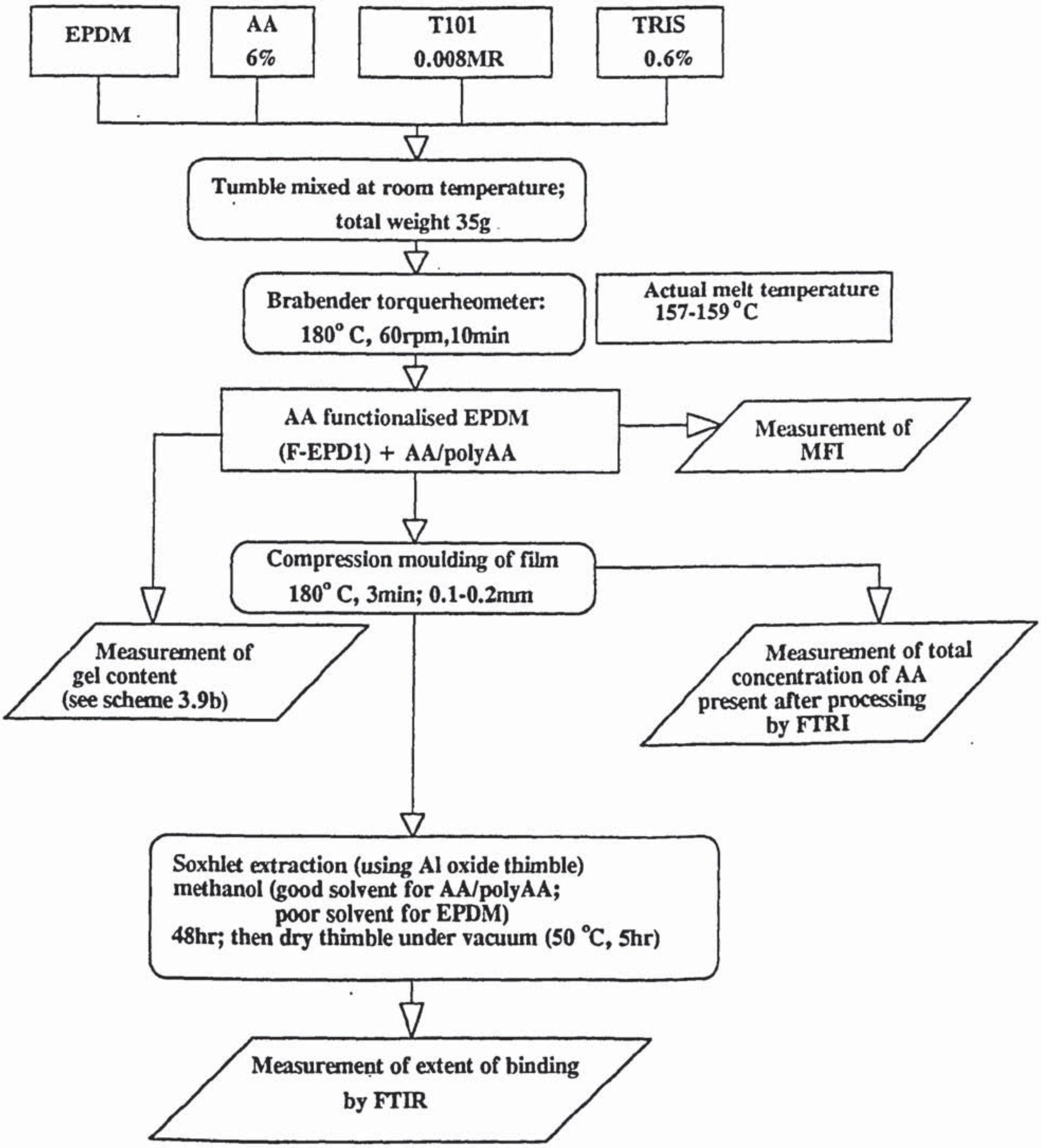


Scheme 3.10: Flowchart of experiments used for qualitative and quantitative assessment of effect of peroxide concentration on the extent of grafting of AA to PS processing condition was 200 C, 100rpm, 10min.

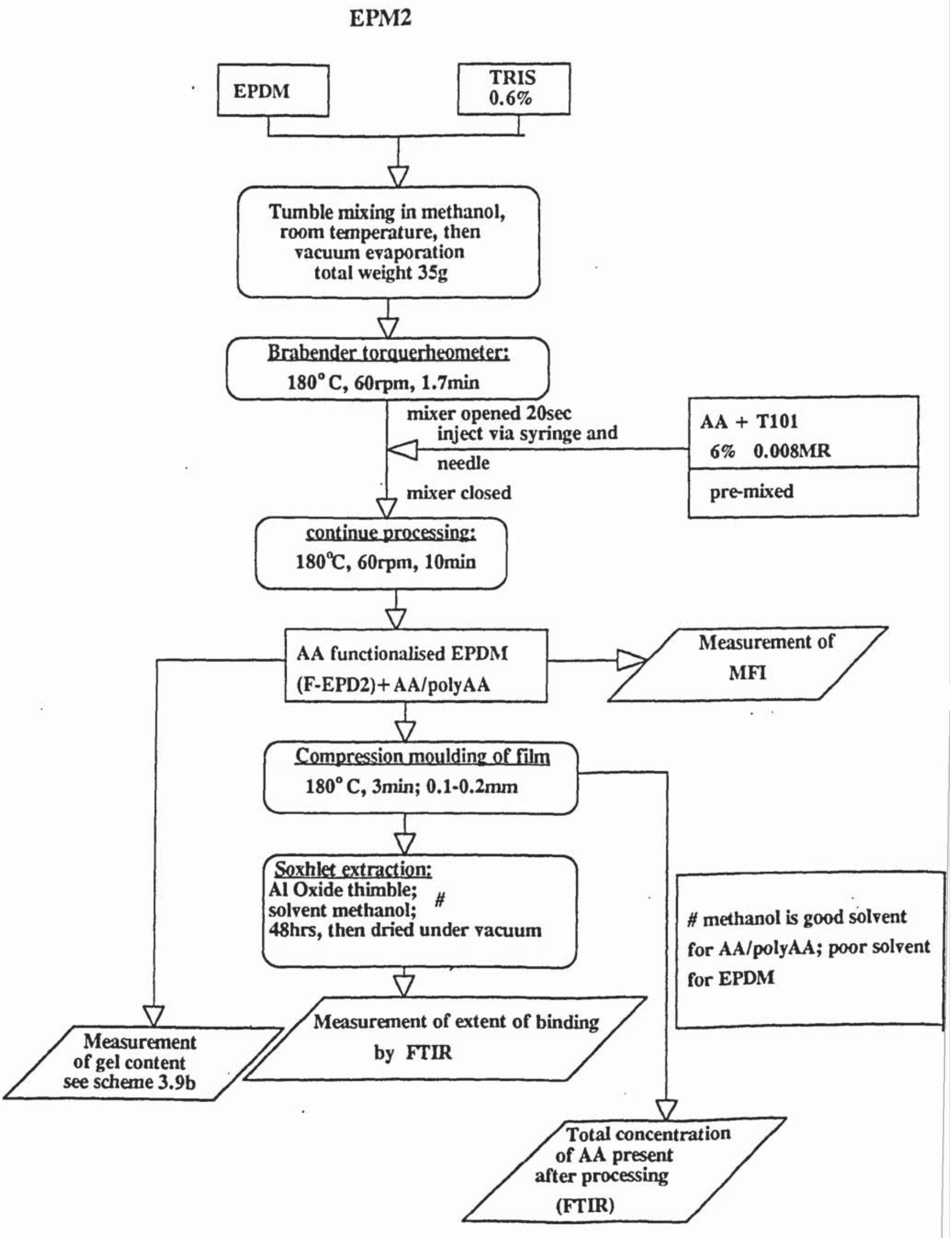


Scheme 3.11: Flowchart of experiments to assess effect of DVB concentration on on the extent of grafting of AA to PS. Processing conditions: 180° C, 60rpm,10min.

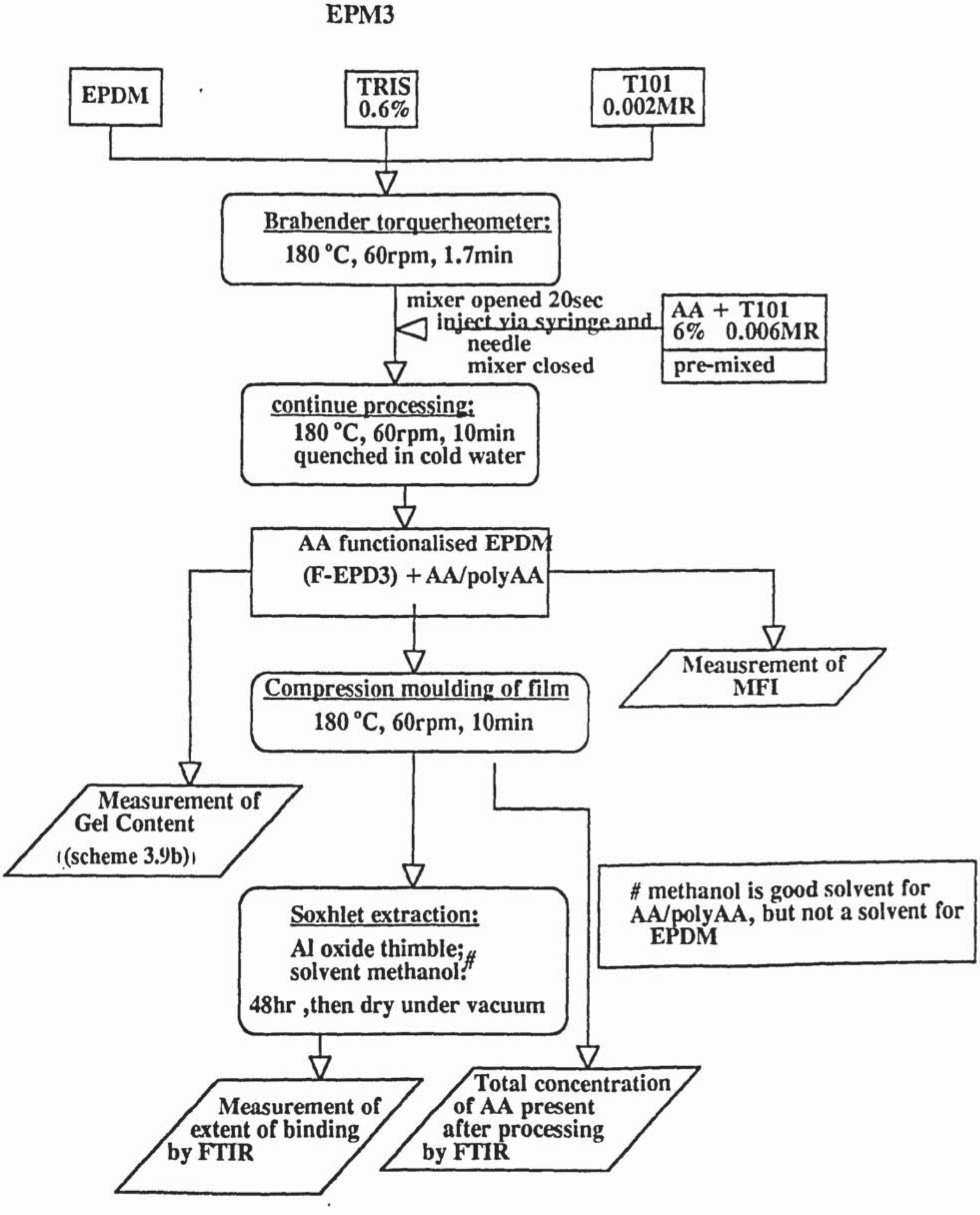
EPM1



Scheme 3.12:Flowchart for functionalisation of EPDM with AA by method EPM1 from mixture of EPDM, AA(6%), T101(0.008MR), TRIS(0.6%); 180°C, 60rpm, 10min; and subsequent treatment and analysis of the F-EPD1.

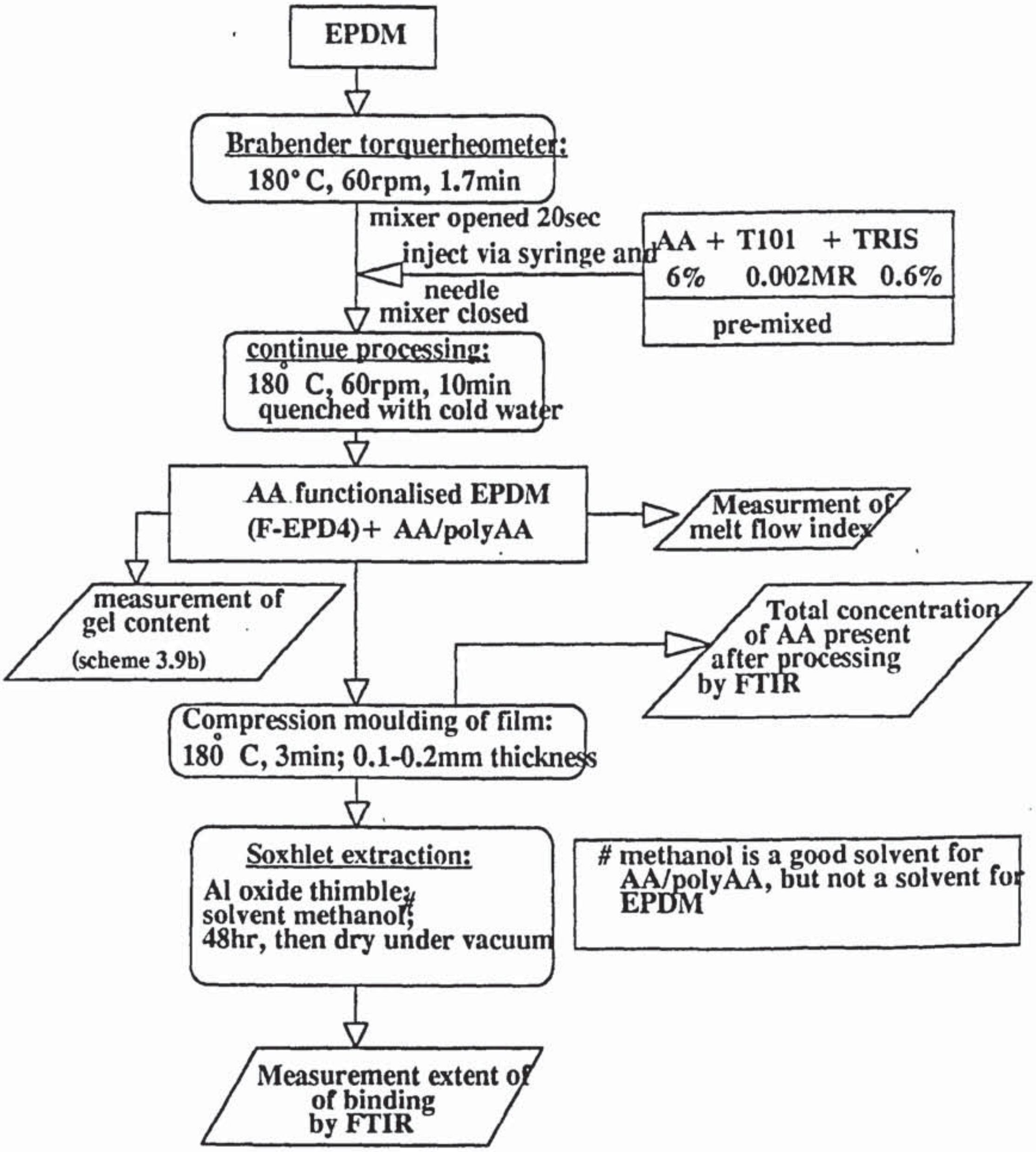


Scheme 3.13: Flowchart for functionalisation of EPDM with AA by method EPM2 and subsequent treatment and analysis of the F-EPD2 samples

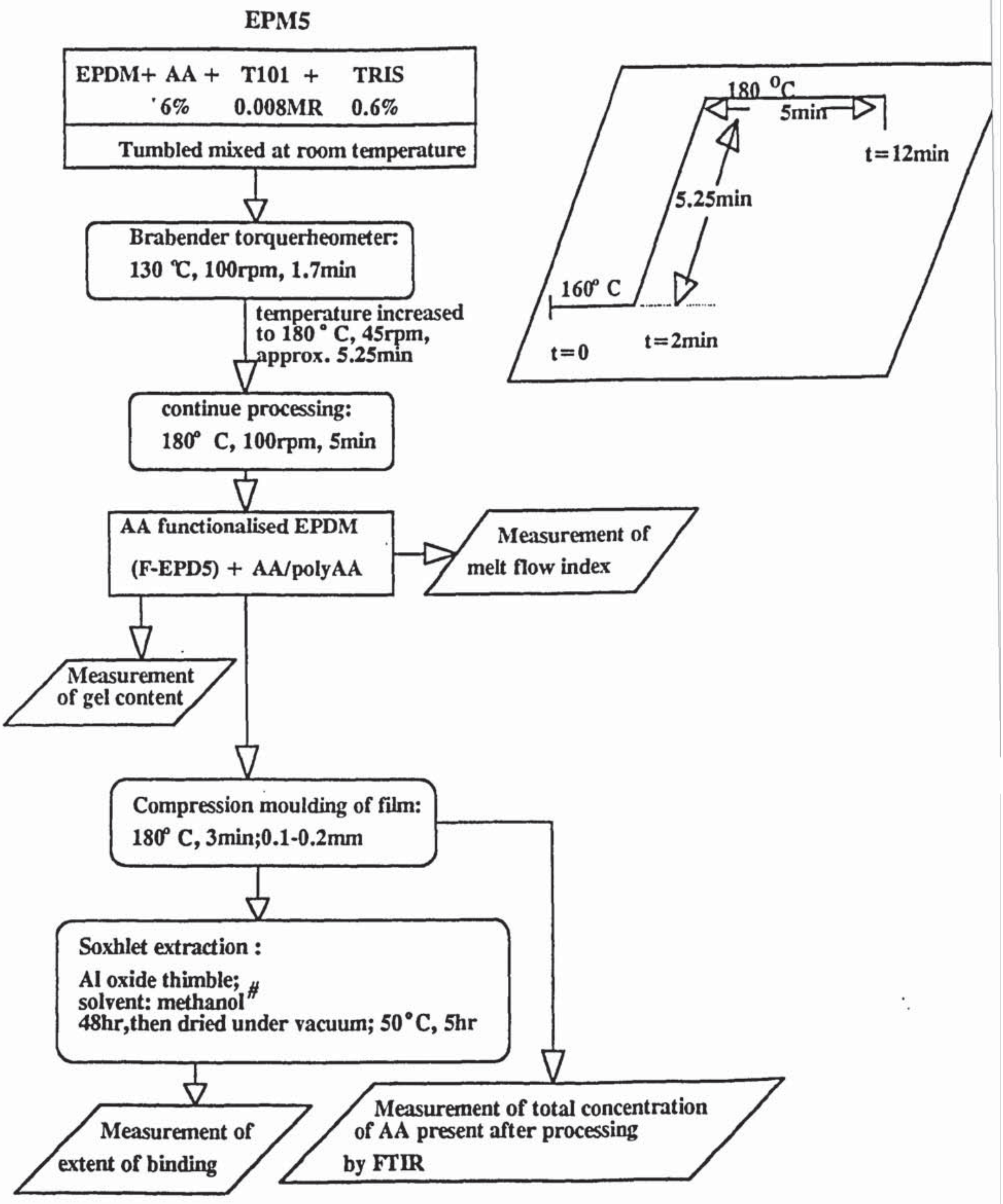


Scheme 3.14: Flowchart for functionalisation of EPDM with AA by method EPM3 180° C, 60rpm,12min (total); and subsequent treatment and analysis of the F-EPD3 sample.

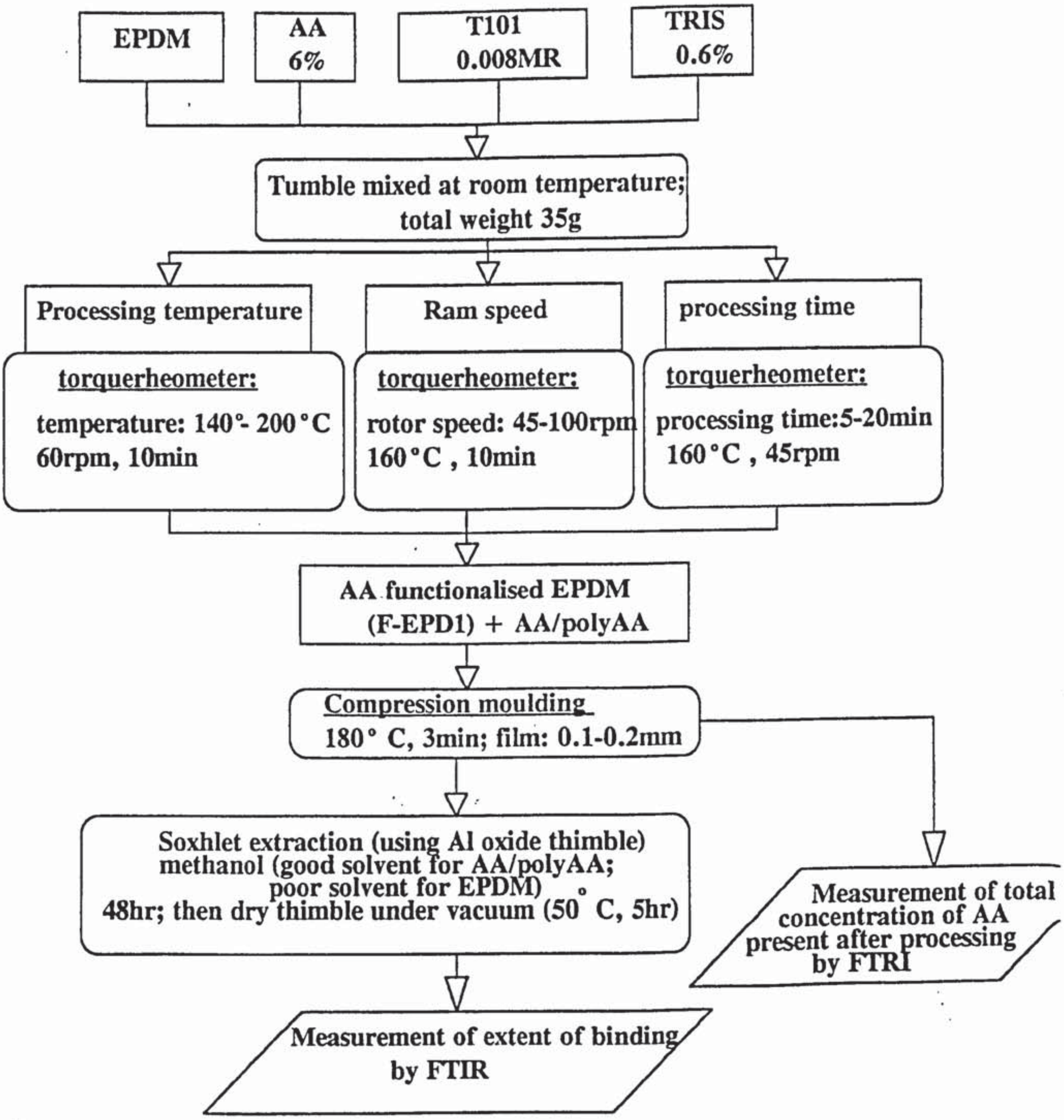
EPM4



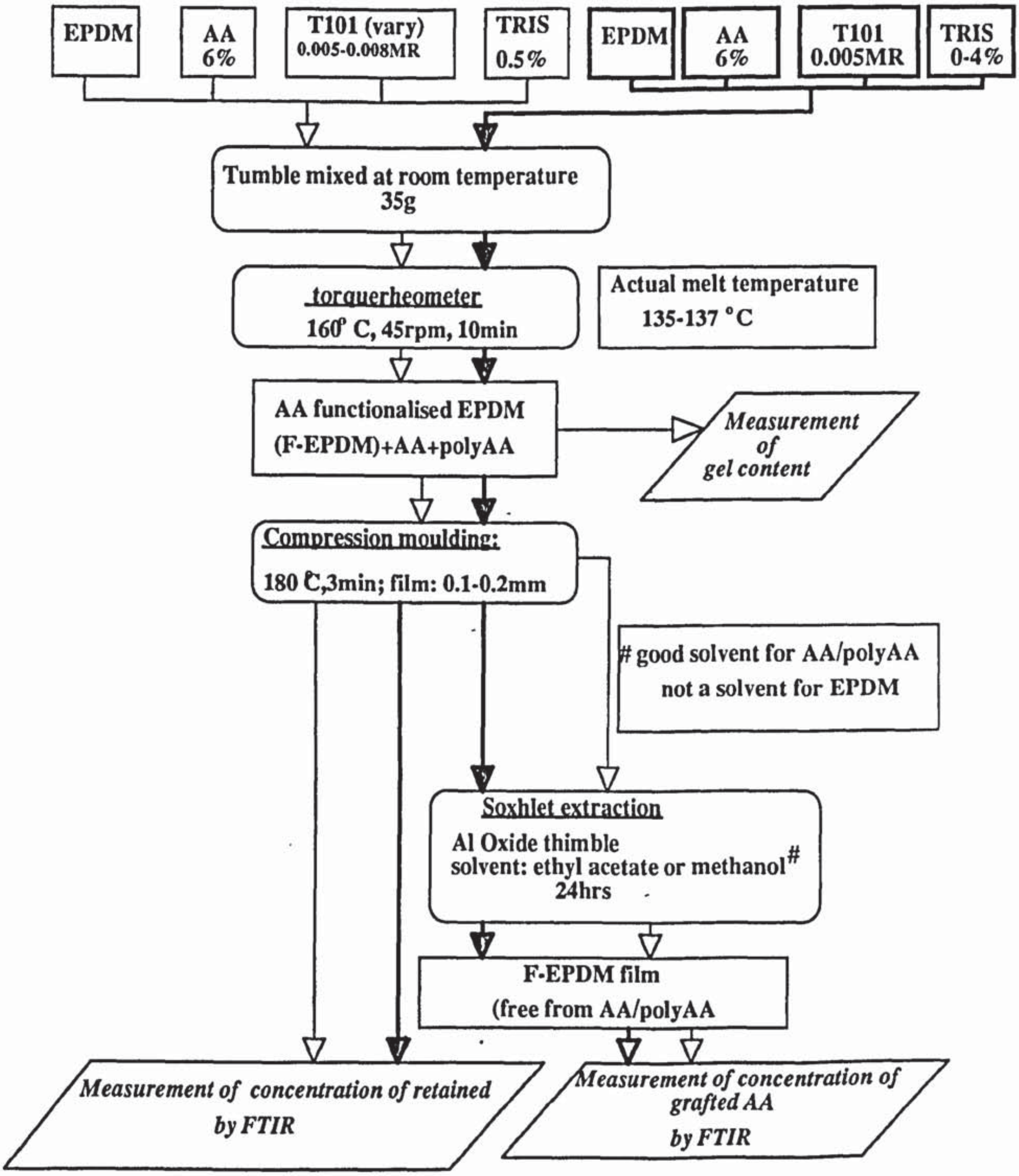
Scheme 3.15: Flowchart for functionalisation of EPDM by method EPM4 and subsequent treatment and analysis of F-EPD4 sample



Scheme 3.16: Flowchart for functionalisation of EPDM with AA by method EPM5, subsequent treatment analysis of F-EPD5 sample



Scheme 3.17: Optimisation of processing conditions: Effect of processing temperature, ram speed and time on grafting efficiency of AA to EPDM.



Scheme 3.18: Flowchart of experiments used for quantitative assessments of effect of peroxide and TRIS (thicker line in the chart) concentration on the extent of grafting of AA to EPDM; processing conditions were 180 C,60rpm,10min.

Figure 3.1C: Effect of processing methods of PM1 and PM5 on infra red of F-PS1 and F-PS5 samples (film :0.1-0.15mm thickness), Stage B, window region 1600-1800cm^{-1}. F-PS samples [PS, AA(6%), T101(0.04MR), DVB(3.0%); 180^{0}C in PM1, 160-180^{0}C in PM5, 60rpm, 10min].

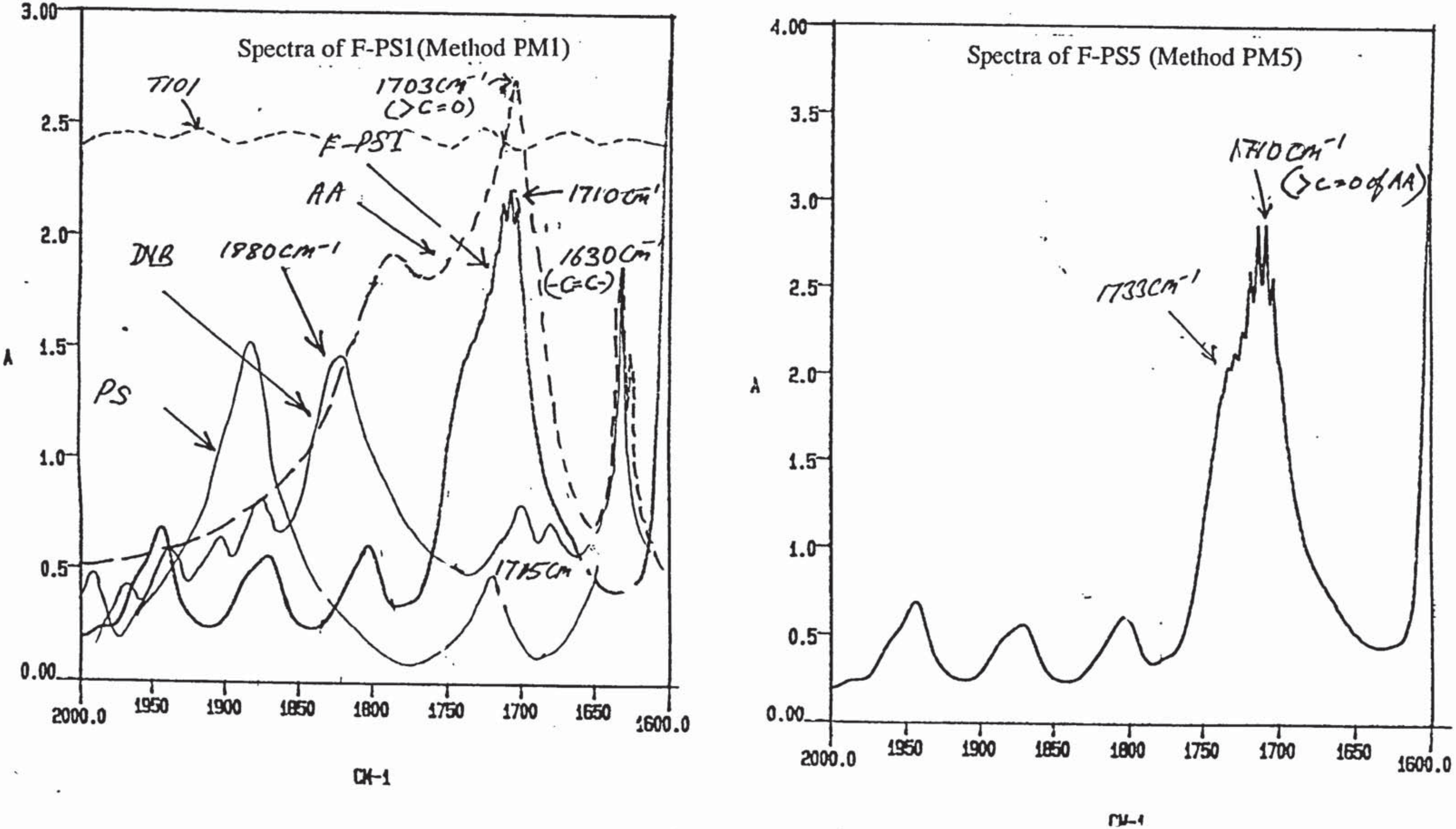


Figure 3.1d : Effect of processing methods (PM2 to PM4) on infra red spectra of F-PS samples (film: 0.1mm thickness) in window region of 1600-1900cm^{-1}.F-PS samples[AA(6%), T101(0.04MR), DVB(3%); 180^{o}C, 60rpm, 10min]

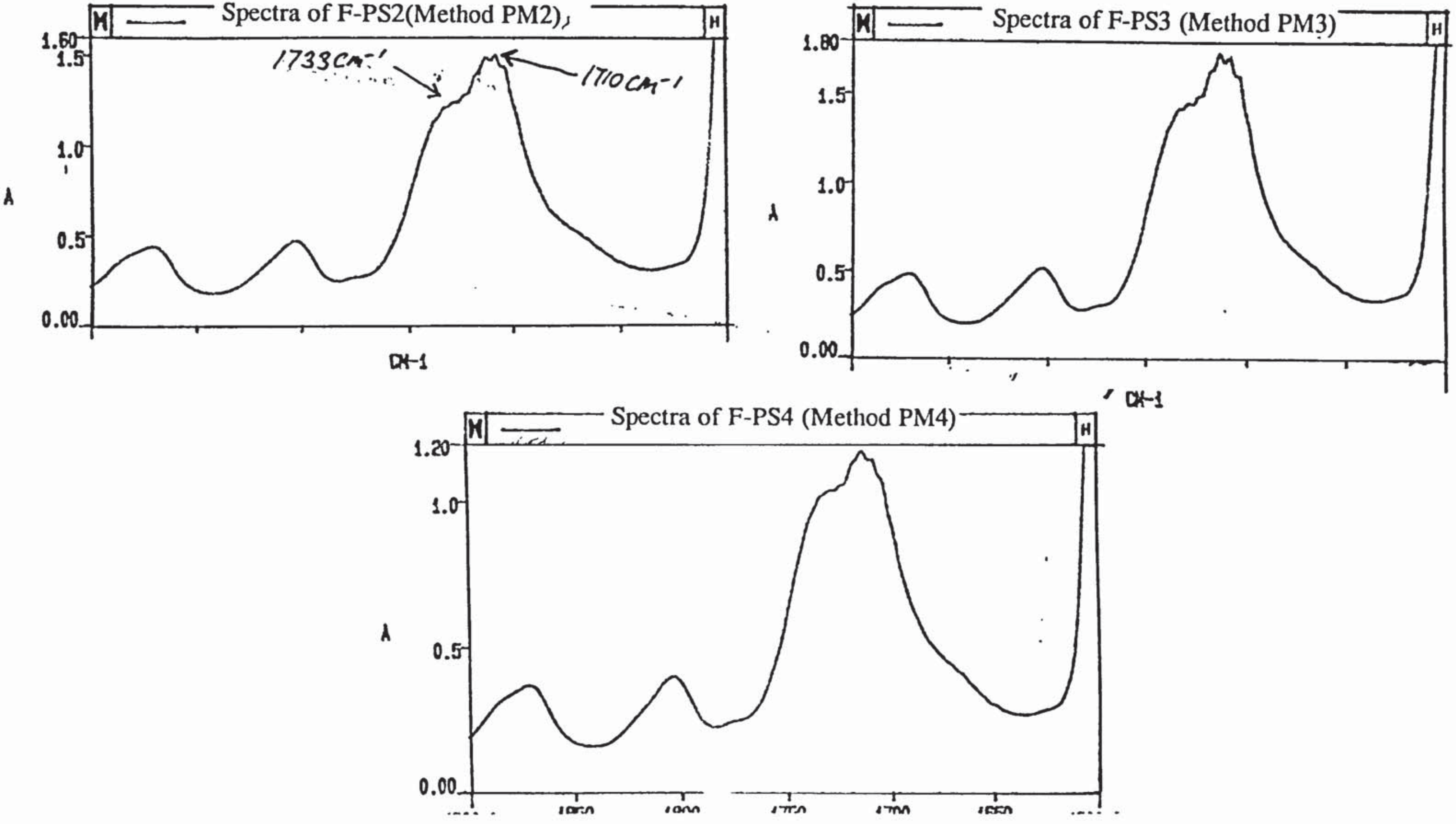
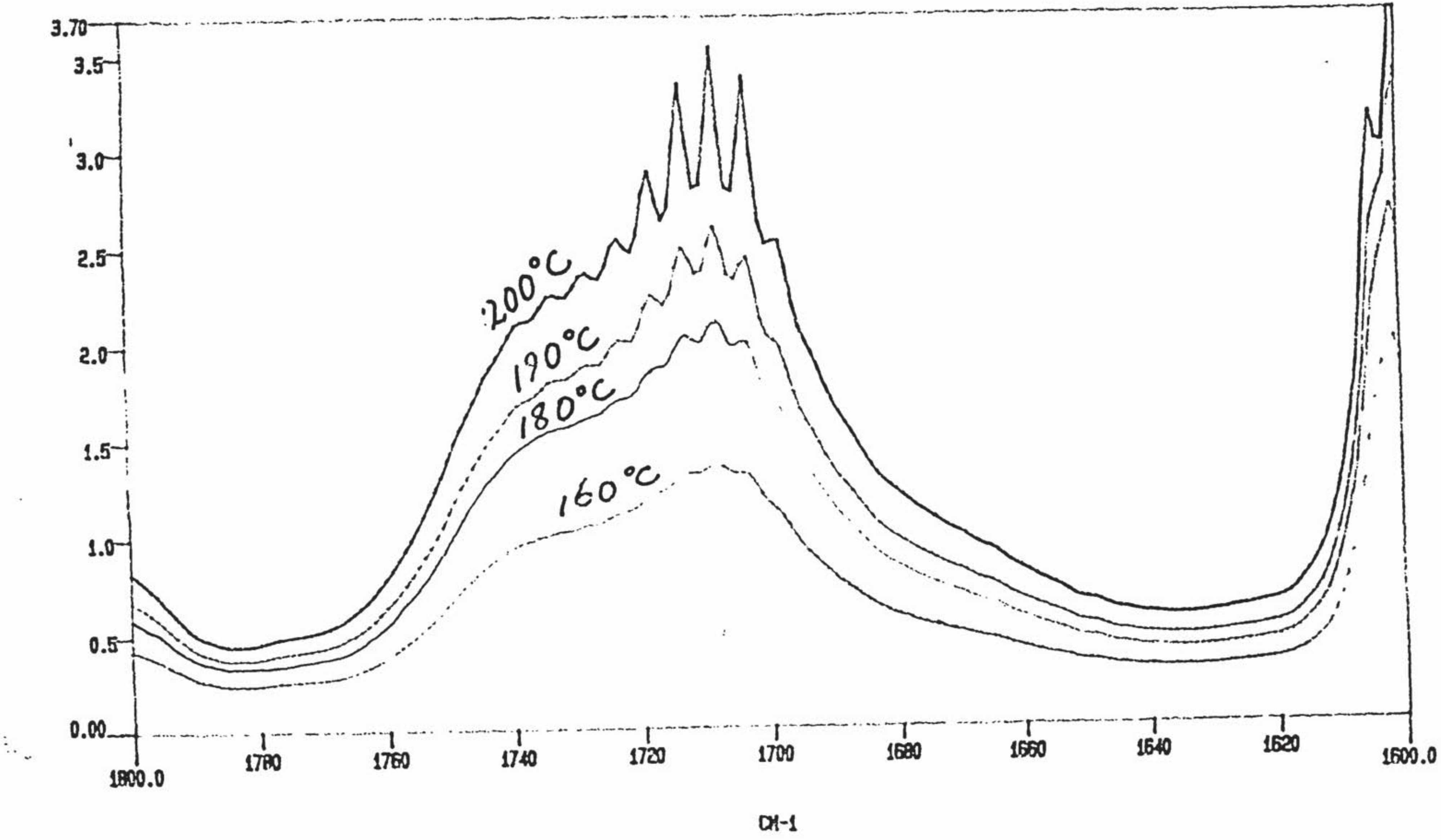


Figure 3.1f : Optimisation of processing temperature: Effect of processing temperature on the peak height (baseline method), absorbance mode, of IR spectra (1800-1600cm^{-1}) of F-PSs [PS, AA(6%), T101(0.04MR DVB(3%); 160^{o}-200^{o}C,60rpm,10min; PM1 method.



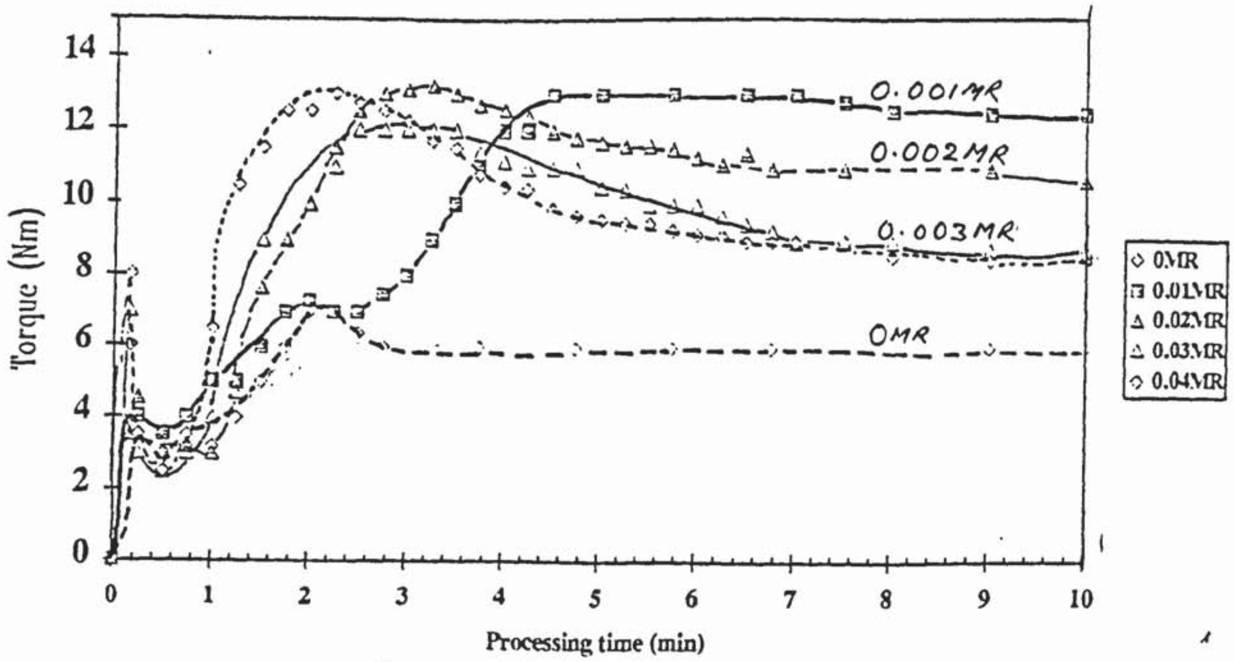


Figure 3.2a: Effect of [T101] on torque during processing of of mixtures PS, AA(6%) , DVB (3%) and varying concentration of T101 (MR 0.0- 0.04), at 200°C, 100rpm,10min using PM1 method.

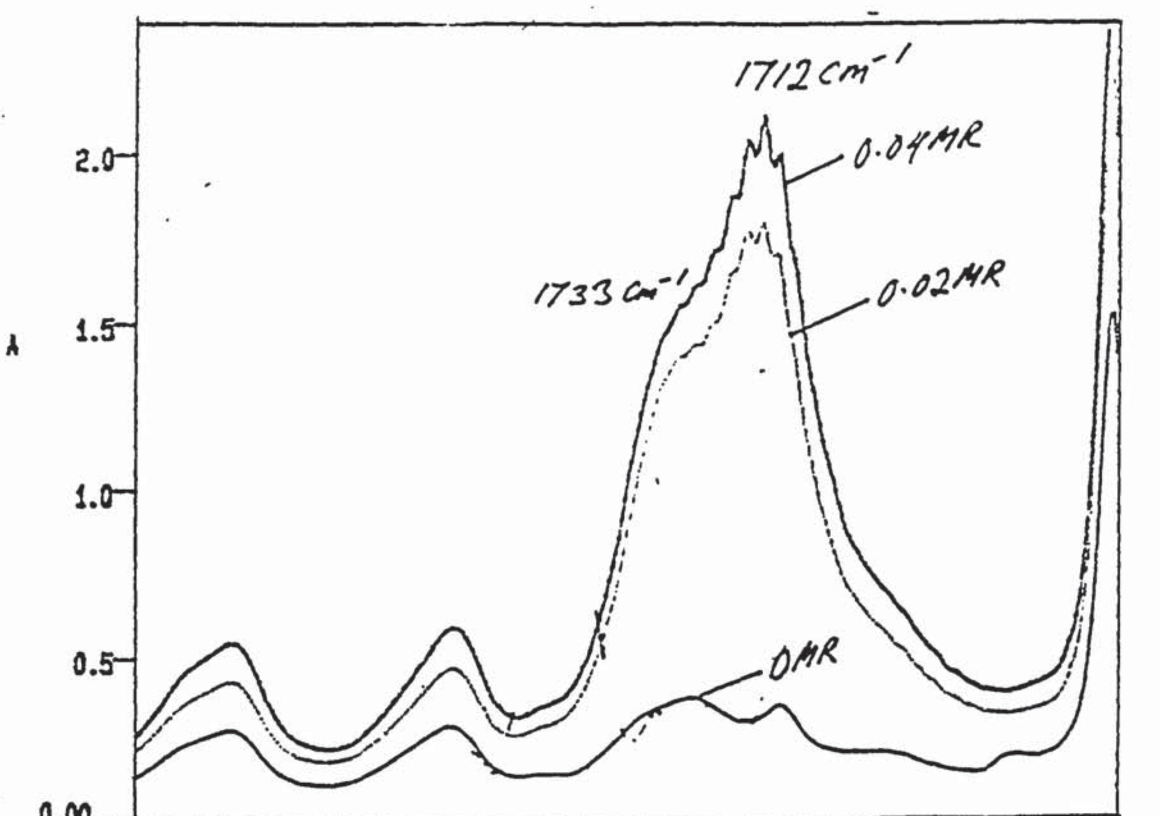


Figure 3.2b: Effect of [T101] on infra red spectra (absorbance mode) of F-PS (StageB) film samples (0.15mm thickness), window of 1600-1900cm^{-1}, obtained by method PM1, see scheme 3.2.

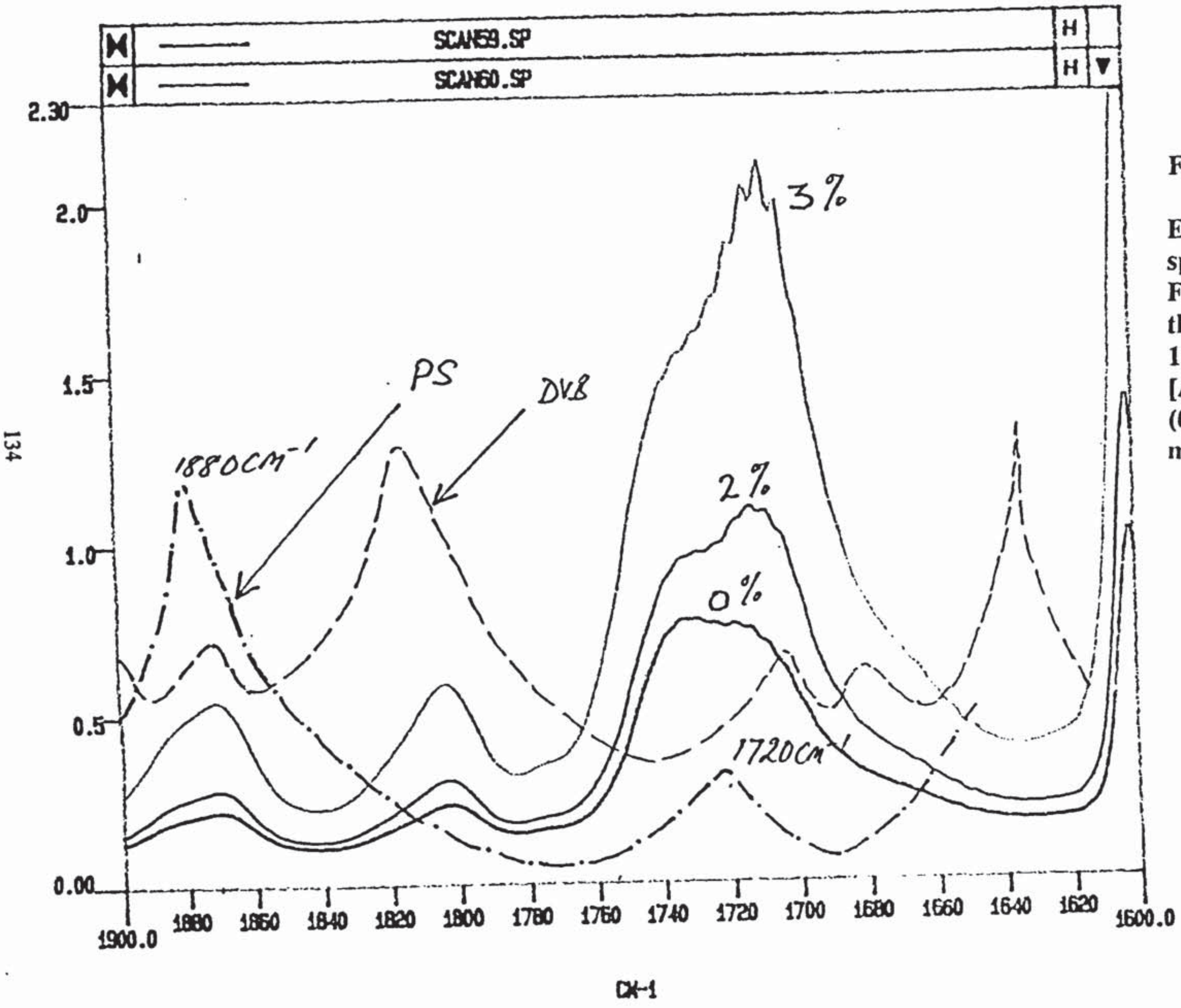


Figure 3.2c:

Effect of [DVB] on infra red spectra (absorbance mode) of F-PS1 samples (film:0.63mm thickness) in window region of 1600-1900cm^{-1}. F-PS1 samples [AA(6%), t101(0.04MR),DVB (0-3%); 180^{0}C, 60rpm,10min; method PM1.

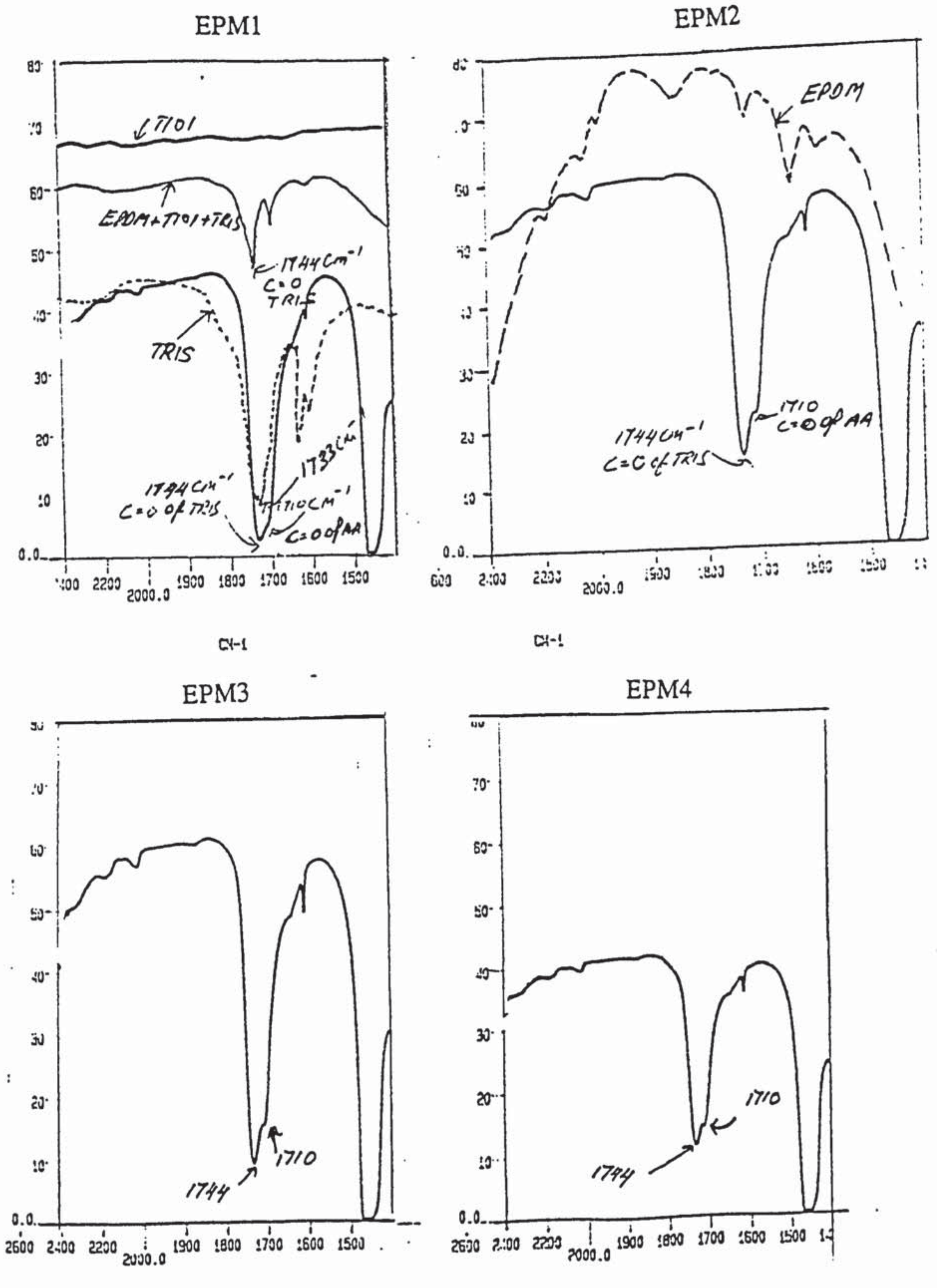


Figure 3.3a: IR spectra of F-EPD1 to F-EPD4 films (0.15mm prepared from mixtures of EPDM with AA(6%), T101(0.008MR), TRIS(0.6%) by methods EPM1-4 see schemes 3.11-3.15.

Figure 3.3b: Effect of temperature on infra red spectra (1800-1600cm^{-1},absorbance mode) of F-EPDI samples [EPDM, AA(6%), T101(0.005MR), TRIS(1.5%); 140-200°C,45rpm; EPM1 method

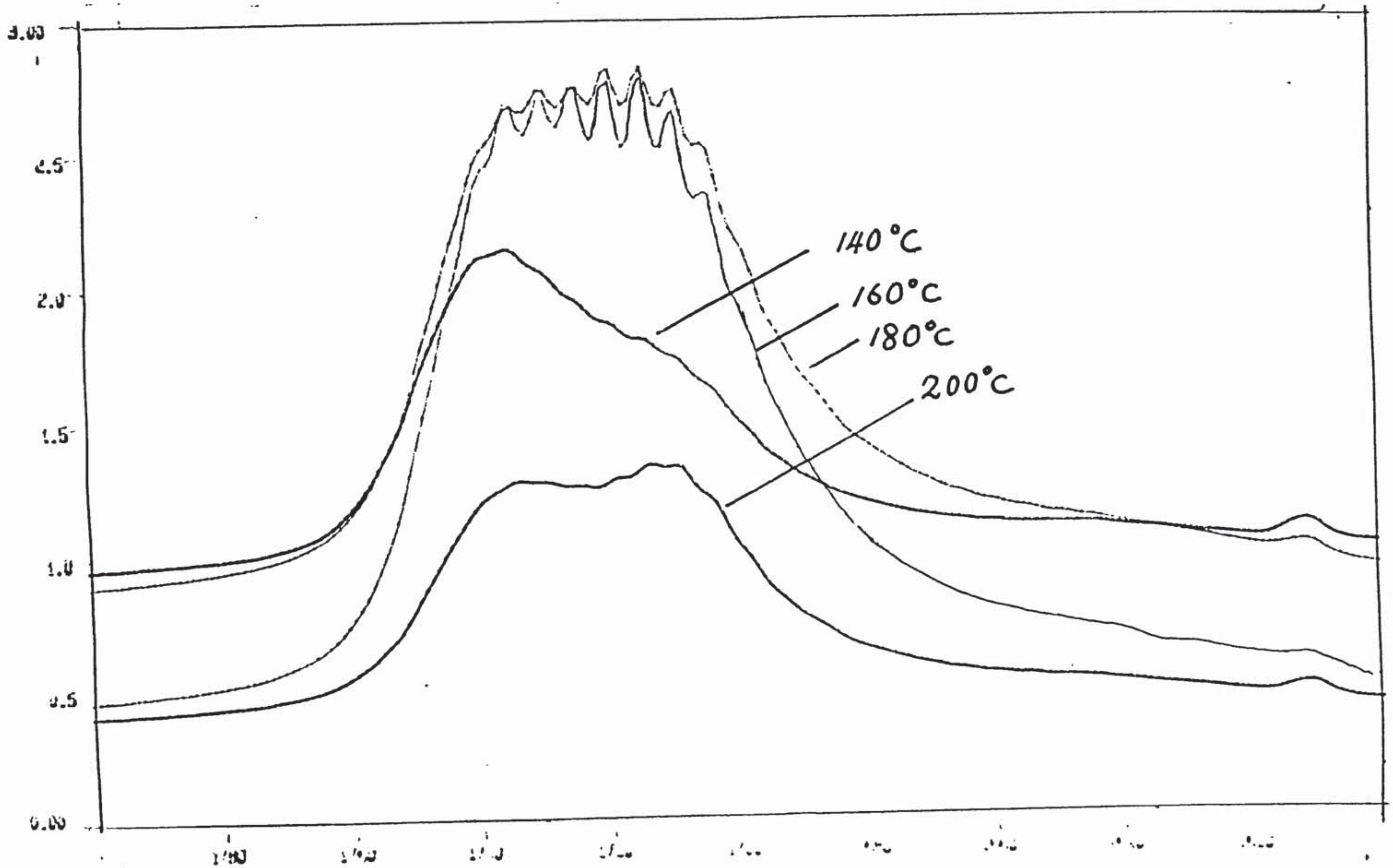
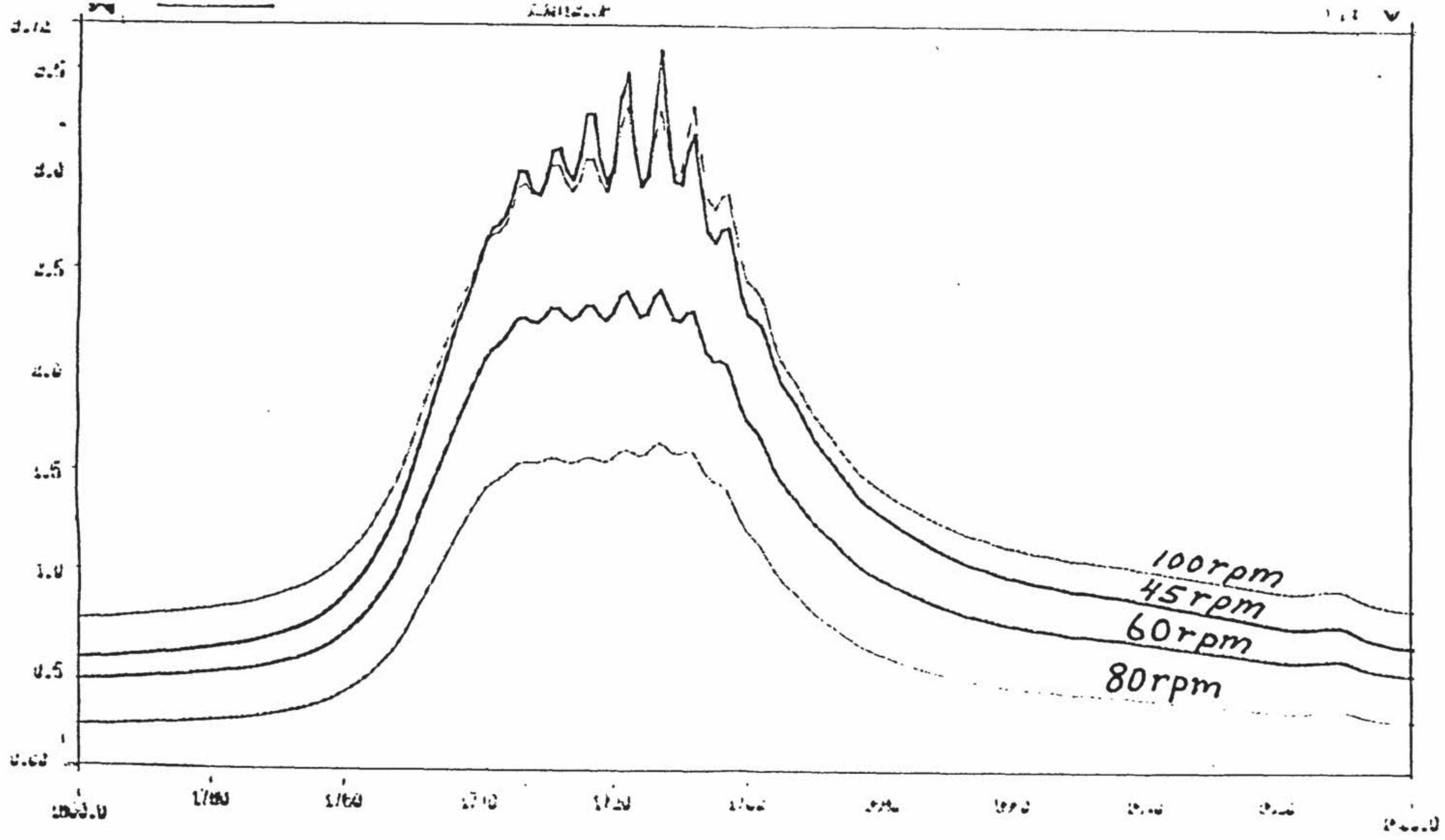


Figure 3.3c: Effect of rotor speed on infra red spectra (1800-1600cm^{-1},absorbance mode) of F-EPD[samples [EPDM, AA(6%), T101(0.005MR), TRIS(1.5%); 140^{0}C,45-100rpm,10min; EPM1 method.



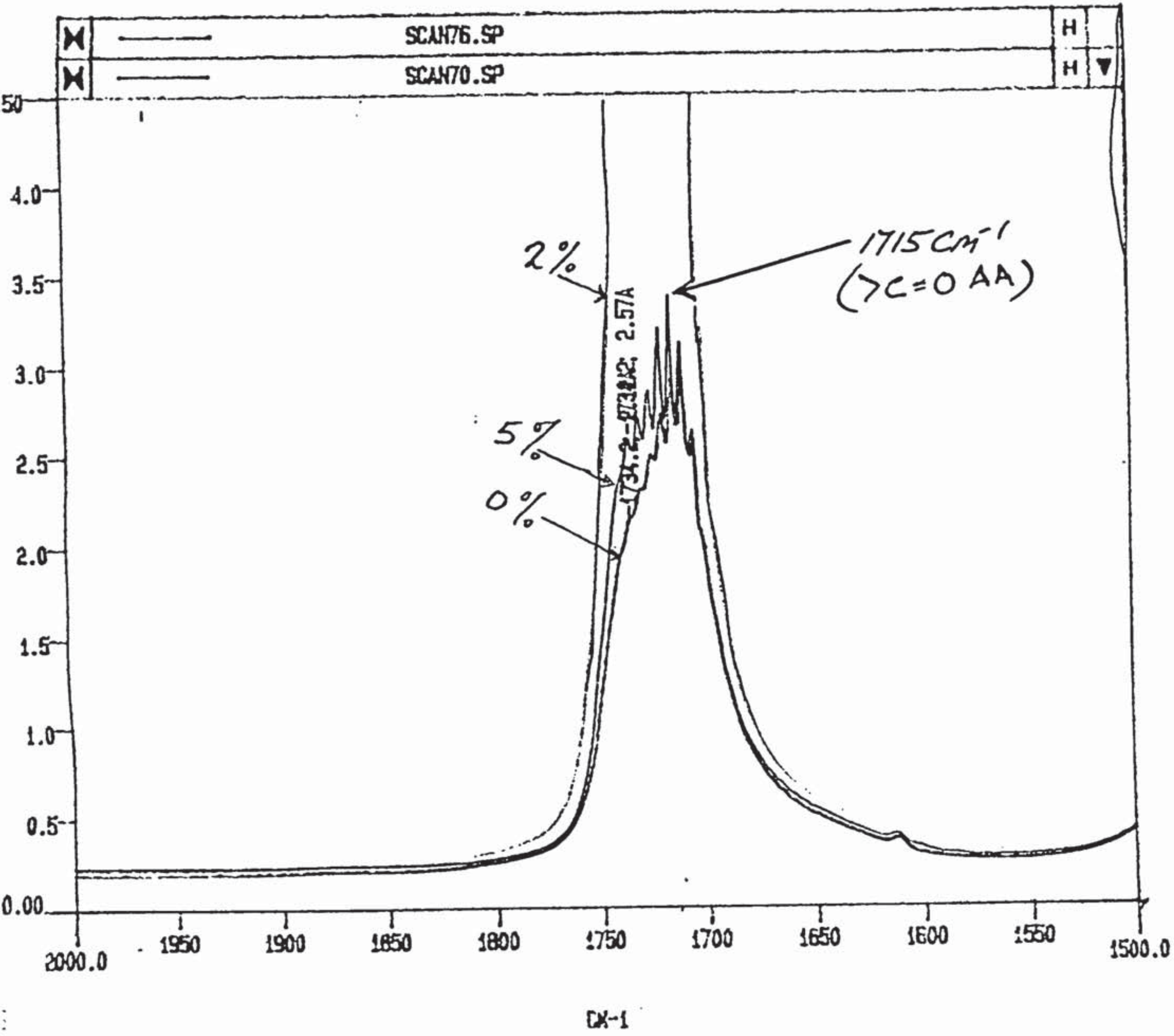


Figure 3.3d

Effect of [TRIS] on infra red spectra (absorbance mode) of F-EPD1samples (film:0.6-0.8mm thickness) in window region of 1500-2000cm^{-1}. F-EPD1 samples [AA(6%), T101(0.005MR),TRIS (0-5%); 140^{0}C, 45rpm,10min]; method EPM1.

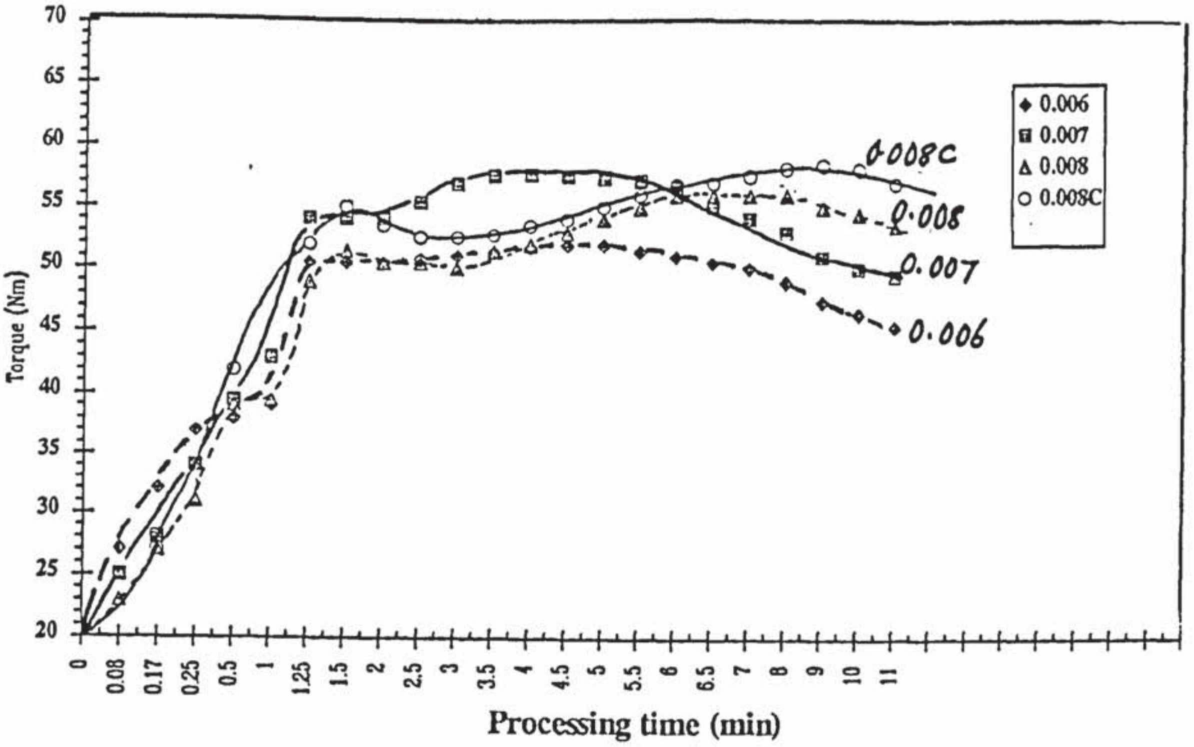


Figure 3.4: Effect of peroxide T101 on torque during processing by EPM1method, for mixtures of EPDM, AA(6%), T101(0.006-0.008MR), TRIS(0.2%), at 180°C, 60rpm, 11min. Mixture 0.008C was without TRIS (0%)

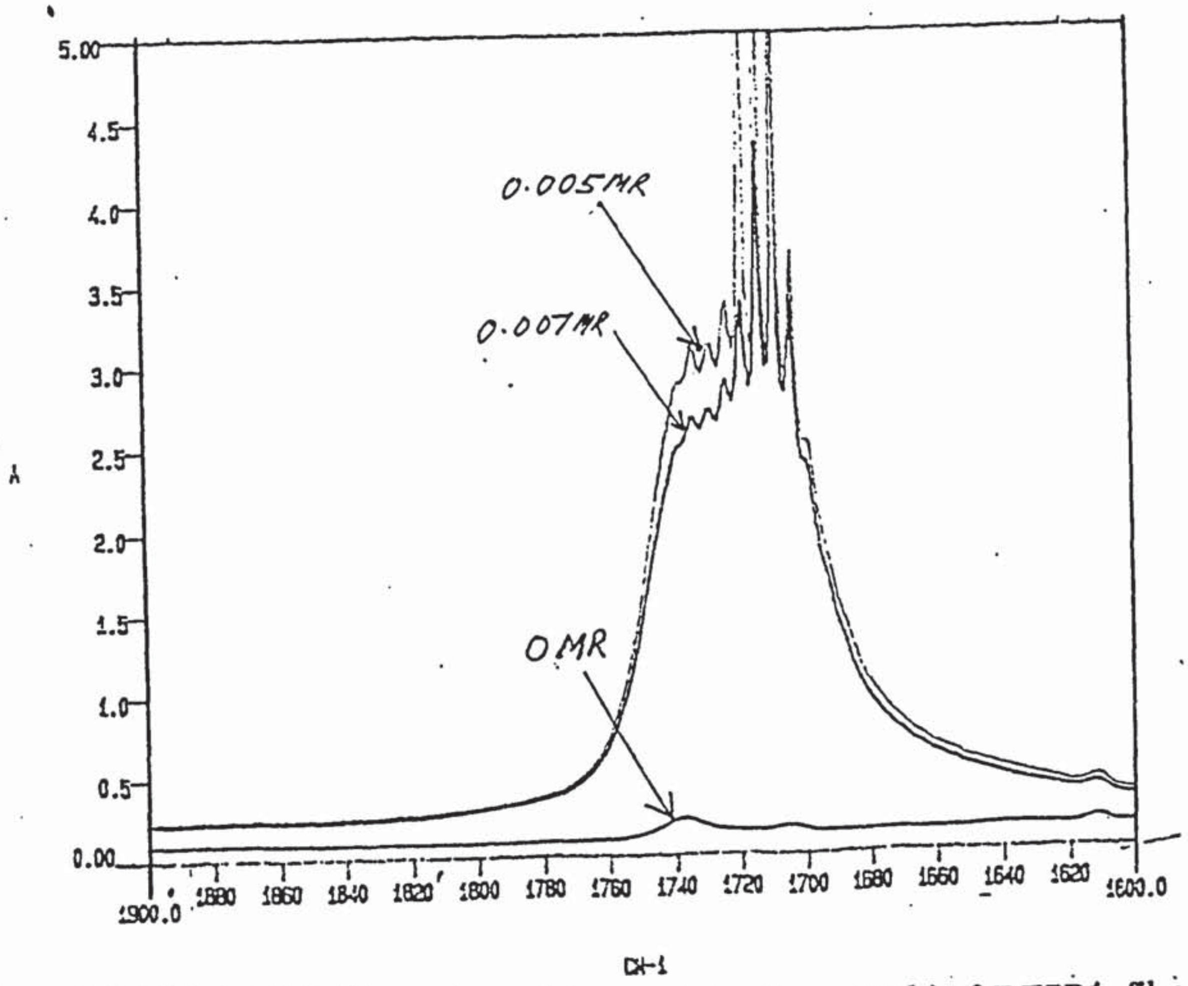


Figure 3.5: Effect of [T101] on infra red spectra (absorbance mode) of F-EPD1 film samples (0.20mm thickness), window region of 1600-1900cm^{-1}. F-EPD1 samples [AA(6%), T101(0- 0.007MR), TRIS(1.5%); 160°C

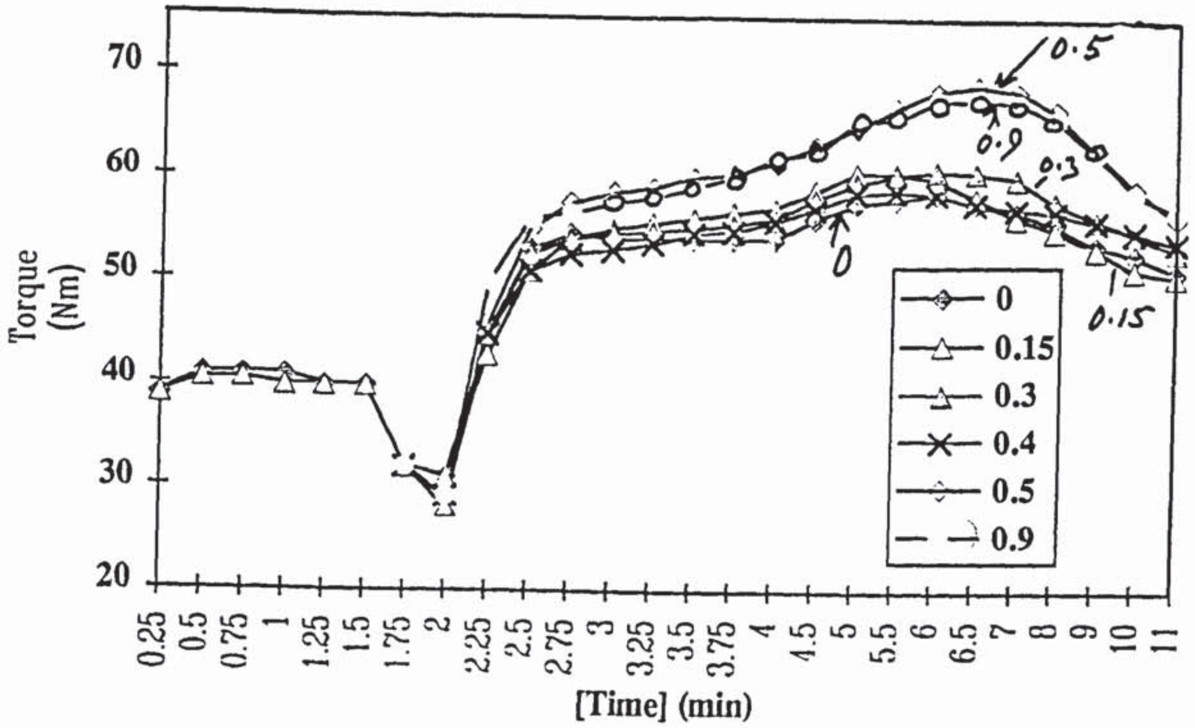


Figure 3.6a: Effect of TRIS concentration on torque during processing for mixture of EPDM, AA(6%), T101(0.008MR), TRIS(0-1.0%) using method EPM4 at 180^{0}C, 60rpm, 10min

PAGE
MISSING
IN
ORIGINAL

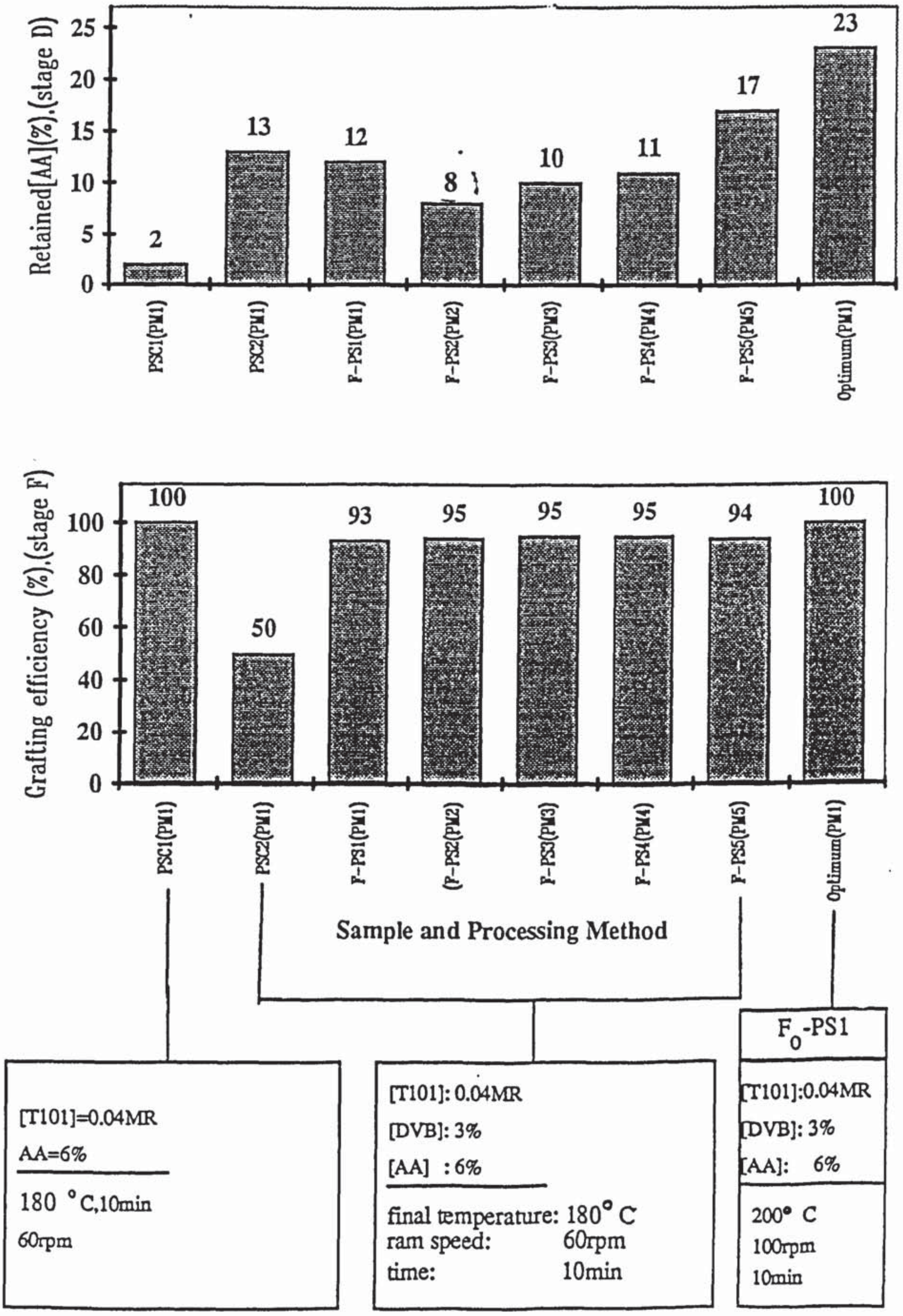


Figure 3.7: Effect of processing method on percentage total concentration of AA retained and the grafting efficiency of AA on PS

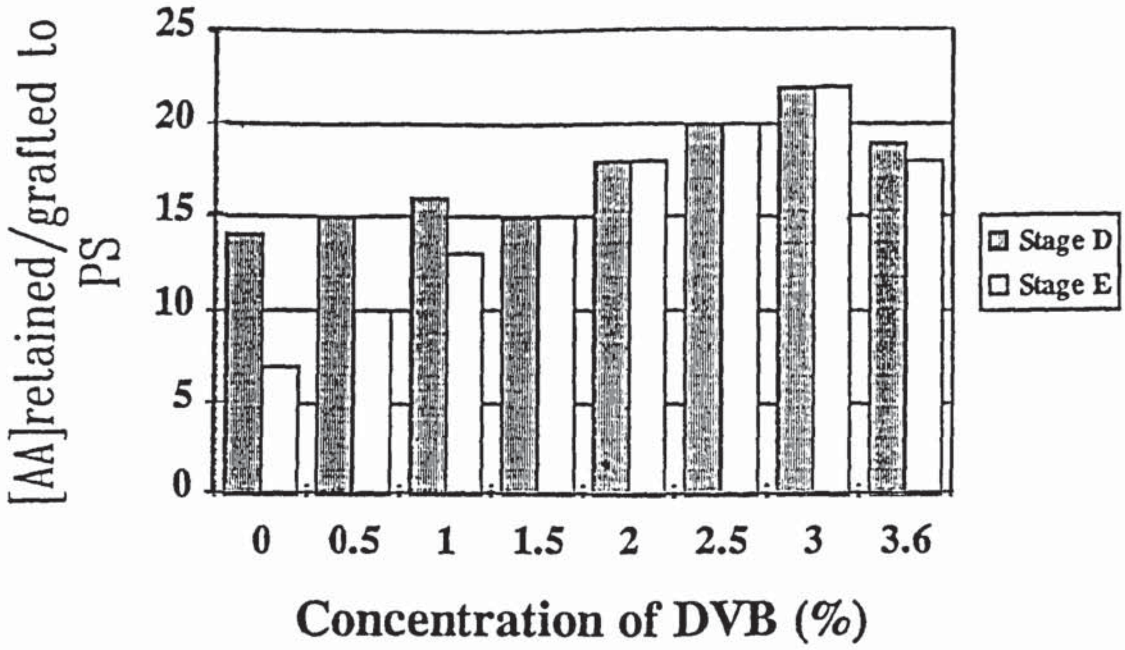


Figure 3.8: Effect of DVB concentrations on retained (stage D, table 3.6) and grafted AA in F-PSs of processed mixtures of PS,AA(6%) T101(0.04%), DVB(0-3.6%) at 180^{0}C, 60rpm, 10min using PM1 method.

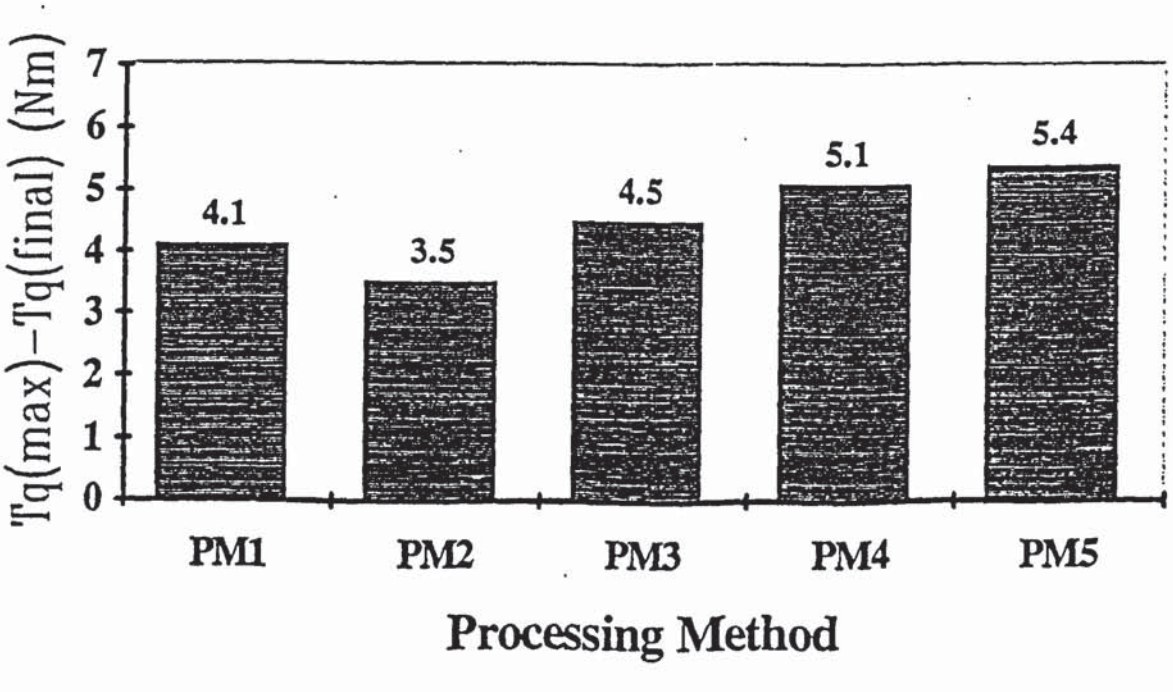


Figure 3.9: Effect of processing methods (method 1 to 5) to the change in tq [$Tq_{(max)}$ of second peak-$Tq_{(final)}$].

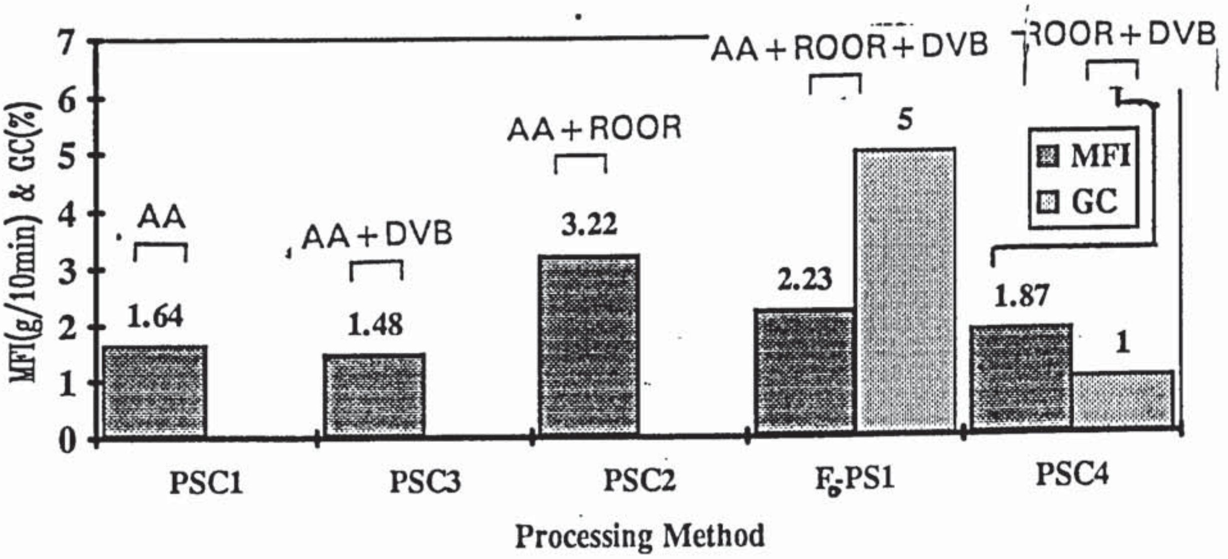


Figure 3.10: The effect of composition on MFI and gel content (GC) of PS processed by method PM1. Concentration of AA(6%), T101(0.04MR) and DVB(3%). Peocessing conditions were 180^{o}C, 60rpm,10min.

Figure 3.11: Effect of processing methods (EPM1 to EPM5), optimum processin condition and chemical composition, on the percentages of retain grafting efficiency of AA in F_0-EPD1 sample.

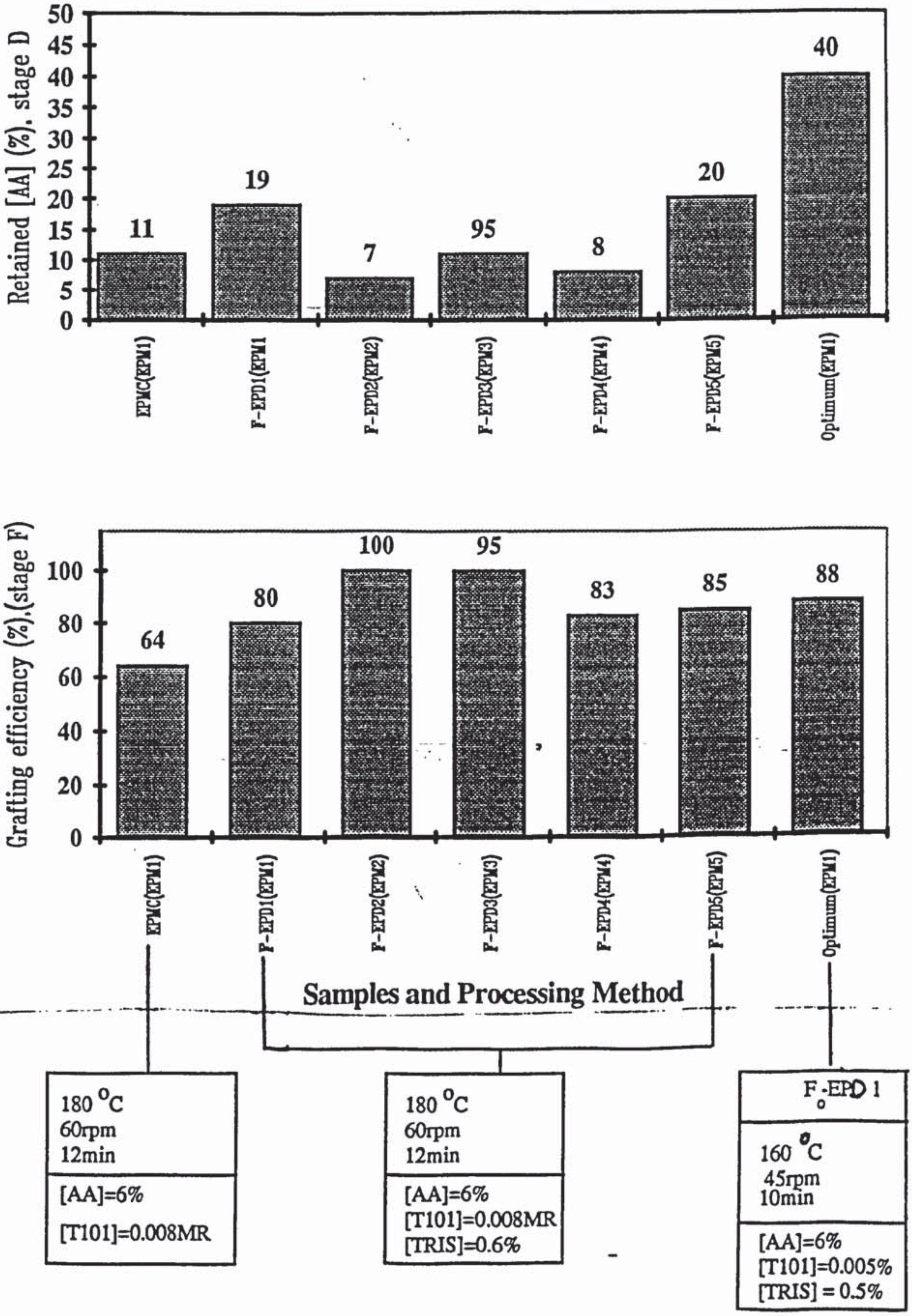
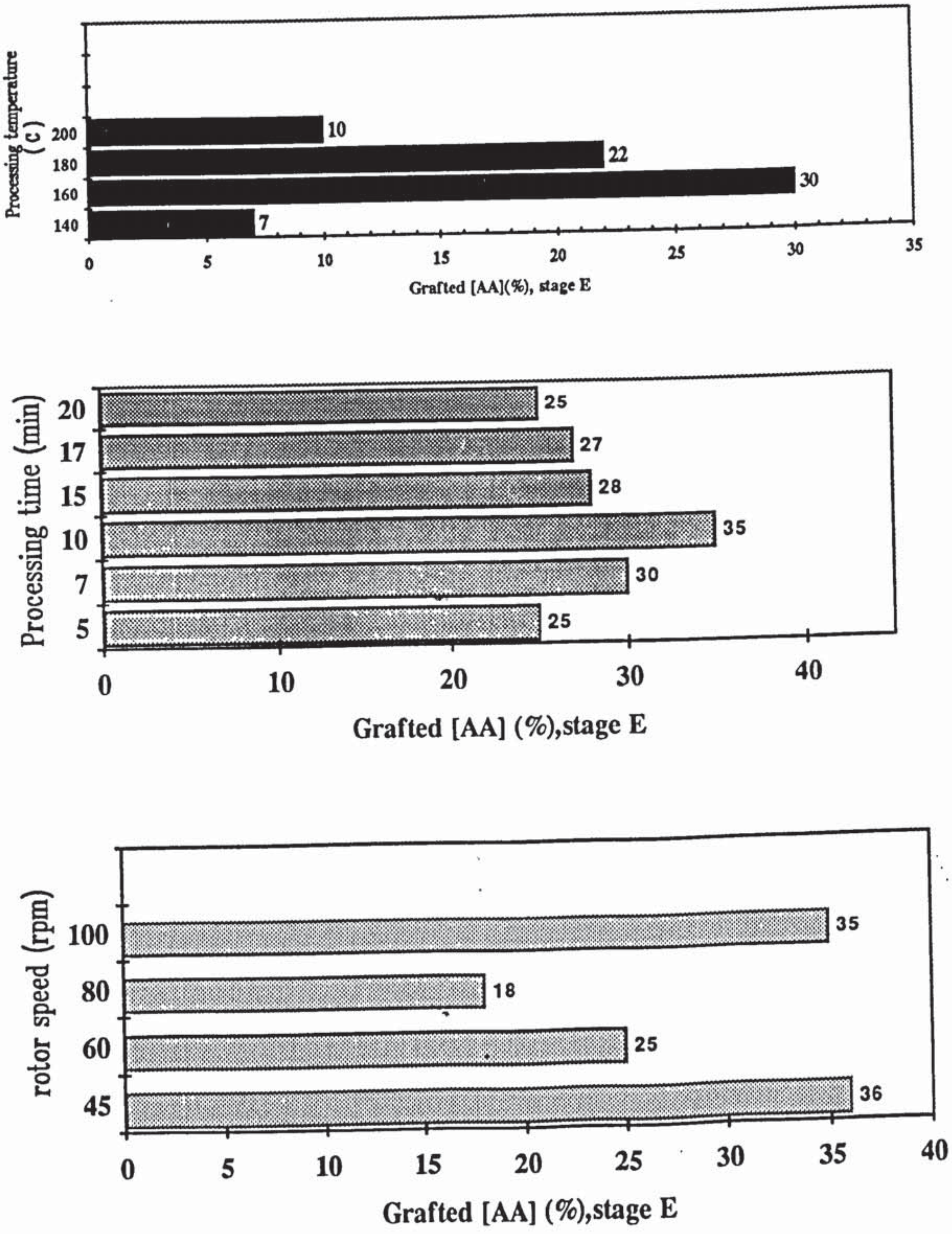


Figure 3.12: Effect of processing conditions on the level of grafting of [AA] in EPDM using method EPM1



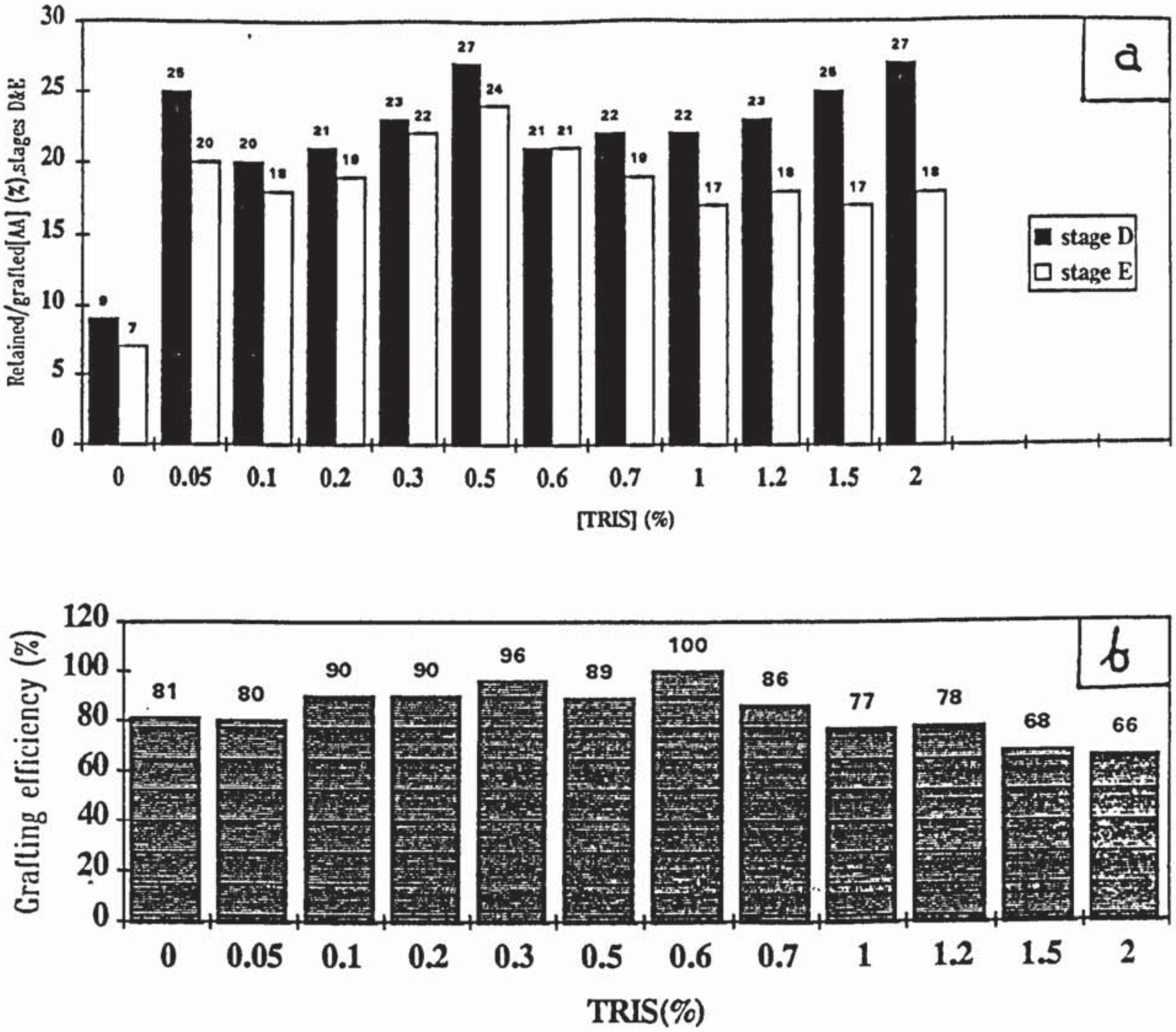


Figure 3.13:Effect of TRIS concentration on amount of AA retained (Stage D and the amount grafted (Stage E), a,as well as the grafting efficiency (Stage F)

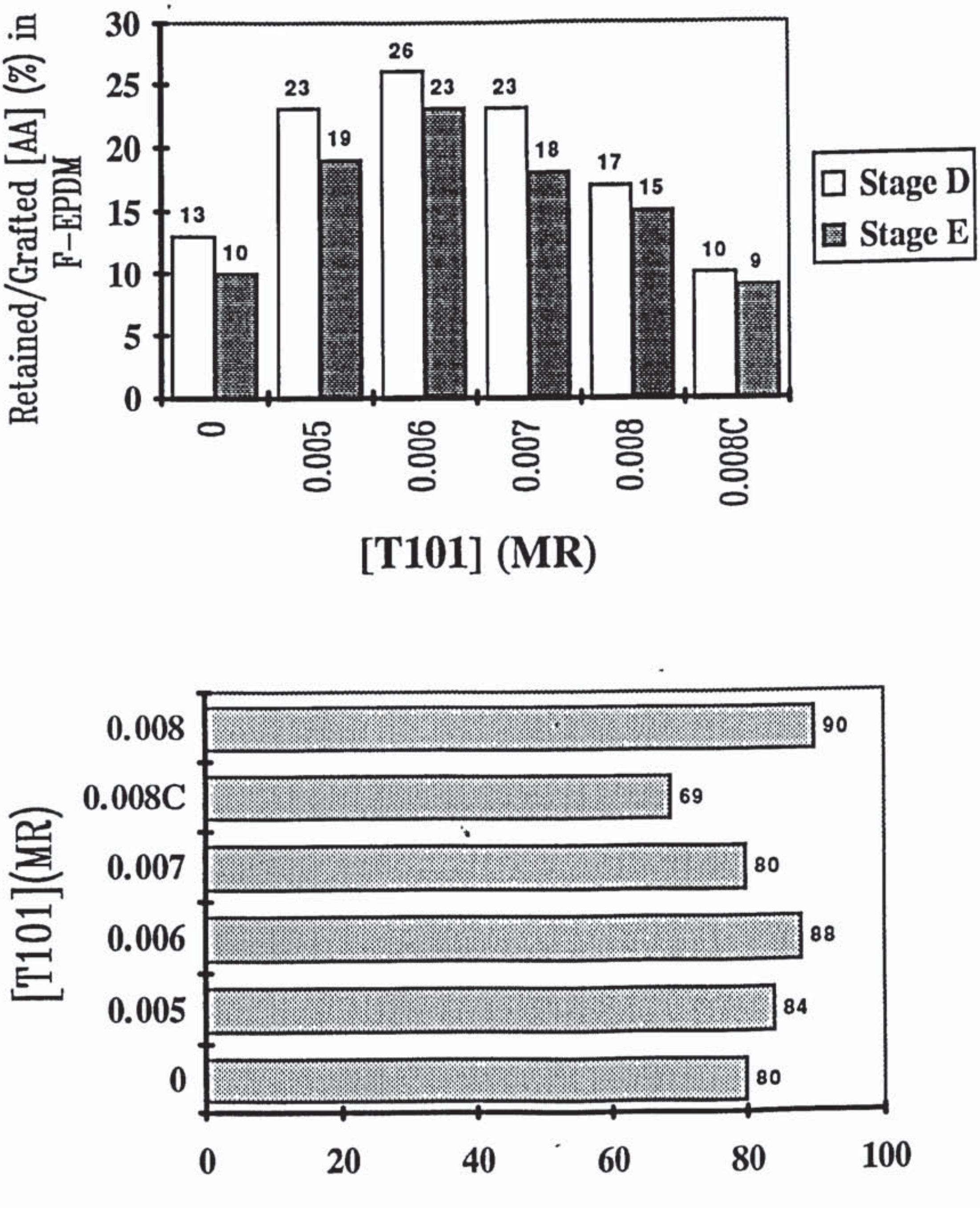


Figure 3.14: Effect of [T101] on the amount of AA retained (Stage D) and amount grafted (Stage E) as well as the grafting efficiency (Stage) in F-EPD1 samples (containing AA(6%),TRIS(0.6%) and variabl concentration of T101; processed at 180°C, 60rpm, 10min using EPM1 method. Sample 0.008C was without TRIS.

CHAPTER 4

BLENDS OF POLYMER COMPOSITIONS BASED ON FUNCTIONALISED PS/FUNCTIONALISED EPDM AND FUNCTIONALISED PP/FUNCTIONALISED EPDM BLENDED IN THE PRESENCE AND ABSENCE OFAN INTERLINKING AGENT

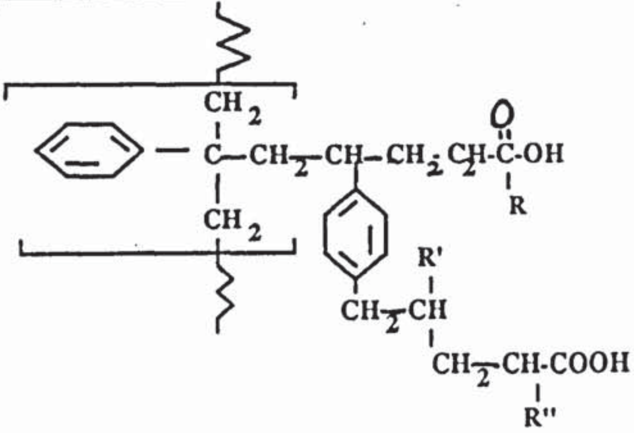
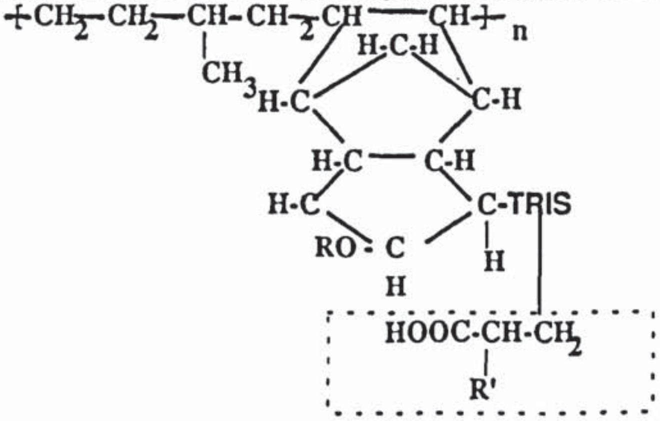
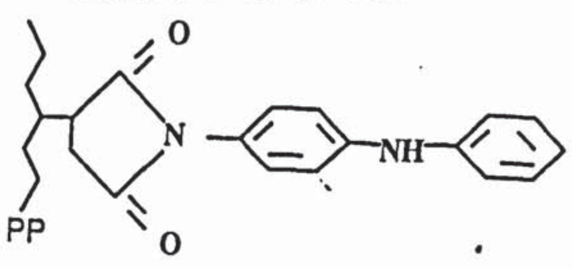
4.1 OBJECT AND METHODOLOGY

In chapter 3, functionalisations of PS and EPDM was investigated to obtain the highest concentration of grafted AA, and the role of both coagents DVB and TRIS in enhancing the level of the grafting of AA to PS and EPDM was examined. A direct melt blending of the functionalised PS (F-PS) and functionalised EPDM (F-EPD) is expected not to result into any significant condensation reaction between the carboxylic group functionalities in both polymers. However, the use of an organic diamine, for example ,ethylene diamine (EDA, structure VII) or hexamethylene diamine (HEMDA, structure VIII) in the melt should function as interlinking agent (IA) which lead to an amidisation reaction between the amine group of the diamine and the carboxylic groups of the functionalised polymers, resulting in a grafted PS to EPDM (PS-g-EPDM).

The main object of the work described in this chapter was to investigate the effectiveness of EDA and HEMDA as interlinking agents in undergoing amidisation reactions with carboxylic groups of the F-PS, (see structure VII), and the F-EPD , (structure VIII), and to examine any improvement in mechanical properties of the F-PS/F-EPDM blends with particular reference to their impact strength. The F-PS and F-EPD used throughout this chapters are the optimised, AA functionalised polymers (F_0-PS1 & F_0-EPD1) the composition and behaviour of which is described in chapter 3, see figure 3.7, page for F_0-PS1, and figure 3.11, page for F_0-EPD1.

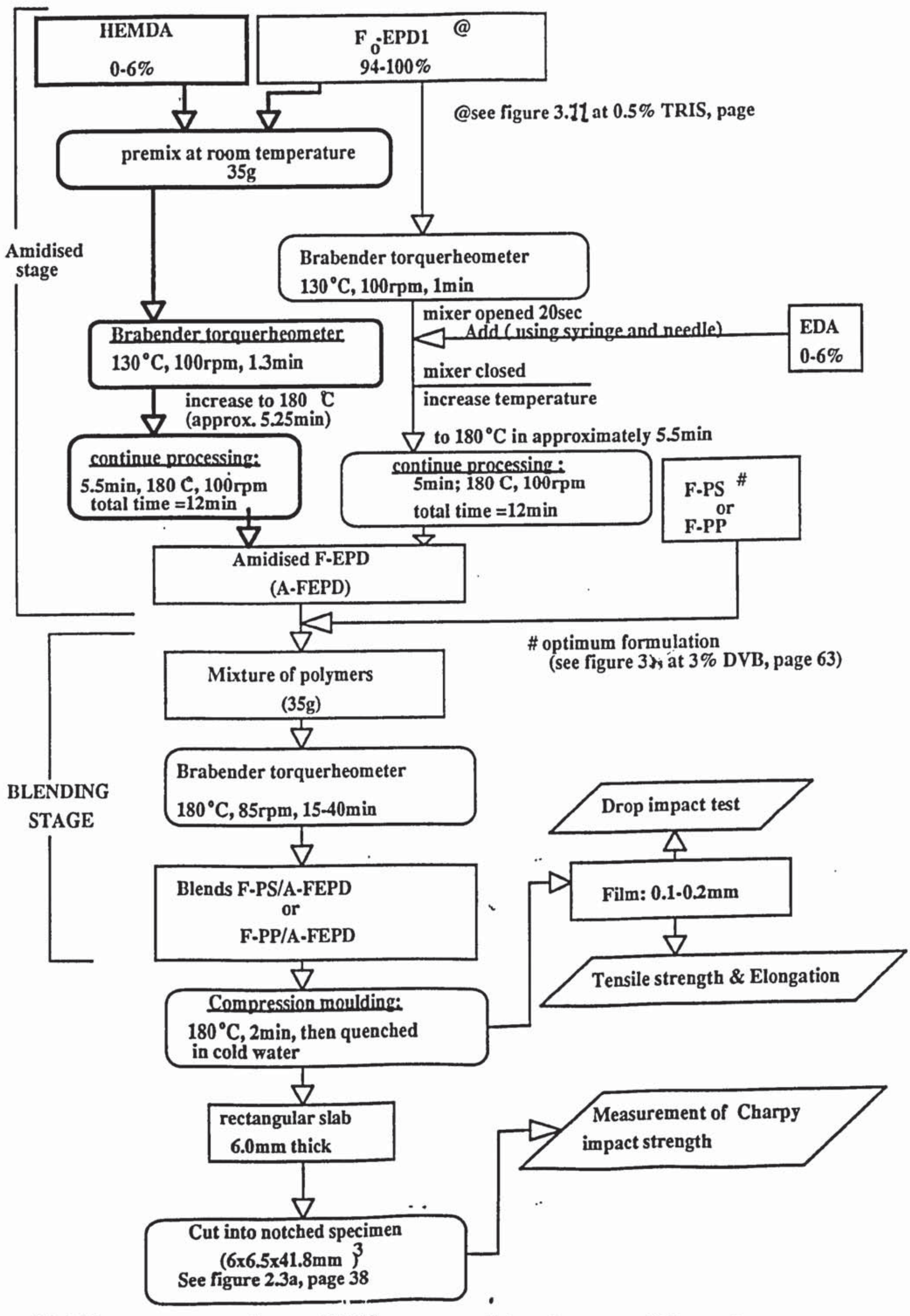
PP was also functionalised and blended with F_0-EPD1. Functionalisation of PP was carried out via reaction of PP with N-(4-anilinophenyl) maleimide, PM, (see structure IX in table 4.1) The PP-g-PM (F-PP) was prepared by reactively processing PP with, PM (1%), dicumyl peroxide (2%) in the presence of (0.25%) in a single screw Busko Kneader at 190°C, 90 rpm and dwelling time of approximately 4min. The modified polymer was then diluted 1:1 with fresh polypropylene (PP) using the same processing condition.The procedure has resulted into approximately 70% bound PM before the dilution.

Table 4.1: Structure ,physical properties and abbreviation of chemical used in chapter 4.

structure number	Chemical structure, name and molecular weight (MW)	Abrevi·ation
VII	$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ 1,2-diamino ethane (MW= 58), liquid.	EDA
VIII	$H_2N\text{-}(CH_2)_6\text{-}NH_2$ 1,6-diamino hexane (MW= 116), solid	HEMDA
IX	 AA grafted PS; one possible structure; solid; grafted [AA] was 15%. R, R' and R'' are alkyl or aryl groups	F-PS
X	 structure; solid; grafted [AA] was 18%) AA functionalised EPDM (F-EPDM); one possible (stage E, scheme 3.17)	F-EPD
XI	 N-(4- anilinophenyl maleimide) grafted PP; solid	F-PP

The general procedure of the work carried out in this chapter is described in scheme 4.1. The F_0-EPD1 (optimum composition, see figure 3.11, page129 for composition and processing conditions) was amidised with IA (3-6%) using a temperature gradient method which involved initially processing a mixture of the F_0-EPD1 with a diamine in torquerheometer at a low temperature (130^{o}C) for 1.3min and then the temperature was gradually increased to 180^{o}C where the processing was continued for a further 5min. The amidised F_0-EPD1 was then blended with F_0-PS1 (optimum composition, see figure 3. page126for composition and processing conditions) or F-PP at a chosen weight ratio at 160^{o} - 200^{o}C. The same F-PS and F-EPD samples which were processed using the same composition and processing condition as stated in figures 3.8 and 3.13 were used throughout the work in this chapter unless otherwise stated.

The blends were then pressed to form films (0.1-0.2mm thickness) or slabs (6mm thick) as previously described (see section 2.4, page29). A portion of the film sample was cut into dumb bell shaped specimens (thin part dimensions: $30 \times 4 \times 0.5 mm^3$) to be used for mesurements of tensile strength and elongation,see chapter2, section 2.7.2.1. The rest of the film was used in drop impact test measurement, see chapter 2, section 2.7.2.2. The slabs were used for Charpy impact test. The cutting of test specimens and introduction of notches are described in section 2.7.2.2, page37.



Scheme 4.1: Flowchart for amidisation of F$_0$-EPD1 ; blending of F$_0$-PS/F$_0$-EPD1 and F-PP/F$_0$-EPD1 in the presence and absence of interlinking agent; measurements of physical and mechanical properties.

4.2 RESULTS

4.2.1 Amidisation of AA Functionalised EPDM (F_0-EPD1) with Interlinking Agents Ethylene diamine (EDA) and Hexamethylene diamine (HEMDA)

The amidisation of F_0-EPD1 was carried out as described in **scheme 4.2a**. A variable concentration of the interlinking agent (0-6%) was processed with F-EPD using a temperature gradient method similar to that used in the EPM5 method (see scheme 3.16). In the case of HEMDA, the F-EPD and the interlinking agent were mixed at room temperature before transfer into the mixer, whereas with EDA, the F-EPD was processed first for one minute prior to the addition of EDA which was done in the next 20sec using syringe with long needle. The processing temperature which was initially set at 130°C for both HEMDA and EDA was , maintained for 1minute and 20sec. After this time the temperature was increased to 180°C
(approximately 5.25min) and processing was continued for further 5min, to a total of 12min. The HEMDA amidised F-EPD (A_H-FEPD) and the EDA amidised EPDM (A_E-FEPD) were quenched in cold water and compression moulded into thin films (0.1-0.2mm) for qualitative FTIR analysis. The results of the analysis are given in **figure 4.1a** (in case of EDA) and **4.1b** (in case of HEMDA); for full IR of EDA and HEMDA , see figures 2.8 and 2.9.

Figures 2.8 and 2.9, (chapter2) show that the peaks due to vibration of amino group ($-NH_2$) are located at 3281cm^{-1} and 1598cm^{-1} for EDA, 3220cm^{-1} and 1609cm^{-1} for HEMDA. IR spectra of amidised functionalised EPDM by EDA and HEMDA (A_H-FEPD and A_E-FEPD), see **figures 4.1a&b** ,show the presence of the $-NH_2$ peaks (3304cm^{-1} and 1550cm^{-1}in the case of EDA; 3310cm^{-1} and 1550cm^{-1}in the case of HEMDA). In figure 4.1a, the carbonyl peak of carboxylic group (1713cm^{-1}) of the grafted AA has significantly deminished while simultaneously a strong peak due carbonyl of newly formed amide group (-NHCO) at 1640cm^{-1}(51) emerged, giving evidence of good efficiency of the amidisation reaction which has taken place. The two $-NH_2$ bands (i.e. 3281cm^{-1} and 1598cm^{-1}) show the presence of free amino ends of the bound diamine in the A-FEPD samples. In figure 4.1b, similar bands are present at 1667cm^{-1}, 3310cm^{-1} and 1550cm^{-1}showing that the amidisation reaction with HEMDA has also taken placed. A complete analysis on the effect of [HEMDA] on the extent of amidisation as indicated by the variation of peak height index for the carbonyl and free amine bands are given in **table 4.2.** The peak height index **(PHI)** is *the ratio of the peak height at the chosen wavenumber to the peak height of a stable peak (reference), which*

Table 4.2: Effect of [HEMDA] on the infra red PHI of the A-FEPD samples
[F_0-EPD+HEMDA(0-6%); 180°C, 85rpm,15min]

	PHI at various wavenumbers in A-FEPD			
[HEMDA] (%)	-OH	-C=O of AA in polymer	$-\overset{\overset{O}{\|}}{C}-NH$	free NH_2
	3310cm^{-1}	1715cm^{-1}	1667cm^{-1}	1550cm^{-1}
0	0	0.96	0	0
1	0.19	0.27	0.17	0.08
2	0.28	0.27	0.26	0.33
3	0.48	0.26	0.44	0.57
4	0.34	0.16	0.36	0.96
6	0.33	0.24	0.40	0.48

does not change when the polymer is subjected to thermal or shear stresses; and was found to be at 1461cm^{-1} band ($-CH_3$ vibration).

Table 4.2 shows that the PHI at 3310cm^{-1}and 1550cm^{-1}($-NH_2$ vibrations), and also at 1647cm^{-1}(stretching vibration of -C=O of the amide group) increased with [HEMDA] up to 3-4%,but decreased at higher HEMDA concentration (above 4%). On the other hand, the PHI of 1713cm^{-1} (stretch vibration of carbonyl of the -COOH group) simultaneously decreased and reached A minimum at 4%[HEMDA], as it progressively changed to the amide functional group.

The amidisation of F-PS with HEMDA was carried out as described in **scheme 4.2b** using a temperature programme to minimise the possible loss of HEMDA due to evaporation during the transfer into the mixer (160° -180°C for 10min). The IR spectrum of the amidised functionalised PS (with 3% HEMDA), A_H-PS is given in **figure 4.2a.** At 3% [HEMDA] the spectrum shows some significant reduction in intensity of the carbonyl band of AA at 1733cm^{-1} , showing that the amidisation reaction (with HEMDA) had taken placed. Unlike the case of the amidised F-EPD, the peaks of the newly formed carbonyl of amide (at 1667cm^{-1}), and the free amine end group of the bound diamine were partially hidden [overlapped by a band of aromatic vibration (peak at 1600cm^{-1}) of PS].

4.2.2 Blending of F_0-PS/F_0-EPD1 and F_0-PP/F_0EPD1 containing interlinking agent

4.2.2.1 Amidisation of AA-functionalised PP-EPDM and PS-EPDM blends

The effect of processing conditions i.e. temperature (180-200°C), ram speed (45-100rpm) and time (5-40min) on mechanical properties of amidised functionalised PS-EPDM and PP-EPDM blends were investigated, see schemes 4.3 and 4.4 and table 4.3 and 4.4. The original unit of tensile strength given by the tensile tester was in N/mm^2. It is converted into MPa using relationship 1N/mm ^{2} =1MPa.

The original unit of drop impact strength of kiloergs/mm is converted into J/m using relationship 1kiloergs/mm= 10^5J/m (52)

Table 4.3: Effect of processing temperature, speed and time on tensile and impact properties of amidised AA-functionalised PS-EPDM blends (F&A-PS/EPDM) ,50:50w/w; 180°-200°C, 90rpm 15min for temperature; 190°C, 45-90rpm, 15min for speed and 190°C, 75rpm, 10-40min for time, see scheme 4.4. @ control (blend in absence of HEMDA) , see scheme 4.4.

Processing temperature (°C)	Mechanical properties of F&A-PS/EPDM, 50:50 w/w blends		
	Tensile strength (MPa)	Elongation (%)	Drop impact strength (x10^5J/m)
180	4.8+0.2	6 + 0.1	51+1.5
185	5.6 +0.2	5 + 0.2	54+1.7
190	**5.2 +0.1**	**8 + 0.3**	**57+1.3**
190@	3.4+ 0.2	7 + 0.3	49+1.3
200	4.6+ 0.2	6 + 0.2	55+1.4
60rpm, 10min			

continue table 4.3

Processing speed (rpm)	Mechanical properties of, F&A-PS/EPDM 50:50 w/w blends		
	Tensile strength (x10^4)MPa	Elongation (%)	Drop impact strength (x10^5J/m)
45	5.0 + 0.2	5+0.7	56+1.5
60	5.2 + 0.3	7+0.4	57+1.3
75	5.1 + 0.2	8+0.7	60+1.3
90	**5.3 + 0.1**	**6+0.6**	**62+1.4**

190°C, 15min

continue table 4.3

Processing time (min)	Mechanical properties of F&A-PS/EPDM, 50:50w/w blends		
	Tensile strength MPa	**Elongation (%)**	**Drop impact strength ($x10^5$J/m)**
10	6.0	6.0	62
15	5.7	6.0	56
20	6.1	5.0	46
30	6.5	5.0	63
40	**6.6**	**7.0**	**72**
190°C, 90rpm			

Table 4.4: Effect of processing temperature on tensile properties of F-PP/F-EPDM, 50:50 w/w prepared at 180-200°C, 100rpm, 15min. Sample (@) was prepared in absence of IA.

Processing temperature (°C)	Mechanical properties of F&A-PP/EPDM, 50:50 blends	
	Tensile strength (MPa)	Elongation (%)
180	17.9	9
190	**19.2**	9
200	16.9	8
200@	11.7	6

The optimum processing conditions for amidised functionalised PS/EPDM (F&A-PS/EPDM) blends are shown to be **190°C, 90rpm and 40min**. In case of amidised functionalised PP/EPDM (F&A-PP/EPDM) blend the optimum conditions were **190°C, 100rpm and 15min.**

The peroxide (T101) was shown to have strong effect on final structure of the elastomer particularly to the degree of crosslinking (see table 3.10in chapter 3, page97). Excessively high degree of crosslinking would adversely affect the processability and mechanical property of the polymer and the blend in which the modified polymer is a component. This situation warrants a search for appropriate level of the peroxide for the preparation of the F-EPD. The F-EPD samples were prepared using method EPM1, see scheme 3.12, page , followed by amidisation with 3% HEMDA (see scheme 4.2a). The amidised F-EPD samples were blended with F-PP using the method as described in scheme 4.3 . The impact strength of the blends were obtained and shown in **table 4.5.**

Table 4.5 :Effect of [T101] used in preparation of F_0-EPD1 [EPDM+AA(6%) +T101 (0.003- 0.006MR)+TRIS(1.5%)]; 160^{o}C, 45rpm, 10min] on the Is off amidised F&A-PP/EPDM, 60:40w/w containing 3% HEMDA, processed at 190^{o}C, 100rpm, 15min .

[T101] (MR)	Sample code	Is of F&A-PP/EPDM blends (J/m)
0.003	EPV1	637 + 30
0.004	EPV2	189 + 17
0.005	**EPV3**	**369 + 18**
0.006	EPV4	301 + 08

Table 4.6 shows that F-EPD prepared by using 0.003MR peroxide concentration has resulted in a blend of highest Is. However, there is a doubt to whether such a strength was genuinely due to the effect of compatibilisation or merely derived from the intrinsic strength of the elastomer itself which was not subjected to relatively more severe molecular changes such as scission or crosslinking as compared to those processed with higher peroxide concentration. Since the Is at 0.005MR was higher than the value at 0.004MR, the compatibilisation effect is very clearly shown . Furthermore the Is at this concentration was maximum and it decreases at higher peroxide concentration, indicating the optimisation at 0.005MR. The functionalised F-EPD of 0.005MR [T101] will therefore be used in further reactive blending described in this chapter.

Different methods were examined to promote reactions between the acid functionalities of the polymer components in blends of PS/EPDM and PP/EPDM by using diamines (EDA or HEMDA) as interlinking agent. **Scheme 4.3** shows the different approaches used which essentially involve either direct addition of the diamine to the acid functionalised polymers or by preamidisation of one functionalised polymers and mixing with second functionalised polymer (a). **Figures 4.2b** and **4.2c** show IR spectra and SEM micrographs of the blends while **table 4.6** shows physical appearance and impact strength (Is) of the amidised functionalised PP-EPDM blends.

Table 4.6 : Effect of EDA (4%) and HEMDA (4%) on impact strength of F&A-PP/EPDM (60:40) blends; processed as described in scheme 4.3. EDA was added direct into polymer mixture; HEMDA was either added direct or preamidised with the F-EPDM.

[IA], %	Blends (see sch. 4.3) & Code	Physical appearance of the blend slab (6mm thick)		Charpy impact strength of F&A-PP/EPDM blends (J/m)
		colour	transparency	
EDA, 3 (direct addition)	F&A_F-PP/EPDM (BE3)	light yellowish brown	semi-transparent (ST1)	343 + 3
HEMDA, 3 (direct addition)	F&A_H-PP/EPDM (BH3)	greenish brown	semi-transparent (ST2)	816 + 3
HEMDA ,3% (pre-amidised)	F-PP/A_H-EPDM (BH)	brown	semi transparent (ST3)	369 + 18
IA ,0	F-PP/F_0-EPD1 (B10)	black	opaque	313 + 2

Improvement in impact strength can be taken to suggest an improvement in compatibilisation of the blend components. Table 4.6 shows that direct addition of HEMDA to functionalised blend of PP-EPDM led to 160% improvement in Is compared to its absence and 120% over the Is obtained via the pre-amidisation route. Higher improvement was achieved with HEMDA (in F&A_H-PP/EPDM) compared to EDA.

4.2.2.2 Effect of HEMDA concentrations on mechanical properties of various weight ratios of the amidised F-PS/F-EPD blend

The effect of [HEMDA] on mechanical properties of F_O-PS/F_O-EPDM blends containing various weight ratios of the functionalised polymers (70:30, 60:40, 50:50) was investigated using the direct mixing method, see **scheme 4.5** . In this work, each blend ratio was independently processed with a range of [HEMDA]. The results on tensile strength and elongation are presented in **table 47** . The impact strength of the F&A_H-PP/EPDM, 70:30 blends containing various concentration of HEMDA was also examined for functionalised polymers of different compositions. The HEMDA was introduced by direct addition and the processing was carried out at 190°C, 90rpm, 40min. The results on impact strength are shown in **table 4.8** . SEM micrograph of selected broken impact specimen surfaces (see section 2.8.1) were investigated and presented in **figure 4.3**. For comparison, blends of PS/EPDM (i.e. non functionalised and non amidised) of the same weight ratios were prepared using the same processing conditions and the tensile properties of the blends were measured. The results are shown in **table 4.9**

Table 4.8 shows that in the 70:30w/w and 60:40 w/w blends, within the concentration range used, HEMDA has increased the ultimate tensile strength (Ts) of the blends at two concentrations i.e. at 0.5%(25% in 70:30w/w and 4% in 60:40w/w) and 4.0% (45%increase in 70:30w/w and 22% in 60:40w/w). In the case of 50:50w/w the maximum strength achieved at 4%was 8% higher than achieved at the 2%concentration. The elongation has generally increased with increasing rubber content, but was not sensitive with HEMDA concentration. Table 4.9 shows that the tensile strength decreased with the increase in rubber content, but simultaneously caused increase in elongation.

Table 4.7: Effect of [HEMDA] (0-9%) on tensile properties of F&A$_H$-PP/EPDM blends, containing various weight ratios of the functionalised polymers, prepared at 190 ^{0}C, 90rpm, 40 min (see scheme 4.5).

[HEMDA] (%)	Tensile properties of F&A$_H$-PS/EPDM blends					
	70:30w/w blends		60:40w/w blends		50:50w/w blends	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0.0	6.2+0.2	2	7.1+0.2	4	-	-
0.5	7.7+0.2	3	7.4+0.2	3	-	-
1.0	6.3+0.2	2	7.0+0.3	5	-	-
1.5	6.3+0.2	2	6.0+0.3	4	-	-
2.0	6.1+0.2	2	6.2+0.3	4	6.2+0.2	8
3.0	8.7+0.3	2	8.4+0.2	4	6.6+0.2	9
4.0	**9.0+0.28**	**2**	**8.7+0.3**	**4**	**6.7+0.2**	**9**
6.0	.2+0.2	2	-	-	6.3+0.2	7
7.0	-		7.3+0.2	3	5.8+0.2	8
9.0	-		-	-	5.6+0.2	9

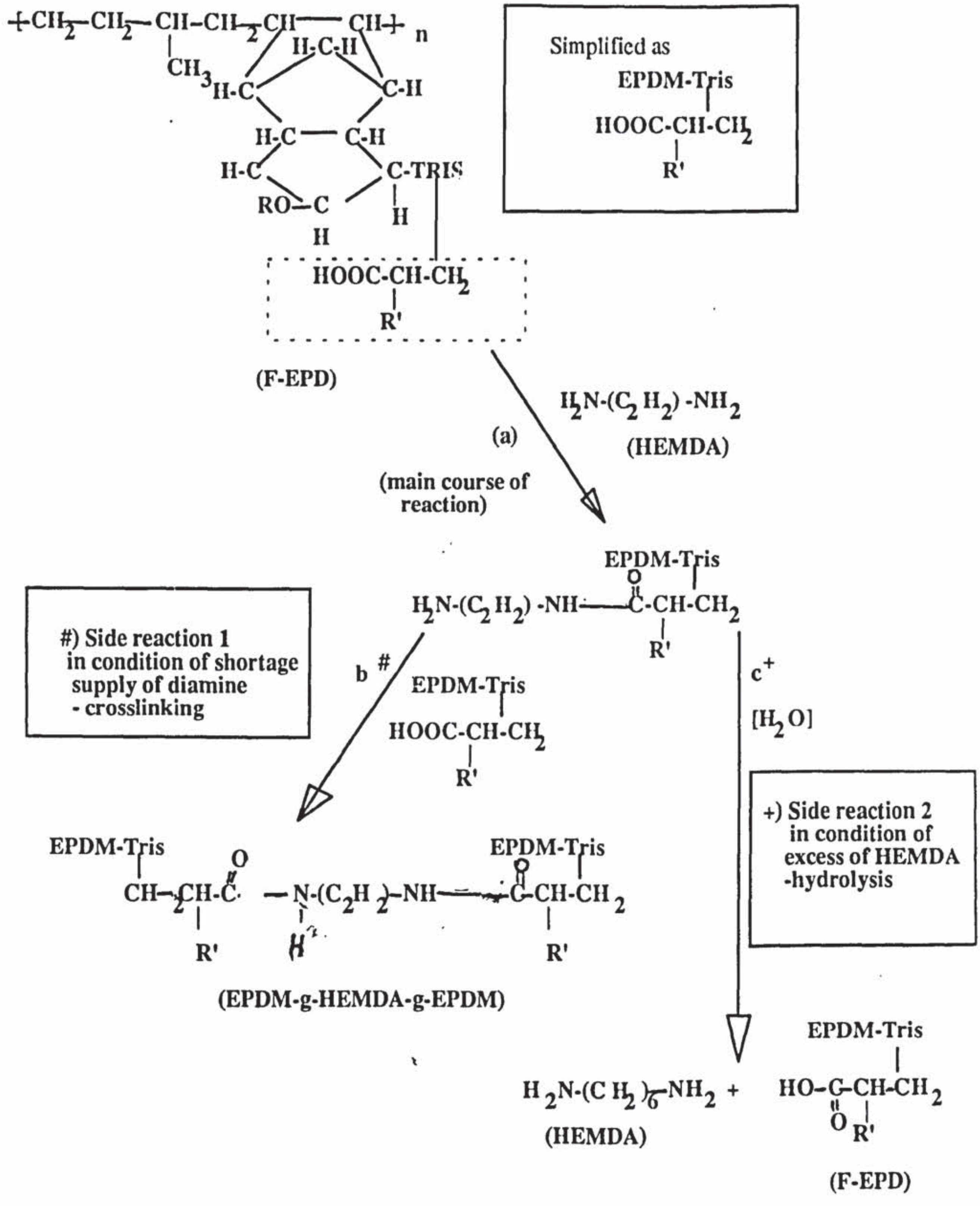
Improvement in impact strength can be taken to suggest an improvement in compatibilisation of the blend components. Table 4.6 shows that direct addition of HEMDA to functionalised blend of PP-EPDM led to 160% improvement in Is compared to its absence and 120% over

Table 4.8. : Effect of [HEMDA] on impact strength (Charpy) of F&A-PS/EPDM, 70:30w/w blends, processed at 190^{o}C, 90rpm, 40min. F-PS [PS+AA(4%)+T101(0.04MR) +DVB(2.5%); 200^{o}C, 100rpm, 10min]; F-EPD1[EPDM+ AA(6%)+T101 (0.003MR) +TRIS(1.5%); 160^{o}C, 45rpm, 10min].

[HEMDA] (%)	Is of F&A$_{II}$-PS/EPDM, 70:30w/w (J/m)
0	22
1	20
2	24
3	33
4	26
6	38

Table 4.9: Tensile properties of various weight ratios of PS/EPDM blends prepared at 190^{o}C, 90rpm, 10min.

weight ratio (%)	Tensile properties of PS/EPDM blends	
	Tensile strength (N/mm^{2})	Elongation (%)
80:20	24	5
70:30	19	11
60:40	11	13
50:50	8	17



Reaction Scheme 4.1: Suggested reaction mechanism of amidisation of F-EPD with HEMDA, in the mel at 180°C.

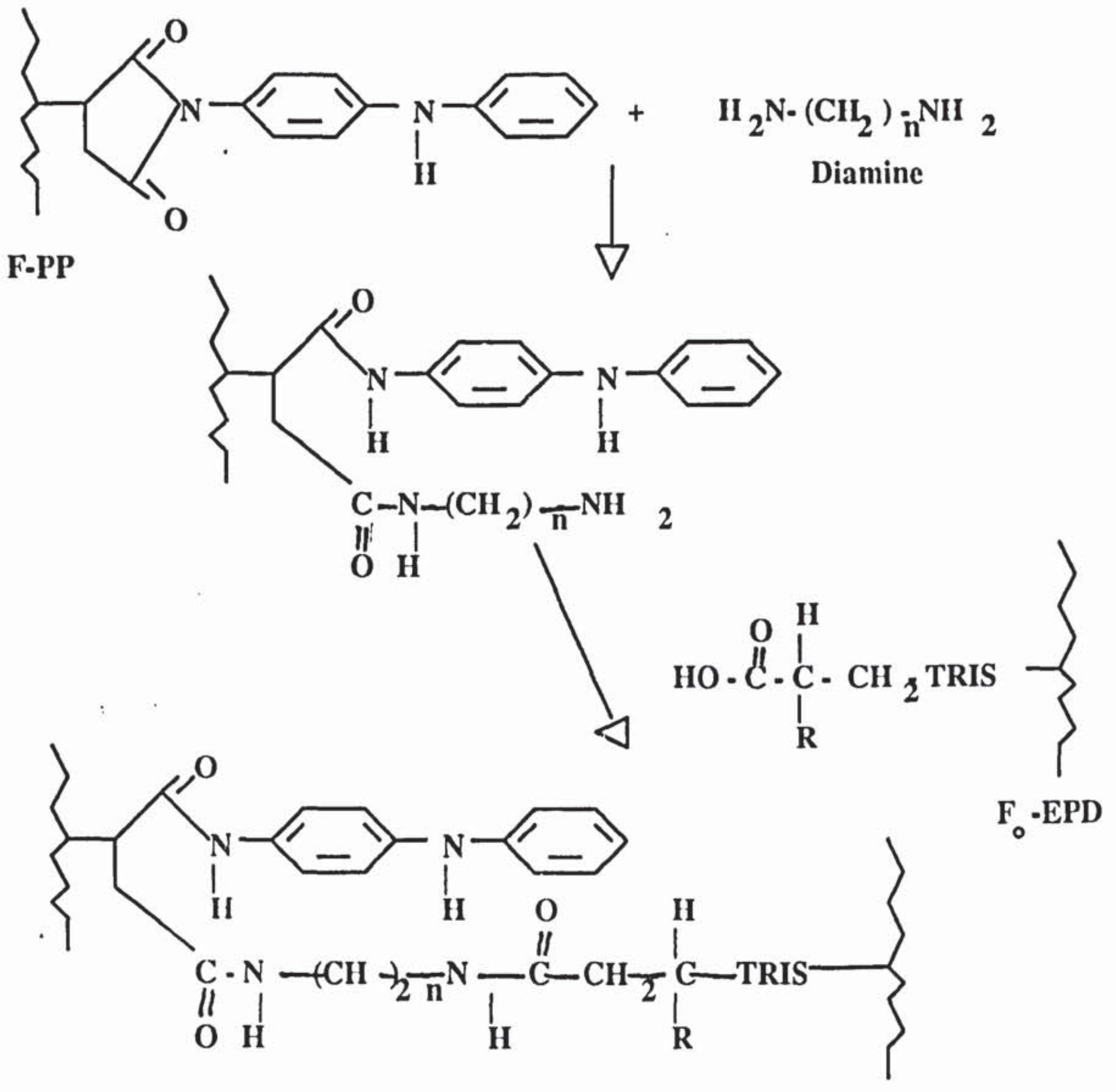
4.3 DISCUSSIONS

4.3.1 The Role of Interlinking Agent In Compatibilising the F-PS/F-EPDM and F-PP/F-EPDM Blends.

Figures 4.1a&b and 4.2 show that both EDA and HEMDA have undergone amidisation reaction with F-EPD and F-PS in the melt. At 3% IA concentration, there was a significant extent of amidisation reaction between the carboxylic functional group of AA (total) and the amino functional group of IA, shown by significant deminishing of the intensity of the carbonyl band of the carboxylic functionality of the grafted AA as it was converted into amide group functionality (-NHCO). **Figure 4.4** shows that a maximum extent of amidisation (indicated by the change in peak height index, PHI) of the carbonyl band of carboxylic functional group, $1734cm^{-1}$, was achieved at HEMDA concentration of 3.5-4%. This was accompanied by the availability of maximum concentration of free (unreacted) $-NH_2$ group of the bound diamine (shown by the maximum PHIs of $3039cm^{-1}$and $1580cm^{-1}$bands). At concentrations higher than this, the HEMDA affects adversely the extent of amidisation, causing a decrease in the concentration of the free amine group of the bound diamine moeity

Amidisation reaction with HEMDA, in F-EPD, at lower or higher concentration than the optimum level, has caused reduction in the extent of the reaction , see table 4.3, which demonstrated the critical limit of IA concentration to affect maximum conversion of the existed carboxyl group in the functionalised polymers into the amide group, see **reaction scheme 4.1.** At concentration below the optimum level, the depletion in the IA concentration could presumably cause pre-mature crosslinking reaction between the remaining unamidised carboxylic group with the second (free) amine group (of the bound IA), see *side reaction route b* in the reaction scheme 4.1, which was disadvantageously reducing the amount of the second free amino group available for reaction in further blending with a second functionalised polymer. At higher concentration than the optimum level, the presence of higher concentration of the amine groups (from the unreacted diamine) could prevent the undesirable side reaction, but the concomitant increase in reaction speed (which was proportional to the IA concentration) could result in the rate of release of water vapour excessively higher than the limited dissipative capacity of the mixer (via any of its natural gap of the non air-tight design of the equipment). In presence of the high level of the water vapour at a particular instant, hydrolysis of the amide bond back to the acid has probably occurred and hence reducing the final level of the amidisation, see *side reaction route c* in the reaction scheme 4.1.

In a blend involving any two of the three functionalised polymers (F-PS, F-EPD and F-PP) in which an IA is present, it is expected that the amidisation reactions between the carboxyl functionality groups of both polymers and the amine group of the IA, see reaction scheme 4.2 lead to formation of crosslinked macromolecule (a copolymer),e.g.F-PPg-PM-IA-AA-g-EPDM , which is consisted of segments of the polymer components. The copolymer is therefore expected to acts as a solid phase dispersant (SPD), compatibilising to certain degree the originally incompatible blend. Figure 4.4a (and table 4.5) show that both EDA and HEMDA have clearly increased the impact strength of the blends. However HEMDA was more effective than EDA; the increase in impact strength due to HEMDA was several order of magnitudes higher than EDA. The evidence of compatibilisation is further supported by the SEM micrographs, see figure 4.2c, which compare the surface structure of the amidised F-PP/F-EPD blends , one without HEMDA (0%), BH0, and the other contained HEMDA (3%), BH3. A very extensive displays of microfibrils in BH3 (as compares to the (BH0) demonstrates the presence of substantially high interfacial adhesion between the dispersed phase (EPDM) and the continuous matrix (PP) which was probably due to the emulsification activity of the copolymer.



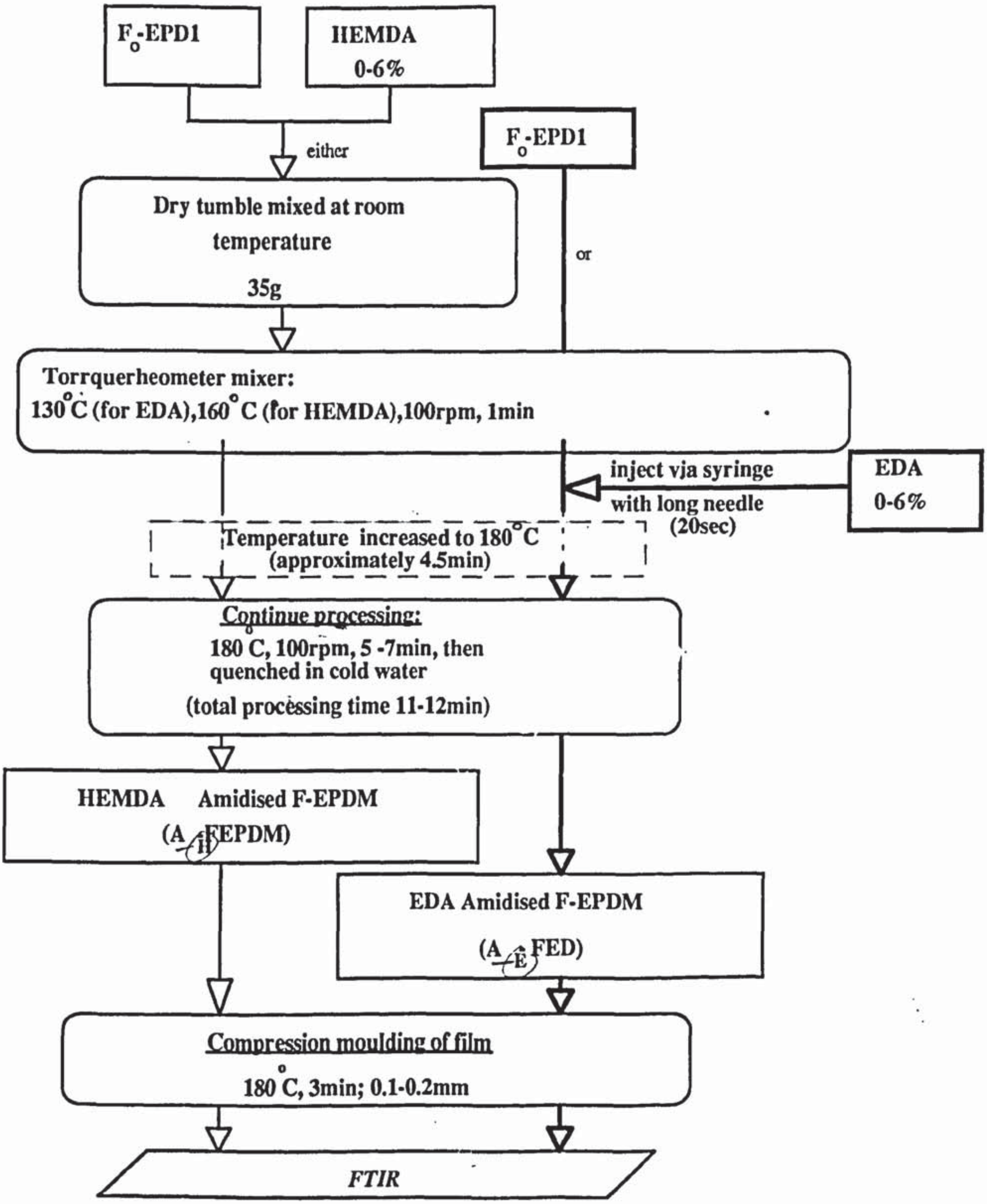
PP-g-PM-IA-AA-g-EPDM

Reaction scheme 4.2: Suggestion mechanism of reaction for amidisation of F-PP with a diamine (EDA or HEMDA); at 180°C, 15min processing conditions.

Figure 4.4a also shows higher enhancement effect of HEMDA over EDA, which was probably due to two reasons i.e. basicity and chain length.The longer carbon chain length in HEMDA (C6) could cause higher basicity over EDA (C2) and hence leading to higher reactivity of its amino group towards the carboxylic group of the AA in F-EPDM, and the anhydridic imide group of the phenyl maleimide of the functionalised PP (F-PP). Furthermore, the longer carbon chain length of the HEMDA could offer flexibility in overcoming (up to certain extent) steric hindrances which are inherent to the F-EPDM and F-PP. Such flexibility is possibly limited in the case of EDA due to its shorter carbon chain length.

Processing mixtures of F-PS/F-EPD using optimum processing conditions, see figures 4.5a&b, 4.6a&b and 4.7a&b has further improved the mechanical properties of the F&A_H-PP/EPDM blends.These processing conditions were used in the preparation of the F-PS/F-EPDM blends of various weight ratios containing various concentration of HEMDA, **Figure 4.8** (see also table 4.7) show that as in the case of the F-PP/F-EPD blends, HEMDA has effectively enhanced the mechanical properties. The maximum tensile strength for blends of various weight ratios was achieved at appeoximately 4%HEMDA for tensile properties, and for the 70:30 composition, the impact strength was achieved 6%HEMDA, see figure 4.9. As in the case of the amidised F-PP/F-EPD blends, the improvement in the mechanical properties was most probably realised, through the *in situ*formation of copolymer of F-PS-HEMDA-g-F-EPDM consisting segments of PS chain and EPDM chains, see **reaction** scheme 4.3., which was preferentiallylocated at the interface and acts as emulsifier, reducing the interfacial tension and hence promoting greater adhesion between the dispersed and continuous matrix phases, resulting into improvement of the mechanical properties. The improved interfacial situation is further verified by the SEM micrograph, see figure 4.3; in which the broken surface of PSH6 sample (contained 6% HEMDA), shows the presence of microfibrils (streched as a result of strong resistance to the fracturing force) of fine diameter (~6um) interconnecting the dispersed phases, which was absent in the PS1 sample (1% HEMDA). Fayt et. al. found similar displays of fibrils in their compatibilised PS/PE ([56]) . As it is well known ([53,54,55]), the graft copolymer such as above ,which contain chain segments of PS and EPDM would be able to compatibilise the PS/EPDM blend. The extent of reaction leading to the formation of the graft copolymers however, competes with other side reactions, particularly those which would lead to the formation of crosslinked macromolecules between similar polymer chain such as via routes b and c, see reaction scheme 4.3. Such possible occurrence would decrease the concentration of the functionalised polymers which would potentially undergo the beneficial 'crosslinking reaction' via route (a), and hence reduced the concentration of graft macromolecule having potential compatibilising characteristic. This aberration can be apparently overcame through the judicious use of suitable concentration of the IA.

Figure 4.10 compares the strength of PS/EPDM and the F&A_H-PS/EPDM blends at their maximum strength (see tables 4.8 & 4.10). Although the IA (HEMDA) has successfully enhanced the strength of the latter, but in all cases their strength was much lower than the strength of the blends of the unmodified polymers. The longer and more severe thermal history undergone by the modified polymers, as compared to that of the polymers which constituted the PS/EPDM blends, have presumably caused excessive degradation to the molecular chains, leading to inevitable decrease in the basic strength of the former, and this situation was further reflected in the mechanical properties of the their blends. Nevertheless, the presence of the copolymer has in the amidised blends have brought up some of the compositions as potential SPD for the PS/EPDM blends.This potential was investigated, as described in the next chapter (see **Chapter 5**).



Scheme 4.2a: Flowchart for amidisation of F$_0$-EPD1 with HEMDA (via thin line arrows) and F$_0$-EPD1 with EDA (via thick line arrows); 130-180^{0}C, 100rpm, 12min.

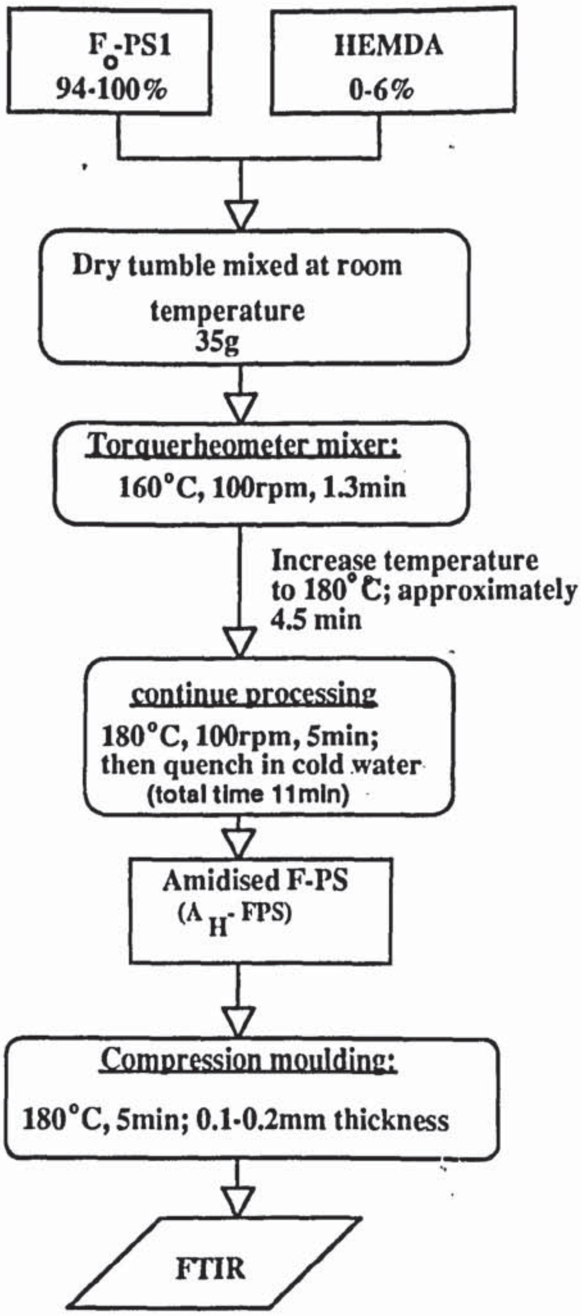
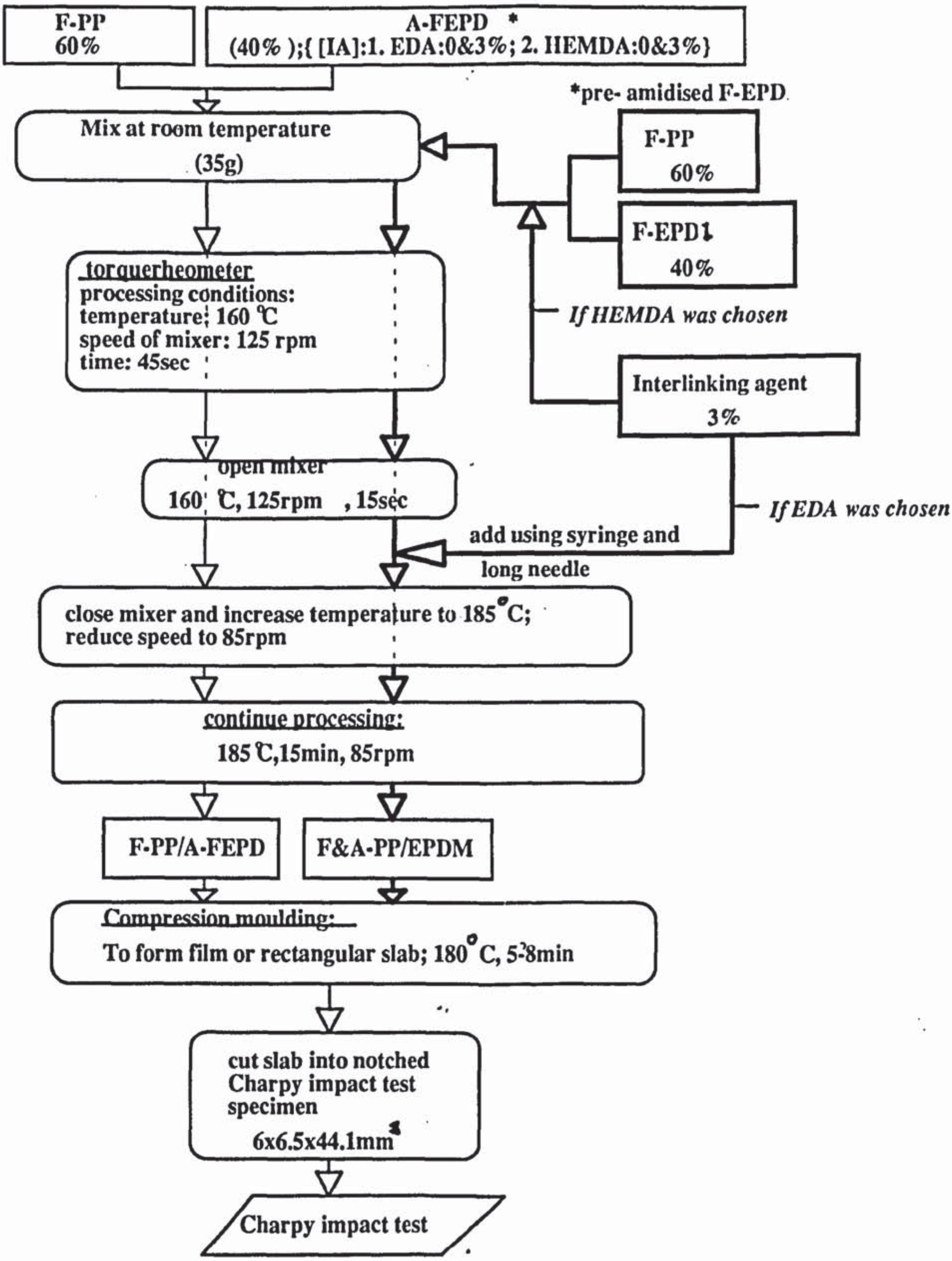
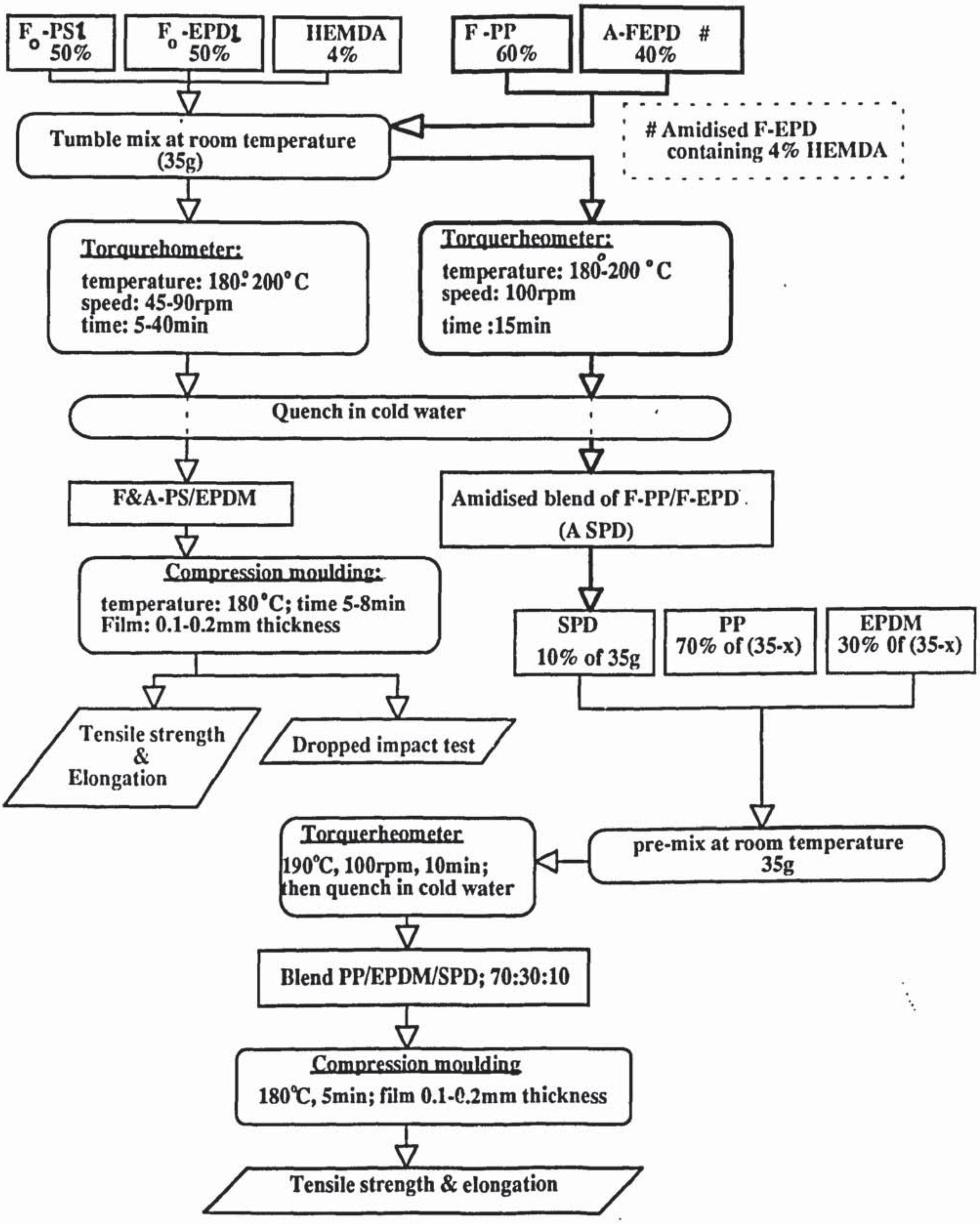


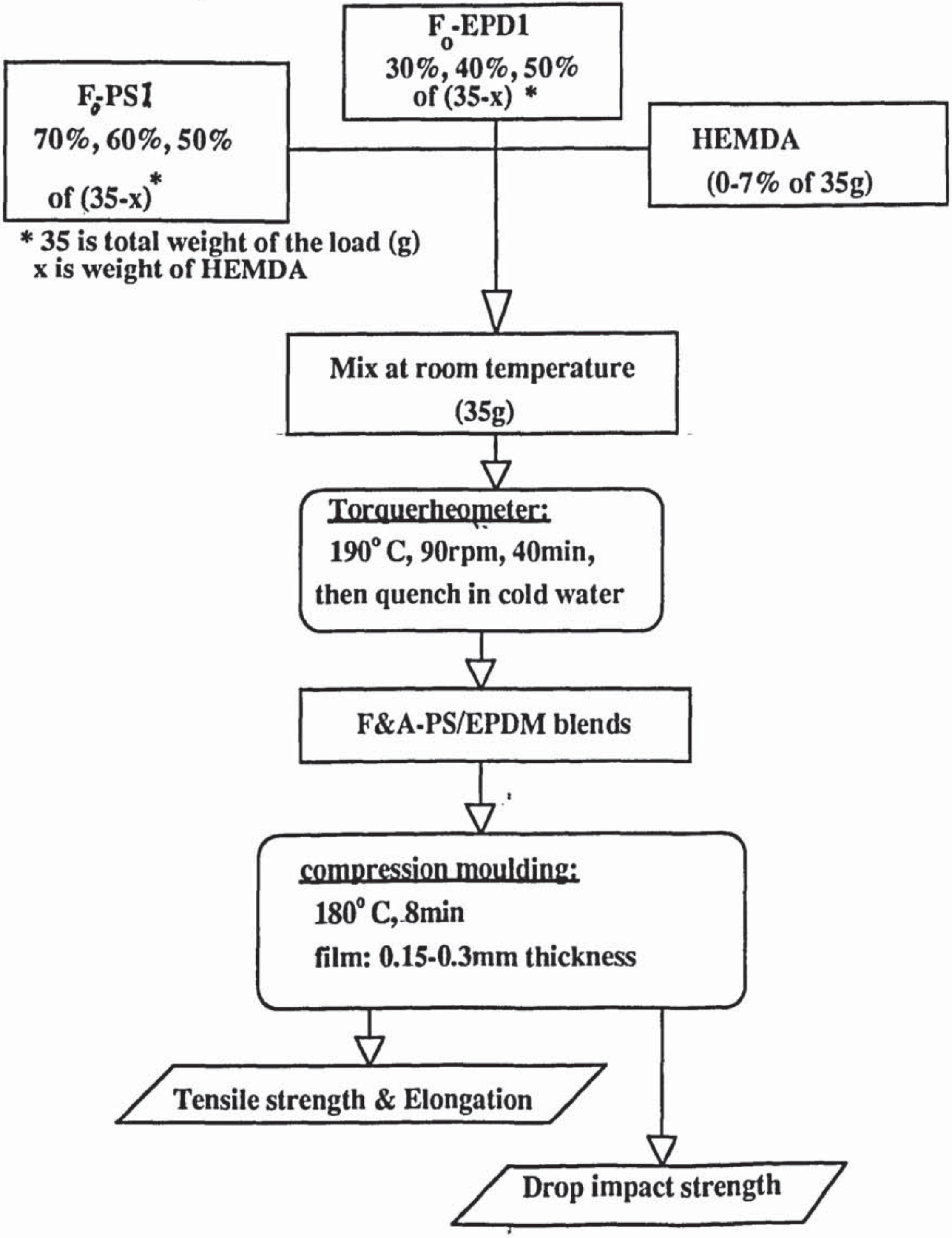
Figure 4.2b: Flowchart of amidisation of F-PS with HEMDA (0-8) and infra red analysis of the amidised F-PS.



Scheme 4.3: Flowchart for evaluation of potential IA (EDA or HEMDA) for blends of F-PP/F-EPD1 (thin line route); and determination of appropriate method of incorporating IA , i.e. by direct addition (thick line route) or pre-amidised (thin line route)

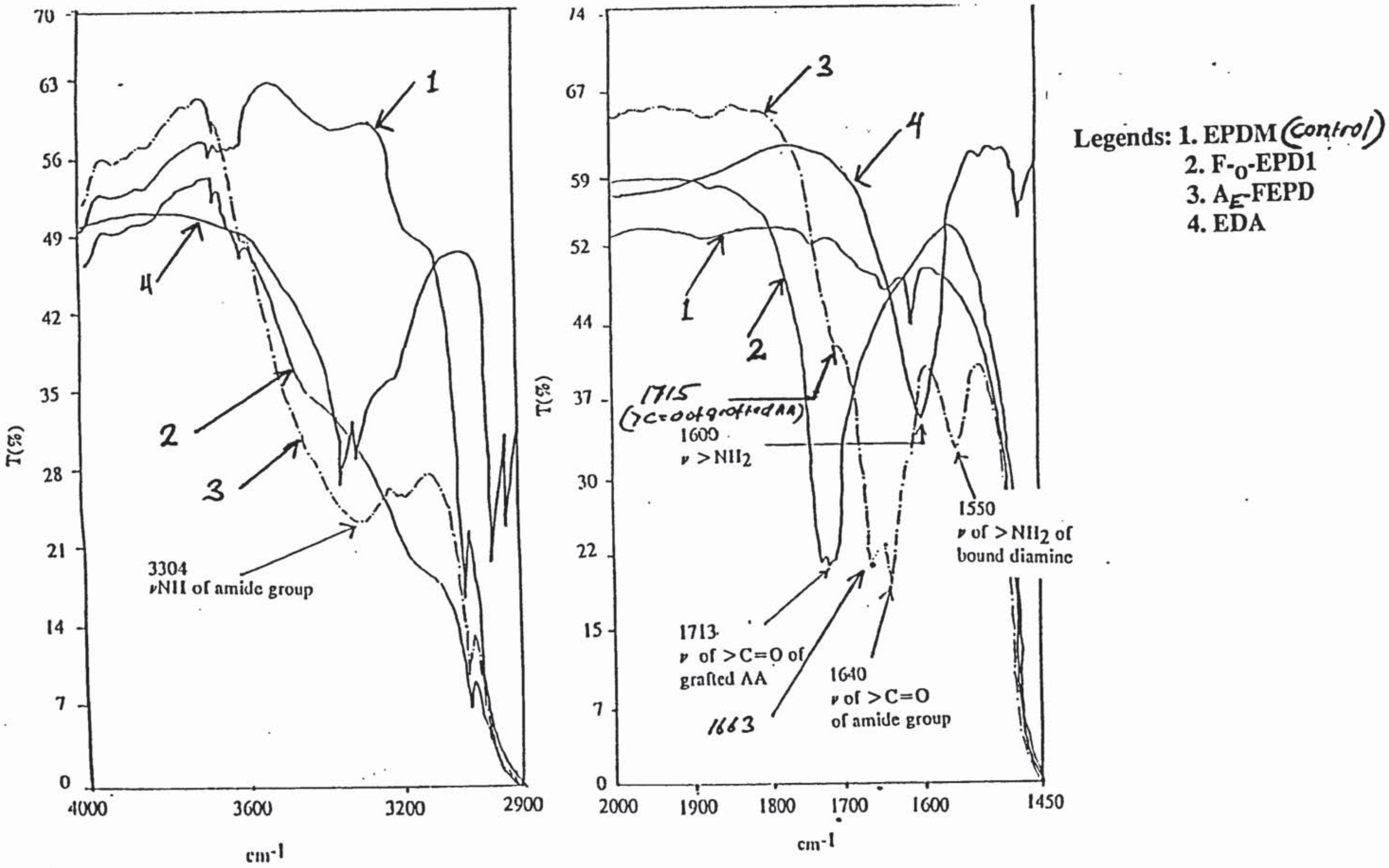


Scheme 4.4: Flowchart for determination of optimum processing conditions; temperature, rotor speed and time for F-PS/F-EPD1/HEMDA , 50:50:(4%) blend, and temperature for F-PP/A-FEPD, 60:40 blend by indirect method (by evaluating it's compatibilising effect on PP/EPDM,70:30 blends.



Scheme 4.5 : Flowchart for blending of F$_0$-PS/F$_0$-EPD1 mixture of various weight proportion of the functionalised polymers in which each weight proportion was blended with a range of concentration of HEMDA (0-9%).

Figure 4.1a: IR showing effect of EDA (3%) on amidisation reaction of AA-functionalised EPDM (F_0-EPD1). EDA was a thin liquid film in between KBr disk; EPDM, F_0-EPD and A_E-FEPD were films (0.1mm) pressed from the processed polymers at 180°C



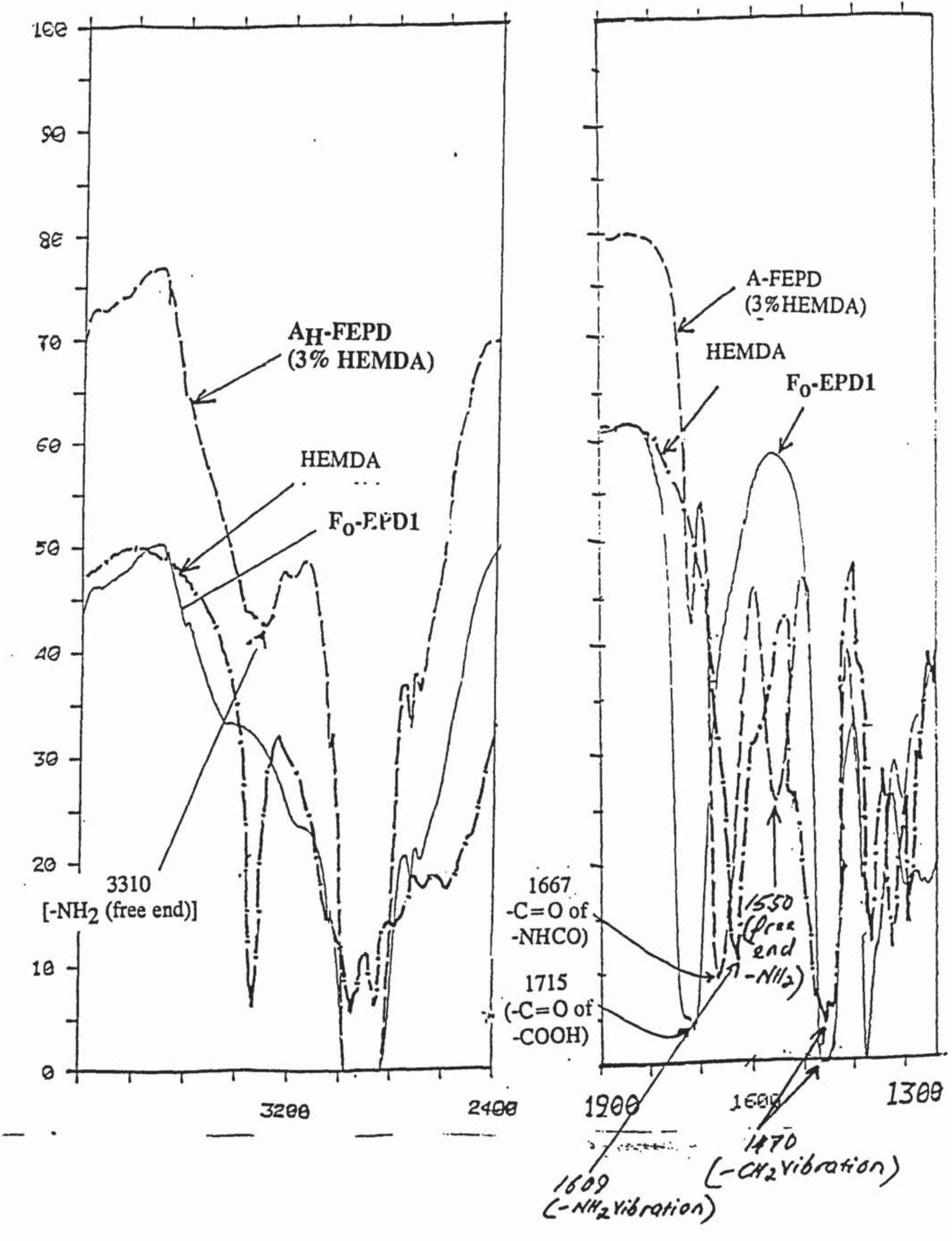


Figure 4.1b: IR showing effect of HEMDA (3%) on amidisation reaction of AA- functionalised EPDM. HEMDA was thin liquid film in nujol; F-EPD1and A-FEPD were polymer films (0.1mm thickness), pressed from processed polymers at 180°C.

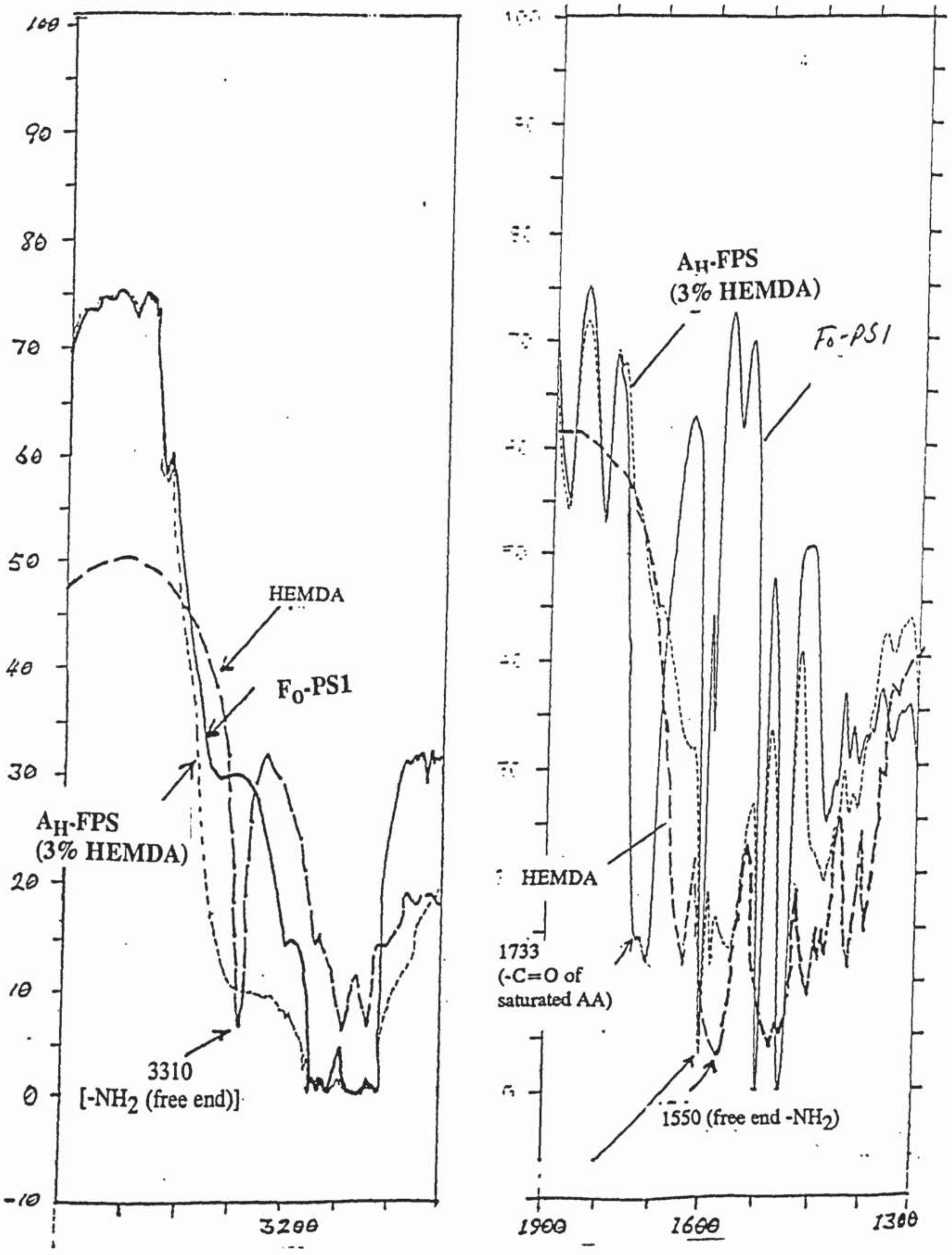


Figure 4.2a: IR showing effect of HEMDA (3%) on amidisation reaction of AA- functionalised PS. HEMDA was thin liquid film in nujol; F-PS and A-FPS were polymer films (0.1mm thickness), pressed from processed polymers at 180^{o}C.

Figure 4.2b: IR spectra showing effects of one level concentration (3%) of IAs (EDA and HEMDA) on the extent of deminishing of the carbonyl band of the carboxylic group of the grafted AA (1733cm^{-1}) and the emergence of carbonyl band of the amide functionality (1641cm^{-1}) in F-PP/F-EPDM , 60:40w/w blends (thin films, 0.1mm thickness). Letters on spectra represents: a. 0% IA, b. 3% EDA and c.3% HEMDA.

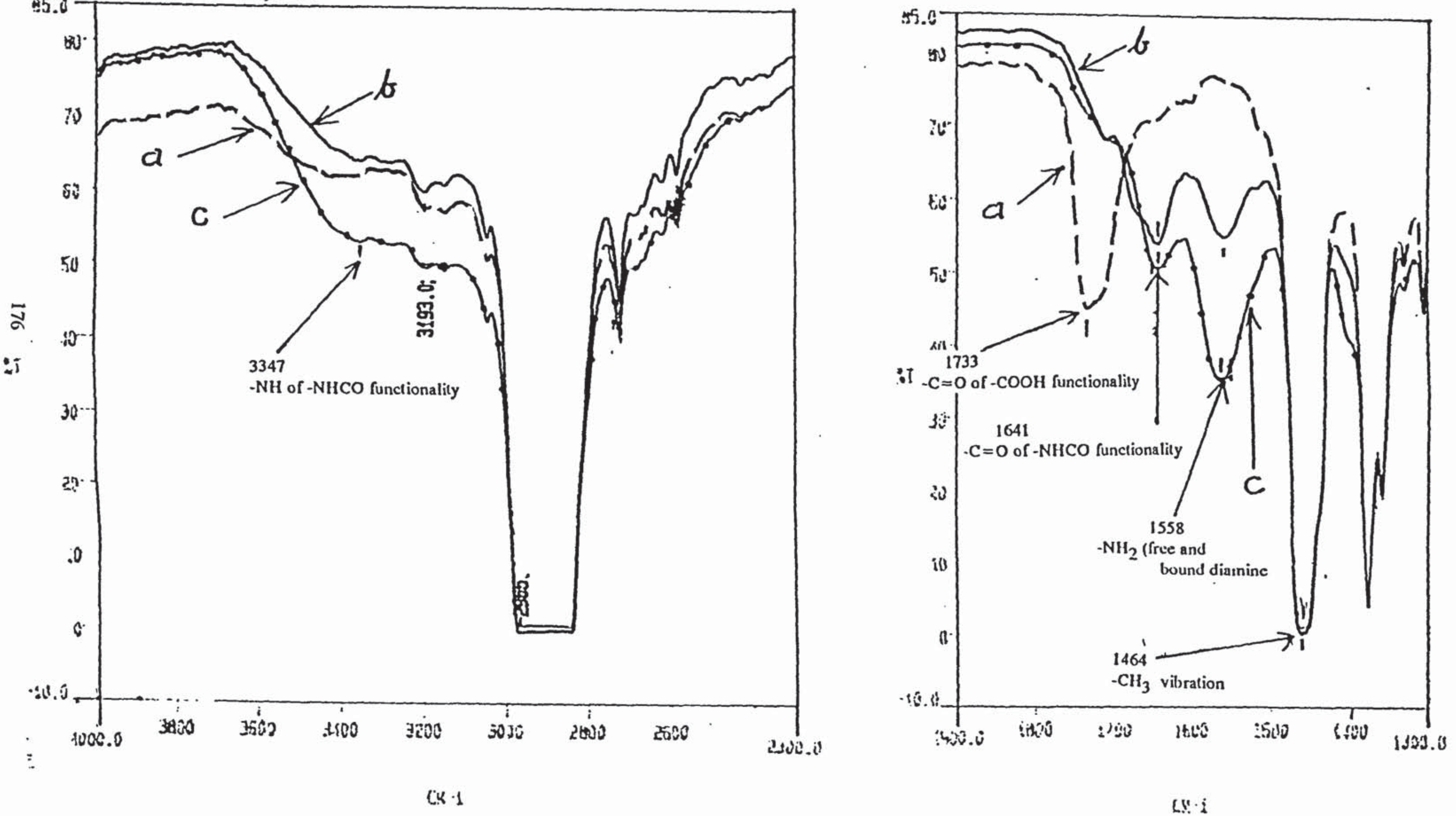


Figure 4.2b: IR spectra showing effects of one level concentration (3%) of IAs (EDA and HEMDA) on the extent of deminishing of the carbonyl band of the carboxylic group of the grafted AA (1733cm^{-1}) and the emergence of carbonyl band of the amide functionality (1641cm^{-1}) in F-PP/F-EPDM , 60:40w/w blends (thin films, 0.1mm thickness). Letters on spectra represents: a. 0% IA, b. 3% EDA and c.3% HEMDA.

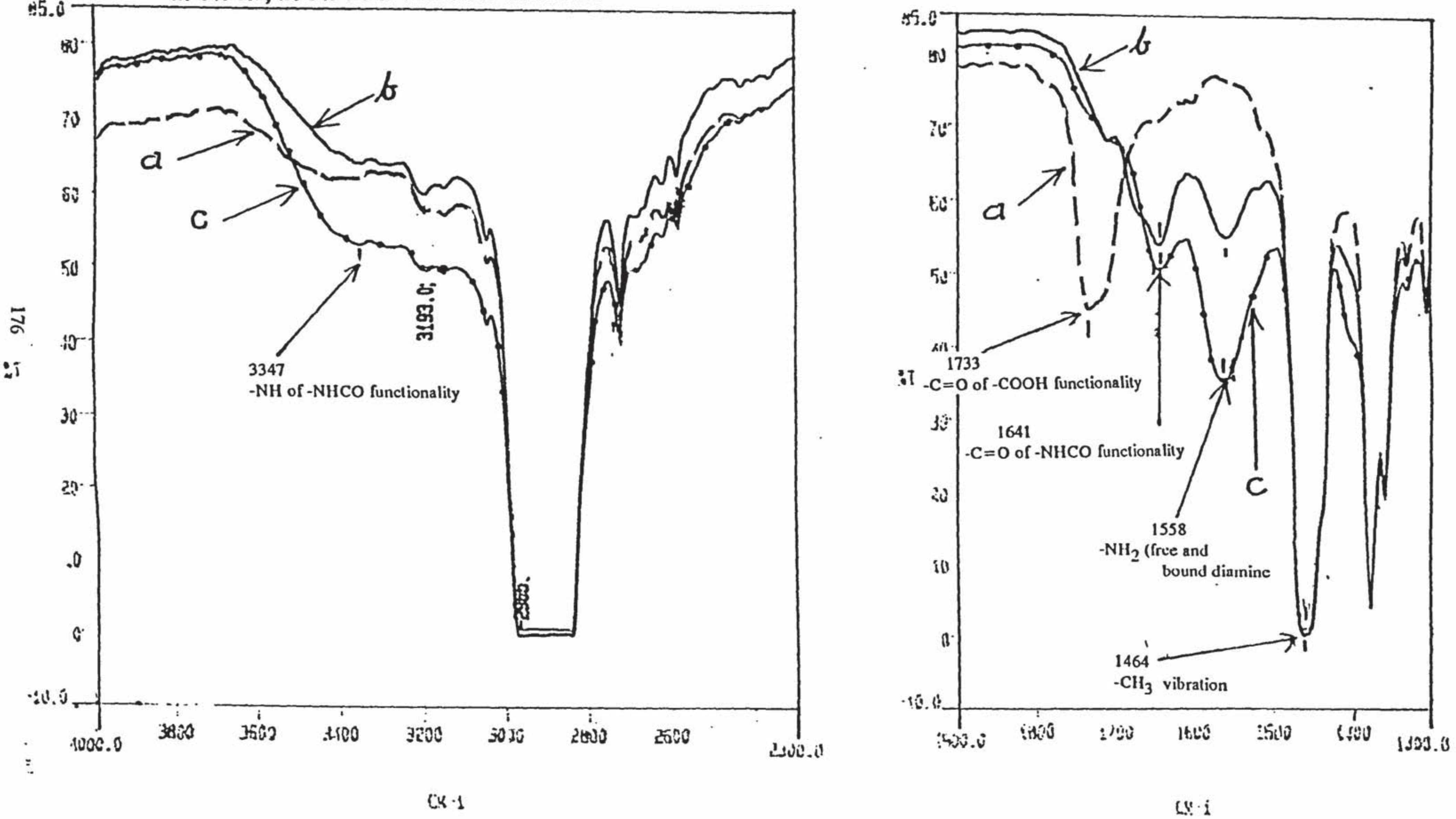
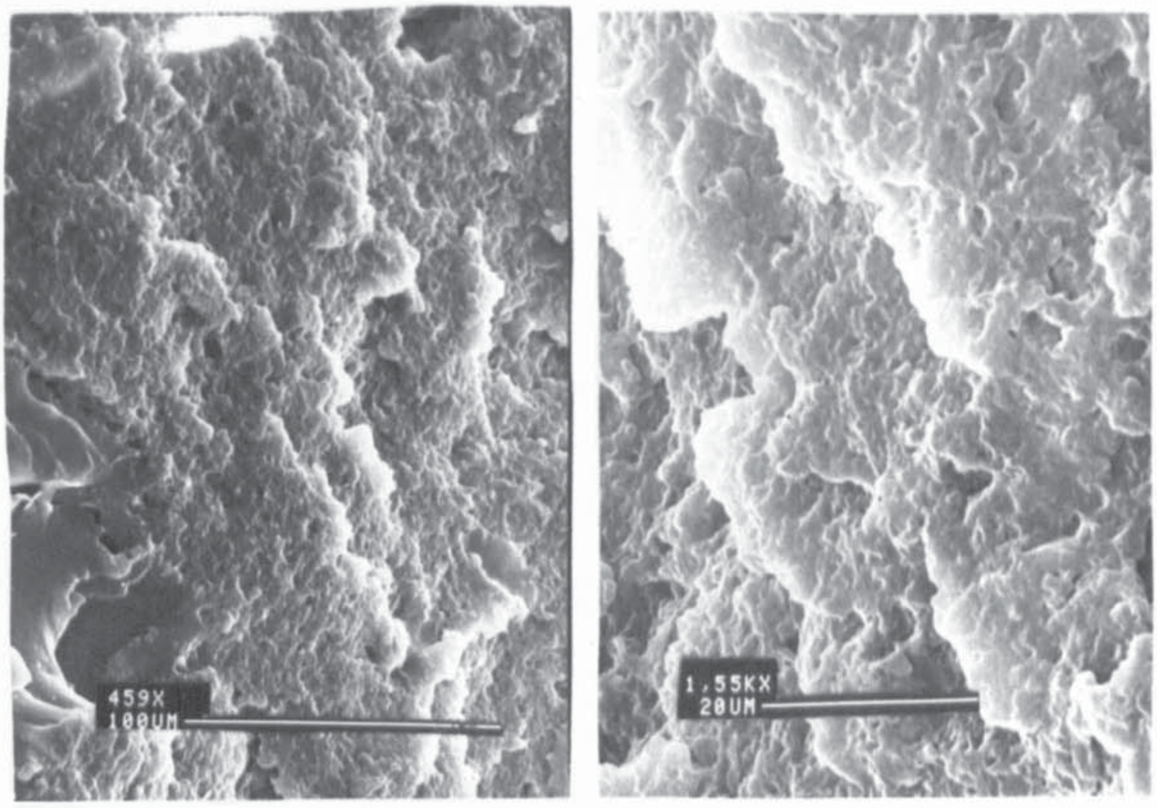


Figure 4.2c: Effects of HEMDA (0, 3%) on SEM photomicrographs of the surface of the broken impact test specimen films (0.1-0.2mm thickness, see section 2.7.3.1, chapter 2) of F-PP/F-EPD, 60:40w/w blends, BI0 and BH3 (see table 4.5).

Sample BIO, 459x magnification **Sample BIO, 1,550x magnification**



Sample BH3, 551x magnification **Sample BH3, 1750x magnification**

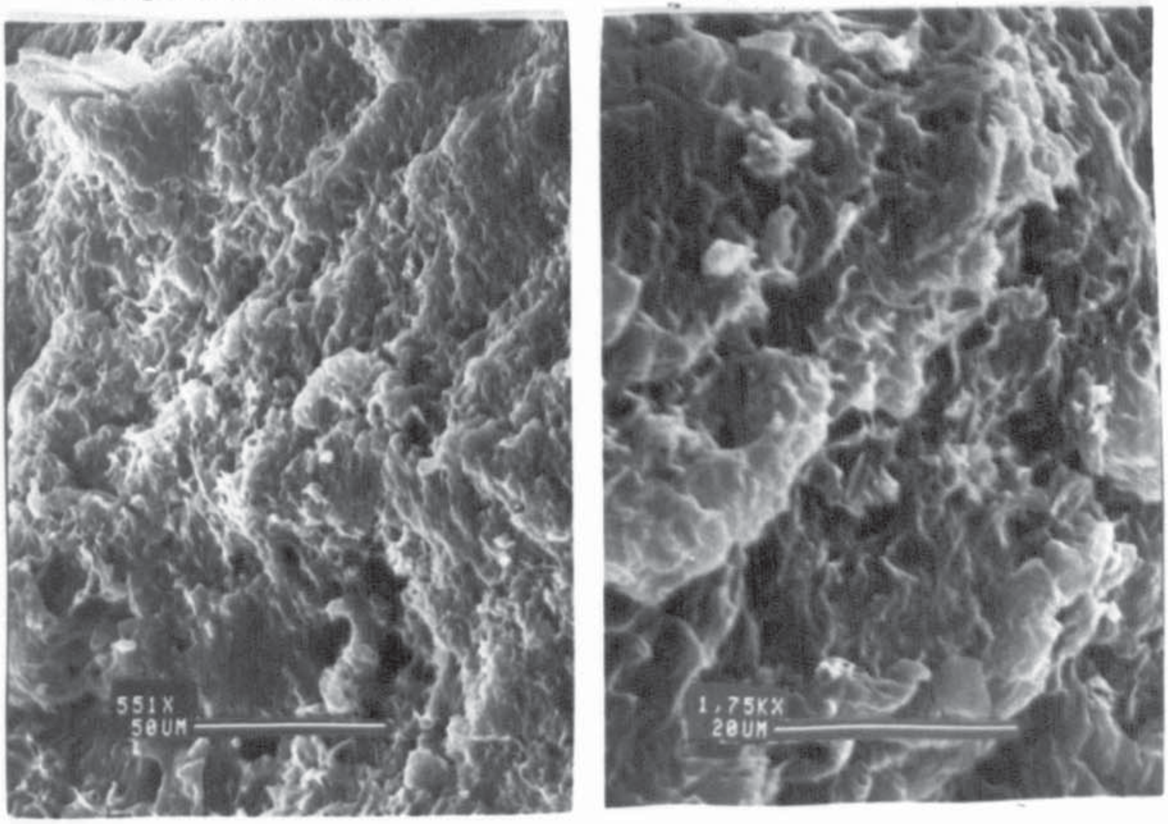
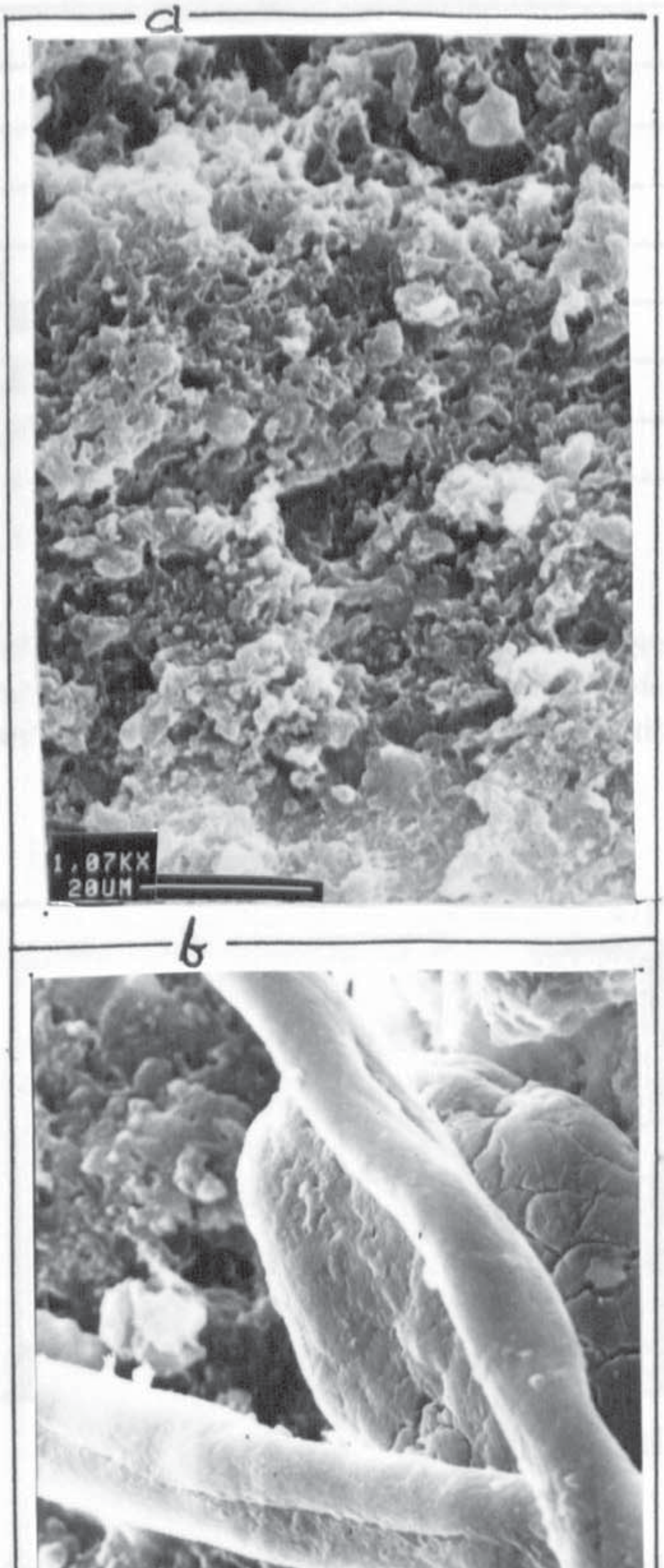


Figure 4.3: SEM micrograph of broken surface of F&A-PS/EPDM blends (F_o-PS1/F_o-EPD1, 70:30w/w, processed at 185°C, 85rpm, 40min). Letters represent: a, 1%HEMDA, b, 6%HEMDA.



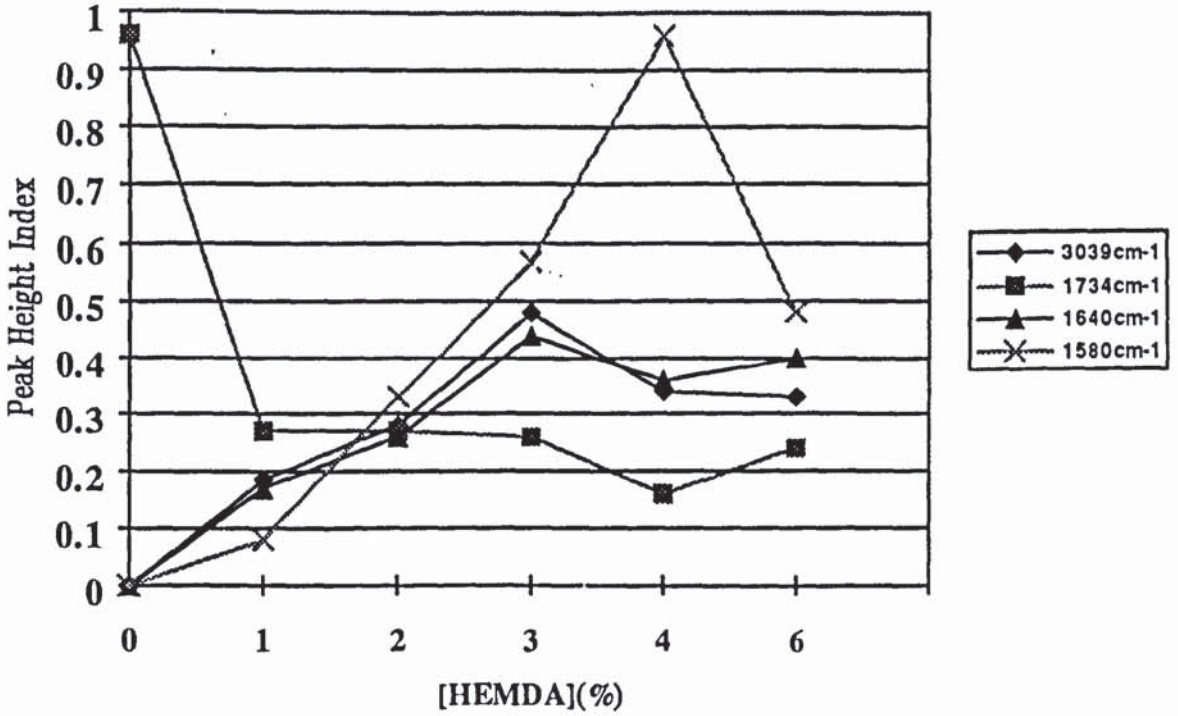


Figure 4.4: Effect of [HEMDA] (0-6%) on the PHI of amino groups ($3039cm^{-1}$ and $1580cm^{-1}$), carbonyl of the carboxylic functionality ($1734cm^{-1}$) and carbonyl group of the amide functionality ($1640cm^{-1}$)

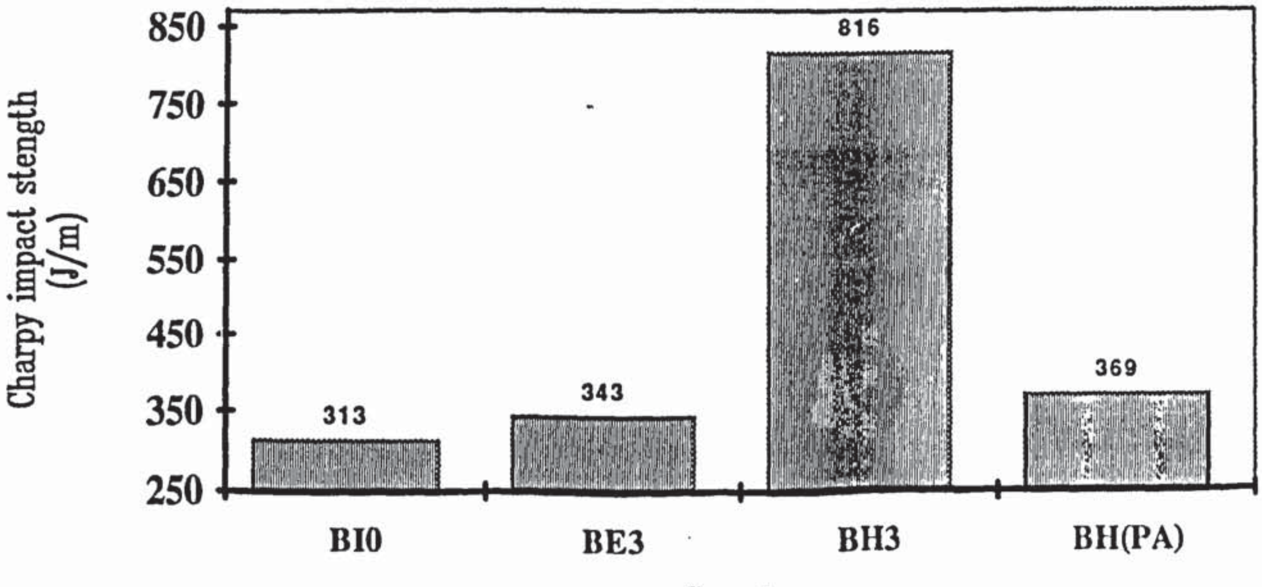
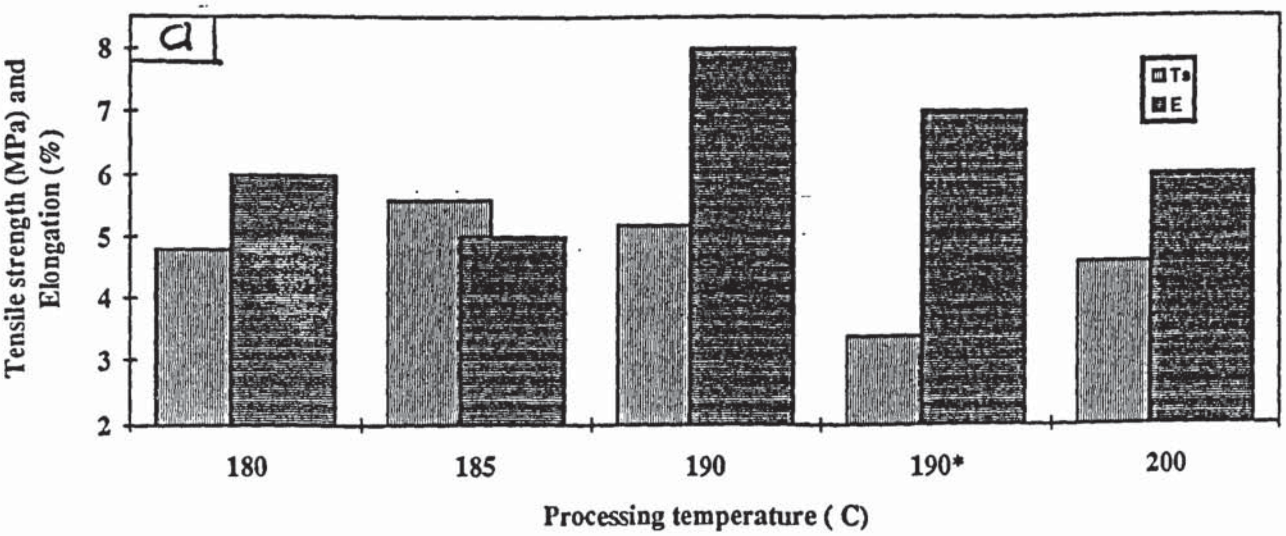
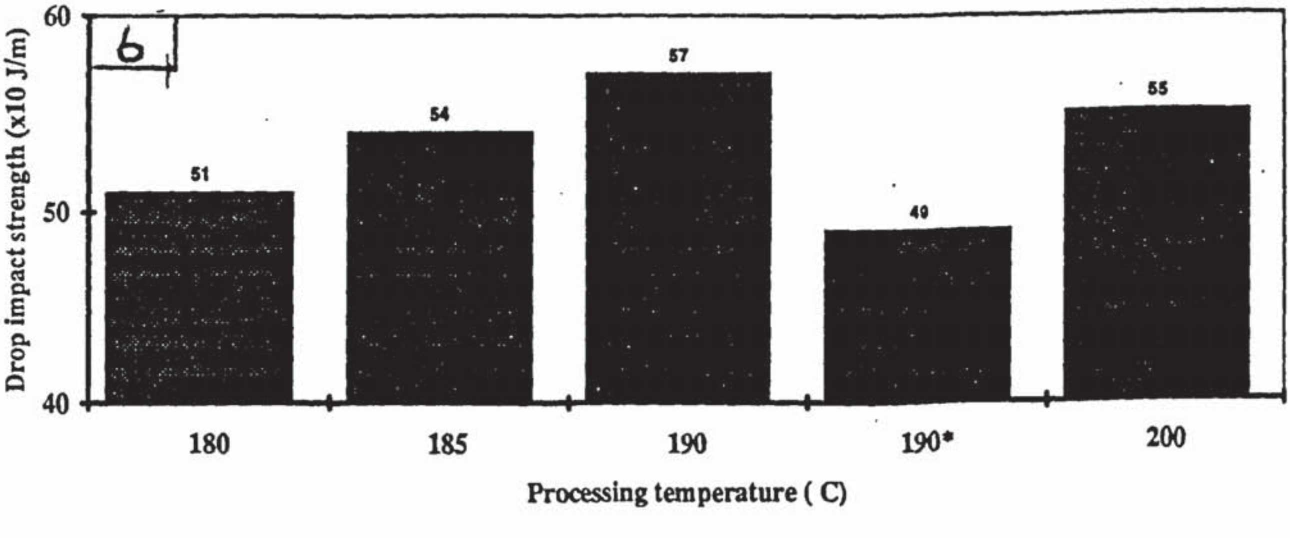


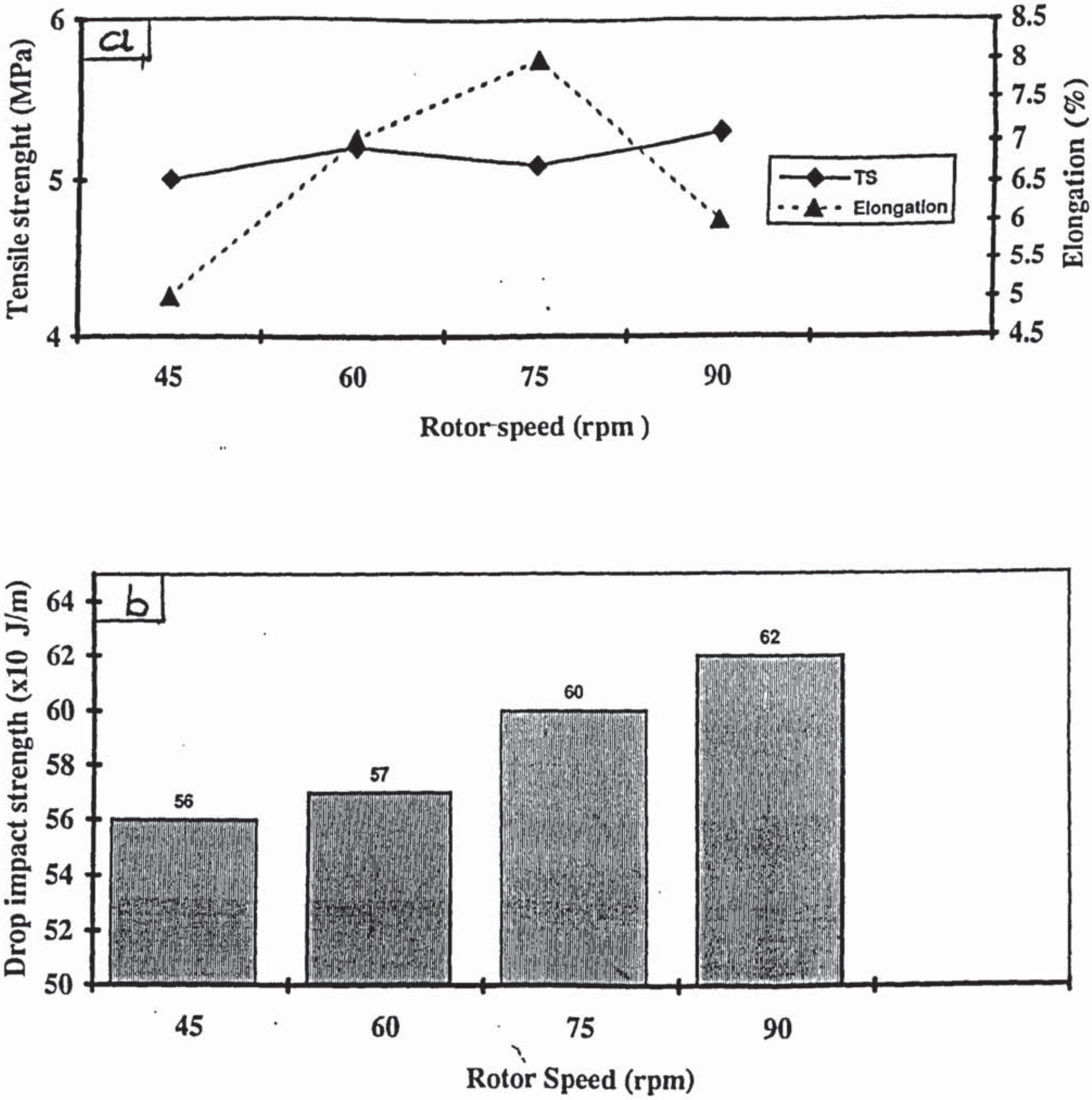
Figure 4.4a: Effect of EDA and HEMDA and methods of addition on Charpy impact strength of F-PP/F-EPD ,60:40 blends, processed using method described in scheme 4.3, see table 4.6 for codes

Figures 4.5a&b: Effect of processing temperature on tensile strength and elongation (a) and drop impact strength (b) of F-PS/F-EPD ., 50:50 blends, containing 3% HEMDA, processed at 180°-200°C, 60rpm, 10min,using method as described in scheme 4.4. mixture (*) was without HEMDA (control).

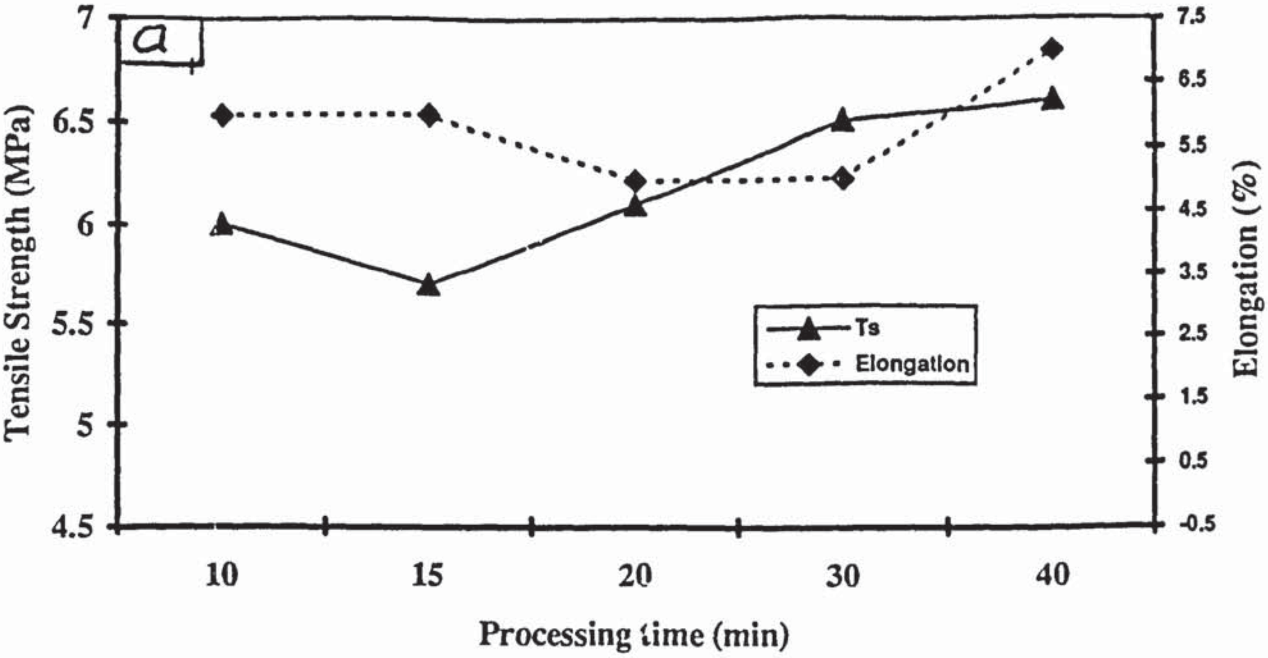


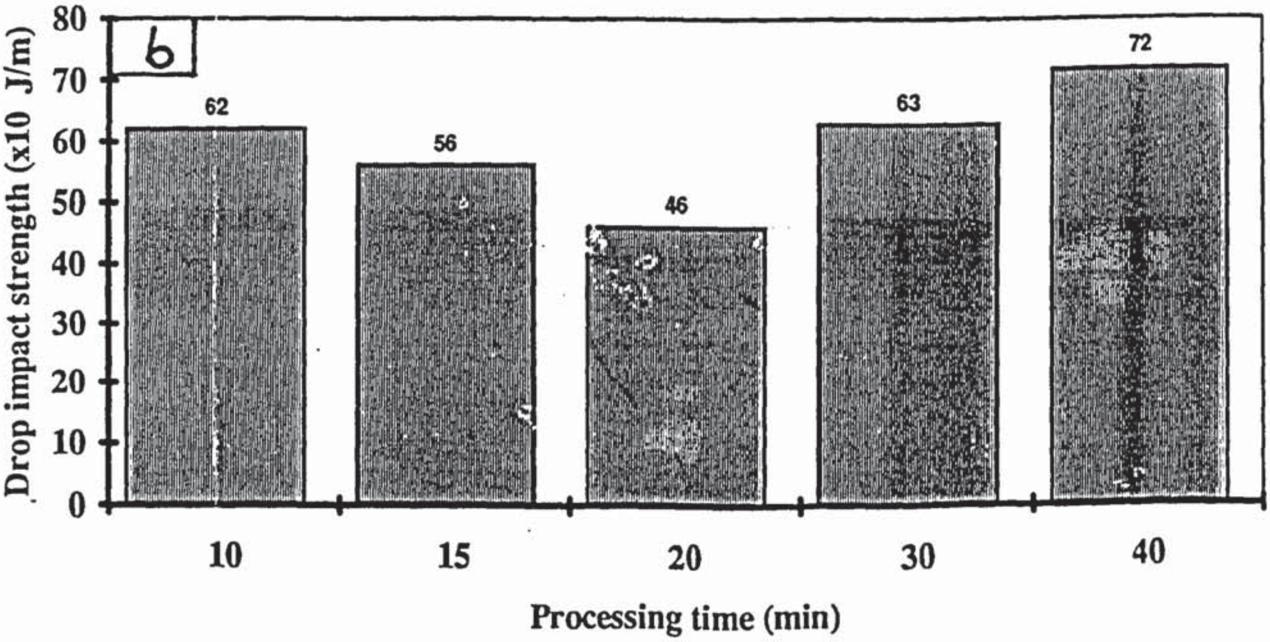


Figures 4.6a&b: Effect of rotor speed on tensile strength and elongation (a) and drop impact strength (b) of F-PS/F-EPD. , 50/50 blends containing 3%HEMDA, processed at 190^{0}C, 45-90rpm, 10min,using method as described in scheme 4.4.



Figures 4.7a&b: Effect of processing time on ultimate tensile strength and elongation (a) and dropimpact strength (b) of F-PS/F-EPD , 50:50 blends containing 3% HEMDA, processed at 190°C, 75rpm, 10-40min, using method as described in scheme 4.4.





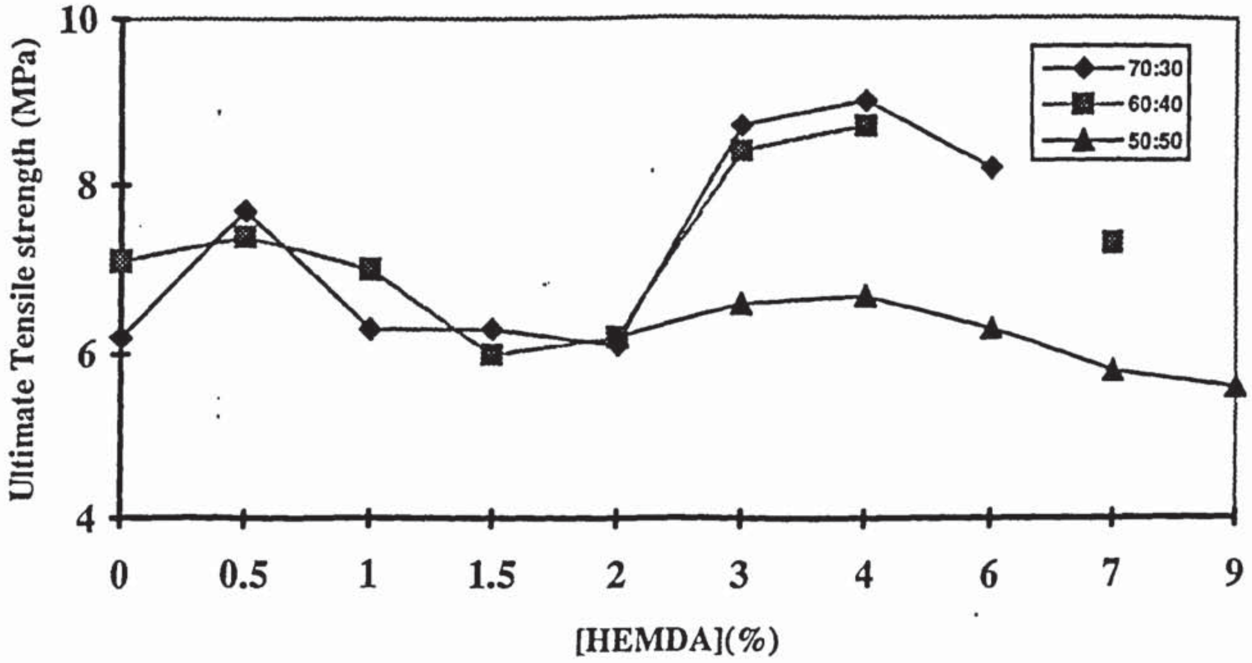


Figure 4.8 : Effect of [HEMDA] (0-9%) on ultimate tensile strength of F&A-PS/EPDM blends (70:30w/w, 60:40w/w and 50:50w/w); processed at 190°C, 90rpm, 40min.

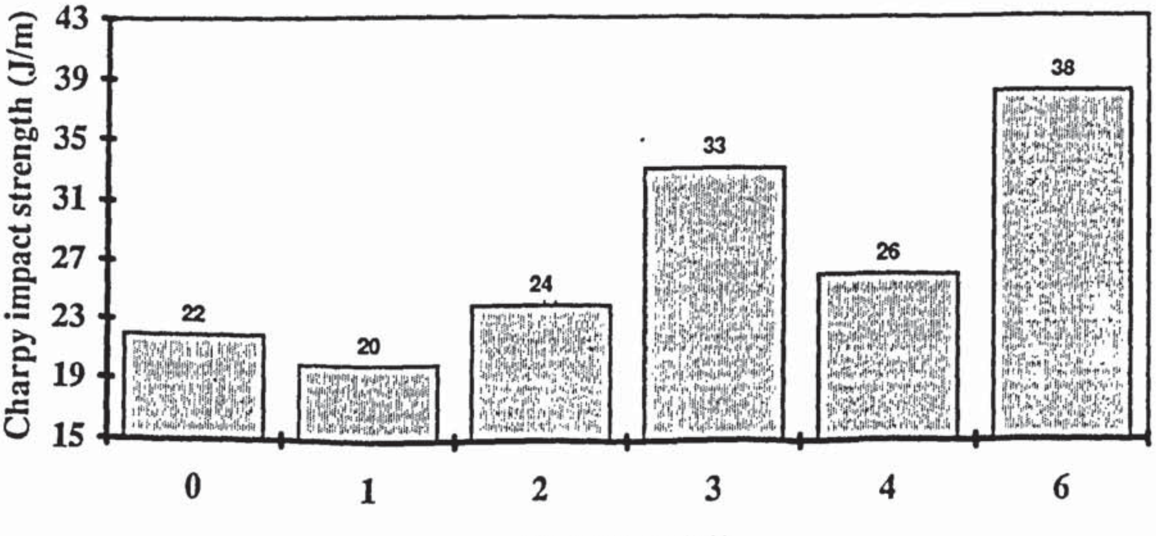


Figure 4.9 : Effect of [HEMDA] on Charpy impact strength of F&A-PS/EPDM blends, 70:30w/w processed at 190°C, 90rpm,40min.

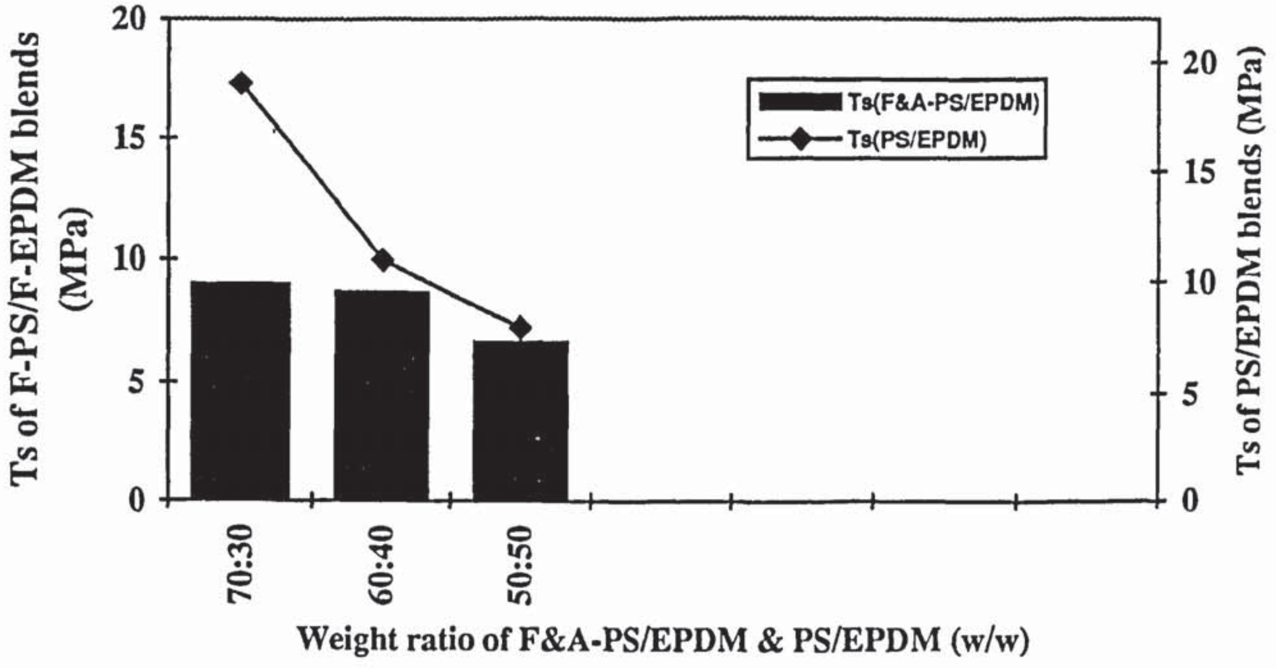


Figure 4.10: comparison of tensile strength of HEMDA (4%) amidised F-PS/F-EPD blends with the PS/EPDM blends of various weight proportions prepared at 190^{0}C, 90rpm, 40min.

CHAPTER 5

COMPATIBILISED AND UNCOMPATIBILISED BLEND OF PS/EPDM AND PP/EPDM

5.1 OBJECT AND METHODOLOGY

Interfacial tension in incompatible polymer blends can be improved by addition of a copolymer with a chemical composition similar or compatible to the polymer components of the blend ([12,21,23]). The copolymer , block or graft, acts as a compatibiliser (or solid phase dispersant, **SDP**) hence reducing the interfacial tension of the polymer components and therefore acts in compatibilising them. A straight melt mixing of PS/EPDM and PP/EPDM are expected to result in incompatible heterogeneous blends. Addition of copolymers of PS-g-EPDM in former and the PP-g-EPDM in the latter should lead to enhanced compatibility. As the F-PS/F-EPDM and F-PP/F-EPDM blends described in chapter 3 contained both of the copolymers, it is possible to compatibilise the PS/EPDM and PP/EPDM blends by incorporating the relevant functionalised polymer blends.

The main object of the work described in this chapter was to investigate the effectiveness of selected blends of F&A_H PS/-EPDM (**SPD_H1**) and F&A_H-PP/EPDM (**SPD_H2**) when used as solid phase dispersants in compatibilising various weight ratios of PS/EPDM and PP/EPDM blends (80/20/, 70/30 and 60/40), see **scheme 5.1a**. The assessments were based on the performances of the uncompatibilised and intended compatibilised blends with respect to their mechanical and morphological properties. Also, since in the case of PP, the functionalisation of PP was with a reactive thermal antioxidant (see section 4.1, chapter 4), the thermal ageing properties of the compatibilised PP/EPDM blends was also measured. The compositions of functionalised polymers and interlinking agents used in preparation of various forms of the SPDs are given in **table 5.1.**

The general methodology adopted is described in **scheme 5.1b**. Mixtures of PS-EPDM or PP-EPDM of various component weight ratios were processed in the torquerheometer mixer (180-200°C, 45-100rpm, 5-30min) in the presence and absence of the relevant functionalised polymer blend used as the SPD (0-30%). The resulting blends were compression moulded into either films for tensile property and for dart impact strength measurements, or into slabs which were cut into suitable test specimens ($6.0 \times 6.5 \times 41.8 mm^3$) for Charpy impact test. Selected broken surfaces of the tested Charpy impact specimen were used for morphological property analysis by SEM.

Table 5.1: Concentrations of functionalised polymers, interlinking agents, methods of amidisation and the SPD nomenclature used in chapter 5. In SPD number 1,2&3, the letters A, P and D stands for AA, T101 and DVB; small letter v stands for 'variations in concentration'. See also scheme 5.1.

SPD Code	Concentration of functionalised polymers			Concentration of interlinking agent		Amidisation method	Nomenclature of SPD
•	F_s-PS1 (%)	F_o-EPD1 (%)	F-PP (%)	EDA (%)	HEMDA (%)		
1. SPD1(Av)	60	40	-	-	3	pre-amidising F_o-EPD1 before blending	F-PS1/A_H-FEPD
2. SPD1(Pv)	60	40	-	-	3		-idem-
3. SPD1(Dv)	60	40	-	-	3		-idem-
4. SPD1(pa)	60	40	-	-	3	pre-amidising F-EPD1 before blending	F_o-PS1/A_H-FEPD
5. $SPD_H(1)$	60	40	-	-	3	pre-mixing before blending	F&A-PS/EPDM
6. SPD2(Tv)	-	40	60	-	3	pre-mixing before blending	F&A-PP/EPDM
7. $SPD_E(2)$	-	40	60	3	-	pre-amidising F-EPD1 before blending	F-PP/A_E-FEPD
8. $SPD_H(2)$	-	40	60	-	3	pre-mixing before blending	F&A-PP/EPDM

5.2 RESULTS

In this chapter, film were prepared as described in section 2.4, from blends and mechanical property tests were carried out as described in section 2.7.2 (chapter 2 section 2.7.2.1 for tensile strength and 2.7.2.2 for impact strength). The thermal and morphological tests (for PP/EPDM/SPD$_H$2 blends) were performed as described in sections 2.6.3 and 2.7.3.1 . In every tensile test performed, a set of 6-12 test specimens were used, the number of which depending on uniformity of the readings obtained. In the case of impact strength test, an average of 5 succesful readings were calculated for the drop and Charpy impact tests. Results from the home built drop impact test are used for comparative purpose only and not for absolute indications of the impact resilience of the samples. Wherever an error is indicated together with the main reading, it is an average of the sum of absolute deviations from the average. As an illustration, a set of readings of 3.14, 3.16, 3.21 and 3.12 will have an average of 3.16, sum of absolute deviation from the average of 12.63 and an absolute value error of 0.03, to give a final reading of 3.16+0.03.

5.2.1 Optimisation of processing conditions for PS/EPDM/SPD1 blends.

The optimum processing temperature, rotor speed of the torquerheometer and duration of processing were determined by processing mixtures of PS/EPDM/SPD1, 70:30:10w/w see **scheme 5.2**. The effect processing conditions were investigated (optimum values were based on evaluation of tensile properties and drop impact strength). The results are presented in **table 5.2a,b&c** and **table 5.3** .

Table 5.2: Effect of temperature (a), rotor speed (b) and time (c) on mechanical properties of PS/EPDM/SPD_H1, 70:30:χ see table 5.1.

Table 5.2a: 180°-200°C, 60rpm, 10min

Processing Temperature (°C)	Mechanical Properties of Compatibilised PS/EPDM/SPD1 blends (70:30:10)		
	Tensile Properties		
	Ultimate tensile strength MPa	Ultimate Elongation (%)	Modulus of Elasticity MPa/cm
180	**15.4+0.05**	**6**	**85+0.13**
190	13.6+0.01	7	65+0.02
200	14.3+0.1	7	68+0.23
60rpm, 10min			

Table 5.2b:45-100rpm, 180°C& 10min

Processing speed (rpm)	Mechanical Properties of Compatibilised PS/EPDM /SPD blends (70:30:10)			
	Tensile Properties			Drop Impact strength (KJ/m)
	Ultimate tensile strength (MPa)	Ultimate Elongation (%)	Modulus Elasticity (MPa)	
45	16.0+ 0.04	11	48+0.06	46.2+1.4
60	14.0+ 0.01	7	67+0.02	45.0+0.4
85	**15.5+ 0.07**	**12**	**43+0.09**	**46.5+0.6**
100	15.1+ 0.07	12	42+0.09	46.3+0.5
110	14.0+ 0.05	12	39+0.06	46.2+0.6
180°C, 10min				

Table 5.2c : 3-25min, 180^{o}C, 85rpm

Processing time (min)	Mechanical Properties of Compatibilised PS/EPDM /SPD , 70:30:10 blends.			
	Tensile Properties			Drop Impact strength ($x10^{3}$KJ/m)
	Ultimate tensile strength MPa	Ultimate Elongation (%)	Modulus of Elascitity MPa/cm	
3	16.0+0.03	11	48+0.1	40.9+1.8
5	15.7+0.08	11	48+0.1	-
10	**15.5+0.08**	**12**	**43+0.1**	**46.5+0.60**
15	16.7+0.06	12	46+0.8	39.4+0.20
20	11.9+0.04	10	40+0.6	36.2+0.20
25	14.5+0.05	10	48+0.8	35.8+0.10
180^{o}C, 85rpm				

Tables 5.1a,b&c show that optimum processing conditions are 180^{o}C, 85rpm and 10min.

Table 5.3: Effect of different addition timing of the SPD1 into PS/EPDM mixture during processing to the mechanical properties of the compatibilised blends.

Addition time of (SPD)	Sample code	Mechanical Properties of Compatibilised PS/EPDM blends
		Charpy Impact strength (J/m)
Simultaneous addition	BT(SA)	26.4
Beginning of second minute	BT(2)	26.9
Beginning of third minute	**BT(3)**	**32.7**
Beginning of fifth minute	BT(5)	29.2
Beginning of sixth minute	B(6)	29.5

Table 5.3 shows that the impact strength (Charpy) of sample BT(3) in which the is SPD at the beginning of the third minute is the highest; 24% higher than when added at the begining of the processing (i.e. sample BT(SA).

5.2.2 Effect ofthe concentrations of the agent (AA), the peroxide (T101) and the coagent (DVB) concentration used in the preparation of F-PS to the efficiency of amidised F-PS/FEPDM blend as SPD1 in compatibilising PS/EPDM blends.

The copolymer formed vis reactions between the AA functionalised polymers in F-PS/F-EPD, 60:40 blends (as discussed in chapter 4) were used as SPD in PS/EPDM blends. It is important to point out that the type of copolymer (graft, block and shape of the block) formed determines the effectiveness of the SPD ([23]). The concentration and distribution of functional groups along the backbone of the modified polymers of the SPD must play an important role.

Experiments were therefore specifically carried out to determine an optimum concentration of the three reactants (AA, T101 ans DVB)used in the preparation of F-PS samples which when blended with a F-EPD sample in the presence of an interlinking agent i.e. HEMDA, resulted in a blend of high performance as an SPD. The effect of chemical composition on F-PS samples was evaluated by examining the performance of the amidised functionalised blends (F&A_H-PS/EPDM, 60:40 containing 4% HEMDA) used as SPD (10% concentration). in PS/EPDM, 70:30w/w , see **scheme 5.3** , (processing condition of 180°C, 85rpm, 10min).The Charpy impact and tensile tests were performed on all the blends obtained and the results are presented in **table 5.4a,b&c** for the three chemical variables, respectively.

Table 5.4a,b&c: Effect of [AA], [T101] and [DVB] used in F-PS1 [PS+AA(0-6%) +T101(0.04MR) +DVB(0-3%)] samples to the effectiveness of F-PS1/A_{II}-F-EPD , 60:40:4 as SPD1 in enhancing mechanical properties of PS/E 70:30:10 blends processed at 180°C, 85rpm,10min.

Table 5.4a: Effect of [AA] (2-6%), at 0.04MR T101 and 3% DVB.

		Mechanical Properties of Compatibilised PS/EPDM/SPD_{II}1 70:30:10 blends			
[AA] in F-PS1 (%)	Sample Code	Tensile Properties			Charpy Impact strength (J/m)
		Ultimate tensile strength MPa	Ultimate Elongation	Young's Modulus MPa/cm	
2	CV(1)	18.8	10	63	41
3	CV(2)	18.1	10	60	28
4	**CV(3)**	**18.6**	**14**	44	**48**
6	CV(4)	15.6	12	43	32

Table 5.4b: Effect of [T101](0.01-0.04MR) at 4% AA and 3% DVB

		Mechanical Properties of Compatibilised PS/EPDM/SPD blends 70:30:10			
[T101] in F-PS1	Sample code	Tensile Properties			Charpy Impact strength (J/m)
		Ultimate tensile strength (σ) MPa	Ultimate Elongation (ε)	Young Modulus MPa/cm	
0.01	PV(1)	16.1	16	3.4	-
0.02	PV(2)	17.4	16	3.6	44
0.03	PV(3)	16.1	16	3.4	39
0.04	**PV(4)**	**18.6**	**14**	**4.4**	**48**

Table 5.4c: Effect of [DVB] (0-3%) at 4%AA and 0.04MR T101.

		Mechanical Properties of Compatibilised PS/EPDM, 70:30:10 blends
Concentration of DVB in F-PS of SPD (%)	Sample code	Charpy impact strength (J/m)
0	COV(1)	72
0.5	COV(2)	64
1.0	COV(3)	64
1.5	COV(4)	72
2.0	**COV(5)**	**80**
2.5	COV(6)	65
3.0	COV(7)	48

From tables 5.4a,b&c, it was shown that the highest mechanical properties were attained by samples Sample CV(3), PV(4) and COV(5) which were corresponding to 4%AA, 0.04MR T101 and 2.0%DVB ,used in the preparation of F-PS1samples. The F-PS sample prepared using agent, peroxide and coagent of these concentrations when used as a component of the SPD would significantly contribute to the effectiveness of the SPD in enhancing the impact strength of the PS/EPDM blend, with relatively high value of tensile strength .

Effect of method of preparation of F-PS on its contribution to the efficiency of the SPD produced was also investigated. Here, the effect of methods PM1 and PM, see schemes 3.2 and 3.6 in chapter 3, were compared, see **scheme 5.4.** The tensile atrength & elongation and drop impact strength of the blends were measured and shown in **table 5.5a.** Results in Table 5.5a show that F-PS processed by method PM1, see scheme 3.2 in chapter 3, has higher contribution to the effectiveness of the SPD than the method PM5 (scheme 3.7, chapter 3).

Table 5.5a: Effect of the procesing method used in processing F-PS1 [PS+AA(4%)+T101(0.04)+ DVB(2%)] on the effectiveness of F_o-PS1/A_H-FEPD, (60:40:4 used as SPD1) in enhancing mechanical properties of PS/EPDM/SPD1, 70:30:10 blends processed at 180^oC, 85rpm,10min.

Processing method	**Mechanical Properties of Compatibilised PS/EPDM/SPD1 blends 70:30:10**			
	Tensile Properties			**Drop Impact strength ($x10^3$KJ/m)**
	Ultimate tensile strength MPa	**Ultimate Elongation (%)**	**Young's Modulus of Elasticity MPa/cm**	
PM1	**18.6+0.09**	**14**	**44+0.1**	**51+0.4**
PM5	17.7+0.03	14	42+0.03	48+0.5

The F_0-EPD1 used (0.74%w/w bound AA) was processed from mixtures of EPDM with 6%AA, 0.005MR T101 and 1.5% TRIS at 160°C, 45rpm,10min. The effect of diluting F-EPDM by melt mixing with 40% fresh EPDM at 160°,60rpm,7min (before being processed with the F-PS) on the enhancement effect of the SPD in PS/EPDM/SPD, 70:30:10 blends was also investigated, and the mechanical properties performance of the blends are shown in **table 5.5b.**

Table 5.5b: Effect of diluting F_0-EPD1 with 40% fresh EPDM on the effectiveness of F_0-PS1/A_H-FEPD, 60:40:4 as SPD1 on the enhancement of mechanical properties of PS/EPDM/SPD1, 70:30:10 blends processed at 180°C, 85rpm,10min.

Nature of F-EPD1 used	Mechanical Properties of Compatibilised PS/EPDM/SPD1, 70:30:10 blends			
	Tensile Properties			Drop Impact strength ($x10^3$KJ/m)
	Ultimate tensile strength (MPa)	Ultimate Elongation (e) (%)	Young's Modulus of Elasticity (MPa/cm)	
Undiluted	18.6+0.09	14	44+0.1	51+0.4
Diluted	**17.4+0.08**	**14**	**41+0.1**	**60+0.8**

The effect of the method of addition of HEMDA to the F-PS/F-EPDM mixtures on the performance of the amidised blend (when used as SPD) was also investigated, see scheme 5.5. The effects studied involved:

1. Pre-amidised F-EPDM with HEMDA followed by blending with F_0-PS1; (F_0-PS1/A_H-FEPD)
2. Pre-mixed HEMDA with mixture of F_0-PS1 and F-EPDM followed by processing; (F&A-PS/EPDM) and,
3. The F-EPDM was firstly diluted with 40%EPDM and then pre-amidised with HEMDA followed by processing with F_0-PS1,(F_0-PS1/A_H-$FEPD_{dil}$)

The mechanical properties of the blends are shown in **table 5.5c**

Table 5.5c: Effect of different method of incorporating HEMDA in to F-PS/F- EPDM mixture during blending processing , blends prepared at 185°C,

Sample number	Mechanical Properties of Compatibilised PS/EPDM blends			
	Tensile Properties			Drop Impact strength ($x10^3$KJ/m)
	Ultimate tensile strength MPa	Ultimate Elongation (%)	Young's Modulus of Elasticity MPa	
F_o-PS1/A_H-FEPD	**7.42**	**6**	**4.12**	**66+0.1**
(F&A-PS/EPDM)	7.51	7	3.58	51+0.4
F_0-PS1/A_H-$FEPD_{dil}$	7.32	7	3.48	60+0.08

The result so far can be summarised as follows:

Optimisation of SPD.

1. The optimum F-PS samples can be prepared by processing mixture of PS with 4%AA, 0.04MRT101and 2%DVB, using method PM1 and processing conditions of 180°C, 100rpm,10min.
2. The F-EPDM (processed as previously described) is to be diluted with 40% EPDM and then preamidised with 4%HEMDA at 160-180°C, 85rpm, 10min.
3. The preamidised F-PEDM (60%) is then processed with F-PS (40%) at 185°C, 85rpm, 40min resulting in blends to be used as the optimised SPD

Optimisation of processing conditions for PS/EPDM/SPD blends

The optimum processing conditions are :
temperature: 190°C,
cam speed:85rpm,

time 10min, and
addition of SPD into the PS/EPDM mixture is at the beginning of third minute.

5.2.3 Mechanical and Morphological Properties of the PS/EPDM Blends in the Presence or Absence of the SPD1.

A more extensive blending experiments to assess the effectiveness of the optimised SPD in PS/EPDM blends formulated to contain various weight proportions of the two polymers and the SPD were carried out as described in **scheme 5.5**. The weight proportion range of the PS/EPDM were 80/20, 70/30 and 60/40 calculated against the maximum load (35g) less the weight of the SPD; whereas those of the SPD was 0-30%calculated against the maximum load . A constant processing conditions was used throughout the experiments. The results on mechanical properties tests are given in **table 5.6a,b,c&d**

Table 5.6a: Effect of SPD1_H concentrations (0-30%) on mechanical properties of PS/EPDM/SPD1_H 80:20:χ blends processed at 190°C, 85rpm, 10min.

		Mechanical Properties of Compatibilised 80:20 PS/EPDM blends			
		Tensile Properties			**Drop Impact strength (x10^{3}KJ/m)**
[SPD] (%)	**Sample Code number**	**Ultimate tensile strength MPa**	**Ultimate Elongation (%)**	**Young's Modulus of Elasticity MPa**	
0	SR1	22.0	5	14.7	69
5	SR2	23.4	7	11.4	58
10	SR3	20.7	5	13.8	133
15	SR4	20.1	7	9.6	165
20	SR5	18.3	6	10.2	60
30	SR6	16.9	4	14.1	33

For 80:20 blend composition, see table 5.5a, the SPD has increased the drop impact strenght by about 93-140% over the uncompatibilised blend.. However increasing concentration of SPD above 15% led to a drop in tensile strength and impact strength.

Table 5.6b: Effect of SPD$_H$ concentrations (0-30%) on mechanical properties of PS/EPDM/SPD, 70:30:χ blends processed at 180^{o}C, 85rpm, 10min.

		Mechanical Properties of Compatibilised PS/EPDM, 70:30w/w blends			
		Tensile Properties			Drop Impact strength (x10^{3}KJ/m)
[SPD] (%)	Sample Code number	Ultimate tensile strength MPa	Ultimate Elongation (%)	Young's Modulus of Elasticity MPa	
0	SR7	17.5	11	5.3	59.1
5	SR8	16.5	7	7.8	46.6
10	SR9	15.6	6	8.7	65.6
15	SR10	14.6	10	4.9	88.0
20	SR11	12.8	5	8.5	53.8
25	SR12	13.7	5	9.1	59.7
30	SR13	13.7	3	15.2	45.3

The SPD improves the impact strength for the 70:30 blend as well, optimum impact performance at 15% SPD, see table 5.5b.

Table 5.6c: Effect of SPDH concentrations (0-30%) on mechanical properties of PS/EPDM/SPD, 60:40:χ blends processed at 180^{o}C, 85rpm, 10min.

[SPD] (%)	**code number**	**Mechanical Properties of Compatibilised PS/EPDM blends**			
		Tensile Properties			**Drop Impact strength ($x10^3$KJ/m)**
		Ultimate tensile strength MPa	**Ultimate Elongation (%)**	**Young'sModulus of Elasticity MPa/cm**	
0	SR14	10.1	7	48	80.4
5	SR15	10.1	8	42	83.9
10	SR16	11.9	8	50	82.7
15	SR17	10.1	6	56	72.2
20	SR18	10.0	6	56	56.0
25	SR19	9.2	6	51	59.1
30	SR20	10.0	5	67	59.3

However, in 60:40 blends, see table 5.6c, the improvement in the compatibilised blend (at 5% SPD) is approximately 4%compared to the uncompatibilised blend. Generally, a flat profile of tensile strength was shown throughout the concentration range of the SPD used.

Table 5.6d: Effect of SPD concentrations (0-30%) on mechanical properties of PS/EPDM/SPD, 40:60:c blends processed at 180°C, 85rpm, 10min.

[SPD] (%)	Sample Code number	Mechanical Properties of Compatibilised PS/EPDM blends		
		Tensile Properties		
		Ultimate tensile strength MPa	Ultimate elongation (%)	Young's Modulus of Elasticity MPa
0	SR21	4.4	8	18
5	SR22	4.5	7	21
10	SR23	4.2	7	20
15	SR24	5.0	7	24
20	SR25	4.4	6	24
25	SR26	5.3	6	29
30	SR27	4.9	6	27

5.3.0 Mechanical and Morphological Properties of the PP/EPDM Blends in the Presence or Absence of the SPD2.

5.3.1 Effect of SPD$_E$2 and SPD$_H$2 on the Impact Strength of the PP/EPDM, 60:40 Blends.

The effect of EDA and HEMDA to the performance of the SPD2 was investigated by preparing PP/EPDM, 60:40 w/w blends containing various concentration of the SPD$_E$2 and SPD$_H$2 (see scheme 5.6) and the impact strength of the blends were determined.. The SPDs were prepared as described in scheme 5.1a. The results are shown in **table 5.7**

Table 5.7: Selection of interlinking agent (IA): Effect of EDA (E) and HEMDA (H) as interlinking agent on the performance of F-PP/F-EPD1/ IA as SPD (0-30%) in PP/EPDM 70:30 blends.

SPD containing IA	Concentration of SPD(%) and Charpy impact strength(J/m)				
	0	1	15	25	30
$SPD_E(2)$	1216+94	1103+46	1010+37	823+56	860+37
$SPD_H(2)$	**1216+94**	**1271+56**	**1178+37**	**954+56**	**991+37**

Table 5.6 shows that all the SPD concentrations, the impact strength achieved by the use of the **$SPD_H(2)$** is higher than that obtain with $SPD_E(2)$, The HEMDA will therefore be used in further processing of the SPD (i.e. the SPD_H2).

5.3.2 Effect of TRIS concentration used in F-EPD1 on compatibilising efficiency of F&A-PP/EPDM, [$SPD_H(Tv)$], in PP/EPDM/$SPD_H(Tv)$ blends.

The TRIS is a coagent added to the reaction mixture of EPDM, AA and T101 with the purpose of enhancing the grafting reaction of AA to EPDM similarly as in case of DVB to PS. In case of using optimised TRIS enhanced AA functionalised EPDM (see chpater 3) in amidised F-PP/F-EPDM blends , the latter would not necessarily perform effectively if used as SPD due to the reasons as being described as in the case of the amidised F-PS/F-EPDM, see section 5.2.1.1.2. Experiments were therefore carried out to determine optimum concentration of TRIS through performance evaluation of the amidised blends of F-PP/F-EPD1 used as SPD in PP/EPDM blends, in which the

F-EPDM samples were prepared from mixtures containing various concentration of TRIS, see chapter 3. The method of preparation of the blends and tests carried out are described in **scheme 5.7**. The results are presented in **table 5.8**

Table 5.8: Effect of [TRIS] used in preparation of F-EPD1 to the F&A-PP/EPDM blends effectiveness as $SPD_H(Tv)$ in enhancing mechanical property (impact strength) of PP/EPDM/$SPD_H(Tv)$ blends processed at 190°C, 85rpm, 10min.

[TRIS] (%)	**Sample code number**	**Charpy Impact Strength of PP/EPDM/$SPD_H(Tv)$, 60:40:3 (kJ/m)**
0	VTR1	1.028
0.7	VTR2	0.329
0.9	VTR3	0.339
1.2	VTR4	1.122
1.5	VTR5	**1.266**

Table 5.8 shows the enhancement effect of TRIS to the impact strength of the blends, which is increased with the increase in the coagent concentration. At 1.5% [TRIS] ,in VTR5, an improvement of 23% in Charpy impact strength was achieved over the VTR1 sample . Use of TRIS (1.5%) is therefore useful in enhancing the impact strength of the blends and will be used in further processing of the SPD.

5.3.3 Optimisation of processing conditions for PP/EPDM/SPD_H2 blends

Optimum processing conditions were determined similarly as in case for PS/EPDM blends and is described in **scheme 5.8.** The results are given in **table 5.9a,b.** Here, a constant 85rpm, was used in all experiments.

Table 5.9a: Effect of temperature on impact strength of PP/EPDM/SPD$_H$(2), 70:30:10 blends prepared at 170°-200°C, 85rpm,10min.

Processing Temperature (°C)	Sample no	Charpy Impact Strength (kJ/m)
170	PRT1	0.74
180	PRT2	0.46
190	**PRT3**	**0.88**
200	PRT4	0.77
85rpm,10min		

Table 5.9b: Effect of time on impact strength of PP/EPDM/SPD$_H$2, 70:30:10 blends prepared at 190°C, 85rpm,10-40min.

Processing time (min)	Sample no	Charpy Impact Strength (kJ/m)
10	**PRC1**	**0.88**
15	PRC2	0.59
20	PRC3	0.50
25	PRC4	0.43
30	PRC5	0.27
40	PRC6	0.42
190°C, 85rpm		

As shown in tables 5.8a&b, the optimum processing conditions are **190°C,85rpm &10min**. Processing time has clearly affected the strength of the blends. The strength progressively decreasing as the time is increased. A highest strength was achieved by sample PRC1 (10min processing) and therefore this was considered optimum and will be used in further processing.

Table 5.10: Effect of SPD$_{H}$2[F-PS/F-EPDM/EDA, 60:40:4] and its concentration (0-30%) on mechanical properties of PP/EPDM blends of 90:10, 80:20 composition ratios processed at 185^{0}C, 85rpm,10min. The letters σ, ε and Is represent the ultimate tensile strength, ultimate elongation and Charpy inpact strength, respectively.

SPD$_{H}$2 Concentration (%)	Mechanical properties of PP/EPDM/SPD blends of weight ratios 90:10&80:20							
	90:10			80:20			70:30	60:40
	σ MPa	ε (%)	Is (J/m)	σ MPa	ε (%)	Is (J/m)	Is (J/m)	Is (J/m)
0	29.2±0.2	275±142	243±2	21.3±0.3	243±76	449±37	1023	1080
1	28.9±1.0	117±5	280±9	28.7±5	91±38	1047±206	1206	1322
2			-	-	-	-	-	1374
3	28.9±1.0	49±7	280±9	28.8±2	66±11	505±19	-	-
4	-		-	-	-	-	1037	1267
5	-		280±9	21.3±1	145±14	692±19	1141	1180
7	-		246±7	28.5±2	107±9	410±37	-	1190
10	26.1±3.0	54±7	247±19	23.7±2	120±4	640±37	1170	-
13	-		374±30	-	-	560±37	1080	-
15	-		-	-	-	620±131		1200
17	-		250±9	-	-	560±94	-	-
20	25.7±2.0	37±6	280±0	28.6±2	88±10	520±74	-	-
25			280±9		-	320±37	1066	-
30			-			-	1047	

5.3.4 Mechanical, Morphological and Thermal Properties of PP/EPDM blends in presence and absence of SPD$_H$(2)

The effectiveness of the optimised SPD, **SPD$_H$(2)** [F&A-PP/EPDM, 60:40w/w blends containing 3%HEMDA], (0-30%), in compatibilising various weight ratios of PP/EPDM , 90/10, 80/20, 70/30 and 60/40w/w blends were determined by carrying out blending processes and testings as described in **scheme 5.9.** The results of the tests on mechanical, and thermal properties (preliminary studies) are given in **tables 5.10** and **5.11(a&b)** respectively. The thermo-oxidative ageing were carried out obtain an indication on the merit of the incorporation of the thermal stabiliser (this area reserved further work) The results of morphological observation (see section 2.7.3.1, chapter 2) by SEM are given in **figure.5.2.**

Table 5.11a: Comparison of the effects of SPD$_H$(2) and Irganox 1010 on resistance to thermal degradation of 70/30w/w PP/EPDM blends ,films 0.15mm thick, (0% and equivalent of 0.05% antioxidant) processed at 190°C, 85rpm, 10min.

Thermal stabiliser	Duration of embrittlement (hrs)
0% Antioxidant	21
SPD$_H$2	220
Irganox 1010	312

Table 5.11b: Effect of [SPD$_H$2] (which contained thermal stabiliser) on the resistance to thermal degradation (duration of embrittlement) of PP/EPDM/ SPD$_H$(2) blends (90:10:x and 80:20:x w/w), in a Wallace oven at 140°Cand air flow rate of 2cm^3/min.

Weight Ratio Blend	SPD2 Concentrations (%) and Duration of Embrittleme						
	[SPD] 0	1	3	5	7	10	
90:10	14	20	40	-	-	80	100
80:20	27	60	-	150	180	210	-

The 90:10 blends have benefited from the incorporation of SPD_H2. In all concentration the Charpy impact strength are higher than the uncompatibilised blend. At 13%[SPD] there is an increase of 55%higher then the strength of the blend without SPD. In 80:20 series, there was no significant effect shown on the impact strength, although some improvement was observed especially in medium range of the SPD concentration. In 70:30 series, improvements were shown in all concentrations, but again it is not very significant.

In 60:40 series substantial improvement over the uncompatibilised blend are shown, which is in average much higher than in other series. The effect of the SPD to tensile strength is more pronounced as compared to the 90:10 series. In some concentrations the tensile strength was enhanced.

Table 5.11b shows clearly that in both blends the embrittlement time increased with the increase in the SPD_H 2 concentration and embrittlement time at any concentration of the SPD_H2 in 80:20 blend is higher than in 90:10 blend. The increased in EPDM content (with 0%[SPD_H2]) itself has prolonged the embrittlement time. Since the active thermal stabiliser agent [N-(4-anilinophenyl maleimide)] has undergone long thermal history (i.e in reactive processing to bind it to PP, preparation of the SPD2 and blending the SPD2 in the PP/EPDM blend itself, the amount of protection (whatever left) to the films in the thermal tests must be from residues of a very much reduced concentrations. Table 5.11a shows that at equivalent concentration the thermal resistance of irganox 1010 is higher than the diphenylmaleimide

5.4 DISSCUSSION

5.4.1 EFFECTS OF SPD$_H$1 CONCENTRATION ON MECHANICAL, MORPHOLOGICAL AND THERMAL PROPERTIES OF PS/EPDM BLENDS

The polystyrene (PS) is a brittle low impact resistance polymer. The primary purpose of blending it with a rubbery polymer (in this case EPDM) , is to increase the impact strength, without causing detrimental change in other properties such as stiffness and tensile strength. By using a combination of optimum processing conditions (see figures 5.1a,b&c), chemical compositions (see tables 5.4a,b&c) and processing methods (see tables 5.5a,b&c) the mechanical properties of the PS/EPDM blends were improved. Figure 5.3a and b show the effect of SPD$_H$1 (F-PS/F-EPD, 60:40w/w containing 3% HEMDA) concentrations on the drop impact strength, compared to that of the uncompatibilised blend. It is clearly shown that the SPD has affected the impact strength of the blend by compatibilising or decompatibilising it over the whole range of concentration used. The SPD is particularly useful in improving the impact strength of blends containing high proportion of PS (i.e. 70% and higher) particularly in concentration region of 10-15%, see figure 5.3b. The SPD however is not effective in blends of lower PS content.

Figures 5.3;c,d&e show photomicrographically the effect of SPD$_H$1 concentrations on the fractured impact test specimens. In 80:20 blends, without the compatibiliser, the dispersed phase is clearly visible in spherical shape with a diameter in between 1.5-12μm. At 2% [SPD], see figure 5.3. , the dispersed phase was nearly dissapeared, and was completely disappeared at 10% concentration, in which both phases was probably homogenised into a single phase. The surface of the fractured specimen acquired relatively more fibroutic appearance showing sign of higher development of crazes to resist the eventual fracture. The appearance of the SEM photographs is in complete agreement to the enahncement effect obtained at 10%[SPD], (see figure 5.3a).

In 60:40 blends, the weight ratio of PS:EPDM remained the same with the addition of the SPD (which was also a 60:40w/w F-PS/F-EPD). Addition of 5% has not caused any significant change the appearance of the fractured surface of the specimen (see figure 5.3e). The extensive displays of microfibrils as a result of shear yielding during the impact, however indicated evidence of strong surface adhesion between the dispersed phase (EPDM) and the continuous matrix (PS). The fact that the impact strength was maintained at the same level up to 10% [SPD], has proven the occurrence of the compatibilisation. Without the enhancement effect of the SPD, addition of increasingly higher amounts of SPD would immediately result in weakening of the blend due to negative contribution effect of the PS and EPDM from the SPD, which have undergone longer detrimental heat and chemical exposure and other reactive agent, as previously described in chapter 3. At higher than 10% however the weakening effect has prevailed and resulted in an overall decrease in the drop impact strength, see figure 5.3b

The evidence of a compatibilisation effect of the SPD can be further confirmed by analysis of the relationship between PS concentration in the blend and its modulus. The general rule is, in a 'straight 'blend (without molecular interaction) , increasing the content of the glassy component will increase the modulus. Addition of SPD of increasingly higher concentration will alter the actual concentration of PS and EPDM. **Figure 5.4a** shows that in 80:20 blends, at SPD concentrations of 15% (PS content is 77% of the total feed load) there is a strong evidences of compatibilisation, whereby the impact strength (Is) increases and the modulus (stiffness) decreases substantially compared to uncompatibilised blend (SPD=0%) , where the PS content is 81.4% of the total feed load. **Figure 5.4b**, shows similar compatibilising effect of [SPD] at 15%,for the 70:30 blends, in which an optimum increase in Is is observed, parallel by a decrease in the modulus. At 30% [SPD] the PS content decrease by 3%and EPDM increase by also 3% but the modulus increased substantially again in defiant to the norm as in case of the 80:20 blend. In the 60:40 blend, the content of both PS and EPDM are constant at 60%and 40% respectively in all compositions. The modulus however, see figure 5.4c, increase as the [SPD] is increased , while the impact strength maintained at the same level up to 10% [SPD] and then decreased as [SPD] increased. The SPD has undoubtebly exert its influence on the physical molecular interaction between the blend component and therefore to the mechanical properties in a pattern almost peculiar to every composition. Within certain concentration ranges the compatibilisation resulting in improvement of mechanical properties are taking place.

In the blend containing PS 70%and higher , the SPD has caused general decrease in the tensile strength, see figures 5.2a and b , including in the concentration region in which the impact strength is greatly improved. The destabilising effect of the SPD to the tensile strength has however decreased, as the concentration of PS decreases, followed simultaneously by increasing evidence of compatibilisation effect resulting in tensile strength higher than the basic blend.

In the blends of 80:20,70:30 and 60:40w/w, see figure 5.4a,b,and c, the increase in impact strength (except in 80:20 composition where [SPD] was less than 10%) was generally accompanied by a decrease in Young's Modulus, indicating a reduction in stiffness of the blends. The regularity of this pattern is more pronounced in the blends where the concentration ratio of PS is .

5.4.2 EFFECTS OF SPD_H2 CONCENTRATION ON MECHANICAL, MORPHOLOGICAL AND THERMAL PROPERTIES OF PP/EPDM BLENDS

In the previous chapter (chapter 4), it was shown that blends of F-PP/F_o-EPD1, 60:40 w/w containing 3% HEMDA have superior mechanical strength over similar blends in absence of the IA and it was proposed that the synergistic effect was due to the in situ formation of the copolymer which has acted as compatibiliser to the amidised functionalised polymer blend.

In very diluted form, the same blends when added to PP/EPDM mixtures were expected to affect a certain degree of compatibilisation which resulted in enhancement of certain properties of the blends . Figure 5.5a shows that the SPD_H2 has caused a general decrease in tensile stength over the entire concentration range used, which was also accompanied by significant changes in the modulus of the blends (higher than the modulus of the uncompatibilised blends). Figure 5.5b (see also table 5.8) shows that in general the SPD has caused favourable effect to the impact strength, affecting some degree of improvements at almost all concentrations used, with greatest synergistic effect prominently shown in the region of 10-15%. It is also shown (see figure 5.5b) that strong enhancement effects, as expected, are always accompanied by reduction in the modulus, suggesting that the blends are more easily deformed under the influence of tensile force. The improvement in Is is most probably realised through compatibilising effect of the SPD, which is probably located at the interfaces and further solubilised the already semi compatible blends of PP/EPDM (104) . This has resulted in stronger interfacial adhesion between the dispersed phase (i.e. EPDM) and the matrix (PP). Figure 5.5c&d showed distinctively the crimping microfibrils which formed during the shearing influences of the impact force. In figure 5.5c the micrograph clearly shows the end of the rubber microfibrils still attached to the PP matrix, after the fracture, an unmistakable evidence of strong interfacial adhesion between the interfaces.

Figure 5.6a, shows that the SPD$_{H}$2 is effective in increasing the tensile strength (Ts) of the 80:20w/w blends while it was in up to 10% concentration. At higher concentrations than this, the Ts seemed to stabilised at constant values. which was approximately 10% lower than that of the uncompatibilised blend. The SPD$_{H}$2 also caused increment in the YM values which have become progressively higher with the higher SPD concentrations. It was found to generally imrproved the Is, see figure 5.6b, but the extent of improvement is small, except within a narrow range of concentration (less than 3%) in which a maximum improvement (70%) was achieved. Figure 5.6d shows that, as in the case of the 90:10 w/w blends that the improvement of the Is was the result of compatibilisation.

In 70:30w/w and 60:40w/w blends see figures 5.7 and 5.8, the SPD$_{H}$2 has enhanced the Charpy Is in all concentrations used. The synergistic effects were particularly high in the low region of [SPD] (i.e. less than 12% in the former and less than 6% in the latter) . The extent of enhancement of Is in the 60:40 blends over a broad spectrum of the [SPD] was the highest as compared to the rest of the blends, see figure 5.8, It shows that the higher compatibilisation effect is achieved when the PP content was decreased from medium and towards lower concentration . Figures 5.7b(1-3)show display of microfibrils, particularly denser in the broken surfaces of the compatibilised blends, which is as mentioned before, the unmistakable indication of occurrence of strong compatibilising activity of the SPD_H2 in promoting stronger interfacial adhesion between the two blend components. In figure 5.8b(1.2) an even a more pronounce contrast in surface appearance is shown between the compatibilised and non compatibilised blends.

Figure 5.9 and table 5.11b show that the SPD_H2 which was incorporated with the diphenylmaleimide (as a potential thermal stabiliser) has affected certain level of protection to the blends against the thermal degradation, in the presence of limited amount of air, at 140°C, with better level of protection was affected in the 80:20 compositions. However, there is no conclusive evidence at this stage to whether such protections were due to the beneficial stabilising activity of the incorporated thermal stabiliser or it was merely due to the inherent resilience of the PP/EPDM in basic composition as well as the resultant composition whenever the SPD was added. The long thermal history undergone by the diphenylmaleimide compared to the irganox 1010 cast further difficulty in evaluating the actual strength of this potential antioxidant. This area therefore warrants further detail investigations. Table 5.11a however shows that at equal concentrations, the SPD2 is unlikely to surpass the performance of the irganox 1010.

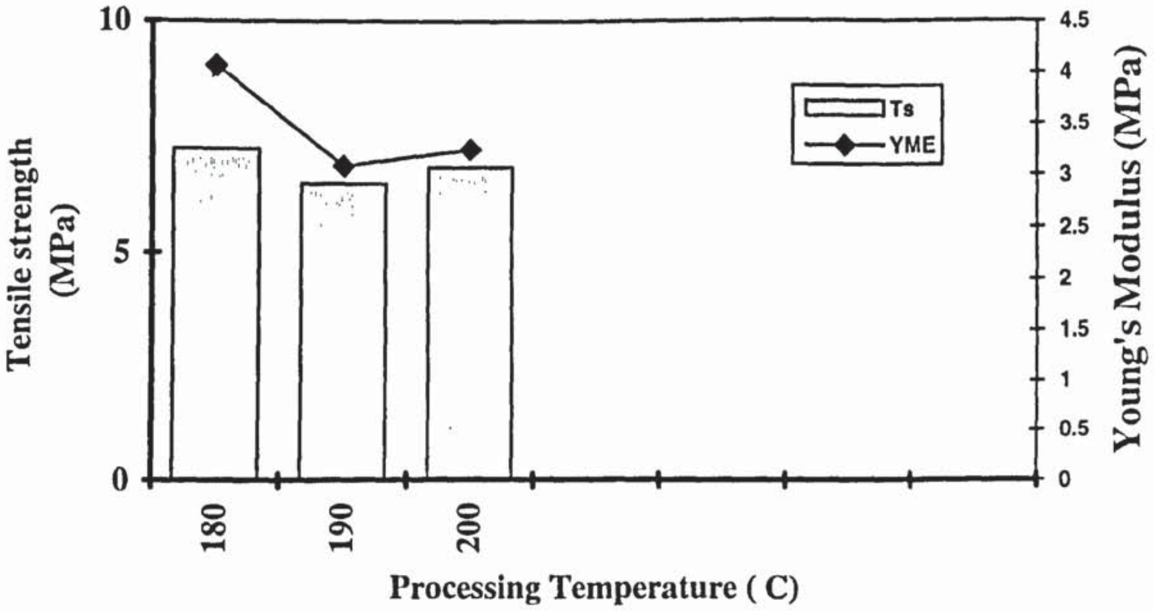


Figure 5.1a: Optimisation of processing temperature: Effect of temperature on tensile and impact strength of PS/EPDM/SPD, 70:30:10 blends, processed at 180-200°C, 60rpm,10min.

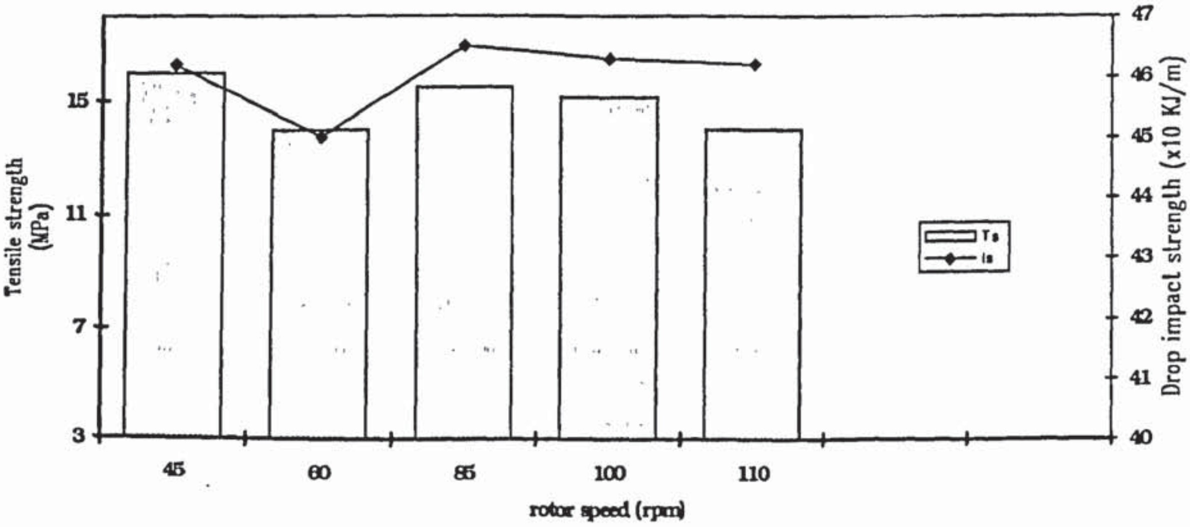


Figure 5.1b: Optimisation of rotor speed: Effect of rotor speed on tensile and drop impact strength of PS/EPDM/SPD$_H$1, 70:30:10 blends processed at 190°C, 45-110rpm, 10min.

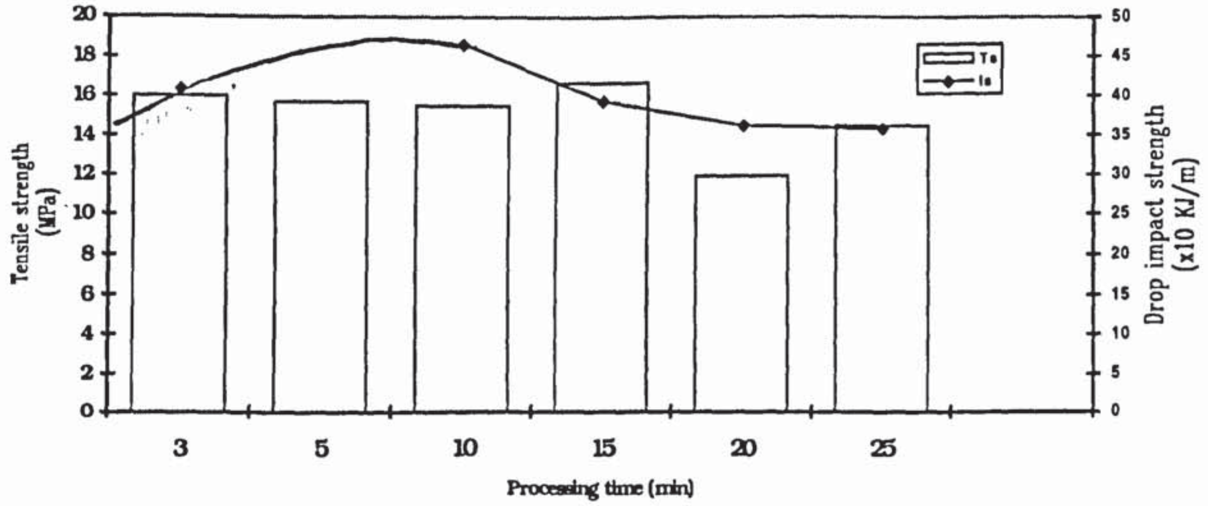


Figure 5.1c: Effect of processing time on tensile and drop impact strength of PS/EPDM/SPD$_H$1 70:30:10 blends processed at 190°C, 85rpm, 3-25min .

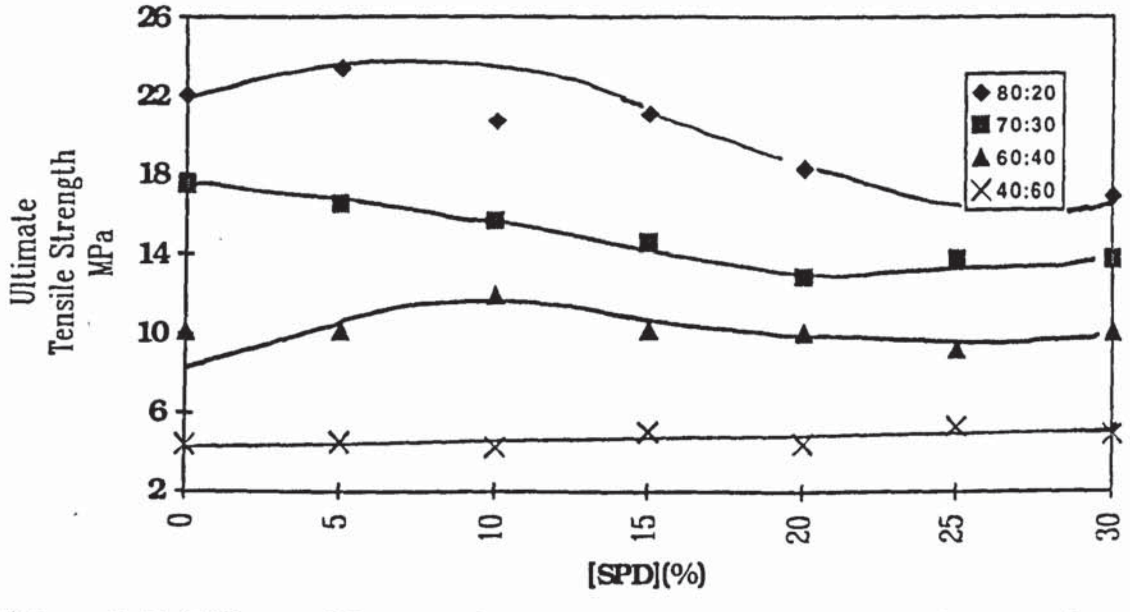


Figure 5.2: Effect of [SPD$_H$1] on tensile strength of PS/EPDM/SPD$_H$1 blends.

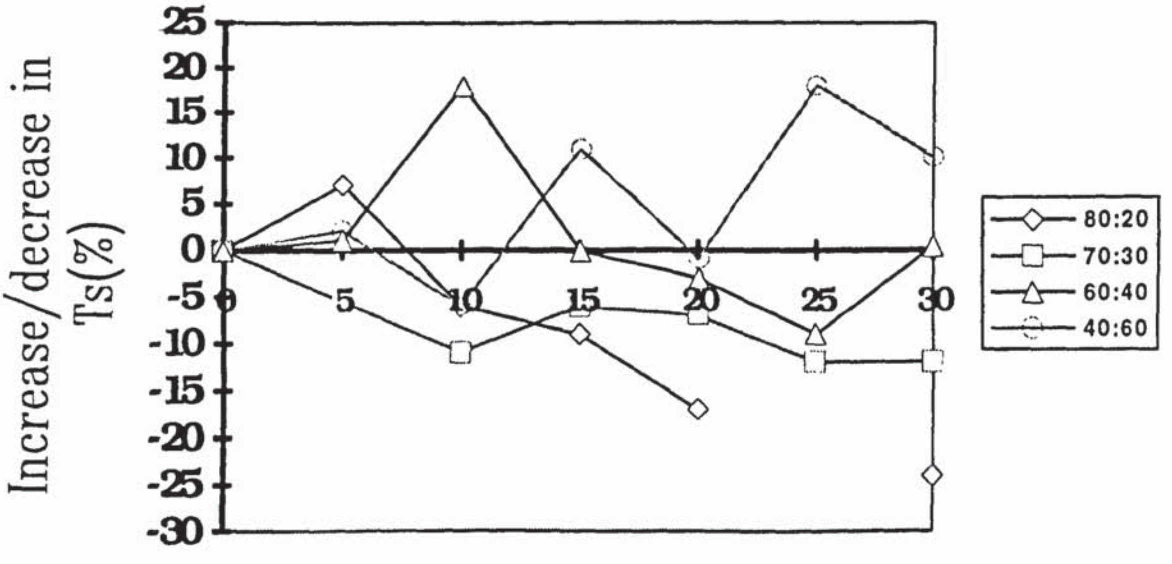


Figure 5.2b: Effect of [SPD$_H$1] on the increase (or decrease) of tensile stress of PS/EPDM (80:20, 70:30, 60:40w/w) blends containing 0-30% SPD.

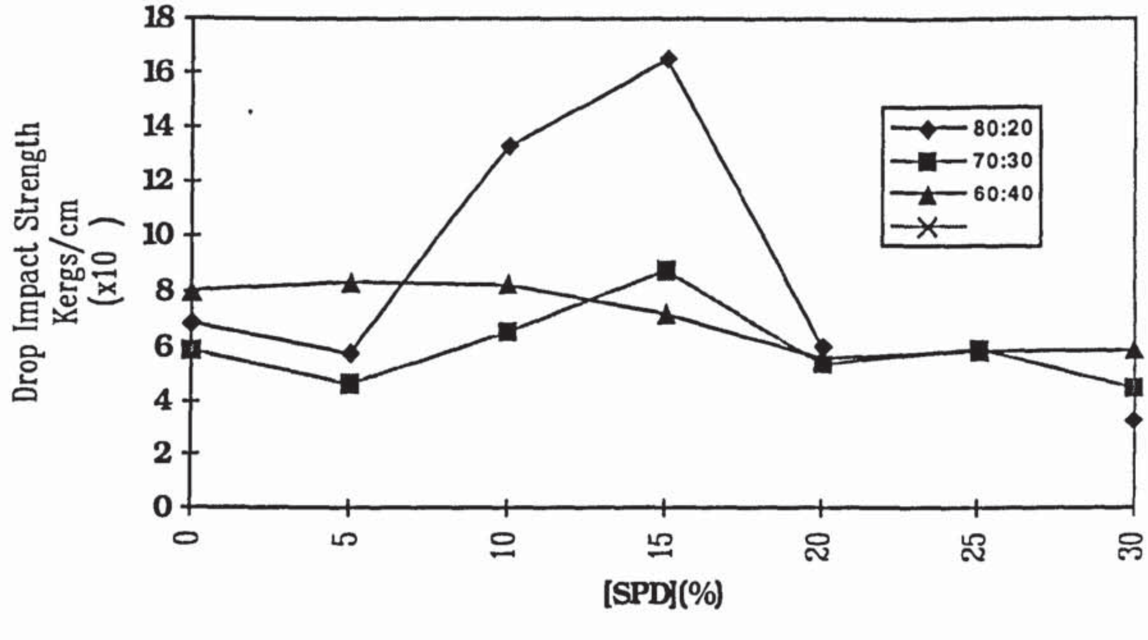


Figure 5.3a: Effect of [SPD$_H$1] on drop impact strength of PS/EPDM/[SPD$_H$1 blends of 80:20, 70:30 and 60:40 of weight composition ratios processed at 180°C, 85rpm, 10min.

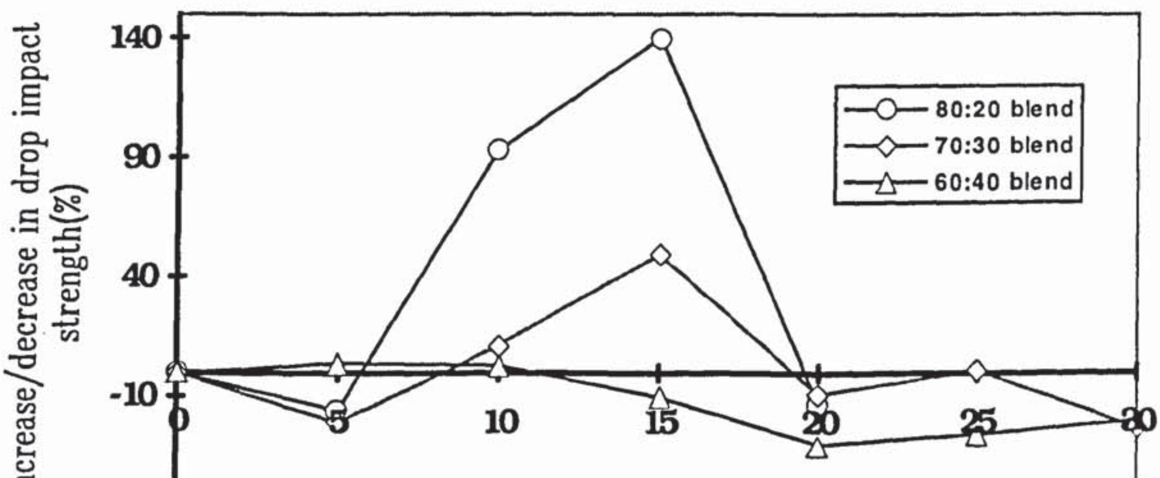


Figure 5.3b: Effect of [SPD$_H$1] on the extent of increase (or decrease) in impact strength of PS/EPDM blends (80:20,70:30&60:40w/w) containing 0-30% SPD.

Figure 5.3C: Effect of SPD$_H$2 concentrations (0-5%) on scanning electron micrographs of 80:20 w/w PP/EPDM blends, processed at 190°C, 85rpm, 10min. SPD$_H$2 [F$_o$-PP/F$_o$-EPD, 60:40w/w containing 3% HEMDA]. The figures represent SPD$_H$2 concentrations (%): 1) 0, 2) 3 & 3) 7.

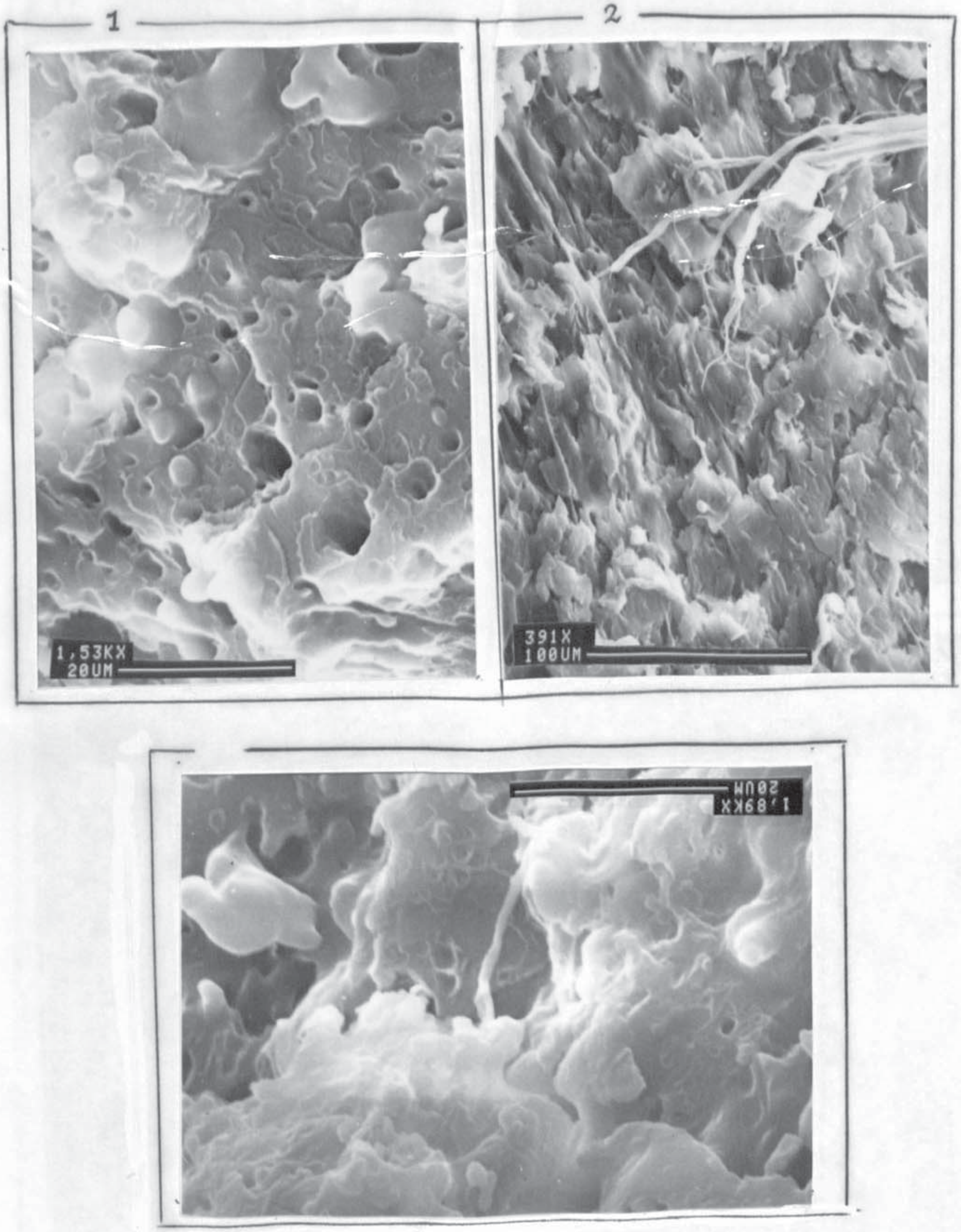


Figure 5.3d: Effect of SPD$_H$1 concentrations on scanning electron micrographs of 70:30 w/w PS/EPDM blends, processed at 185°C, 85rpm, 10min. SPD$_H$1 [F$_o$-PS/F$_o$-EPD1, 60:40w/w containing 3% HEMDA]. The figures represent SPD$_H$1 concentrations (%): 1) 0, 2) 4

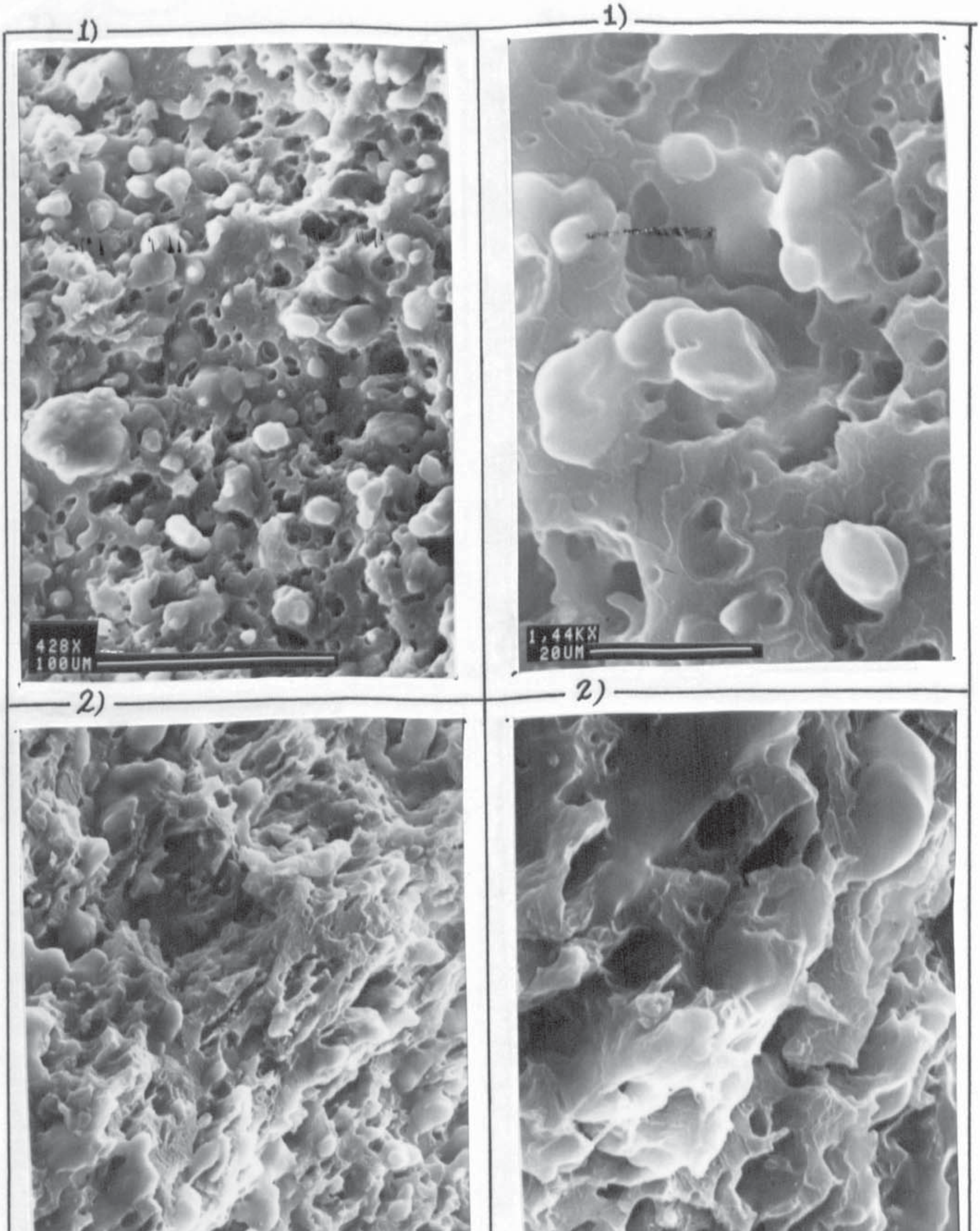
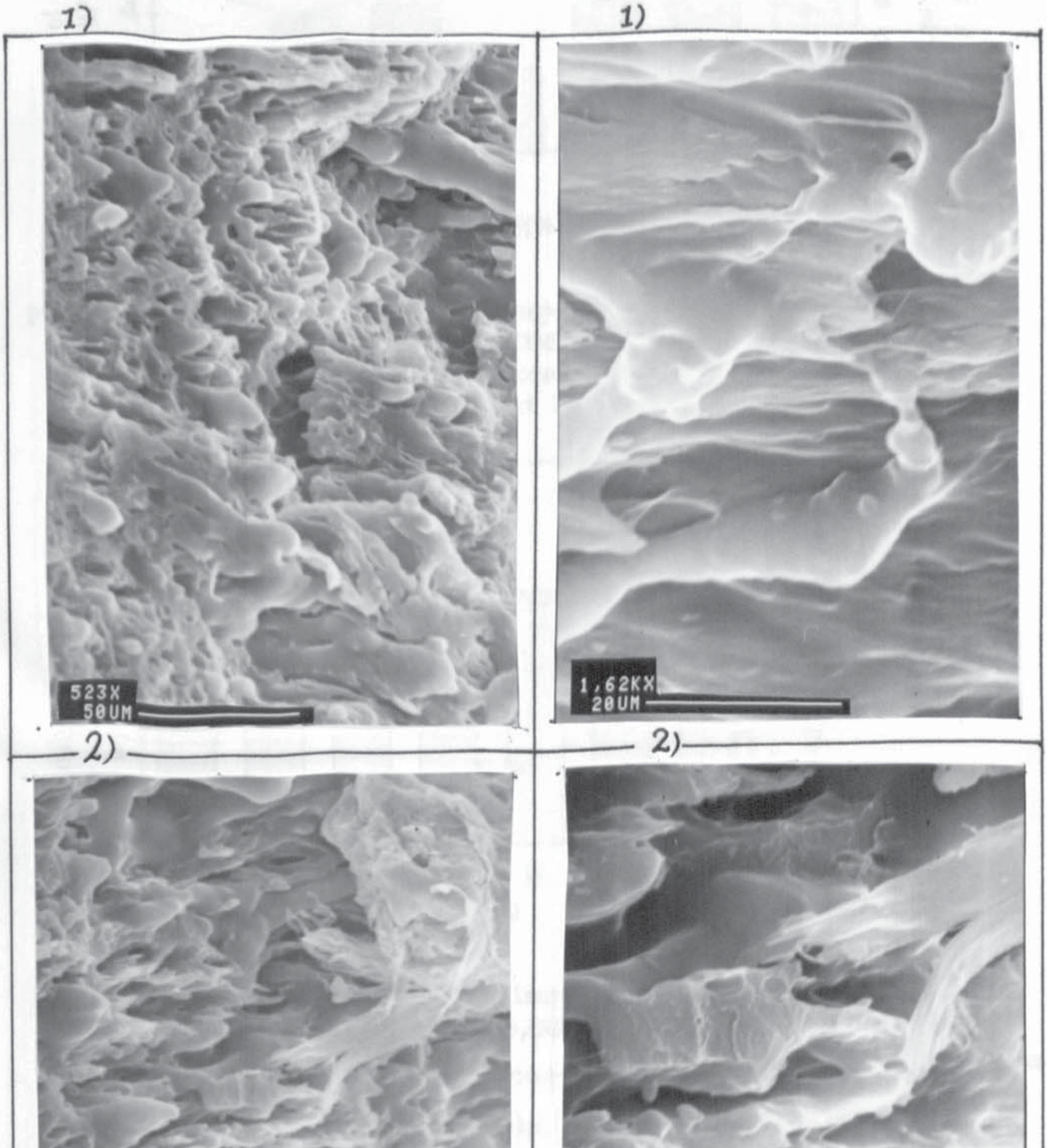


Figure 5.3e: Effect of SPD_H1 concentrations on scanning electron micrographs of 60:40 w/w PS/EPDM blends, processed at 185°C, 85rpm, 10min. SPD_H1 [F_o-PS/F_o-EPD1, 60:40w/w containing 3% HEMDA]. The figures represent SPD_H1 concentrations (%): 1) 0, 2)2



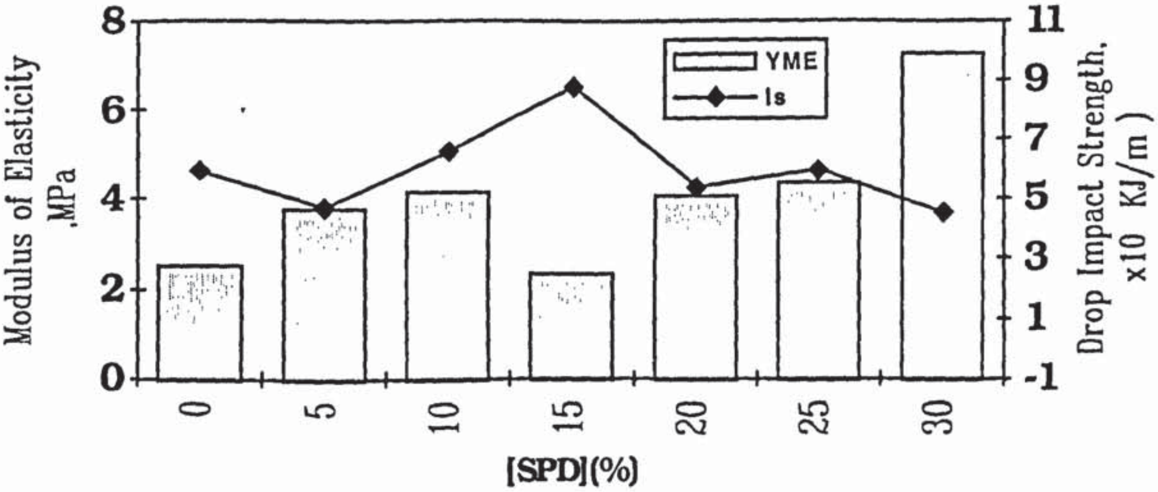


Figure 5.4b: Comparison of drop impact strength with modulus of elasticity of PS/EPDM/SPD1, 70:30 blends containing various concentration of SPD1 (0-30%), processed at 180°C, 85rpm, 10min.

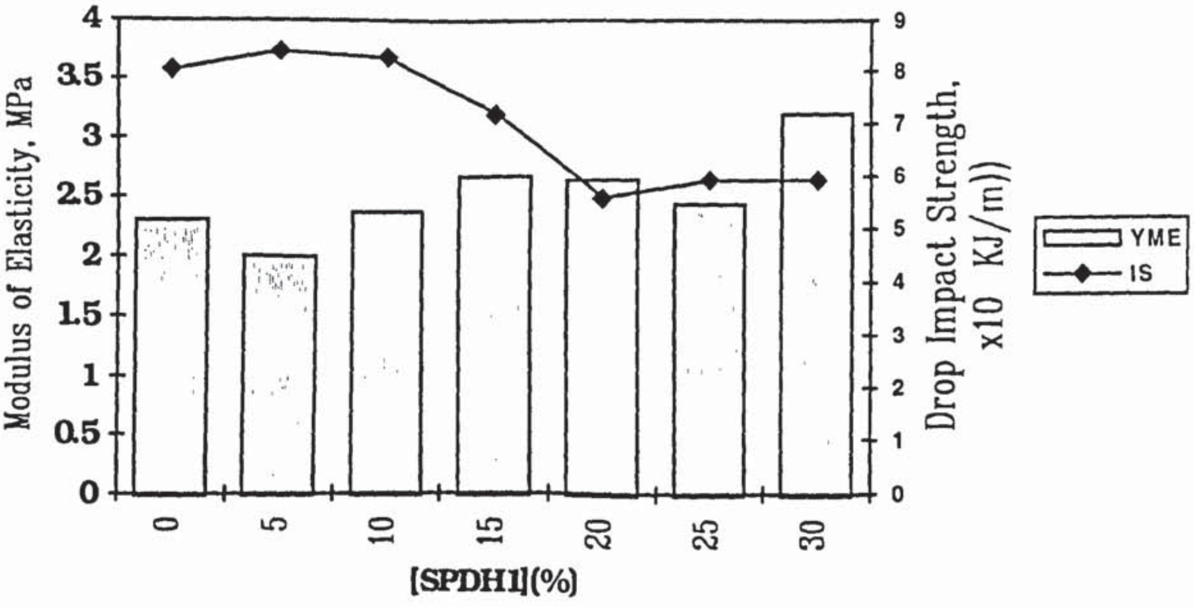


Figure 5.4c: Comparison of drop impact strength with modulus of elasticity of PS/EPDM/SPD_H1, 60:40w/w blends containing various concentration of SPD (0-30%), processed at 180°C, 85rpm, 10min.

Figures 5.5a&b: Effects of SPD$_H$2 concentrations on tensile strength and Young's modulus (a) , and Charpy impact strength (in comparison to Young's modulus), b, of PP/EPDM 90:10w/w blends processed at 185°C, 85rpm,10min.

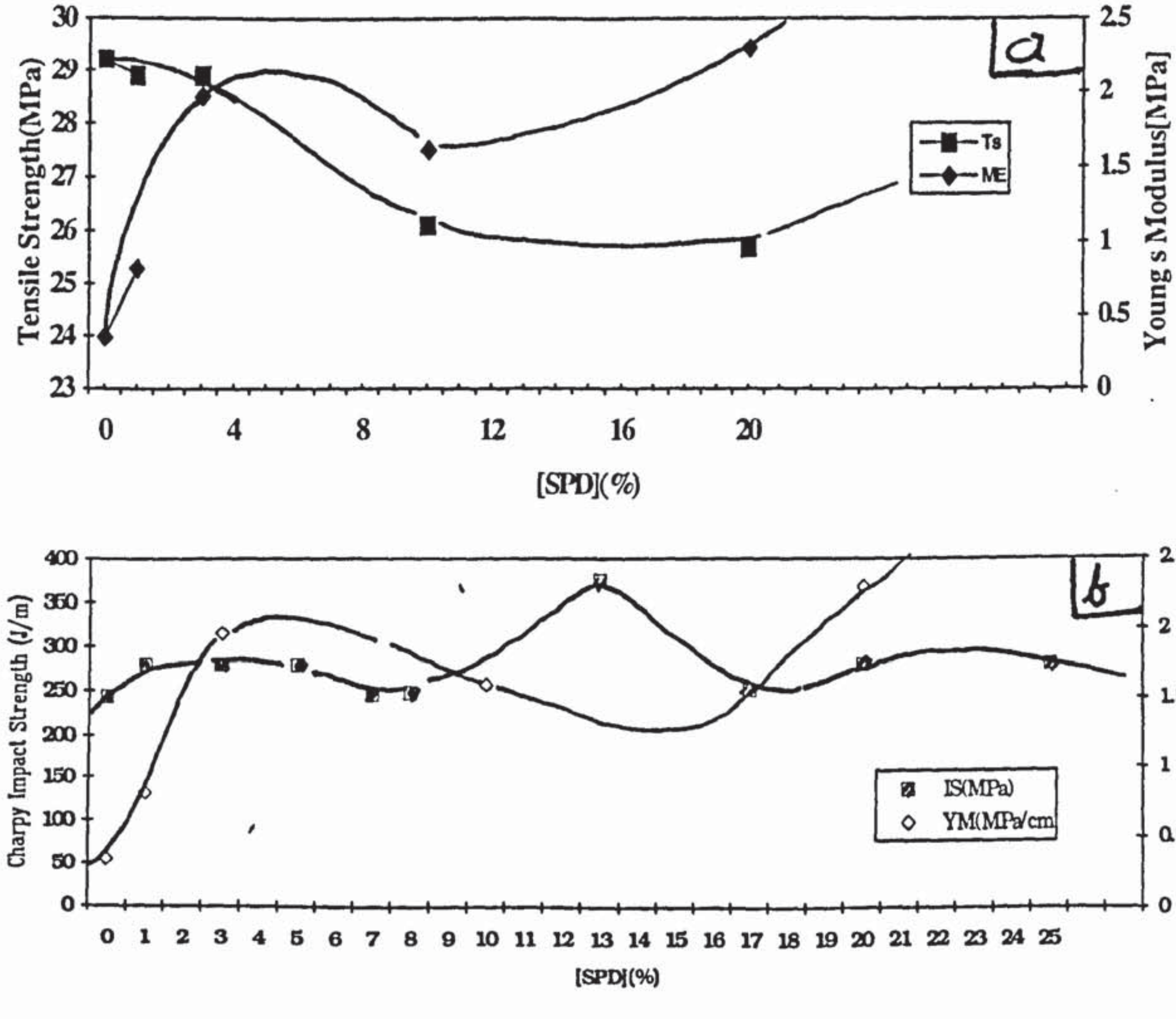
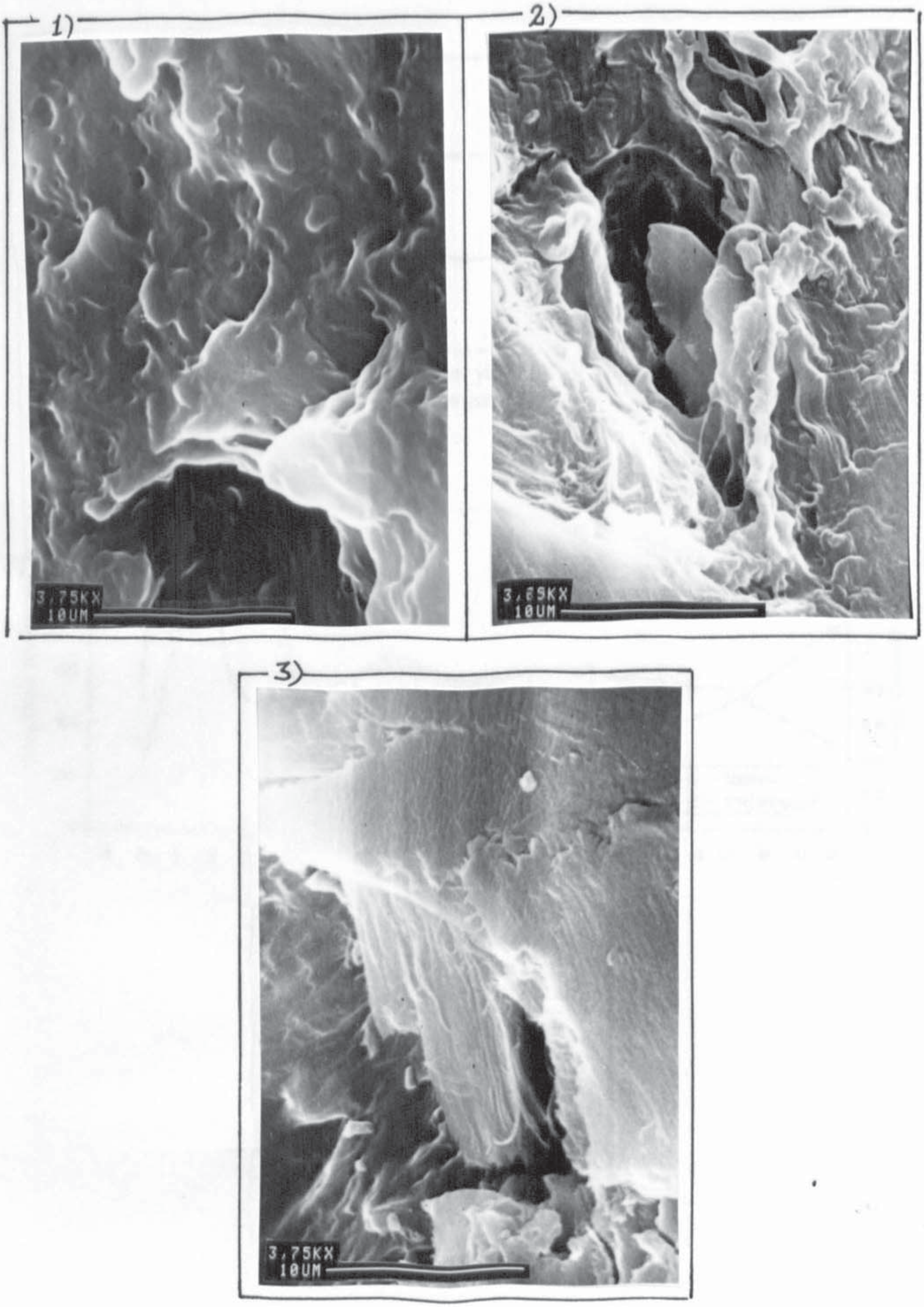


Figure 5.5c : **Effect of SPD$_{H}$2 concentrations (0, 5&13%) on scanning electron micrographs of 90:10 w/w PP/EPDM blends, processed at 190^{o}C,85rpm,10min. SPD$_{H}$2 [F$_{o}$-PP/F$_{o}$-EPD, 60:40w/w containing 3% HEMDA]. The letters represent [SPD] : 1) 0% 2) 5% and 3) 13%.**



Figures 5.6a&b: Effects of SPD concentrations on tensile strength and Young's modulus (a) , and Charpy impact strength (in comparison to Young's modulus), b, of PP/EPDM 80:20w/w blends processed at 185°C, 5rpm,10min.

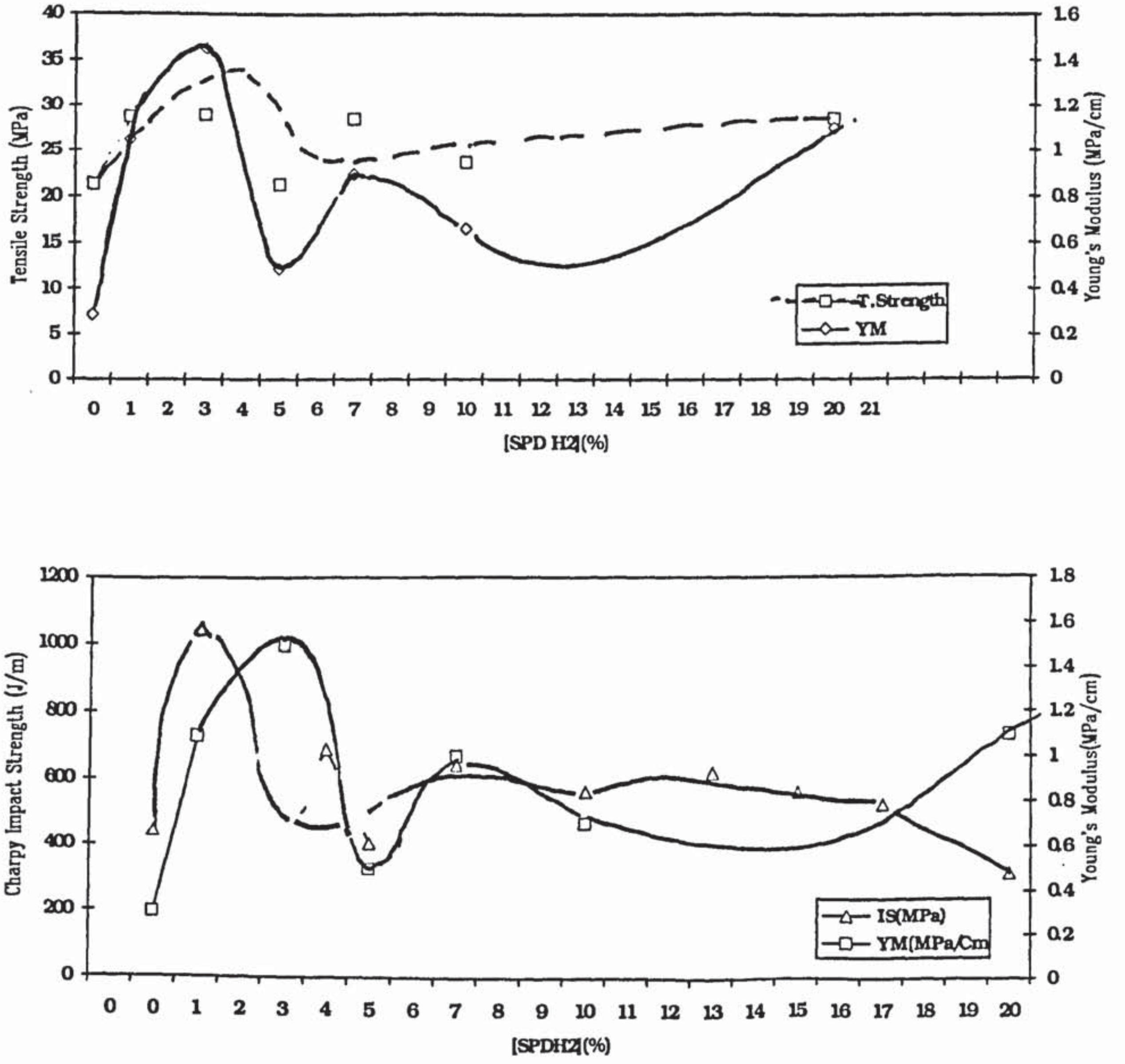
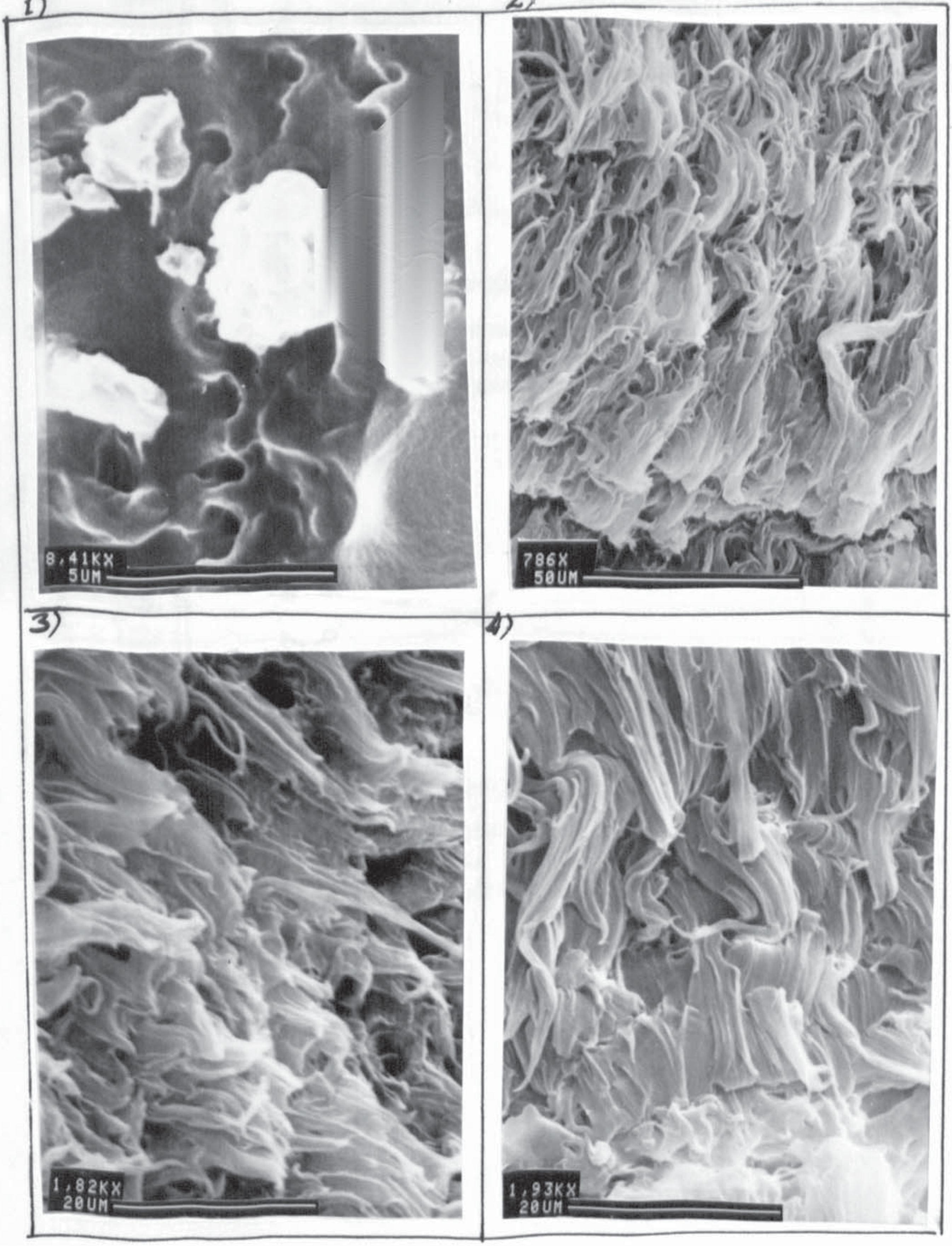


Figure 5.6c: Effect of SPD$_H$2 concentrations (0-10%) on scanning electron micrographs of 80:20 w/w PP/EPDM blends, processed at 190°C, 85rpm, 10min. SPD$_H$2 [F$_o$-PP/F$_o$-EPD, 60:40w/w containing 3% HEMDA]. The figures represent SPD$_H$2 concentrations (%): 1) 0, 2)1 3)4 & 4) 10



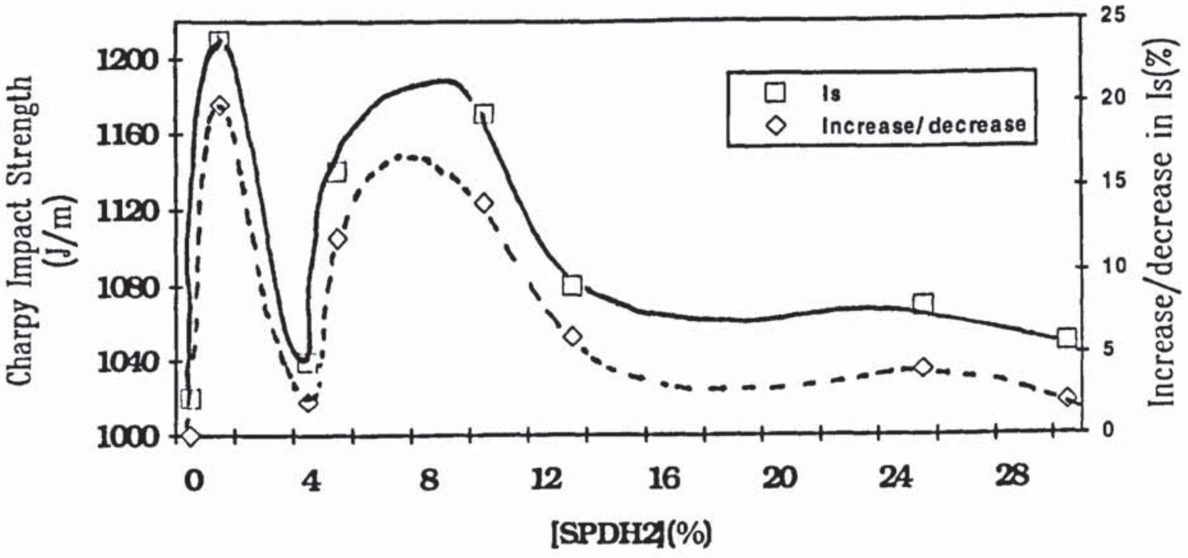


Figure 5.7: Effect of SPD$_H$2 concentrations on Is of PP/EPDM, 70:30w/w and percentage variation of Is against the Is of the uncompatibilised blend (0%SPD)

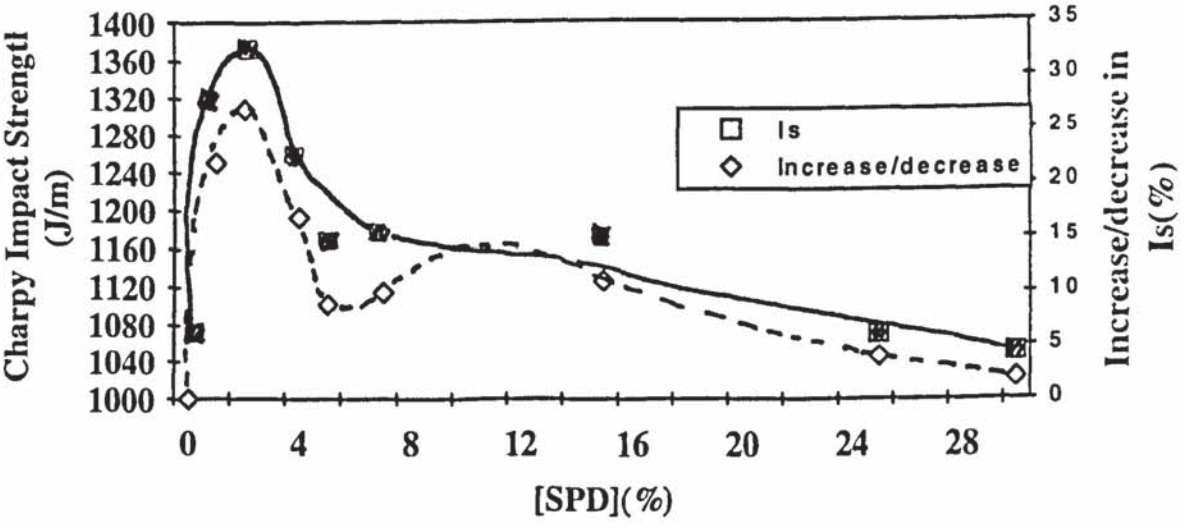


Figure 5.8: Effect of SPD$_H$2 concentrations on Is of PP/EPDM, 60:40w/w and percentage variation of Is against the Is of the uncompatibilised blend (0%SPD).

Figure 5.7b: Effect of SPD$_{H}$2 concentrations (0-5%) on scanning electron micrographs of 70:30 w/w PP/EPDM blends, processed at 190°C, 85rpm, 10min. SPD$_{H}$2 [F$_{o}$-PP/F$_{o}$-EPD, 60:40w/w containing 3% HEMDA]. The figures represent SPD$_{H}$2 concentrations (%): 1) 0, 2) 1 & 3) 5.

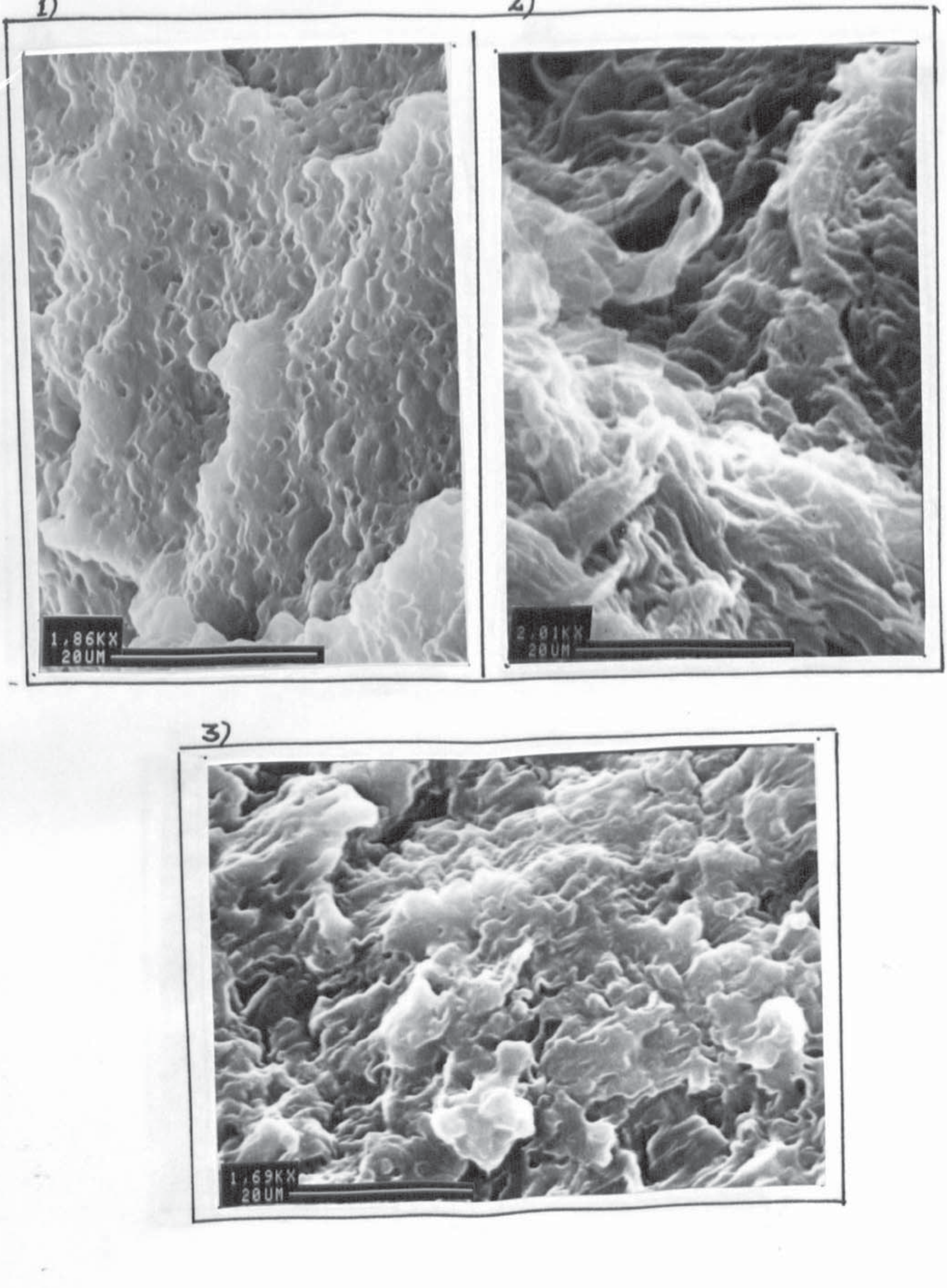
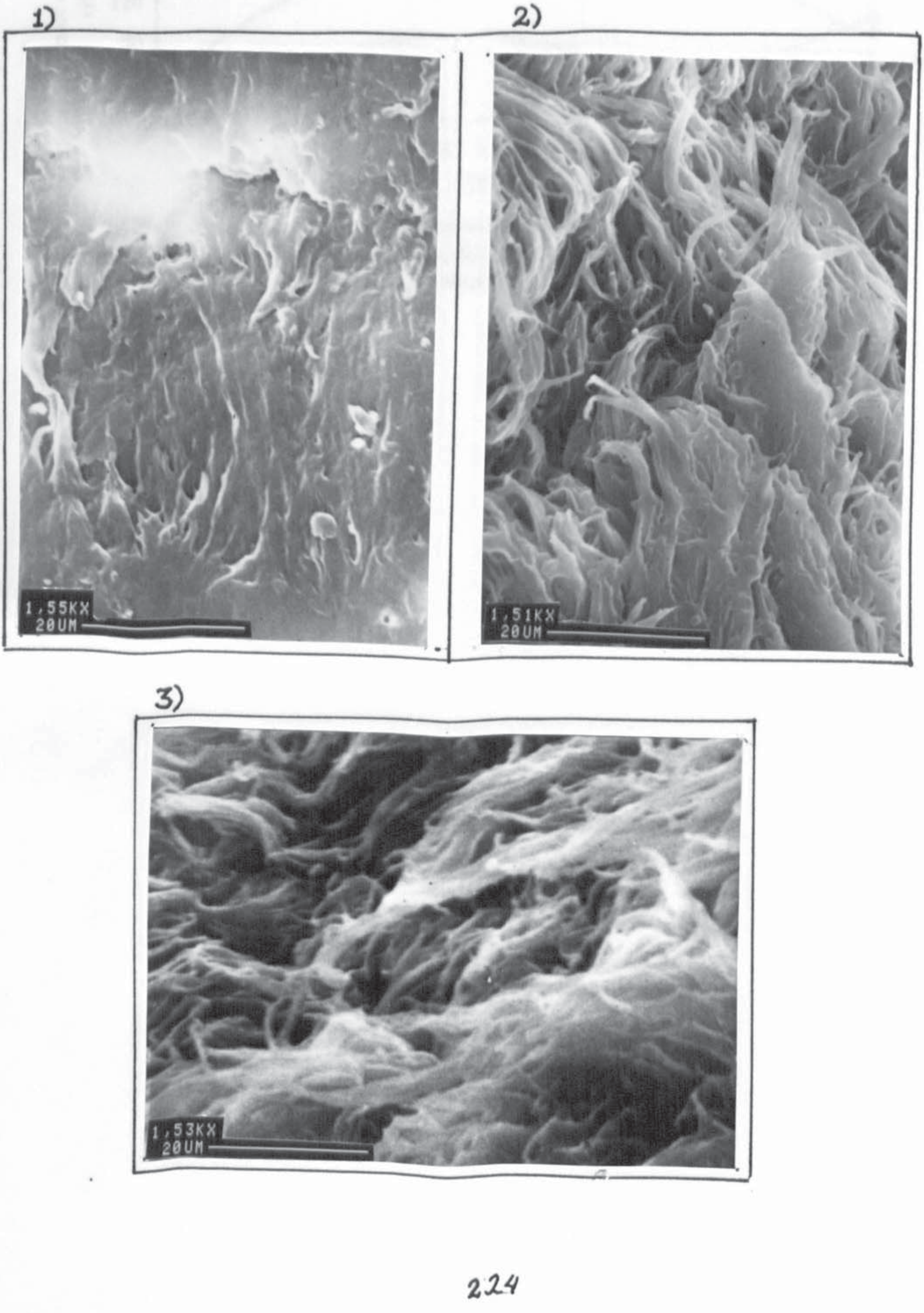


Figure 5.86: Effect of SPD$_H$2 concentrations (0- %) on scanning electron micrographs of 60:40 w/w PP/EPDM blends, processed at 190°C, 85rpm, 10min. SPD$_H$2 [F$_o$-PP/F$_o$-EPD, 60:40w/w containing 3% HEMDA]. The figures represent SPD$_H$2 concentrations (%): 1) 0, 2) 2 & 3) 5


1) 2) 3)

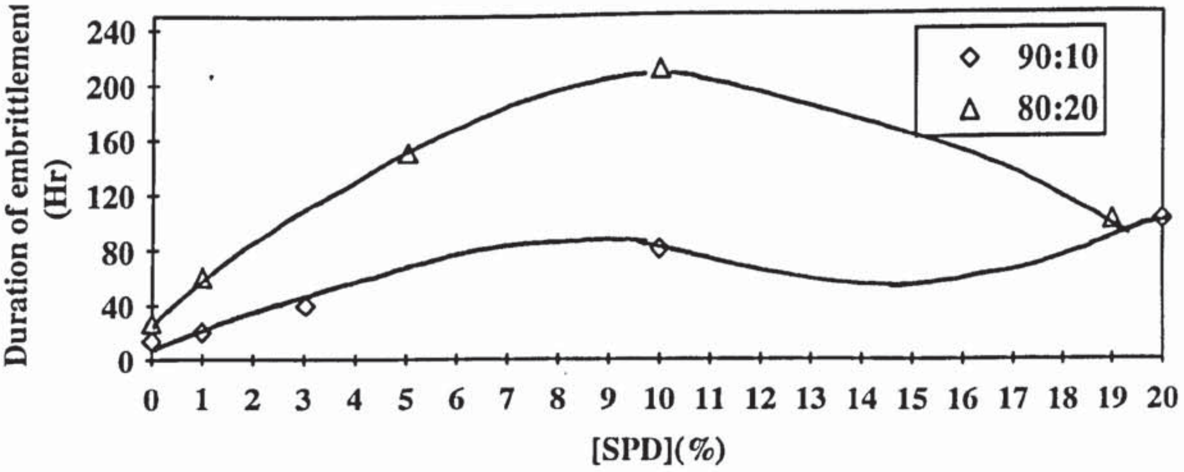
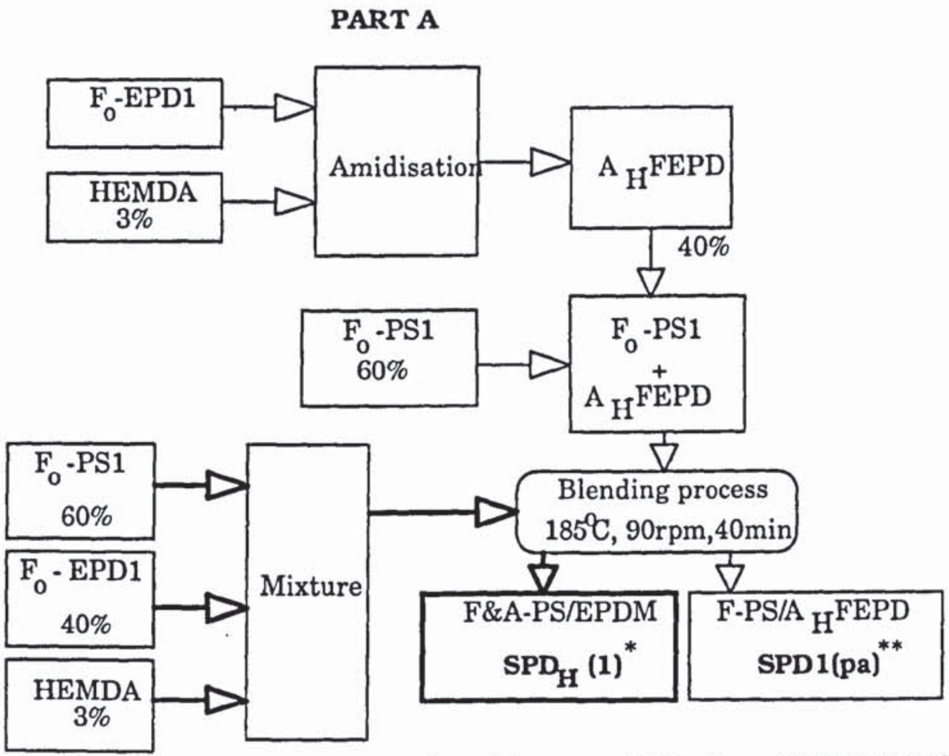
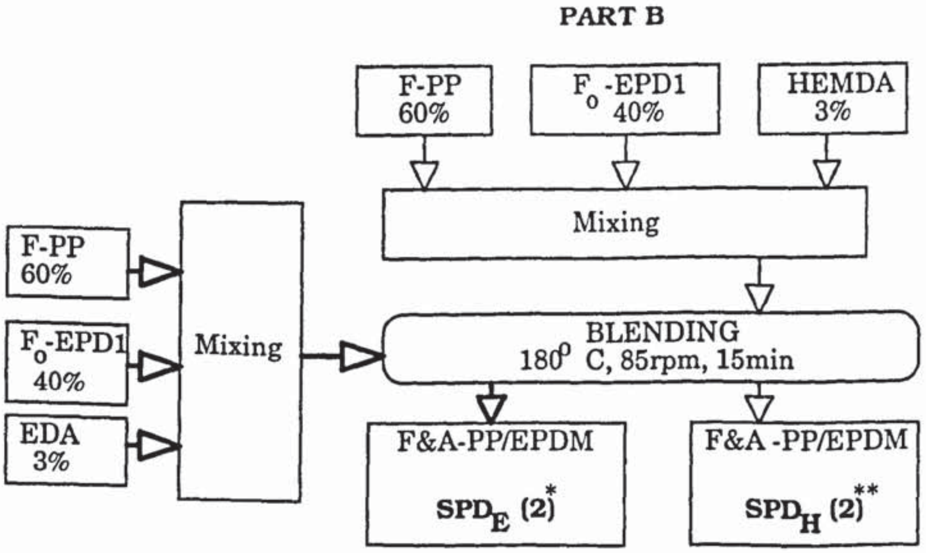


Figure 5.9: Effect of [SPD_H2] on resistance to thermal degradation of PP/EPDM, 90:10 and 80:20w/w blend films (0.15mm thick) in a Wallace oven at 140°C, air flow rate of $2cm^3/min$.



* used in compatibilisation of PS/EPDM blends (see section 2.5.3)

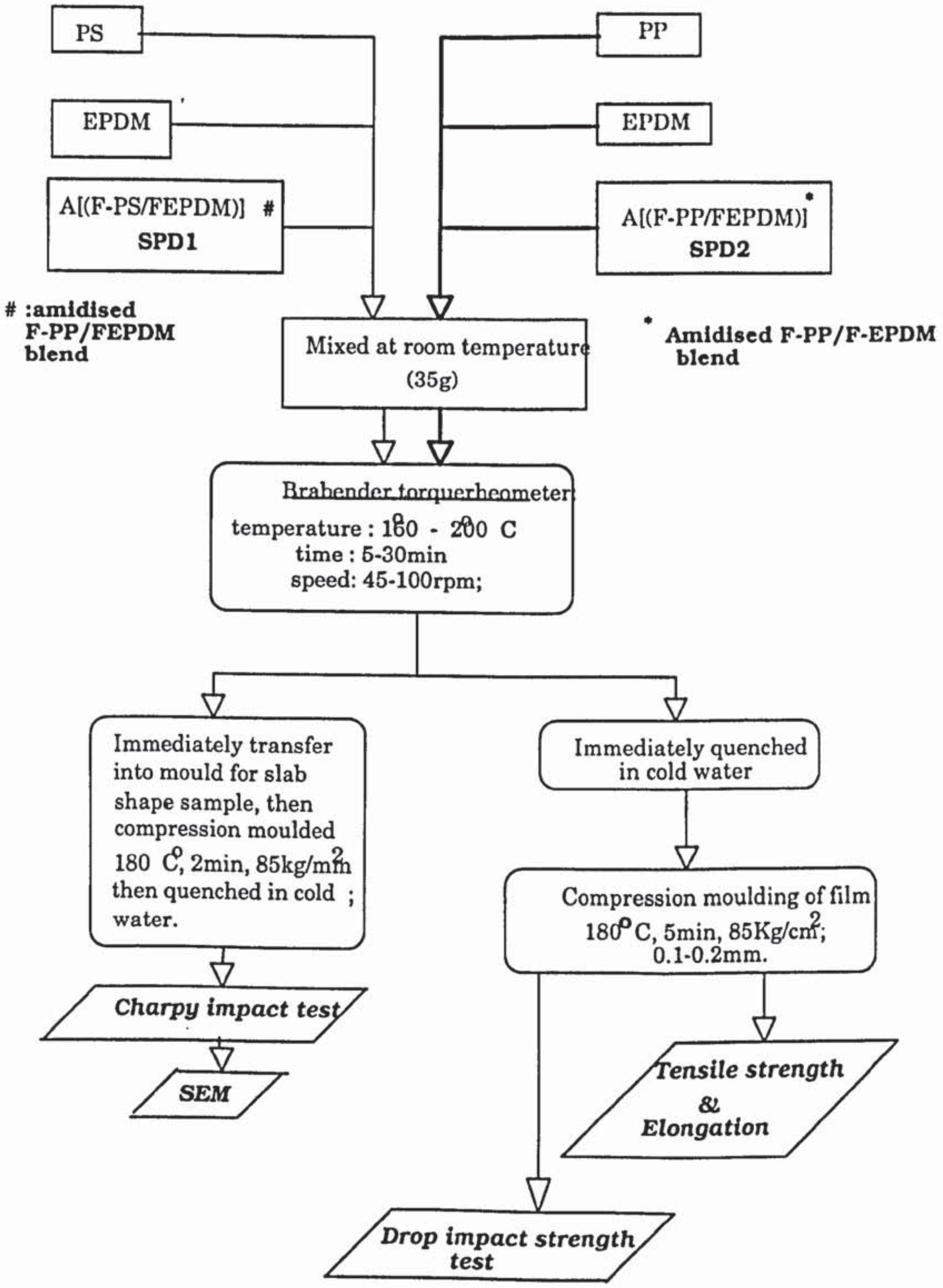
** used in optimisation experiments (see section 5.2.1&5.2.2)



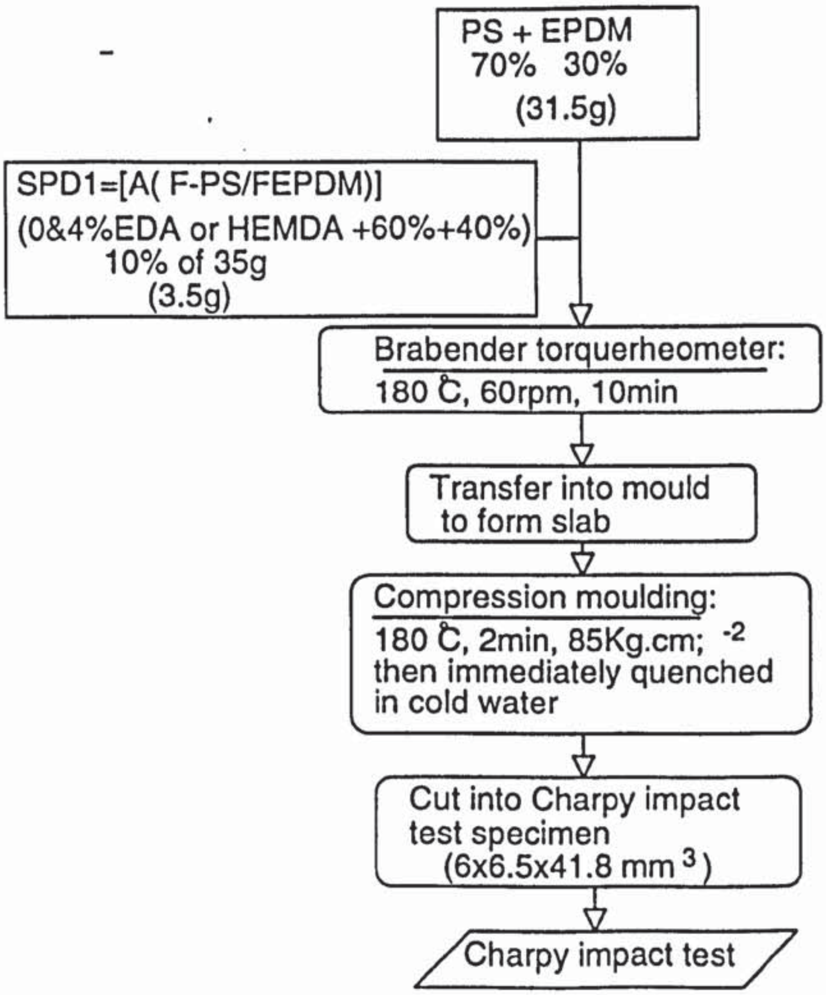
* used in experiments described in table 5.7

**used in blend of PP/EPDM

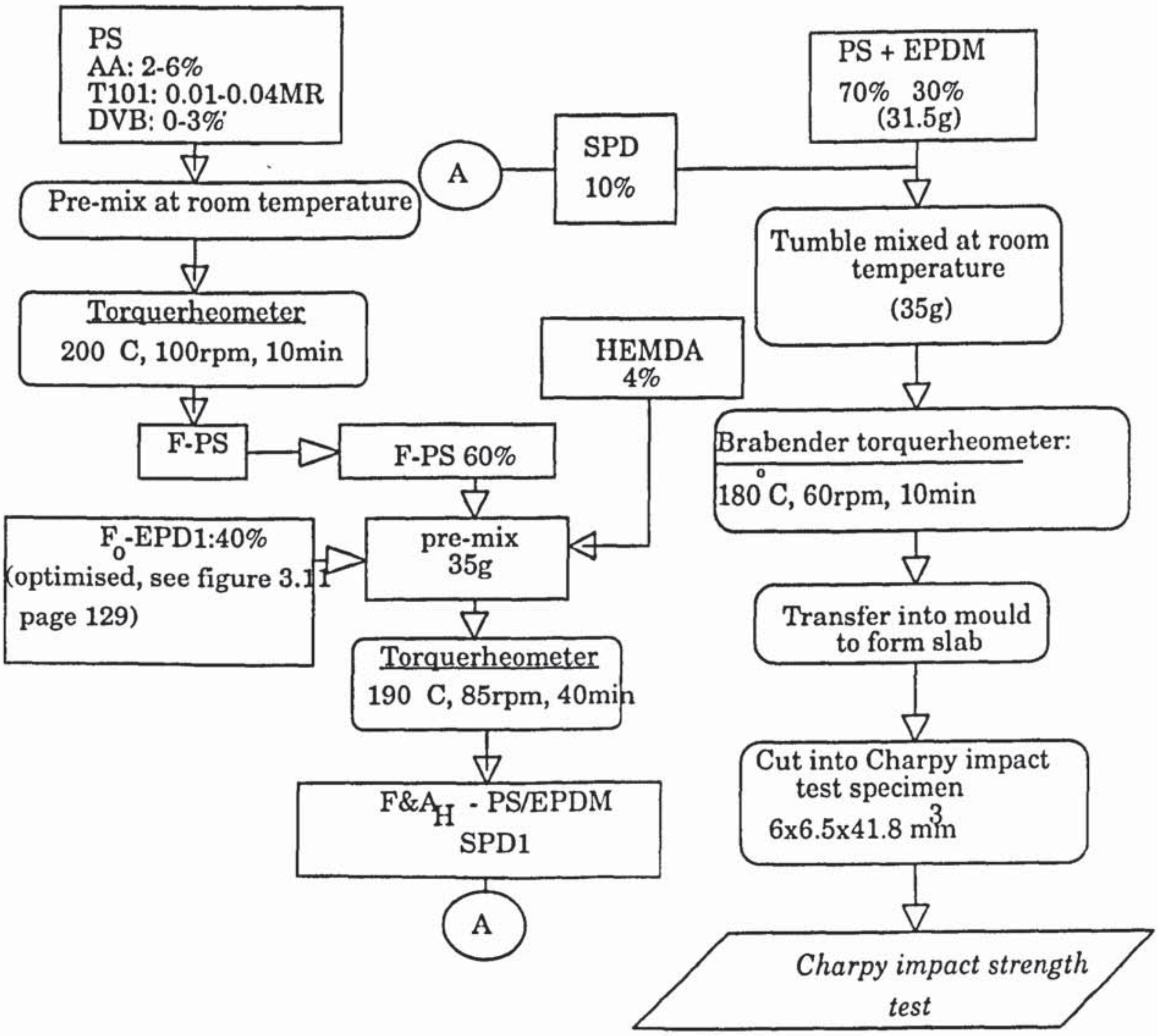
Scheme 5.1a: Flowchart (simplified) showing the compositions of SPDs used in chapter 5; Part A for preparation SPD involving PS and EPDM and part B for the SPD consisting of PPand EPDM



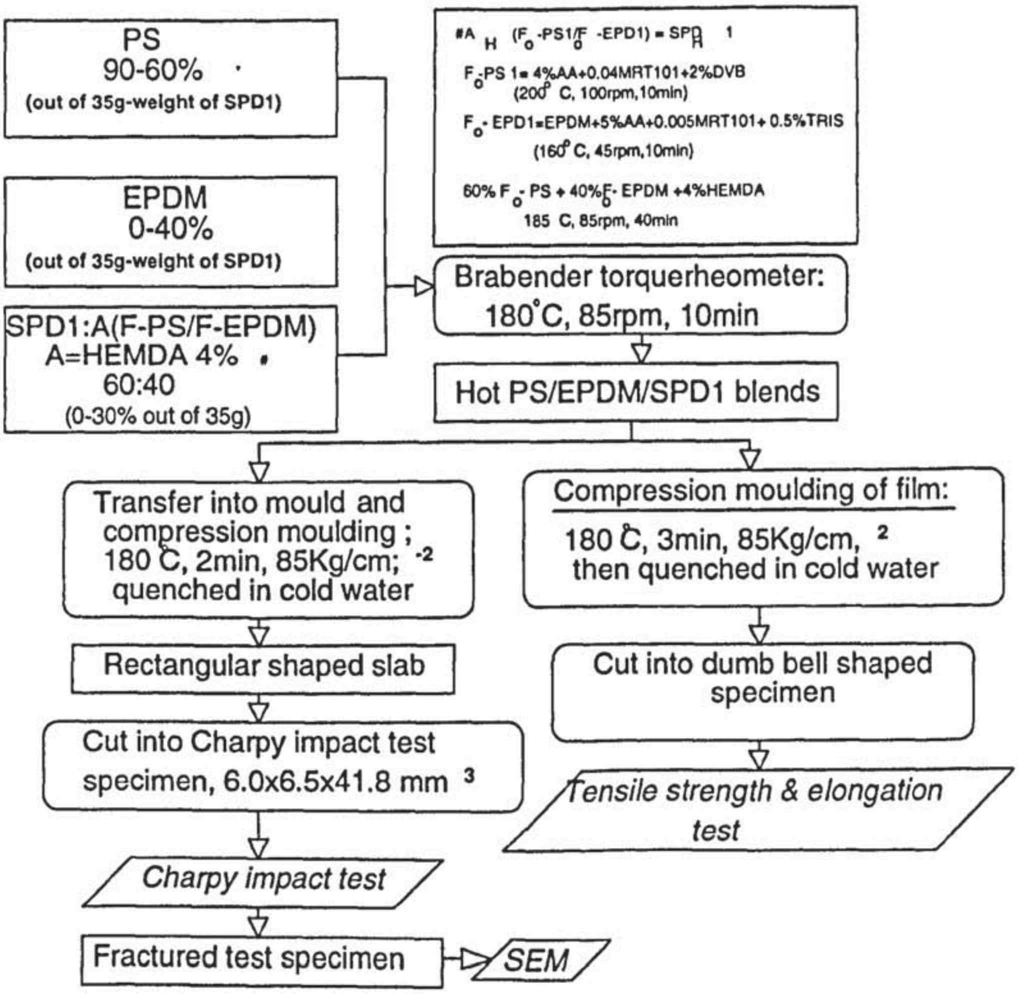
Scheme 5.1b: Flowchart for general processing and tests of PS/EPDM and PP/EPDM blends (with or without SPD); 160-180 C 45-100rpm, 5-30min.



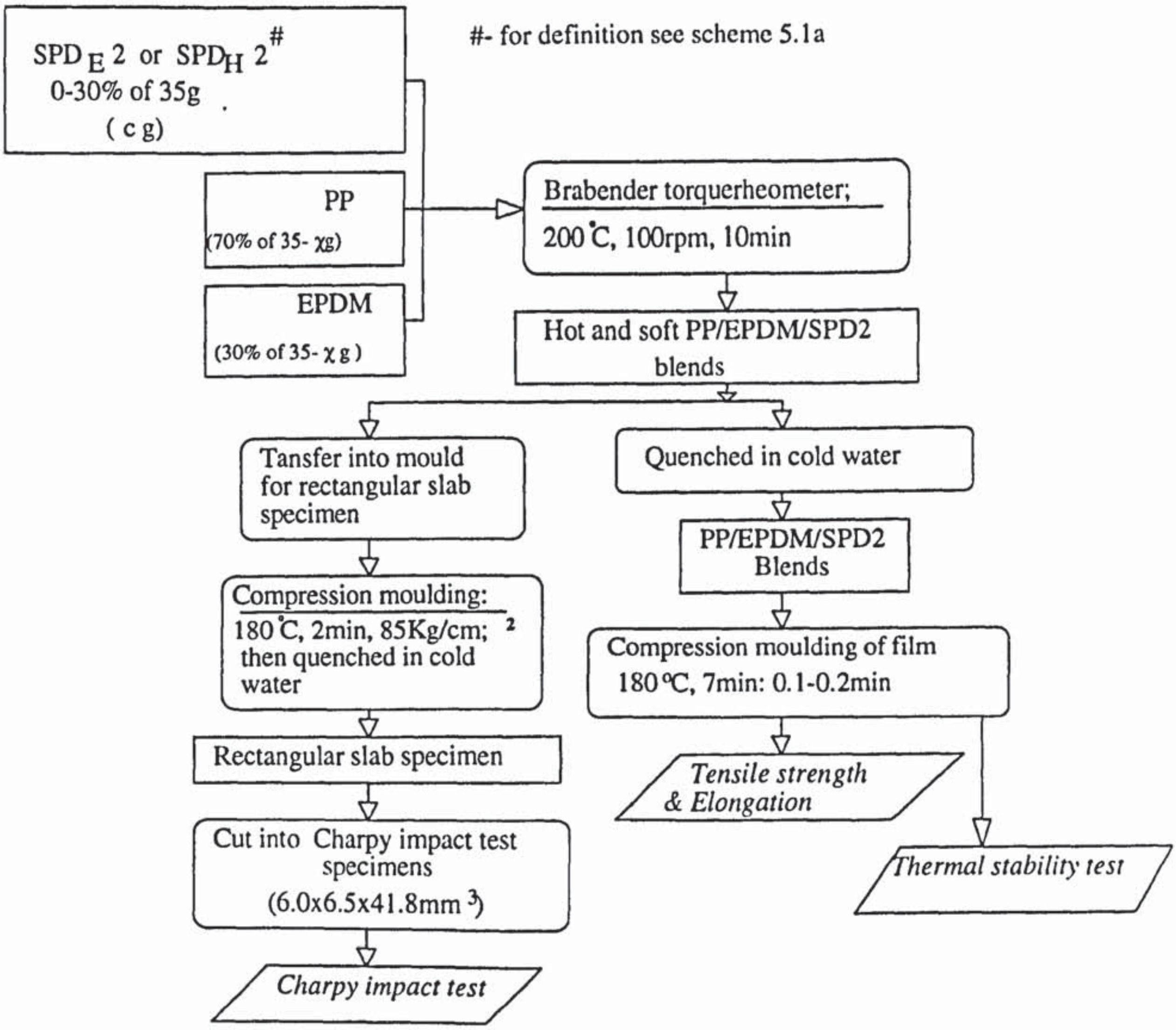
Scheme 5.2: Flowchart for effect of presence and absence of EDA and HEMDA in F-PS/F-EPDM blends, on effectiveness of the blends as SPD in compatibilising PS/EPDM, 70/30/(10) blends.



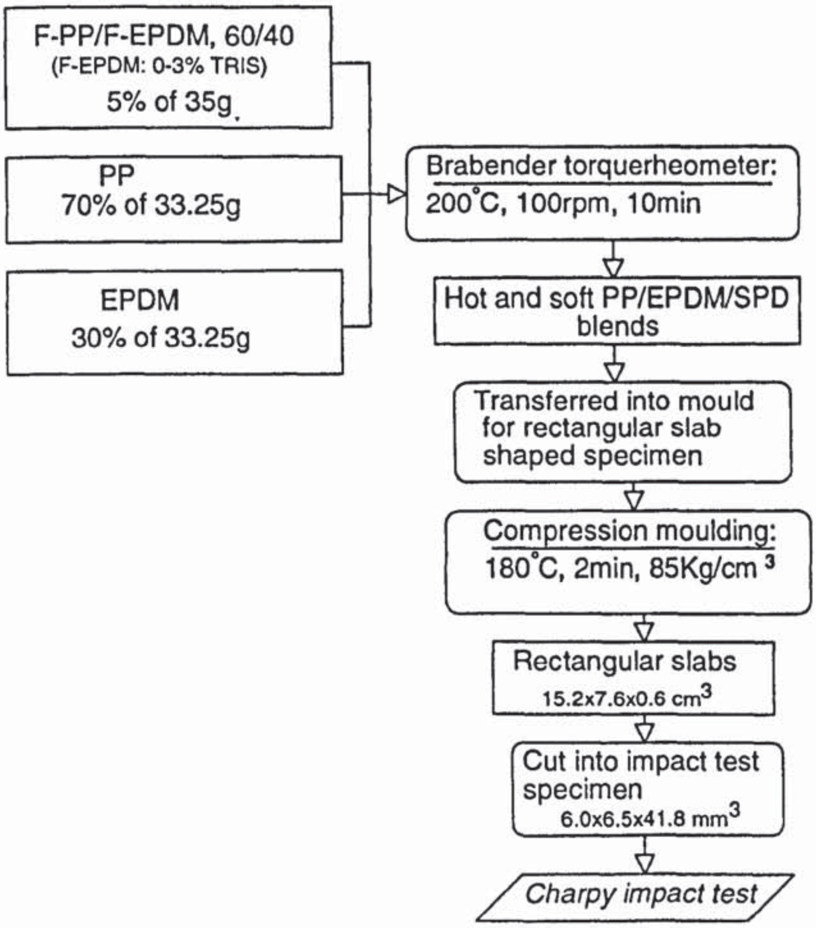
Scheme 5.3: Effects of F-PS samples prepared using various concentrations of AA, T101 and DVB on effectiveness of the F-PS/F-EPD, 60:40w/w blends as SPD in PS/EPDM/SPD, 70:30:10 blends as evaluated via Charpy impact strength.



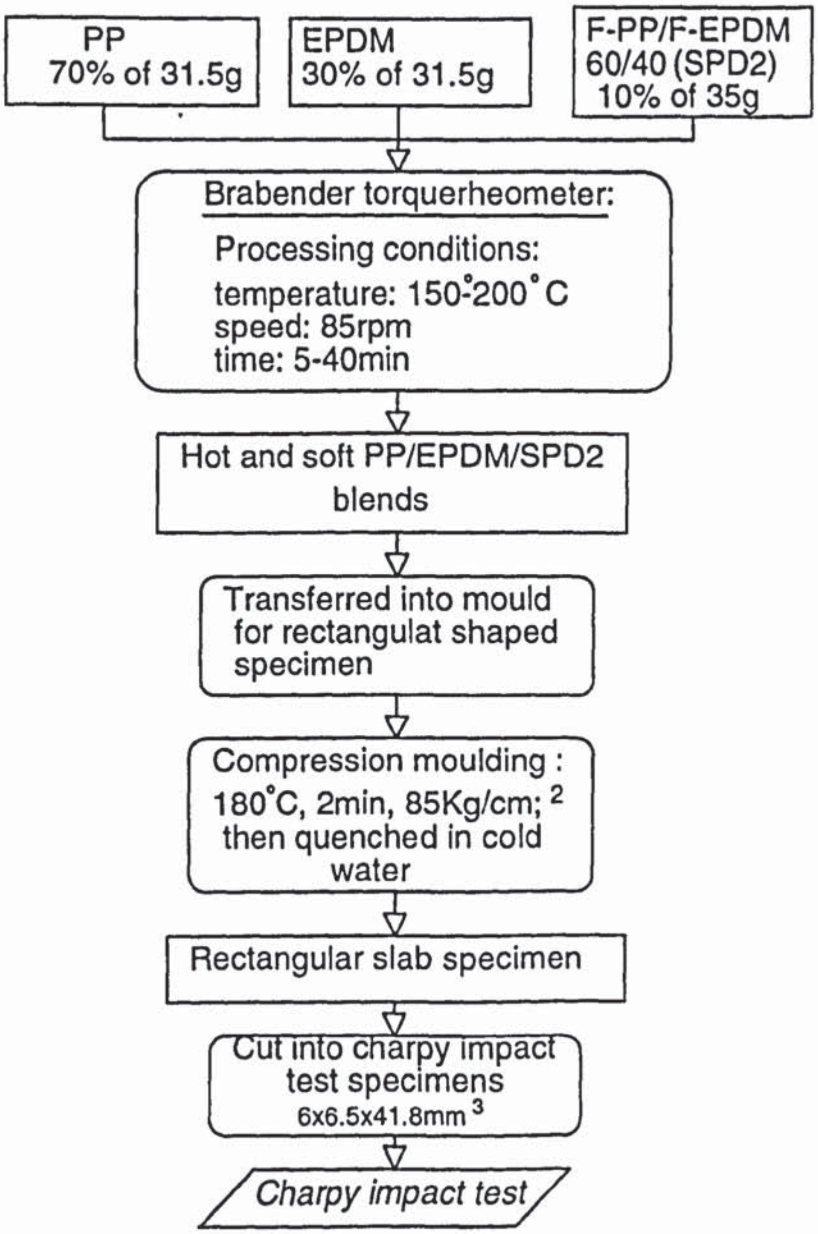
Scheme 5.4: Flowchart for PS/EPDM/SPD1 blends containing various weight proportions of the components processed at at 180°C, 85rpm, 10min;l and mechanical, thermal and morphological tests carried out.



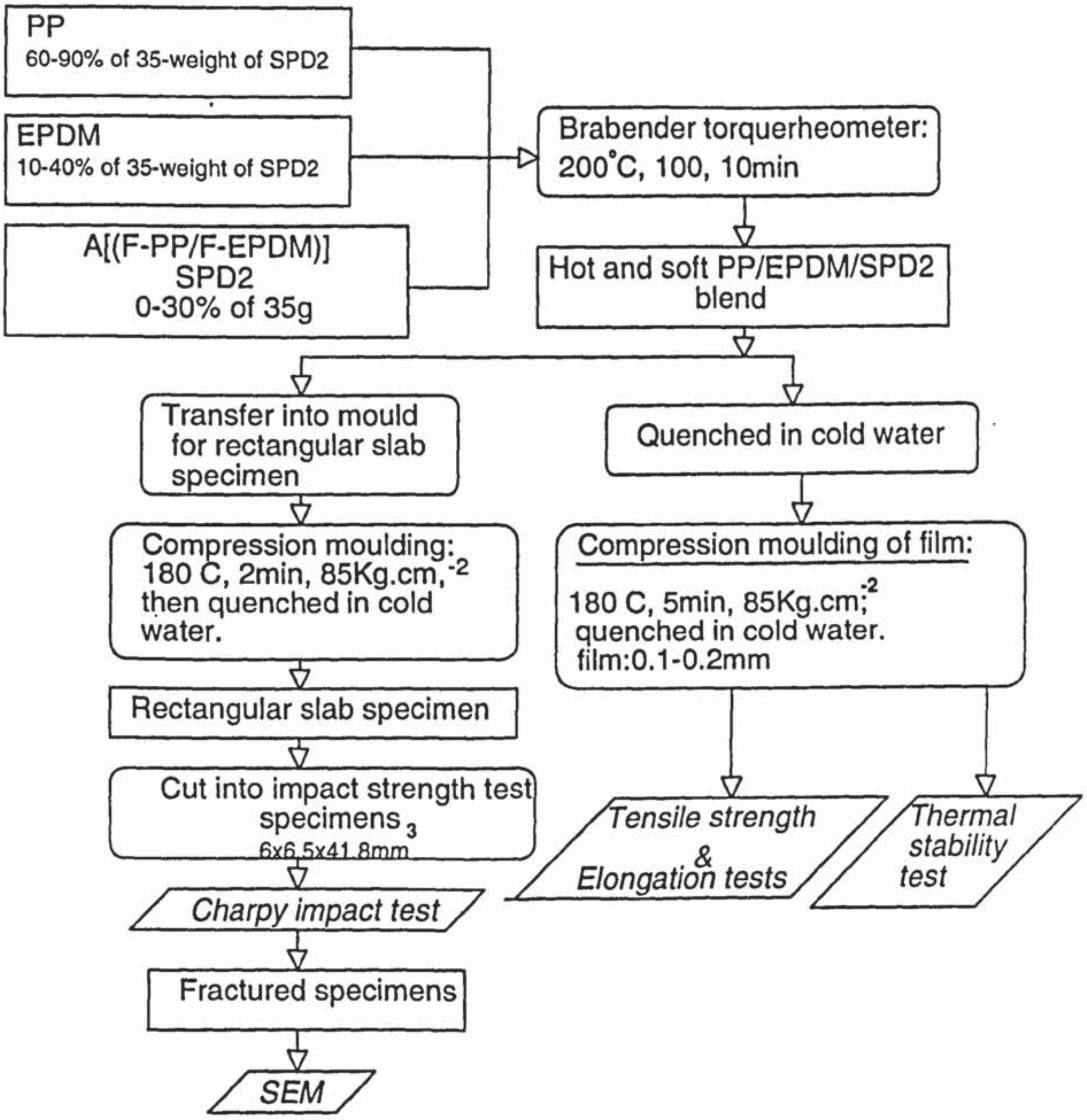
Scheme 5.5: Effect of presence and absence of EDA or HEMDA in amidised F-PP/F-EPDM,60/40 blends on effectiveness of the blends as SPD in compatibilising PP/EPDM,70/30/(0-30) blends at 200°C 100rpm, 10min.



Scheme 5.6: Effect of TRIS concentration (0-3.0%) in F-EPDM of the amidised F-PP/F-EPDM/(4%HEMDA) blends (SPD2) on effectivity of the SPD2 in compatibilising PP/EPDM/SPD2, 70/30/(5) blends as evaluated through Charpy impact test.



Scheme 5.7: Effect of processing conditions (temperature, speed & time) on Charpy impact strength of PP/EPDM/SPD2, 70/30/(10) blends.



Scheme 5.8: Mechanical, thermal and morphological properties of PP/EPDM/SPD2 blends containing various weight proportions of the components processed at 200°C, 100rpm, 10min.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORKS

6.1: CONCLUSIONS

1. Functionalisationof the inert hydrocarbon polymer, polystyrene (PS) with acrylic acid (AA), the agent, in the presence of a coagent, mainly divinyl benzene (DVB) can be successfully carried out in the melt by reactive processing using an internal mixer. At 6% [AA], the optimum level of peroxide (Triganox 101) and coagent (DVB) was 0.04MR and 2%, respectively; and optimum processing conditions were 200°C, 100rpm and 10min, using the 'premix method (PM1). At this compositions and conditions a grafted AA concentration of 1.3%(to the weight of the processed PS) or 22%(to the initial amount of AA added) was achieved. The F-PS obtained was free from insolubles but suffered a certain extent of molecular chain degradation.

2. The expectation (based on previous work in other system [100]) that addition of a coagent e.g. DVB during the functionalisation of PS with AA in the presence of peroxide may enhance the level of grafting was brought to realisation. Addition of certain concentration of the coagent (e.g. 2%) has remarkably increased the level of grafting (see figure 3.8), much higher than achievable by the mixture in the absence DVB (i.e. 22% vs 7% respectively). However a judicious of the coagent was shown to be very important in order to strike a balance between the achievement of sufficiently high level of grafting with reasonably low level of crosslinking and degradation. The coagent also promotes the grafting efficiency of the total amount of the retained AA and reducing the extent of chain scission/degradation (see table 3.4).

3. Functionalisation of EPDM with AA in the presence of a peroxide (T101) and a multifunctional coagent, trimethylolpropane triacrylate (TRIS), in a reactive processing procedure has been successfully carried out. As in the case of functionalisation of PS, the premixing prior to processing procedure (EPM1) has over the other sequential addition methods affected higher grafting efficiency of AA to EPDM. Addition of peroxide was shown to be important in order to

affect significant level of grafting (22% binding at 0.006MR versus 10%binding at 0.00MR of T101) but must be used judiciously to strike a balance between the achievement of reasonably high concentration of grafting and amount of crosslinking. Care had to be taken with the use of peroxide concentration as higher (than the optimum concentration), led to excessively high fraction of insolubles, due to crosslinking (even though accompanied by higher AA grafting levels) rendered the F-EPD1 unsuitable for further use.

3. The expected role of the coagent TRIS in enhancing the level of grafting of AA to EPDM was realised. The coagent has significantly enhanced the level of retained AA and increased the grafting efficiency . A judicious use of the coagent could promote an increase in concentration of the grafted AA up to an order of magnitude (24% at 0.5%TRIS versus 7% at 0%TRIS) (see figure 3.13).

4. The mechanical properties of functionalised PS/EPDM and PP/EPDM blends were enhanced by the incorporation of diamine (e.g. HEMDA in the case of F-PS/F-EPDM blend; EDA and HEMDA for F-PP/F-EPD blends), which acted as interlinking agent (IA), promoting the *in situ* coupling reaction between the carboxylic groups (of the funtionalised polymers) and the amino group of the IA. The enhancement effect was probably derived from the beneficial activity of the copolymer(s) which have probably acted as SPD(s). The enhancement effect of HEMDA was particularly strong in the F-PP/F-EPD system, as shown by the remarkable increase in the impact strength over the unamidised blend (816J/m at 3% HEMDA versus 313J/m at 0% HEMDA, see table 4.6). Use of IA at proper concentration is important in order to maximised the amidisation reaction (both in pre-amidised and direct addition methods), and minimise the side reactions, which would reduced the eventual in situ formation of the copolymer which might act as an SPD.

6. The F&A-PS/EPDM, 60:40w/w (SPD1) and F&A-PP/EPDM, 60:40w/w (SPD2) when used as additives in blends of similar polymer mixtures of various compositions proven to have beneficial effect whereby the impact strength (drop and Charpy) of the basic blends (PS/EPDM or PP/EPDM) were enhanced, without causing detrimental reduction in the tensile strength. In the PS/EPDM blends, the SPD$_H$1was particularly effective in compositions containing high weight proportions of PS; whereas in the PP/EPDM blends the SPD$_H$2 was more effective in lower weight proportions (70% or less) of the PP in improving

the impact strength. In the case of the tensile properties, the both SPDs were enable to maintained or slightly improving the properties when the weight proportion of PS or PP in the blends were lower than 70%.

6.2. SUGGESTIONS FOR FURTHER WORK

1. The encouraging results on the enhancement effect of the coagent DVB and TRIS in the functionalisation of PS and EPDM with AA could be further investigated using twin screw extruders (scale up operation), closer to commercial practice, can be explored. In this case, a completely closed system should be used in the stages of mixing and pumping of liquid mixture into the mixer, in order to minimise the loss of the low boiling point liquid components. The main idea is to plan a temperature gradient in such a way that a thorough mixing can be affected and the liquid components are well inside the extruder barrel (in an airtight condition), before the liquid reaching their boiling point. When the boiling point is reached, a situation of saturated vapour pressure is achieved in which there is an equilibrium between the liquid and vapour phases.

2. Different functional coagent may lead to even higher grafting Since TRIS is a strong polar compound while the EPDM is a non polar copolymer, the inherent repulsive force between the polar branch of TRIS and hydrocarbon chain of EPDM could be a strong factor, inhibiting further promotion of higher extent of grafting reaction of TRIS to EPDM (after which provides a bridge for further reaction with the AA ,via TRIS). The situation could be alleviated if one of the three TRIS polar branches which carries the double bond is to be modified to contain a longer aliphatic hydrocarbon part which carries the double bond located at the end of the chain. This modified branch could undergo more vigorous grafting reaction with EPDM, as the polar estereal linkage and the double bond is far apart, and the likeness in structure to the EPDM chain provides by the longer HC (of the midified TRIS) could prove beneficial. The other two polar branches (reserved to react with the polar AA) should be left unaltered .

3. The use of the diamine as IA was clearly advantageous in enhancing the mechanical properties of the functionalised F-PS/F-EPD and F-PP/F-EPD blends. The stronger effect of HEMDA (6 carbon chain) over EDA (2 carbon chain), could be due to the chain length as a factor. To investigate this effect: Diamines which contain variably longer HC chain can be studied. In the case of

F-PS/F-EPD blend, incorporation of benzylic ring into the IA structure could prove beneficial to further deminish the gap of solubility parameter with concomitant decrease in repulsive forces, reactive energy for amidisation and therefore may result in further enhancement.

4. One step reactive processing for the polymer pairs involving modifier, peroxide and coagent could be one step ahead as an attempt to simplified the processing procedure, shortening the time of thermal exposure which could result in minimising the heat of degradation and could provide a model of feasibility study toward industrial scale application.

5. the effect of coagent can be investigated in other blend system. The first polymer can be functionalised with a monomeric amine and the second with a monomeric carboxylic acid in the presence and absence of the coagents. Subsequent coupling reactions between the amine and carboxylic group should be accomplished without the use of an IA.

6. Amidisation reaction of the functionalised polymer pair in a full size extruder. using the best interlinking agent can be studied. The effect of temperature, screw speed and thoroughput to the extent of compatibilisation and final properties would be the parameters which could be investigated.

REFERENCES

1 Witt W. , "Polymer Blends and Their Importance as Engineering Plastics". International Polym. Sci. Tech., **12**, T/4(1985)

2 L.A. Utracki, Polym.- Plast. Technol. Eng., **22**, 27(1984).

3 L.A. Utracki, 'Recent Advances in Engineering Polymer Alloys and Blends. ANTEC, 1339(1987).

4 Olabisi O. , " Polyblends," review prepared for "Kirk- Othmer Encyclopedia of Chemical Technology," J. Wiley & Sons, New York, (April 1982)

5 Shaw M. T. , Paper presented at the "Polyblend '81" Mini Symposium, NRCC, *Industrial Material Research Institute,* Montreal (April 1981); Polym. Eng. Sci., **22**, 115(1982).

6 Utracki L.A. ," Economics of Polymer Blends", Polym. Eng. Sci., **22**, 1166(1982).

7 Robeson L. M. , "Application of Polymer Blends: Emphasis on Recent Advances", Polym. Eng. Sci., **24**, 587(1984)

8 C. B. Bucknall, 'Compatibility and Copolymerisation' in Toughened Plastics, Applied Science Publishers Limited, 10 (1977) .

9. J. W. Barlow and D. R. Paul, "Polymer Blends and Alloy -A Review of Selected Consideration", Polym. Eng. Sci., **21**, 985(1981).

10 P. J. Flory , *Principle of Polymer Chemistry*, Cornell University Press. 1953.

11 D.R.Paul and S.Newman, Eds., "Polymer Blends", ch.6, vol. 1, Academic Press, New York (1978).

12 D.R. Paul , "Intrefacial Agents for Polymer Blends", in Polymer Blends Vol. 2,Paul D.R. and Newman S., Academic Press Inc.(London) Ltd., Ed., p.35(1978).

13 Olabisi O. , Robeson L. M. ,and Shaw M. T., *Polymer-Polymer Miscibility*,Academic Press, New York, 1979

14 A.Y. Coran and R.Patel, Rubber Chem. Technol., **56**, 1045(1983).

15 Paul D.R., Barlow J.W. Keskkula H, "Polymer Blends", in Encyclopaedia of Polymer Science and Technology, 2nd Ed., Vol.12, John Wiley and Sons Inc., New York, p.399(1989).

16 J.M.G. Cowie, "Miscibility", in The Encyclopaedia of Polymer Science and Technology", 2nd Ed., Supplement Volume, John Wiley and Sons Inc., New York, 455-480(1989).

17 D.W. Fox, R.B. Allen, "Compatibility" in The Encyclopaedia of Polymer Science and Technology, 2nd ed. ,Vol.3, John Wiley and Sons Inc., New York, p.758(1989).

18 Bucknall C. B. , "Characterisation of Structure", in Toughened Plastics, Appl. Sci. Publishers Ltd., p.39(1977).

19 Gaylord N. , "Compatibilising Agents: Structure and Function in Polyblends", J. Macromol. Sci.-Chem., **A26(8)**, p. 1211(1989).

20 Kryszewski M. , "Recent Progress in the Studies on the Preparation and Properties of Polymer Blends", in Polymer Blends *Processing, Morphology and Properties*, Martuscelli E. , Palumbo R. , and Kryszewski M. , Plenum Press New York . p.1(1980).

21 Xanthos M., Dagli S. S. , Compatibilisation of Polymer Blends by Reactive Processing", Polym. Eng. Sci. , **31**, 929(1991).

22 Noshay A. and McGrath J. E. , " Block Copolymer- Overview and Critical Survey". Academic Press, New york (1977).

23 Bywater S. , "Block Polymers. Characterisation and Use in Polymer blends", Polym. Eng. Sci., **24**, 104(1984).

24 Molau G. E. , Heterogeneous Polymer Systems I. Polymeric Oil-in-Oil Emulsions", J. Polym. Sci. , Part A **3**, **1267**, 4235(1965).

25 Molau G. E. , and Wittbrodt W. M. , " Colloidal Properties of Styrene -Butadiene Block CopolymersMacromolecules, **1**, 260(1968).

26 Inoue T. , Soen T, Hashimoto T, and H Kawai H, "Studies on Domain Formation of the A-B Type Block Copolymer from Its Solutions. Ternary Polymer Blend of the Styrene-Isoprene Block Copolymer and Polystyrene and Polyisoprene" Macromolecules, **3**, 87(1970).

27 Moritani M. , Inoue T. , Motegi M. ,and Kawai H. , " Light Scattering from A Two Phase Polymer System. Scattering from A Spherical Domain Structure and Its Explanation in Terms of

Heterogeneity Properties" Macromolecules, **3**, 433(1970).

28 Heikens D., Hoen N. , Barentsen W. , Piet P. , Ladan H. , "Mechanical Properties and Morphology of Copolymer Modified Polymer Blends" , J.Polym. Sci. : Polymer Symp. , **62**, 309(1978).

29 Legge N. R. , Holden G. , Davison S. , and DeLaMare, "Applied Polymer Science" , Ch. 29, A.C.S. Organic Coating, Plastics Chemistry Division, Washington D. C. (1975).

30 Lewis P. R. , and Price C. , Electron Microscopy of Sym-SBS Block Polymers". Polymer, **13**, 20 (1972).

31 Falk J. C. , J. Polym. Sci., A1, **9**, 2617(1971)

32 S. Nakanishi and H. Hisanaya, Japanese Pat. 17,839 (1961).

33 K.Herrle and F. Lees (to Badische Anilin- & soda-Fabrik), British Pat. 1,063,056(1967).

34 Shell Oil Co. , British Pat. 1,031,130 (1966).

35 G. S. Schaufelberger (to Union Carbide), U.S. Pat. 3,216,885 (1968).

36 J. T. Paul, Jr. (to Hercules), U.S. Pat. 3,437,550 (1969).

37 A. Portalani, E. DiGiulio, and M. Milani (to Montedison), U.S. Pat. 3,427,183 (1969).

38 Y. Minoura, M. Ueda, S.Mizunuma, and M. Oba, " The Reaction of Polypropylene with Maleic Anhydride", J. Appl. Polymer Sci.,**13**, 1625 (1969).

39 Avella M, Greco R., Lanzetta N., Maglio G., Malinconico M., Martuscelli M., Palumbo R., Ragosta G., " Synthesis of Interfacial Agents and Their Use in Nylon 6/Rubber Alloys", from Polymer Blends: Processing Morphology and Properties: 1st Joint Italian-Polish Seminar on Multicomponent Polymeric Systems, Capri, 16-21 October 1979, Martucelli E, Palumbo R., Kryszewski M. (eds), Plenum Press, New York, (1980)

40 Adur A., "Enhancement of Properties of Reinforced Polypropylene by Grafted Polyolefin Coupling Agents", at Reactive Processing Practice and Possibilities, A two day seminar at RAPRA Technology Ltd., Shwbury, UK, 11-12 September 1989.

41 Al-Malaika S., "Reactive Modifiers for Polymers", 409-425 in Chemical Reactions on Polymers, ACS Symposium Series 364, Washington (1988).

42 Brown S. B. ,Orlando C. M., "Reactive Extrusion" in The Encyclopedia of Polymer Science and Technology, 2nd Ed,, Vol. 14, 169-189, John Wiley & Sons Inc., New York (1989).

43 Frunz Z. N. , "Reactive Extrusion", Plast. Compounding, **9**, (5) , 24(1986)

44 Brown S. B. , Orlando C. M. , "Reactive Extrusion" in The Encyclopaedia of Polymer Science and Technology, 2nd Ed. , Vol. 14, John Wiley & Sons Inc., New York, p.169 (1989).

45 Gaylord M. G. , Mehta M. , " Role of Homopolymerisation in the Peroxide Catalised Reaction of Maleic Anhydride and Polyethylene in the Absence of Solvent". J. Polym. Sci. : Polym. Lett. Ed. , **20**, 481 (1982).

46 Frunz Z. N. , "Reactive Extrusion", Plast. Compounding, 9, 24(1986)

47 Ide F. , Hasegawa A. , "Studies on Polymer Blend of Nylon 6 and Polypropylene or Nylon 6 and Polystyrene Using the Reaction of Polymer", J. Appl. Polym Sci. , **18**, 963(1974)

48 Callais P. A. , Kazmierczak R. T. , "The Use of Organic Proxide in the Graft Modifications of Polyolefins with Maleic Anhydride", in ANTEC '89 Conference Proceedings, Society of Plastics Engineers 47th Annual Technical Conference, New York, May, 1368(1989).

49 Gaylord N. G. , Mehta M. , Kumar V. , Org. Coat. Appl. Polym. Sci. Proc. , **46**, 87(1982).

50 De Vito G. , Lanzetta N. , Maglio G., Malinconico M. , Musto P., and Palumbo R. , " Functionalisation of an Amorphous Ethylene-Propylene Copolymer by Free Radical Initiated Grafting of Unsaturated Molecules", J. Polym. Sci. , **22**, 1335(1984).

51 Galucci R . , Going R. , "Preparation and Reaction of Epoxy-Modified Polyethylene", J. Appl. Polym. Sci. , **27**, 425 (1982).

52 Gaylord N. G. , Mishra M. K. , "Nondegradative Reaction of Maleic Anhydride and Molten Polypropylene in the Presence of Peroxide", J. Polym. Sci. : Polym. Lett. Ed. , **21**, 23(1983).

53 Baker W. E. , Saleem M., Polystyrene- Polyehttylene Melt Blends Obtained Through Reactive Mixing Process', Polym. Eng. Sci., **27**, 1634(1987).

54 Batailie A. , Boisse S. and Schreiber H. P. , "Mechanical Properties and Permeability of Polypropylene and Poly(ethylene terephthalate) Mixturea; Polym. Eng. Sci. , **27**, 622 (1987).

55 Choudhury N.R., Bhowmick A. K., 'Compatibilisation of Natural Rubber-Polyolefin Thermoplastic Elastomers Blnds by Phase Modification, J. Appl. Polym. Sci., **38**, 1091(1989).

56 Ide F. and Hasegawa A., Studies on Polymer Blends of Nylon-6 and polypropylene or Nylon 6 and Polystyrene Using the Reaction of Polymer', J. Appl. Polym. Sci., **18**, 963(1974).

57 Cimmico S. , D'Orazio L.,Greco R., Maglio G., Malinconico M., Mancarella C., Martucelli E. ,Palumbo R. , and Ragosta G., Polym. Eng. Sci., **24**, 48(1984).

58 Dagli S.S., Xanthos M., and Biesenberger J.A., ' Modification of Nylon-6 /Polypropylene Blends through Reactive Processing', SPE ANTEC Tech. Papers, **36**, 1924(1990).

59 Gelles R., Modic M., and Kirkpatrick J.. SPE ANTEC Tech. Papers 34, 573(1988)

60 Curto D, Valenza A, and LaManta F. P.,' Blends of Nylon 6 with a Polyethylene Functionalised by Photooxidation,', J. Appl. Polym. Sci., **39**, 865 (1990).

61 Miettinen R.H., and Seppala J., 'Effect of Compatibilisers on the Properties of Polyamide/ polypropylene Blends', Polym. Eng. Sci., **32**, 868(1992).

62 MacKnight W., Musto P, Senz R., and Somani R., "Binary Alloys of Nylon 6 and Ethylene-Methacrylic Acid Copolymers: Morphological, Thermal and Mechanical Analysis", Polym. Eng. Sci., **25**, 1124(1985).

63 Mondragon J., Gaztelumendi M., and Nazabel J., "Mechanical Behaviour of Polycarbonate/Phenoxy Blends Before and After Interchange Reactions", Polym. Eng. Sci., **28**, 1126(1988).

64 Devaux J., Devaux P.,Goddard P., 'Study Exchange Reactions in Polycarbonate/Polyaryllcarboxylate Mixture with Model Compounds', Macromol. Chem., **186**, 1227(1985).

65 Dolovoy A., Cheung M.F., and Oene V., 'The Phase Behaviour and Mechanical Properties of Polyarylate and Polycarbonate Blends', Polym. Eng. Sci., **27**, 1642 (1987).

66 Teh J. W., and Rudin A., 'Compatibilisation of a Polystyrene-Polyethylene Blend Through Reactive Processing in a Twin Screw Extruder', Polym. Eng. Sci., **32**, 1678(1992).

67 Xanthos M. , Riahi F. , and Boussida, "Compatibilisers for PP/Plastisised PVC Injection Molded Blends and Laminated Films" , SPE ANTEC, 963(1985).

68 Shaul M. A. , Willis B. H. ,John S. S. , and Divakar M . , "Reactions in the Presence of Organic Phosphites, I: High Temperature Amidisation in the Absence of Solvent", J. Polym. Sci. ; Polym. Chem. Wd. , **22**, 2567(1984).

69 Pillon L. Z. , and Utracki L. A. , Compatibilisation of Polyester/ Polyamide Blends Via Catalytic Ester- Amide Interchange Reaction", Polym. Eng. Sci. , **24**, 1300 1984).

70 Bucknall C. B., "Manufacture of Toughened Plastics", in Toughened Plastics, Bucknall C. B. , Applied Sci. Publishers LTD., p.99 (1977).

71 Fayt R. , Jerome R. , and Teyssie P. , " Characterisation and Control of Interfaces in Emulsified Incompatible Polymer Blends" , Polym. Eng. Sci. , **27**, 328 (1987).

72 Locke C. E. , Paul D. R. , " Graft Copolymer Modification of Polyethylene-Polystyrene Blends. II. Properties of the Modified Blends" J. Appl. Polym. Sci. , **17**, 2791(1973).

73 Heikens D., Hoen N., Barentsen W. M., Piet P., and Ladan H., " Mechanical Properties and Morphology of Copolymer Modified Polymer Blends", J. Polym. Sci. : Polym. Symp., **62**, 309(1978).

74 Barentsen W. M. ,Heikens D., " Mechanical Properties of Polystyrene/ Low Density Polyethylene Blends", Polym., **14**, 579 (1973)

75 Barentsen W.M., Heikens D. , Piet P. "Effect of Addition of Graft Copolymer on the Microstructure and Impact Strength of PS/LDPE blends". Poly. **15**, 119(1974).

76 Heikens D. , Barentsen W. M. , " Particle Dimension in Polystyrene/ Polyethylene Blends as A Function of their Melt Viscosity and the Concentration of Added Graft Copolymer", Polym., **18**, 69 (1977).

77 Sjoerdsma S. D. , Bleijenberg A. C. A. M. , Heikens D., "Tensile Properties and Morphology of Copolymer Modified Blends of Polystyrene and Polyethylene" , in Polymer Blends; Processing , Morphology and Properties: Proceeding 1st Polish- Italian Joint Seminar on Multicomponent Polymeric Systems, Capri, 16-21 October 1979 ; Martucelli E. , Palumbo R. , Kryszewski M (eds.) , Plenum Press, New York, (1990)

78 Barentsen W. M. , Heijdenrijk P. J. ,Heikens D . , Piet P. , Mechanical Properties of Polystyrene/ Ethylene Propylene Copolymer Blends" , Brit. Polym. J. ,**10**, 17(1978).

79 Lindsey G. R. , Paul D. R. , Barlow J. W. , "Mechanical Properties of HDPE-PS-SEBS blends", J. Appl. Polym. Sci. , **26**, 1(1981)

80 Lambla M. . Yu R. X. , Lorek S. . "Coreactive Polymer Alloys", Chapter 3 in Multiphase Polymers: Blends and Ionomers, Utracki L. A. , Weiss R. A. (eds.) . ACS Symposium Series 395, (1989).

81 Ghaffar A. , Sadrmohaghegh C., and Scott G. , Polymer Blends-II. The Use of Solid Phase Dispersants to Improve the Properties of Binary Mixtures of Incompatible Polymers", European Polym. J. , **17**, 941(1981)

82 Hajian M. , Sadrmohaghegh C. , Scott G. , " Solid Phase Dispersants Synthesised by A Mechanochemical Procedure" , Eur. Polym. J. , **20**, (2), 135(1981).

83 Fayt R. , Jerome R. , Teyssie Ph. , " Molecular Design of Multicomponent Polymer Systems. XIV. Control of the Mechanical Properties of Polyethylene-Polystryrene Blends by Block Copolymers" , J. Polym. Sci. : Part B: Polym. Phys. , **27**, 775 (1989).

84 Fayt R. , Jerome R. , Teyssie Ph. , " Molecular Design of Multicomponent Polymer Systems. II. Emulsifying Effect of A Poly(hydrogenated butadiene- b-sturene) Copolymer In High Density Polyethylene/Polystyrene Blends ", J. Polym. Sci. : Polym. Phys. Ed. , **19**, 1269(1981).

85 Fayt R. , Jerome R. , Teyssie Ph. " Molecular Design of Multicomponent Polymer Systems III. Comparative Behaviour of Pure and Tapered Block Copolymers In Emulsification of Blends of Low Density Polyehylene and Polystyrene Blends" , J. Polym. Sci. : Polym. Phys. Ed., **20**, 2209 (1982).

86 Fayt R. , Hadjiandreou P. , Teyssie Ph. , " " Molecular Design of Multicomponent Polymer Systems . VII . Emulsifying Effect of Poly(ethylene- b- styrene) Copolymers In High Density Polyethylene/ Polystyrene Blends ", J. Polym. Sci. : Polym. Phys. Ed. , **23**, 337(1985).

87 Fayt R. , Jerome R. , Teyssie Ph. " Molecular Design of Multicomponent Polymer Systems XII. Direct Observation of the Location of A block Copolymer In Low Density Polehtylene-Polystyrene Blends", J. Polym. Sci. : Polym. Phys. Ed. , **24**, 25(1986)

88 Fayt R. , Jerome R. , Teyssie Ph. " Molecular Design of Multicomponent Polymer Systems. XIV. Control of Mechanical Properties of Polyethylene-Polystyrene Blends By Block Copolymers" , J. Polym. Sci.. : Par B: Polym . Phys. , **27**, 775(1989)

89 Baker W. E. , Saleem M. , "Coupling of Reactive Polystyrene and Polyethylene in Melts", Polymer, 28, 2057(1987).

90 Baker W. E. and Saleem M. ,"Polystyrene Polyethylene Melt Blends Obtained Through Reactive Mixing Process", Polym. Eng. Sci. , **27** (20), 1634(1987)

91 Baker W. E. and Saleem M. , "*In Situ*Reactive Compatibilisation in Polymer Blends: Effect of Functional Group Concentration", J. Appl. Polym. Sci., **39**, 655(1990).

92 Molau G. E. , and Keskkula H., J. Polym. Sci., A-1, **4**, 1955(1966)

93 Wagner E. R. , and Robeson L. M. , " Impact Polystyrene: Factors Controlling the Rubber Efficiency " Rubber Chem. Technol., **43**, 1129 (1970)

94 Nata G. , Pegoraro M. , Severini F. and Dabhade S. , "Improvement of Impact Strength by Compounding with Styrene-Grafted Ethylene Propylene Elastomeric Copolymers" , Rubber Chem. Tech. , **39**, 1667 (1966).

95 Shultz D. C., Rubber World, **36**, 184(1981)

96 Shaw S., Singh R. P. , "Study of Compatibility of Polystyrene with Ethylene

Propylene- Diene Rubber" , European Polym. J., **23**, 547 (1987).

97 Shaw S., Sing R. P., Studies on Impact Modification of PS by Ethylene-propylene Diene Rubber (EPDM) and Its Graft Copolymers. I. PS/EPDM and PS/ EPDM-g-styrene blends", J. Appl. Polym. Sci., **40**, 685 (1990).

98 Shaw S., Sing R. P., Studies on Impact Modification of PS by Ethylene-propylene Diene Rubber (EPDM) and Its Graft Copolymers. II. PS/ EPDM-g-(styrene-co-methyl methacrylate) Blends", J. Appl. Polym. Sci., **40**, 693 (1990).

99 Chang E. P., and Takahashi A., " Factors Influencing the Impact Strength of High Impact Polystyrene", Polym. Eng. Sci., **18**, 350(1978).

100 Shaw S., Sing R. P., Studies on Impact Modification of PS by Ethylene-propylene Diene Rubber (EPDM) and Its Graft Copolymers. III PS/EPDM and PS/ EPDM-g- Maleic anhydride blends", J. Appl. Polym. Sci., **40**, 715 (1990).

101 Karger J., Kocsis A. K., Szaffner A., and G. Bodor, "Morphological Study on the Effect of Elastomeric Impact Modifier in Polypropylene Systems", Polymer, **20**, 37(1979).

102 Kresge E. N., " Rubber Thermoplastics Blends", in Polymer Blends Vol. II, Paul D. R. and Newman S., (ed.), Academic Press N. Y., 293(1978).

103 Jang B. Z., Uhlman P. R., and Vander Sande J. V., "The rubber particle size dependance of Crazing in Polypropylene", Polym. Eng. Sci., **25**, 643(1985).

104 Speri W. M., and Patrick C. R., "Fiber Reinforced Rubber Modified Polypropylene", Polym. Eng. Sci., **15**, 668(1975).

105 George W.O., and McIntyre P.S., "Quantitative analysis", chapter 6 in Infra Red Spectrocopy, John Wiley and Sons, New York, page 238 (1987).

106 Bucknall C.B., "SI unit conversion table"in Toughened Plastics, Applied Science Publishers LTD., London, page 345 (1977).

107 Al-Malaika S. and Scott G., UK Patent Application, Aug. 1988.

108 S. Al-Malaika and G. Scott, UK Patent application, Aug. 1988.

109 Peron P. J. "Unique material produced by reactive compounding", Plast. Eng., Dec ., 47-49, (1988).

110 Pike M. and Warson W.F., 'Mastication of rubber I. Mechanism of plasticising by cold mastication', J. Polym. Sci.,**9**, 229(1952).

111 Al-Malaika S., Ibrahim A. Q., and Scott G., in Polymer Degradation and Stability,**22**, p.233 (1988).

112 Al-Malaika S., and Neng S. S., unpublished work.

113 Al-Malaika S., and Sheena H. H. , Unpublished work.

114. Teh J.W. and Rudin A., 'Compatibilisation of a Polystyrene -Polyethylene Blend Through Reactive Processing in a Twin Screw Extruder', Polym. Eng. Sci., **32**, 1679 (1992).

115. Nakanishi K., Philippa H. S., "Infra Red Absorption Spectroscopy', Ed. 2, p.40 (1977).

116. G. Reiss, 'Le Role Des Copolymeres Sequences et greffes dans les alliages de polymeres', in Polymer Blends: Processing, Morphology and Properties, E. Martuscelli, R. Palumbo, and M. Kryszewski, Eds., Plenum ,New York ,p. 123 (1980).

117 R. Fayt, R. Jerome and P. Teyssie, 'Characterisation and Control of Interfaces in Emulsified Incompatible Polymer Blends', Polym. Eng. Sci., **27**, 328(1987).