MECHANICAL, CHEMICAL AND FLAMMABILITY PROPERTIES OF ABS/PVC BLENDS

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PENGHARGAAN

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UNIVERSITI TEKNOLOGI MALAYSIA UTM/RMC/F/0024

BORANG PENGESAHAN
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK : MECHANICAL, CHEMICAL AND FLAMMABILITY PROPERTIES OF PVC/ABS BLENDS

Saya DR SHAHRIR BIN HASHIM

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CHAPTER I

INTRODUCTION

1.0 Introduction

The first completely synthetic plastic, phenol-formaldehyde, was introduced by Baekeland in 1909, nearly four decades after Hyatt had developed a semisynthetic plastic-cellulose nitrate (Chanda and Roy, 1993). In 1927 poly(vinyl chloride) (PVC) and cellulose acetate were developed, and 1929 saw the introduction of urea-formaldehyde (UF) resins (Chanda and Roy, 1993). The development of new polymeric materials proceeded at an even faster pace after the war. Epoxies were developed in 1947, and acrylonitrile-butadiene-styrene (ABS) terpolymer in 1948 (Chanda and Roy, 1993). The next two decades saw the commercial development of a number of highly temperature-resistance materials. More recently, other new polymer materials were introduced, including several exotic materials which are mostly very expensive.

There are hundred of homo polymers commercially available today. Since one type of polymer does not possess all the physical and mechanical properties desired in a finished product, blending of polymers were introduced to meet the requirements. The continuing pressure to improve productivity and quality has generated the research in polymer blends. Blending also offers the possibility of tailor-making products to meet specific end needs. For this reason, much attention had received from academia and industry and thus blending of polymers are experiencing significant growth. From the economic point of view, blend development is far less costly and time consuming than the development of new polymers (Datta and Lohse, 1996).

This present study focuses on the blending of ABS with PVC. The large diversify of end uses makes ABS one of the most successful of the engineering thermoplastics available. It is a bridge between commodity plastics (e.g., polystyrene) and higher-performing engineering thermoplastics (e.g., polycarbonate). Its position in terms of both properties and price between the more highly priced, high performance engineering plastics and the lower priced commodity plastics makes ABS the material of choice for many applications (Adams *et al.*, 1993).

ABS resins are composed of over 50% styrene and varying amounts of butadiene and acrylonitrile. Styrene provides rigidity and ease of processability, acrylonitrile offers chemical resistance and heat stability, and butadiene supplies toughness and impact strength. ABS having high rubber content possesses higher impact strength than those with low content of rubber. Increase in rubber content results in greater ductility of these blends. Large-volume applications for ABS resins include plastic pipe and automotive and appliance parts. Although ABS has many desired properties as engineering thermoplastic, its still has some limitation for example, easily burn with high flammability value and poor resistance to outdoor UV light (Chanda and Roy, 1993).

ABS itself is already a blend of polybutadiene and styrene acrylonitrile (SAN). It can be further blended with other materials to introduce new and improve resin grades. Thus, the scope of possible applications is broadened (Jin *et al.*, 1998), and resulting in overall demand growth for ABS. Demand in the U.S. for ABS is projected to advance 4% per year through 2006 to 1.6 billion pounds, valued at $3.1 billion (Freedonia Industry Study, 2002).

The low price of PVC renders its use desirable in many applications. Besides, this material is popular with its inherent flame retardancy and UV stability. When blended with ABS, the result is a material with good impact strength, toughness and inherent flame resistance (Hofmann, 1985). ABS/PVC is used in a wide variety of applications which include electrical components, appliances, business machine housings and automotive parts (Manson and Sperling, 1976). The inherent flame retardancy of PVC makes it suitable for applications where the more expensive flame retardant ABS could be employed (Landrock, 1983).

Blending of ABS with other polymers is widely reported. Many studies have been carried out on ABS/Polycarbonate (PC) blend (Chiang and Hwang, 1987; Lee *et al.*, 1988; Steeman and Maurer, 1994; Ogoe *et al.*, 1996; Jin *et al.*, 1997; Balakrishnan and Neelakantan, 1998; Lim and Bertilsson, 1999 and Choi *et al.*, 2000) Among the interesting finding of these studies are that ABS provides the benefits of economics, processability and more reliable impact resistance, while PC contributes the improvements of tensile, flexural, thermal properties and flammability to the blends.

The study on ABS/PVC blend had received less attention compared to ABS/PC blend. According to Adam *et al.* (1993), ABS/PVC blend possessed U.S. annual consumption growth rate (1990-1996) of 12-18% or 3-9% higher than ABS/PC blend (Growth rate: 9%). Thus, more research study should base on ABS/PVC blend since it has a convinced growth rate but less research study is being reported.

The studies on polyblend of PVC and ABS were conducted by Maiti *et al.* (1992). PVC compositions ranging from 50 to 100% were used. Maiti *et al.* discovered that this polyblend possesses advantages like the tensile strength and rigidity of PVC and impact strength of ABS. TGA analysis revealed a substantial improvement in thermal stability of PVC/ABS blends over that of PVC.

The compatibility enhancement of ABS/PVC blends was also conducted by Jin *et al.* (1998). The composition for PVC was ranging from 50 to 100 %. When a compatibilizer, SAN 25 was added into the blend, the compatibility was enhanced and about twofold increase of impact strength was observed.

Bensemra and Bedda (2001) studied the properties of PVC/ABS blends. Blends with variable composition, 0 to 100 wt % PVC were used. The researchers concluded that addition of plasticizer, di(ethyl-2hexyl) phthalate into the blends greatly improved the impact properties where the higher the PVC content, the higher the impact value.

Besides studying the mechanical properties of ABS/PVC blend, flammability of the blend was also investigated by Carty and White (1994). According to Alexander (2000), the annual loss of life and the property caused by fire around the world is extraordinary, since thousand of death and billion of property were loss each year. Most of the fires involve the combustion of polymeric materials. So, the method to reduce the flammability of polymers and hence reduce the loss of life and the property has been the subject of increasing interest over the past several years. As mentioned, one of ABS main drawbacks is its inherent flammability and therefore a need exist to improve this property by incorporation of halogenated polymers, such as PVC.

In the study conducted by Carty and White (1994), ABS/PVC blends containing up to 30 phr of PVC were examined. In this work, addition of PVC into ABS has successfully reduced the flammability of ABS, where the LOI value increased from 18.3% to 33.8%. The flame retarded ABS currently has a great deal of interest in the computer and business equipment market. Alexander (2000) also mentioned that European regulators were considering requiring flame retarded polymer in electronic equipments and other products.

1.2 Problem Statement

As mentioned earlier, the studies on ABS/PVC blend have received less attention compared to PC/ABS blend. The previous studies on PVC/ABS blends concentrate mainly on the use of ABS as the added polymers, with PVC as the main component. The present study will focus on the effect of adding PVC into ABS. The effect of adding PVC of different molecular weight into different types of ABS (with different ratios of monomer content) has not yet been reported. It is expected that both, PVC molecular weight and polybutadiene content in ABS will influence the properties of ABS/PVC blend. The study on blending acrylic grafted PVC with ABS has also not been reported. This proposed study hopefully will contribute to further the knowledge in the area of ABS/PVC blend and extend the applications of ABS.

1.3 Objectives

The main objectives of the proposed research are as follows.

- to study the effect of PVC molecular weight and content, and acrylic grafted PVC on the mechanical and flammability properties of ABS/PVC blends.
- to study the effect of different grades and composition of ABS on the mechanical and flammability properties of ABS/PVC blends.
- to determine the optimum ABS/PVC content in terms of mechanical properties, flammability, and cost.

1.4 Scope

The study involved preparing various samples of ABS/PVC at blend composition of 100/0, 90/10, 85/15 and 80/20. A mixer, single screw extruder and injection moulding were used for sample preparation. The types of the testing and analysis are as follows:

(a) Mechanical Properties

Two types of mechanical properties were conducted, that is Pendulum Izod impact and flexural test.

Pendulum Izod impact was used to determine the impact strength of each blend.

Flexural test was also carried out to determine the stiffness of the ABS/PVC blend.

(b) Flammability

Oxygen Index Test was used to determine the flammability properties of the blends.

(c) Thermal Properties

Heat defection temperature (HDT) was used to determine the temperature at which it loss the rigidity.

(d) Material Characterization Test

DMA (Dynamic Mechanical Analysis) was used to correlates the T_g and with the miscibility of the blends.

SEM (Scanning Electron Microscopy) analysis was carried out to correlate the surface fracture with the impact strength results.
MFI (Melt Flow Index) test was conducted to obtain the melt flow rate and to determine the processibility of the ABS/PVC blends.

CHAPTER II

LITERATURE REVIEW

2.1 Acrylonitrile Butadiene Styrene (ABS Polymers)

2.1.1 General Introduction and Historical Background

The name ABS polymer is derived from the initial letters of three main monomers – acrylonitrile, butadiene and styrene, used in its preparation. ABS is not a random terpolymer of acrylonitrile, butadiene and styrene. Industrially important ABS polymers are two-phase polymer systems that consist of dispersed polybutadiene (or a butadiene copolymer) rubber particles and a matrix of styrene-acrylonitrile copolymer (SAN). The rubber particle is grafted with styrene and acrylonitrile to enhance their compatibility with the matrix.

The fraction of rubber content in ABS is varies from 10-25% for common commercial grades and special grades, e.g. for blending with poly(vinyl chloride) can even contain over 45% rubber. The higher rubber content and the different type of polymer forming the continuous phase result in the ABS polymers having a number of properties better than common grades of high-impact polystyrenes.

Introduced commercially in the 1940s, ABS is a polymer whose sales have grown over the years to become the largest engineering thermoplastic in the world. In 1982, the consumption of ABS polymer in the individual Western countries varied from 0.3 to1.5kg per person (Svec *et al.,* 1990). In the U.S. alone, sales in 1989 exceeded 1.2 billion pounds (Brisimitzakis, 1994). Demand in the U.S. for engineered plastic is projected to advance four percent per year through 2006 to 1.6 billion pounds, valued at $3.11 billion. The demand for engineering thermoplastics in the year of 2001 is shown at Figure 2.1, with ABS has the largest consumption rate (28.8%) compare with the others (Freedonia Industry Study, 2002).

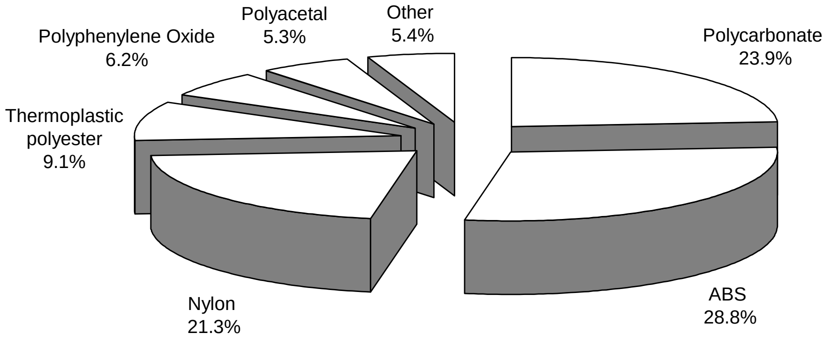


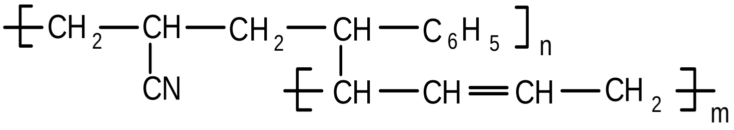
Figure 2.1 : Engineered plastics demand, 2001 (Freedonia Industry Study, 2002)

2.1.2 Chemistry and Manufacturing

ABS consists of two phases, a continuous phase of styrene-acrylonitrile (SAN) copolymer, and a dispersed phase of grafted polybutadiene particles. Each of these phases contributes unique characteristics to the polymer.

2.1.2.1 Chemistry

Each of the three monomers, acrylonitrile, butadiene, and styrene, is important component of ABS. The fundamental repeating unit of the ABS chain is:



$$\left[CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-\underset{\displaystyle \left[CH-CH=CH-CH_2 \right]_m}{\underset{|}{CH}}-C_6H_5 \right]_n$$

Common types of ABS polymers have an average composition of 21 to 27% acrylonitrile, 12 to 25% butadiene and 54 to 63% styrene. Acrylonitrile primarily offers chemical resistance and heat stability; butadiene delivers toughness and impact strength; and the styrene component provides ABS with balance of clarity, rigidity, and ease of processing (Svec *et al.,* 1990).

Styrene and acrylonitrile can be copolymerized to form SAN copolymers, typically at a 70/30 ratio of S/AN. Like polystyrene, SAN is a clear copolymer, but with the additional characteristics of higher chemical resistance, better surface hardness, and improved toughness (Pillichody and Kelly, 1990). This copolymer is a commercially significant product, with major applications in markets such as battery cases, disposable cigarette lighters, and house wares.

ABS polymer systems typically contain between 70 and 90% SAN. In forming the continuous phases of the ABS, the SAN contributes its characteristics of easy processing, high strength, and rigidity, chemical resistance, and good surface hardness and appearance. The second phase of the two-phase ABS system is composed of dispersed polybutadiene (rubber) particles, which are grafted on their surface with a layer of SAN. The layer of SAN at the interface forms a strong bond between the two phases, which allows the polybutadiene rubber to add toughness to the ABS system, forming a rigid, impact-resistant product. The rubber phase is typically present in the range of 10-30% (Glenn and Cathleen, 1985).

Manipulations of the two phases produce the range of polymer characteristics seen in the different ABS products. The major variables of the SAN phase are the acrylonitrile level and molecular weight. The rubber level can be varied to adjust the impact strength of the polymer. Resin properties are also strongly affected by the rubber particle size distribution, the molecular weight, and cross-link density of the rubber as well as by the molecular weight, composition, and level of the SAN graft on the rubber particle surface. Normally, ABS with high rigidity has higher styrene content. Super high impact ABS possesses higher composition of butadiene if compare to medium impact ABS.

2.1.2.2 Manufacturing

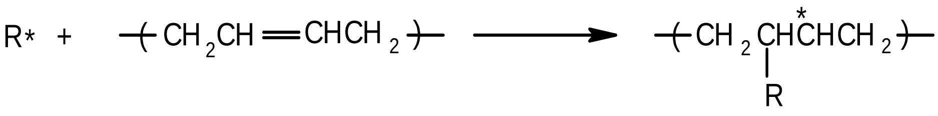
ABS polymers can be prepared by mechanical blending of the individual components or by grafted polymerization of a mixture of styrene with acrylonitrile in the presence of suitable rubber component. There are three commercial polymerization processes for manufacturing ABS: emulsion, suspension and bulk. The most common technique for producing the grafted polybutadiene phase is emulsion polymerization.

2.1.2.2.1 Mechanism of Grafting

Grafting of the styrene-acrylonitrile copolymers onto an elastomer is achieved by copolymerization in the presence of the elastomer. Possible mechanisms include radical abstraction from the polybutadiene (Bach and Knorr, 1989):

$$R{*} + -\!\!\left(CH_2CH{=}CHCH_2\right)\!\!- \longrightarrow RH + -\!\!\left(\overset{*}{C}HCH{=}CHCH_2\right)\!\!-$$

or radical addition to polybutadiene:



$$R^* + -(CH_2CH{=}CHCH_2)- \longrightarrow -(CH_2\underset{\displaystyle R}{\underset{|}{C}}H\overset{*}{C}HCH_2)-$$

R^* is an initiator radical from a growing copolymer chain. Radical attack on the substrate polybutadiene competes with formation of styrene-acrylonitrile copolymer

$$R^* + nM \longrightarrow RM_n^*$$

with M = Styrene or acrylonitrile monomer.

M_n^* = linear styrene-acrylonitrile polymer radical.

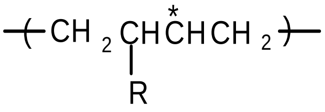
$L^* + nM \longrightarrow LM_n^*$ (grafting by addition)

$L^* + M_n^* \longrightarrow LM_n$ (grafting by termination)

$L^* + L \longrightarrow L-L^*$ (cross-linking)

$L^* + RSH \longrightarrow LH + RS^*$ (chain transfer)

where L^* = $-(\overset{*}{C}HCH{=}CHCH_2)-$ or



$$-(CH_2\underset{\displaystyle R}{\underset{|}{C}}H\overset{*}{C}HCH_2)-$$

RSH = chain-transfer agent.

2.1.2.2.2 Emulsion Technology

It is possible to produce the final product in a single step by grafting in emulsion. A typical commercial emulsion process is shown in Figure 2.2. It involves five steps: rubber polymerization, agglomeration, grafted polymerization, polymer recovery and compounding (Chang *et al.*, 1997).

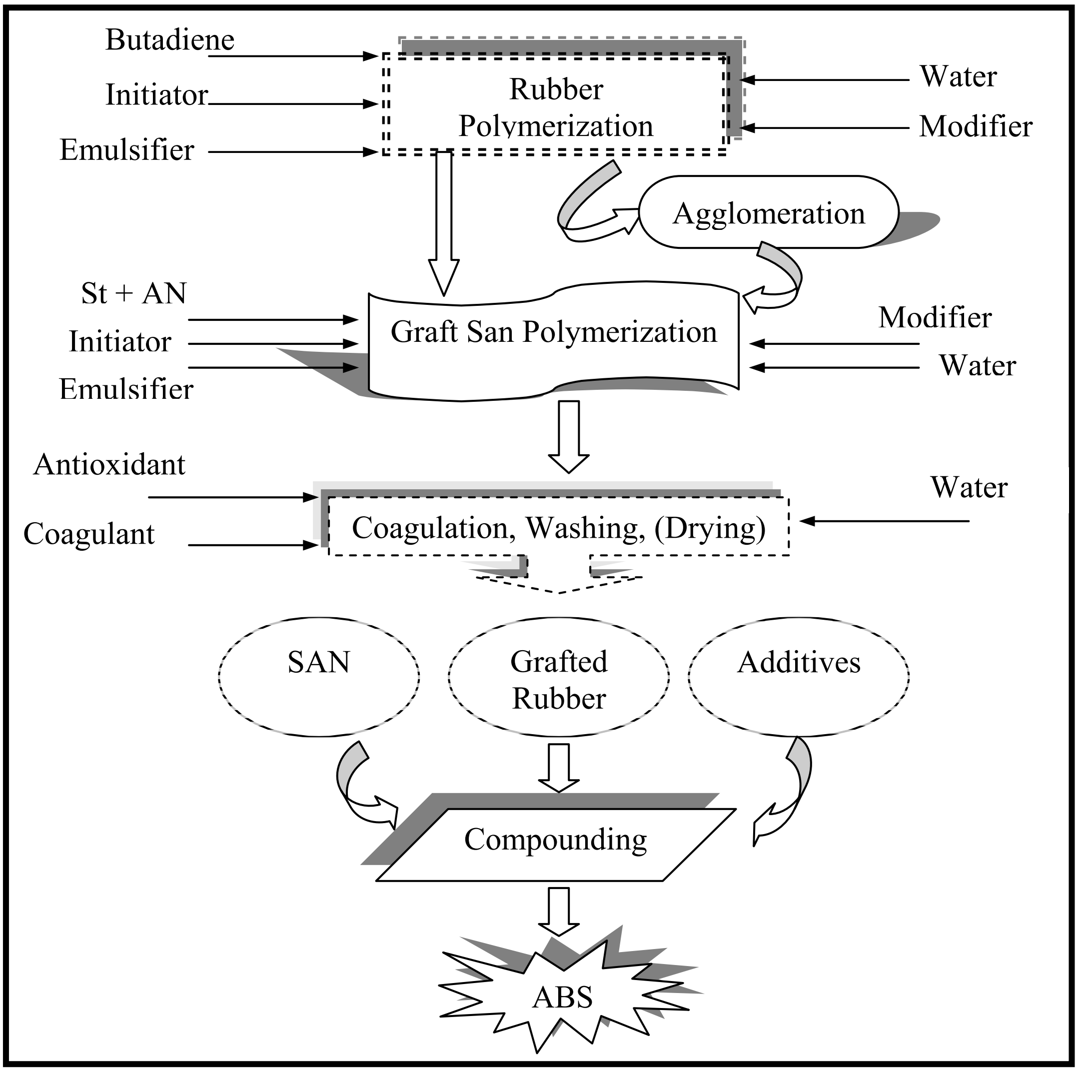


Figure 2.2 : Emulsion ABS polymerization process

The emulsion-mass procedure is used by Toray Industries to prepare ABS polymer. First, part of the styrene and acrylonitrile are grafted onto the polybutadiene in emulsion. The latex particles are then extracted into a newly added monomer mixture in the presence of a coagulant. After separation of the aqueous phase, the partially grafted polybutadiene forms a stable dispersion in the styrene-acrylonitrile mixture. Further polymerization is a continuous mass process; the first stage (up to conversion of 40 to 70%) is carried out in a stirred autoclave and the next stage in a tower plug-flow reactor. The heat of reaction is removed by a cooling jacket. The polymerization is maintained at the boiling point. The unreacted monomers are removed in the evacuated zone of the extruder. A schematic diagram is shown in Appendix A.

2.1.3 Properties

The properties of ABS polymers are strongly affected by the molecular characteristics of both the elastomers phase and the SAN copolymer forming the matrix. Table 2.1 summarized the effects, which will occur under some situations. The properties of this multi-phase system are also affected by conditions at the interface between the rubber and the thermoplastic matrix (Svec *et al.*, 1990). The effect of rubber level is extremely important, and the major trade-offs from increased rubber level are shown in Figure 2.3.

ABS polymer has low density (1020 to 1060 kgm^{-3}) and the bulk density of the pellets is also low, usually 500 to 600 kgm^{-3}(Pillichody and Kelly, 1990). The material is opaque as a result of the different refractive indices of the two phases. The presence of the polar nitrile group results in certain affinity of the ABS polymer for water or water vapour. An increase in the humidity content will lead to complications in processing and to deterioration in some properties.

Table 2.1 : Effect of molecular characteristics of the elastomer phase and SAN copolymer forming the matrix (Svec *et al.*, 1990)

Increase molecular weight of the SAN	Narrow molecular weight distribution	Broad molecular weight distribution	Increase the content of elastomers
Increase resistance to surface-active substances	Improve dimensional stability	Increase heat and pressure sensitivity of the melt	Decrease heat deformation resistance
Impact strength increase	Decrease in shrinkage	Improve flow properties	Increase melt viscosity
Suppression of creep	Increase creep resistance		Improve the impact strength
Tensile strength increase	Tensile strength increase		Ageing resistance decrease
Fluidity decrease			Stiffness increase

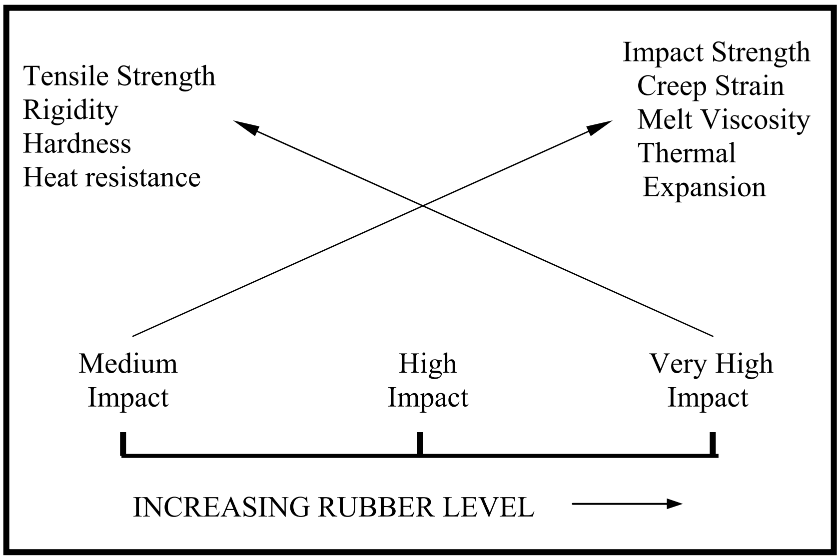


Figure 2.3 : Major property trade-offs for ABS with increasing rubber level. (Glenn and Cathleen, 1985)

2.1.3.1 Mechanical Properties

The overall toughness offered by ABS materials is the prime mechanical property that prompts most users to select ABS for their applications. The standard measure of impact strength used for ABS is notched Izod impact strength, as measured by ASTM D256A. Depending on its impact strength, material is classified as very high-, high- or medium-impact polymer. As pointed out previously, its value determines in which class of standard product a material belongs. Although ABS is notch sensitive, it is much less so than many other polymers, including polycarbonate and nylon. In addition to good impact strength at room temperature, ABS retains significant impact strength at very low temperatures (Svec *et al.,* 1990). This has led to the use of ABS in critical low-temperature applications. ABS materials can deform in a ductile manner over a broad temperature range and at high strain rates. This deformation is accompanied by a significant whitening of the specimen resulting from craze formation and separation of the rubber phase from the matrix polymer.

Another important characteristic of engineering thermoplastics is their stress-strain behavior in flexure. Such measurements are usually made using a simple supported beam test specimen loaded at mid-span according to ASTM D790. As with tensile properties, the flexural strength at yield and flexural modulus can be used to determine the resistance of a product to short-term loadings (Norbert, 1971). They are also useful in comparing the strength and rigidity of the many ABS products.

For many applications, multiaxial impact strength, typically measured using a falling or driven dart, is as important as Izod impact strength. Reporting of multiaxial impact strength is not yet common practice; however, data is now available from manufacturers for many products. Although the two types of tests do not directly correlate, products demonstrating high Izod impact strength in general demonstrate high multiaxial impact strength. Neither of these impact tests produce in- formation that is mathematically applicable to design. The anticipated level of abuse a product will see in a particular application, combined with the designer's experience, will determine the impact class selected (Bucknall, 1977).

The Rockwell hardness (RH) of products is useful in comparing the ability of the surface of a part molded from different products to resist becoming blemished by intermittent loads (Norbert, 1971). The specific gravity of different standard ABS products does not vary much. However, it does vary significantly for many of the specialty grades and alloys.

2.1.3.2 Thermal Properties

The critical thermal properties for ABS are heat distortion, coefficient of linear thermal expansion, thermal endurance, thermal conductivity, and specific heat.

The most common measure of heat distortion is the deflection temperature under load as measured by ASTM D648. High-heat ABS, ABS/polycarbonate (PC) alloys, and ABS/styrene-maleic anhydride (SMA) alloys all extend applications of ABS into the temperature up to 110^{o}C at 1.8 MPa for short-term exposures (Jenker and Köln, 1983).

In general, plastics have significantly higher thermal expansion co-efficients than metals. Consequently, in applications where parts are constrained, thermal stresses must be accommodated in part design or expansion may induce failure in the part. This property is especially important in ABS products designed for electroplating (Moh *et al.*, 1997).

The thermal properties of ABS polymers are characterized mainly by the glass transition temperature, Tg. An increase in temperature of the material leads to a decrease in the tensile strength and an increase in the ductility and toughness. However the modulus of elasticity in tension decreases (Svec *et al.*, 1990).

2.1.3.3 Flammability

Basically, ABS has a low LOI index with a range of 17-18 % (Pál and Macskásy, 1991). ABS materials without flame retardant are easily burned with a luminous yellow flame, smoking strongly and continue to burn after removal of the ignition source. The high impact ABS will has a smell of burnt rubber (Troitzsch, 1980).

ABS grades that meet various standards for flammability performance are available. The non-flame retardant (FR) general-purpose grades are generally classified as 94HB according to Underwriters' Laboratories Test Method UL94, and also meet Motor Vehicle Safety Standard 302. These grades are used in applications having a reduced fire risk. For applications requiring higher degrees of flame retardancy, ABS grades have been developed based on alloys with PVC or through an additive approach using halogen in combination with antimony oxide. Included among the FR grades are materials that meet the Underwriters' UL94 VO requirements beginning at a minimum thickness of 1.47 mm (Bach and Knorr, 1989).

2.1.3.4 Rheology

Factors influencing melt flow behavior of ABS include (Moh *et al.*, 1997):

(1} The presence of the grafted rubber domains, their weight fraction, graft to rubber ratio, particle size and distribution;
(2) The composition, molecular weight and molecular-weight distribution of the matrix;
(3) Additives, ie, lubricants, stabilizers, fillers, pigments, etc;
(4) Residual components from the polymerization process; and
(5) Water.

The presence of the grafted rubber increases viscosity; the viscosity effect increases with decreasing shear rates and increasing rubber content. Residual volatile components and lubricants can function as diluents to reduce viscosity. It has been suggested that their influence on viscosity may depend on whether such materials preferentially reside in the rubber or matrix phase (Glenn *et al.*, 1985).

2.1.3.5 Ultraviolet Resistance

Exposure to ultraviolet (UV) radiation will induce irreversible chemical changes in most organic polymers, including ABS. The extent of degradation depends on the polymer structure, the influencing of prior processing conditions, the effects of additives, the exposure conditions and the presence of protective coatings. UV degradation results in appearance changes characterized by increasing yellowness and an initial embrittlement of the plastic’s outer surface.

ABS is used successfully in many products that are subjected to outdoor exposure for brief periods of time. However, for extended outdoor exposure, measures must be taken to minimize property reduction and changes in appearance. Protection is afforded by UV stabilizer, pigments, paints and film laminates (Glenn *et al.*, 1985).

2.1.3.6 Chemical Resistance

ABS products show very good resistance to chemical attack and most products have good environmental stress-cracking resistance (Svec *et al.*, 1990). ABS is resistant to acids (except concentrated oxidizing acids), alkalis, salts and essential oils. It is, however, attacked by many solvents including ketones and esters.

2.1.4 Processing

2.1.4.1 General Processing

ABS material can be processed by injection molding, extrusion, blow molding or calendaring. However, injection molding and extrusion account for more than 93 % of all ABS material usage. ABS polymers process very easily and can be fabricated into very complex parts. ABS requires significantly lower processing temperatures and is less sensitive to processing conditions (Brisimitzakis, 1994).

2.1.6.2 Preheating and Predrying

ABS materials are hygroscopic, and have an equilibrium moisture content of 0.3-0.4 % at 23 °C and 50 % relative humidity. While mechanical properties in the finished part are not greatly affected by this moisture, its presence during processing can affect the part appearance greatly. Maximum moisture levels of 0.2 % are suitable for injection molding and maximum levels of 0.03 % are suitable for extrusion of ABS materials. These moisture levels can be reached by drying the material prior to processing in a dehumidified air drier (Glenn and Cathleen, 1985).

2.1.5.3 Extrusion

An extruder with a minimum L/D ratio of 24:1 is recommended to ensure a uniform mixing and melt temperature over the die. A screen pack consisting of a 20-40 mesh combination is recommended. Single or two-stage screws are suitable. However, the latter part is preferred since it also aids in devolatilization and results in an improved extrudate quality (Pillichodyand Kelly, 1990).

2.1.5.4 Injection Moulding

ABS polymers can be processed in all types of injection molding equipment, but optimum results are obtained with reciprocating screw machines since it provides more uniform melt and higher available pressure. Processing temperatures range from 177 to 288 ^{o}C, depending on the specific grade. Injection pressure of 69-138 MPa and clamp pressure of 281-422 kg/cm^2 of projected part surface are usually sufficient. Screw having a length to diameter (L/D) ratio of 20:1 are recommended (Glenn and Cathleen, 1985).

2.1.5 Advantages and Disadvantages

ABS, being copolymerized from three different monomers, has high impact strength and competes well with polypropylene, although it is more expensive. Its dimensional stability is good; it replaces die-cast metal components and can be electroplated. ABS is excellent for vacuum-forming and blow-moulding for the production of articles such as fire extinguishers, bus wheel arches, industrial containers, refrigerator shells and protective helmets. Basically, ABS is preferred for its favorable balance of strength, toughness, high gloss, colorability, processability and price.

The balances of properties which are exhibited by ABS are not found in any other plastics material. Specialist applications can be tailor-made by adjustment of the proportions and arrangement of the three parts of the copolymer, thus emphasizing the character of the components.

Besides the advantages, the material has also a number of limitations. The disadvantages are as follows:

1) Limited chemical resistance to hydrocarbon and concentrated acids and alkalis.
2) It is mostly opaque.
3) Electrical properties are not outstanding; however, they are adequate for most purpose.
4) It is easily burn with high flammability value.

2.1.6 Specialty Grades

High Heat Grades. High-heat grades of ABS are produced by increasing the molecular weight, and the acrylonitrile content, while reducing the total rubber present. Most recent work has employed an additive approach (Adam *et al.,* 1993). These products have property balances similar to those of standard ABS except for significantly improved heat resistance. They are somewhat more difficult to process because of the higher melt viscosity, and they are relatively expensive. Alloys of ABS with styrene-maleic anhydride (ABS/SMA) offer similar property balances with a lower melt viscosity at a similar cost (Glenn and Cathleen, 1985).

Chemical Resistance. One of the advantages of ABS relative to reinforced polyolefins and high impact polystyrene is its chemical resistance. The polar nitrite groups make ABS quite resistant to a variety of solvents and uptake of water is relatively low (<1 %) (Adam *et al.,* 1993). This chemical resistance has allowed ABS entry into a wide variety of home appliances and some automotive areas.

Flame Retardant Grades. Standard grades of ABS are considered slow burning polymers, and most meet Underwriters Laboratories requirements for a UL94 HB rating. ABS can be modified using halogenated additives to meet more stringent flammability requirements. These flame-retardant grades offer a balance of properties similar to medium-impact standard ABS grades (Glenn and Cathleen, 1985). Grades with high flexural modulus or with improved light stability are also offered. Many ABS/PVC alloys also meet these flammability requirements. These grades are important for electrical housing applications and contribute to a significant fraction of ABS usage. Halogenated and phosphorus additives are generally used as flame retardants, though halogenated styrene can be copolymerised into the ABS (Uhlmann, 1993).

Clear ABS. Clear ABS is a transparent ABS material, which the basis is the matching of the refractive indices of each of the rubber core, graft and matrix phases (Adam *et al.,* 1993). Clear ABS grades use methyl methacrylate as a fourth monomer to match the refractive indices of the other monomers (Glenn and Cathleen, 1985). The process is complicated by the fact that the refractive indices have to match over the temperature range of use, so that the change in refractive index with temperature must also match (Jalbert, 1991). Properties are similar to those of medium-impact standard ABS grades.

Plating Grades. ABS can be electroplated in the same process used for metals after being prepared via a preplate system, which etches the surface using chromic acid and deposits an electroless layer of copper or nickel, rendering the surface conductive. ABS also lends itself to plating (Glenn and Cathleen, 1985). Such grades are commonly used in car mirrors, headlight bezels and faucets (taps). Chrome plated ABS faucets can be made in styles that cannot be made in metal (Adam *et.al,* 1993). These products also offer a relatively low coefficient of linear thermal expansion which reduces stresses between the metal plate and the ABS during exposure to extremes in temperature.

Filled ABS. A filled ABS has a higher strength, rigidity, modulus and high temperature dimensional stability by adding glass fiber and is suitable for stressed structural applications (Adam *et al.*, 1993). This filled ABS is commonly used is in skis and applications in the automotive industry such as car dashboard supports. Stainless steel filled ABS can be used when more effective shielding from electromagnetic interference is required.

2.1.6 Application

Their broad property envelope, wide processing latitude, and favorable price and performance balance has allowed ABS based products to participate in a wide variety of markets.

Transportation is the largest market for ABS in U.S. Automotive uses are many and include interior and exterior applications. For interior injection molded application, high heat, general purpose, and low-gloss grade have been developed for application. A unibody plastic trailer was designed by using coextruded sheets of Bayer's Lustran ABS is shown in Figure 2.4. This prototype design won in an Automotive Award and People's Choice Award (Molinaro, 1999a). Besides, ABS resin is thermoformed to produce an electric motorbike called the Lectra VR24 (see Figure 2.5) (Molinaro, 1999b).

In the U.S., about 250 million lb. of resin were consumed in appliance market in 1989 (Brisimitzakis, 1994). Most of this consumption was for major appliances with extruded/thermoformed door and tank liners leading the way. Other applications include injection molded housings for kitchen appliances, power tools, vacuum sweepers and hair dryers.

Business machine is a large “value added” market for ABS. Flame-retardant grades have found strong market fits in computer housings and consoles. Closely related is the telecommunication market where by virtue of its exceptional esthetics and good flow/impact balance, ABS resin is enjoying healthy growth in applications such as telephones and modems. A new invented printer/embosser enclosure for a tabletop card personalization system which made by flame retardant ABS had won an Industrial Enclosure Award (Johnson, 1998) (see Figure 2.6).

ABS is used widely in building and construction industry, particularly in extruded drain, waste and vent pipe and injection fittings applications. Consumer and industrial markets contain numerous ABS applications crossing many market segments. These include toys, medical devices, furniture, cosmetic packaging and luggage (Brisimitzakis, 1994). The manufacturers of ABS polymers are constantly introducing new types, with better technical, application and aesthetic characteristics.

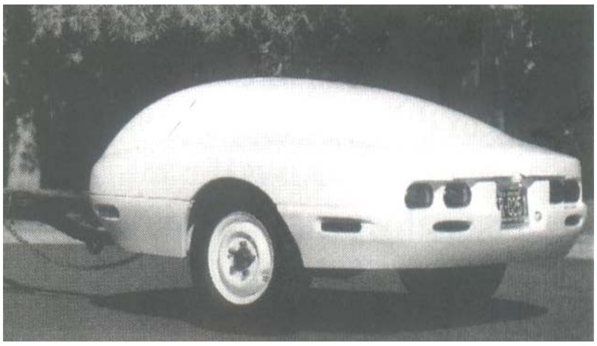


Figure 2.4 : Automotive Award and People’s Choice Award : Unibody plastic trailer

Figure 2.5 : ABS resin speeds motorbike to market

Figure 2.6 : Industrial Enclosure Award: Printer/embosser enclosure for a tabletop card personalization system

2.2 Poly(vinyl chloride) (PVC)

2.2.1 What is PVC ?

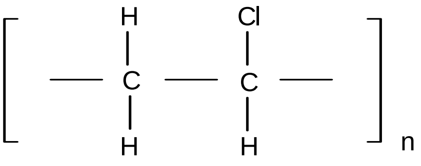
According to Titow, the abbreviation ‘ PVC ’ has one of two meanings, depending on the context in which it appears, viz.

(a) ‘ Poly(vinyl chloride) ’, i.e. the homopolymer of vinyl chloride, or

(b) *as a noun* : a member (or, collectively, the whole) of the large family of plastics materials based on poly(vinyl chloride) and /or vinyl chloride copolymers;
as an adjective : of the nature of, or pertaining to, such member or family.

PVC is the second most widely used thermoplastic polymer. The resin produced in 1999 (15 billion pounds) translates into over 100 billion pounds of compound worldwide. As an amorphous polymer, PVC resin is extensively formulated to produce an extremely large variety of compounds (Blanco, 2000).

The fundamental repeating unit of the PVC chain is:



$$\left[- \overset{H}{\underset{H}{C}} - \overset{Cl}{\underset{H}{C}} - \right]_n$$

Where “n” denotes the degree of polymerization. In general, the higher the molecular weight, the greater the difficulty in processing and the higher the physical properties. In commercial resins, the number average molecular weight is in the range of 50,000 to 100,000^6.

2.2.2 Historical Background

The early development of PVC is highlighted in Table 2.2 (Titow, 1990).

Table 2.2 : Historical background of PVC

Year	History
1835	VCM was first prepared by Regnault.
1872	Baumann discussed the reaction of vinyl halides and acetylene in a sealed tube.
1921	Plausen discovered how to polymerize PVC from dry acetylene which made PVC more than a laboratory curiosity.
1928-1930	Patent disclosures of VC/VAC copolymers and polyvinyl halides. Introducing of emulsion polymerization to prepared vinyl chloride.
1930	Plasticisation of PVC by phthalate ester. Introduction in non-rigid vinyl chloride plastics. Suspension polymerization of vinyl chloride in England and Germany. Technical production of chlorinated PVC polymer and fibres. Commercial production of PVC polymers in Germany and USA.
1942-1943	Commercial production of PVC polymers in England.

The outbreak of the world II was a boost to the PVC industry. It was during this period that PVC substituted highly costly rubber in some important applications, notably as insulation and covering for electrical wires and cables (Titow, 1990). Now, PVC has been used extensively to become one of the worlds leading synthetic polymers since it is relatively cheap and versatile.

2.2.3 Chemistry and Manufacturing

2.2.3.1 Vinyl Chloride Monomer (VCM)

Acetylene, ethylene, chlorine and oxygen feedstocks are necessary to manufacture vinyl chloride monomer. The process by which feedstock is converted to VCM is shown in Figure 2.7. In the early days of VCM production, acetylene was the dominant method; today, only 7 % of the VCM is so manufactured. The remainder is produced by oxychlorination (Figure 2.8) (Titow, 1990).

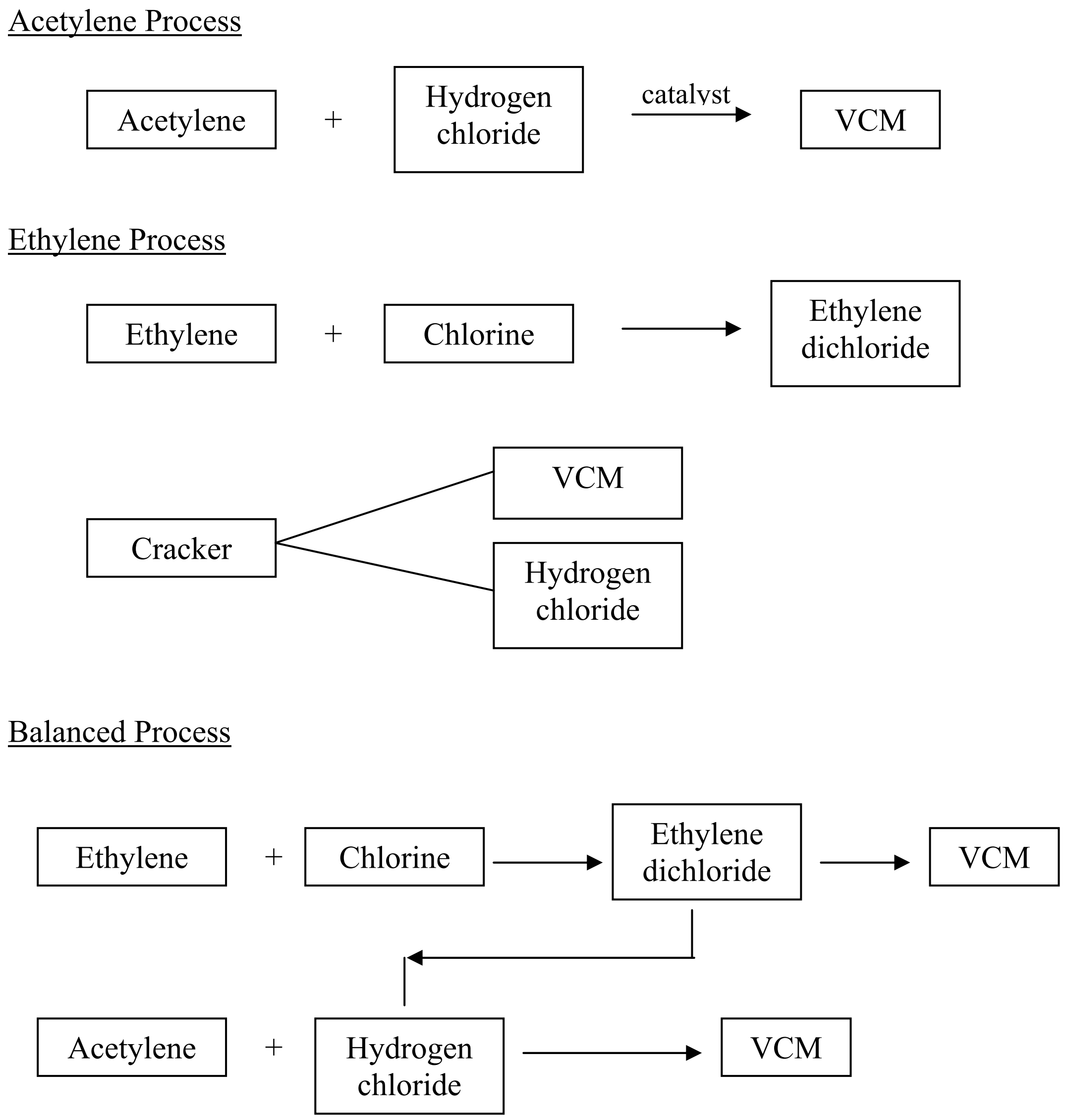


Figure 2.7 : Feedstock conversion to vinyl chloride

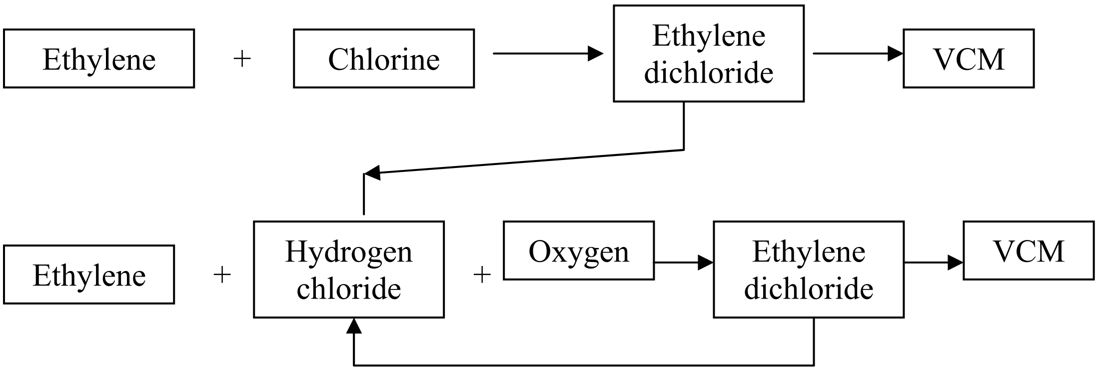


Figure 2.8 : Oxychlorination process

At normal temperature and pressure, VCM is a colorless, dense, pleasantly sweet-smelling gas. VCM is soluble in aliphatic and aromatic hydrocarbons and insoluble in water. Since 56.7 % of the monomer is chlorine, neither VCM nor PVC prices is dominated by oil and gas prices (Gobstein, 1990).

2.2.3.2 Polymerization Process

The polymerization techniques used to produce PVC polymers are suspension, mass (bulk) and emulsion routes. Due to technological and economic advantages, the suspension polymerization process dominates 76% share of the market (Kunststoffe, 1989). The difference between the three types of polymerization process is shown in Appendix B.

Commercial PVC materials are often classified according to the polymerization method, and the molecular weight of the materials. The molecular weight of the polymer is often quoted in terms of a K-value. It is a measurement of the viscosity of dilute solution. The molecular weight of PVC is controlled by the polymerization temperature (Coaker and Wypart, 1993). Block diagram of each method is stated at the Appendix C-G.

The PVC resin used in this research is suspension grade. The suspension polymerization process is sometimes referred to as pearl, bead, or granular processing. PVC so produced has relatively large particles (40 to 200 mesh), low levels of impurities and resembles in particle form (Gobstein, 1990).

2.2.4. Morphology and Properties

Commercial PVC polymers is a “head to tail”, essentially amorphous in nature (Katz, Shkolnik, & Ron, 1976) with low degree of crystallinity (8-10% as determined by X-ray diffraction). The crystallinity is associated with the stereo regular (syndiatactic) polymer fraction: high syndiotactic polymer has a higher crystallinity (De Coste, & Hansen, 1962). It contains 0.4 to 1.1 branches per 100 carbon atom chain.

The PVC resin particle is unusual in structure. After polymerization, PVC possesses a specific morphology as illustrated in Figure 2.9. Powder particles which are visible to the naked eye are known as grains. Its glass transitional temperature (T_g) of about 80-84 ^oC varies with the polymerization temperature. The melting point varies with molecular weight, molecular weight distribution and polymerization temperature (Gobstein, 1990).

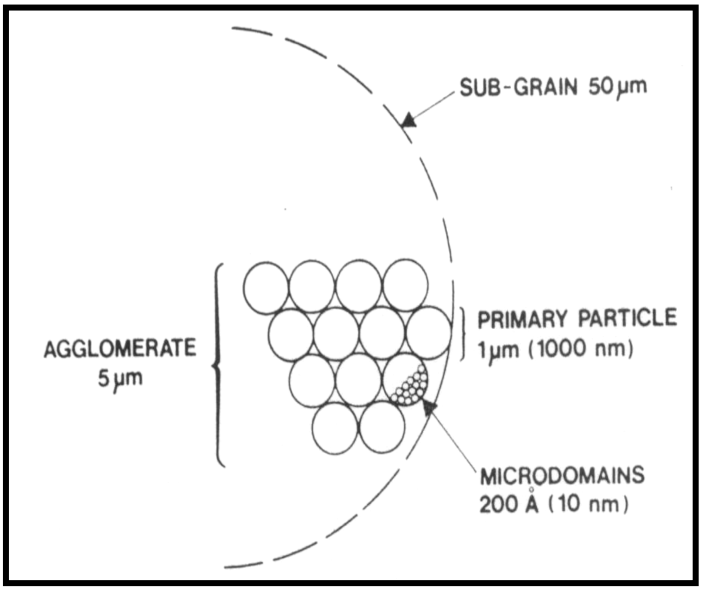


Figure 2.9 : PVC particle morphology

2.2.4.1 Mechanical Properties

The general relationship of physical properties to molecular weight can be represented as in Figure 2.10. As the molecular weight is increased, the mechanical properties (strength) increase. The effect is generally most pronounced for low molecular weight, where properties such as tensile strength, elastic modulus, and impact strength are all low or perhaps even essentially nonexistant. As molecular weight increases, almost all useful mechanical properties are increased but with sequentially diminishing returns. The only useful property lost with increasing molecular weight is melt flow, as described in the preceding section. Thus chosing the right molecular weight is an optimization between mechanical properties and process ability.

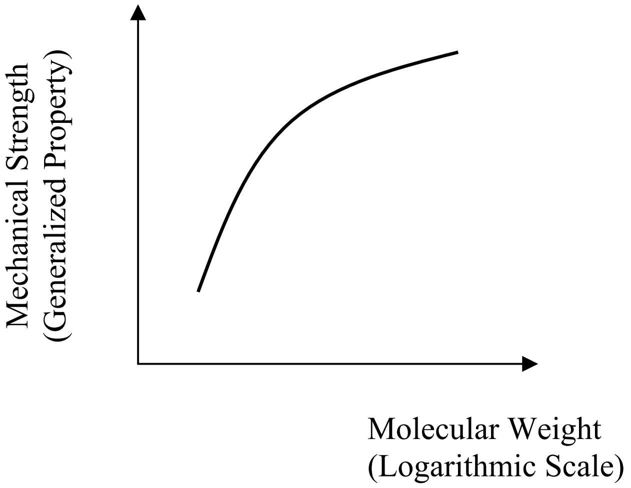


Figure 2.10 : Schematic curve showing the effect of molecular weight on most mechanical properties of PVC. The exact nature of the plot will depend on the mechanical property selected (Donald, 1986)

According to Donald (1986), a great variables ranging from the degree of crystallinity and the state of the glass to the detailed morphology of the specimen, as determined by the compounding ingredients, the starting particles morphology, and the degree of fusion (processing conditions), can all play an important role for the mechanical properties of PVC particles. Small changes can and do make substantial and sometimes quite surprising difference in the outcome.

2.2.4.2 Thermal Properties

The thermal degradation of PVC is considered by most experts to be a major disadvantage of this material. Upon exposure to temperature as low as 100 to 120 ^{o}C or upon exposure to ultraviolet radiation, PVC undergoes a degradation reaction that releases hydrochloric acid and forms long polyene sequences of conjugated double bonds.

The longer polyene sequences are intensely colored and only small amount of them can make the PVC appear black. The following values have also been quoted for *Welvic* (ICI, UK) rigid PVC moulding materials (Titow, 1990):

Specific heat at 20 ^{o}C	110 $Jkg^{-1}\,^{o}C^{-1}$
Thermal conductivity at 20 ^{o}C	0.17 $Wm^{-1}\,^{o}C^{-1}$
Appproximate total heat (moulding)	270 X 10^{6} Jm^{-3}

2.2.4.3 Melt Viscosity

Melt flow of PVC is a complex situation. At low melt temperature (probably below 200 ^{o}C and high syndiotactic polymer), a model of tiny elastic balls that might be lubricated to flow past one another if lubricant is present in the compound might be a more accurate flow model than melt. At higher melt temperatures and low syndiotacticity, and without lubricant, the PVC melt might be more like a true melt.

Basically, molecular weight and shear rate both can change the melt viscosity. PVC with lower molecular weight can reduced the melt viscosity and shear heat generation in the melt significantly (Titow, 1990).

2.2.4.4 Flammability Properties

The flammability of PVC (resin and solid uPVC composition) as determined in standard test is one of the lowest among those of the common plastics. The low flammability is due to the large chlorine content: like the other halogens. Chlorine acts as a retardant in the process of combustion. However, the smoke emission is relatively high and the smoke is irritant and toxic. The smoke evolution can be limited by adding smoke suppressants such as $CaCO_3$ and $MgCO_3$ (Troitzsch, 1980).

The performance of PVC compositions in flammability test falls with increasing dilution of the polymer by the other formulation components (which decrease the overall chlorine content). This is the well known fact that plasticisation increases flammability.

2.2.5 Processing

PVC, in its predominantly dry compound form, is processed mainly by extrusion, calendering and injection moulding. It can also be blow molded into bottles and other parts or made into film on a blown film line. In the extrusion process, PVC compound is fused in an extruder by heat and pressure. The melt is forced through a die to produce a continuous flow. Whereas the injection moulding process develops melt in a method similar to the extrusion process. The melt is injected into a mold cavity by the forward movement of the screw, filling the mold to form the part. After cooling, the mold opens to remove the finished part (Bramfitt and Heap, 1962).

2.2.6 Advantages and Disadvantages

PVC, in all its forms and compounds, is the second largest volume plastic in the world. PVC exists as rigid PVC (RPVC), which is stiff, hard and sometime brittle. It also exists as flexible PVC (FPVC), which is soft and pliable. Basically, PVC can be compounded to posses any degree of rigidity or flexibility between these two extreme, depending on the required properties of the final product. As noted, 56.7 % of the molecular is chlorine. This means that the polymer's availability and pricing are not wholly related to oil or gas feedstock.

Other advantages of PVC are:

1) Relatively cheap and versatile
2) Excellent physical, chemical, electrical and weathering properties
3) Processability by a variety of techniques
4) Nonburning
5) Low water absorption
6) Good surface appearance

The disadvantages are:

1) Poor thermal stability makes processing difficult
2) Low heat deflection temperature (low rise temperature)
3) Poor creep at elevated temperature

2.2.7 Additives

Additives are incorporated into PVC to overcome the limitation of the polymer. The final properties of PVC product are highly dependant on the type and amount of additives presents in the compound. For example, depending on the amount of plasticizer added, PVC can either rigid or extremely flexible. The typical additives used in PVC product are (Gobstein, 1990):

1) Processing aids
2) Lubricants
3) Stabilizers
4) Fillers
5) Impact modifiers

The additives used in this research are lubricant and stabilizer. Further discussion will be based on these two additives.

2.2.7.1 Lubricant

A lubricant is a substance that, when added in small quantities, provides a disproportionate decrease in resistance to movement of chains or segments of polymer of at least partly amorphous structure, without disproportionate change in observable properties (Grossman, 1989).

The two major classes of lubricants are designated “internal” and “external”. It is important to obtain a balance between the external and internal lubricant. Lubricants perform several functions (Titow, 1990):

- Reduce frictional forces between resin chains (internal).
- Reduce frictional forces between the resin chains and the metal surface (external).
- Promote melt flow by reducing melt viscosity.

Calcium stearate act as an internal lubricant in PVC, to promote fusion and modify melt viscosity during extrusion processing. It also act as a co-stabilizer in many PVC applications when combined with a number of primary heat stabilizers (Mesch, 1994).Fatty acids are particularly effective as external lubricants in PVC when used in small amounts. These acids are compatible with PVC, making them particularly useful in applications where clarity is important (Mesch, 1994).

2.2.7.2 Stabilizer

PVC resin is heat sensitive and will degrade if it is exposed to a source of energy such as heat, light, pressure, and shear forces. It tends to cause chemical changes in the polymers that result in noticeable unwanted changes in their properties. Such changes include loss of mechanical strength, fluctuations in melt viscosity and lubricity that make processing more difficult.

The indication of PVC degradation is a dehydrochlorination. Dehydrochlorination is often detected in a compound through discolouration, for example, as the degree of chain unsaturation increases: white, cream, yellow, orange, red, light brown, brown, and finally black. Degradation leads to chain scission and cross linking; hence a loss in physical properties. More changes can occur during the service life of the finished article. Stabilizers, then, are chemical additives that prevent, arrest, or at least minimize such changes, and so “stabilize” the polymer (Kauder, 1989).

The thermal stabilizers commonly available in the market can be divided into 3 main groups. There are (Rabinovitch, Lacatus, and Summers, 1984):

- lead salts, soap, and other metal soaps or salts (Cd, Ca, Zn, Ba)
- organo-tin compounds, organic and miscellaneous stabilizers
- mixed stabilizers (synergistic mixture)

Organo-tin compounds with at least one tin sulfur bond are generally called organo-tin mercaptides. Stabilizers on the basis of these compounds are also called sulfur containing tin stabilizers or thiotins (Andreas, 1984).

2.2.8 PVC Industries and Their Products

The Freedonia Group forecasted that U.S. demand for PVC would increase by 3.4%/yr to 14.4 billion lbs in the year 2002, valued at $6.2 billion (Molinaro, 1999f). This would be driven by PVC’s cost and performance advantages over wood and metal, improvements in production and processing technologies, and the development of improved resin grades with enhanced properties.

Construction constitutes the largest market for PVC, according for 72% of the total demand in 1997 (Molinaro, 1999f). Despite declining housing starts, vinyl products will increasingly be used in remodeling and renovation projects, in which installation ease and low maintenance are highly desirable. Outside of construction, the largest volume PVC markets are insulated wire and cable; and packaging, including film, sheet, and bottles.

Three PVC compounds have been developed by the Geon Co. for a drum and pail pump in fluid-handling applications involving exposure to strong chemical and tough use (Molinaro, 1999g) (refer figure 2.11). A boots manufacturer used ultra-high molecular weight (UHMW) PVC polymer, which are said to offer increased strength, abrasion-resistance, and elasticity to manufacture the Flex3 footwear as shown in Figure 2.12 (Molinaro, 2000). Another example is a robust cash box moulded in PVC material (GAM Report, 2000).

An electric fencing consists of extruded PVC decorative fencing that is affixed with two aluminum conductive rails, is tasked with providing a psychological as well as a physical barrier for large animal (Molinaro, 1999h) (see Figure 2.13). Package for medical components which made of clear PVC had won a Critical Barrier Packaging Award (Johnson, 1998) (see Figure 2.14).

It is not surprising that PVC is currently one of the world’s most important plastics and the second largest after polypropylene in consumption, despite fierce pressure in recent years from environmental group concerning the controversial issue of chlorine chemicals. The release of chlorinated dioxins from the VCM during incineration, as well as the use of health hazardous additives in PVC compounds do not favour the profile of the industry. Issue centers around phthalate plasticizers in PVC intended for food-contact products, medical supplies and toys, but this concern has not yet affected the broad-based PVC market. So far, bans and limitations have been instituted only in the toy industry (Johnson, 1999). The industry itself regards PVC as an environmentally friendly material, given its use in high performance, long-life and maintenance free products and its very low energy demands (making it in fact the most energy efficient of all plastics). In spite of some negative attitude, the market has grown. (see Figure 2.15) (Blanco, 2000).

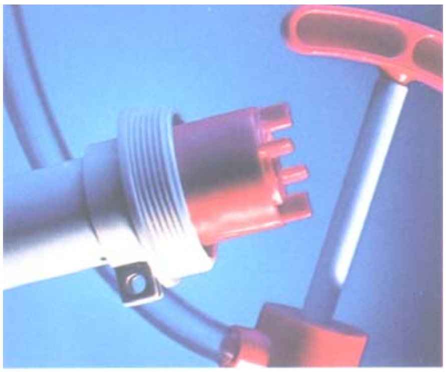


Figure 2.11 :
PVC pumps stand up
to chemicals, rough use

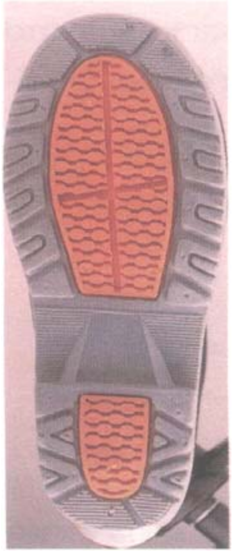


Figure 2.12 :
Vinyl outsoles resist
Harsh chemicals and oils

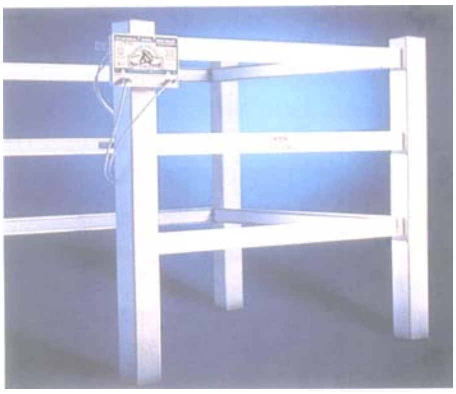


Figure 2.13 : High impact PVC
sparks electric fence

Figure 2.14 : Critical Barrier
Packaging Award: Package for
medical components

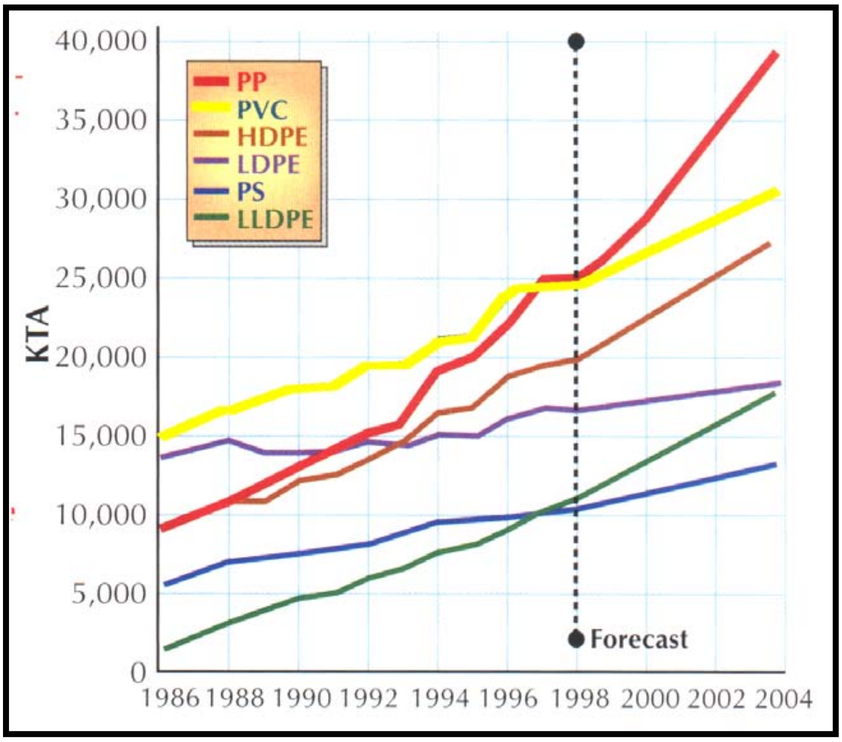


Figure 2.15 : Thermoplastic worldwide forecast (Blanco, 2000)

2.3 Polymer Blends

The concept of physically blending two or more existing polymers to obtain new products (polymer blends) or for problem solving is now attracting widespread interest and commercial utilization. Polymer blends are often referred to by the contraction “polyblends” and sometimes as “alloys” to borrow a term from metallurgy (Modern Plastic Magazine, 1994). The need for improved balance of properties and the potential ability of polymer blends to satisfy this need have converged in the development of polymer blending as a major area for rigorous growth in the past several years. Properties of plastics that have most often been improved by polymer blending include processability, tensile strength, ductility, impact strength, abrasion resistance, heat deflection temperature, low-temperature flexibility, flame retardancy, and environmental stress-crack resistance.

2.3.1 ABS Blends

ABS is itself a blend of PB and SAN, but can be further blended with other materials and thus the scope of possible applications is broadened. Commercial blends with ABS are given in Table 2.3 (Adam *et al.*, 1993) and some of these will be discussed in more detail below.

Table 2.3 Blends with ABS (Adam *et al.*, 1993)

Blend	Key Properties	Application	Growth Rate[a]
PC/ABS	heat resistance, low temperature impact, processability, ease of flame retarding	automotive, computer housing, lawn and garden, power tools, recreational vehicles	9 %
PVC/ABS	impact strength and toughness, flame retardance, UV stability, processability	electrical components, applicances, business machine housings, housewares	12-18 %
Nylon/ABS	high impact, chemical resistance, heat resistance, low moisture sensitivity	Automotive body panels and underhood components, vacuum cleaner housing	7 %
TPU/ABS	Chemical and abrasion resistance, low temperature toughness	Auto bumper fascia	
PBT/ABS	Processability, impact strength, heat and chemical resistance	Lawn and garden equipment, small appliances, fluid engineering industry	8 %
Polysulphone/ABS	Processability, low cost, heat resistance, ccan be plated	Appliances, auto window handles, faucets, food trays	
Miscellaneous*			

[a] U.S. annual consumption growth rate 1990-96. Source: ref. (CEH, 1992)

* miscellaneous blends: ABS/PVC/polyester, ABS/Acrylic acid ester, ABS/EVA, ABS/CPE, ABS/EPDM, ABS/SMA

2.3.2 PVC/ABS Blends

The low price of PVC renders its use desirable in many applications. When blended with ABS, the result is a materials which provide high impact strength, toughness and flame retardance, PVC provides the inherent flame retardance with UV stability, whereas ABS provides the impact strength and process ability (Manson and Sperling, 1976). PVC/ABS is used in a wide variety of applications which include electrical components, appliances, business machine housings and automotive parts. The inherent flame retardance of PVC makes it suitable for applications where the more expensive FR ABS could be employed.

Compatibilized blends of PVC and ABS have been demonstrated by Lindner and Ott, 1989. The compatibility occurred due to the similarity of the solubility parameters of the SAN matrix of ABS and PVC. The effect of this compatibilization was the improvement in the impact strength of the PVC blends. In particular, the data in Table 2.4 showed that the impact strength of PVC blends containing a minor amount of ABS increased with the total amount of polybutadiene in the blend (Datta and Lohse, 1996). These blends were made by melt blending the components at 200 ^{o}C on a mill.

Table 2.4 : Impact strength data for various PVC/ABS blends (Datta and Lohse, 1996)

	ABS		PVC	Impact Strength NI-A (J/m)	
Wt % PBD	wt % SAN	Phr	phr	20 ^{o}C	0 ^{o}C
75	25	7	93	491	400
50	50	7	93	357	290
75	25	15	85	2160	800
50	50	15	85	1330	673

Meredith and Ferguson, 1988 have extended the idea of the compatibility of PVC and SAN to form essentially transparent blends of PVC and ABS by closely matching the refractive indices of the ABS and the PVC phases by either changing the composition (S/AN ratio) or by inclusion of minor amounts of comonomers in the rubber phase. Thus, the refractive index of the rubber phase could be altered by adding minor amounts of styrene or AN without significant effect on the elastomeric properties. This procedure reflects the versatility of the synthetic process for ABS since the free radical procedure could accommodate a large variety of monomers.

In the data shown in Table 2.5, the ABS polymers were made with slightly different composition and blended with PVC by milling the mixture on a two roll mill at 173 °C for 8 min with a thermal stabilizer. The data compared the impact strength of blends containing 100 phr of PVC and 14 phr of ABS-type polymers. It illustrated the significant improvement in the impact strength with rather small increases in the amount of the rubber (PBD and copolymers of butadiene) phase of the blends (Datta and Lohse, 1996). All of the ABS polymers in this collection of the data contained 65% of an elastomer phase, 28% styrene and 7% AN.

Doak, 1984 had suggested the formation of compatibilized blends of PVC and ABS type polymers from styrene copolymers such as SMA, SAN and (S, MA, MMA). There were no definite results available to indicate the mechanical properties of the blends which were believed to be compatibilized because of the similarity in the solubility parameters of PVC and the styrene copolymers.

Table 2.5 : Impact strength data for various ABS compositions blended with PVC (Datta and Lohse, 1996)

ABS-type		PVC	Impact Strength NI_A
% PBD	Phr	phr	J/m (@ 23 °C)
69	80	20	110
74	80	20	480
79	80	20	480
84	80	20	450
89	80	20	490
94	80	20	560

2.3.3 Polycarbonate/ABS Blends

The second class of alloys is produced through blends made with polycarbonate (PC). Nearly all PC/ABS is used in automotive and business machine applications, with a small amount in lawn and garden equipment, power tools and recreational vehicles. PC/ABS properties and price are intermediate between those of the more expensive PC and the less expensive ABS; thus it is a good choice for customers who would like better performance than is available with ABS but do not wish to pay the high price for PC. The blends/alloys of PC/ABS provide heat resistance as well as low temperature impact strength and process ability. ABS improve the processibility and reduced cost whereas the PC provides the heat resistance and toughness and impact, higher tensile properties and improved ease of flame retarding (Bonner and Hope, 1993). These alloys exhibit excellent toughness, good heat distortion and high rigidity (Glenn and Cathleen, 1985).

PC/ABS are processed mainly via injection moulding, and because of their relatively high-melt viscosity, they are somewhat more difficult to process than standard ABS. Care must be taken not to exceed temperatures that will result in degradation of the rubber, but a sufficiently high temperature is required so that the PC is not too viscous (Glenn and Cathleen, 1985).

2.3.4 Nylon /ABS Blends

Nylon/ABS alloys provide high impact at both low and high temperatures as well as reduce moisture sensitivity and chemical resistance. The nylon contributes to the key thermal and chemical resistance properties, whereas ABS provides the impact strength and low moisture absorption. Nylon/ABS alloys are used in automotive interior, vacuum cleaner and power tool housings (Bucknall, 1977). Nylon and ABS or SAN are not compatible and simple blends of nylon and ABS display poorer properties than either component. The addition of some maleic anhydride (MA) copolymerised in the SAN matrix for example acts as some sort of compatibilisation (Triacca, 1991).

2.4.1 Flame Retardant

The burning and non-burning characteristics of plastics have been given great deal of attention by the scientific community in the last twenty years (Landrock, 1983). A flame retardant is used to inhibit or even suppress the burning process. (Troitzsch, 1980). In this study, ABS is a highly flammable material. Whereas PVC itself does not burn easily, and act as flame retardant.

2.4.2 Fire and Polymers: An Overview

Our environment is largely one of polymers and all polymers burn whether natural or synthetic. The issue is not whether polymers burn but rather if a given polymer has a proper profile appropriate to provide for an acceptable level of risk in a given application. Here, we should know that hazard is the potential for harm, with the probability of the event (fire), P_{ev} equal to one and the probability of exposure (e.g. people), P_{ex} equal to one. Risk is the product of the probability of the event times the probability of exposure, times the potential for harm, μ_h (Nelson, 1995).

$$\text{Risk} = P_{ev} \times P_{ex} \times \mu_h$$

$$\text{Risk} = \text{Hazard, when } P_{ev} = P_{ex} = 1$$

$$\therefore \text{ Risk} = \text{Hazard} = \mu_h$$

2.4.3 Combustion of Plastics

The burning of a solid polymer or polymer composition involves four stages:

1. Heating of the polymer
2. Decomposition
3. Ignition
4. Combustion

Heating the polymer. During this initial stage, thermoplastic materials soften or melt and begin to flow. The amorphous or crystalline linear polymers begin to lose their rigidity at the glass transition temperature and a continuous decrease in the viscosity of the melt takes place up to the decomposition point (Landrock, 1983).

Decomposition of the plastic occurs, with the elimination of volatile gases or chemically degraded polymer fragments, as shown in Figure 2.16 (Landrock, 1983). The temperature and the rate at which this occurs depend upon the thermal stability of the polymer and the chemical decomposition reaction occurring under the existing conditions (Pál, and Macskásy, 1991).

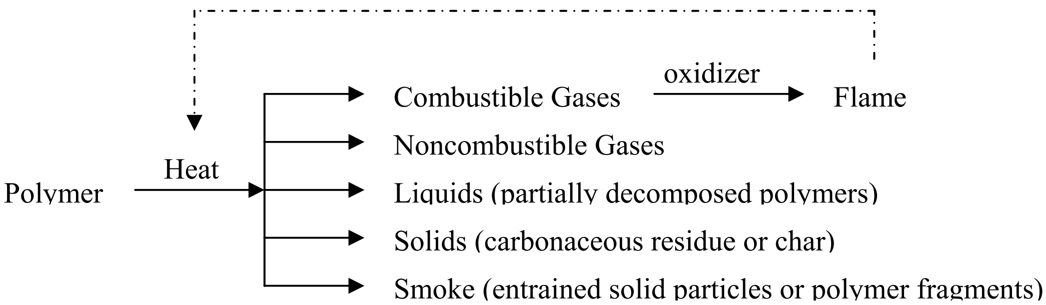


Figure 2.16 : Schematic representation of polymer degradation.

Ignition. The combustible gases and vapours evolved in the coarse of thermal decomposition are mixed with oxygen and ignited with or without the mediation of an external ignition source (Landrock, 1983). Ignition is influenced by the ignition temperature, which is generally lower in the presence of an igniting flame as compared to the self-ignition temperature (Pál, and Macskásy, 1991).

Combustion. After the ignition, the rapid heat generation raises the temperature both of the combustion products and of the environment, including the materials still not burning (Pál, and Macskásy, 1991). If this latter part of heat is sufficient for attaining the ignition temperature of the material, a self-supporting combustion will take place. Otherwise, burning can only be maintained by a continuously acting external heat source (Landrock, 1983).

The burning characteristics of some polymers are summarized in Table 2.6 (Chanda and Roy, 1993; Landrock, 1983).

Table 2.6 : Burning characteristics, burn rates and LOI index of polymers

Polymer	Burning characteristics	Burn rate (cm/min)	LOI index (%)
Polyethylene	Melts, drips	0.8-3.0	17.4
Polypropylene	Melts, drips	1.8-4.0	17.5-18.0
Poly(vinyl chloride)	Difficult to ignite, white smoke	Self-extinguishing	37.0-42.0
Poly(tetrafluoroethylene)	Melts, chars, bubbles	Nonburning	30.0
Fluorinated ethylene propylene copolymer	Does not ignite	Nonburning	> 95.0
Polybutylene	Burns	2.5	18
Acetal	Burns, bluish flame	1.3-2.8	14.8-15.0
Cellulose acetate	Burns, yellow flame, sooty smoke	1.3-7.6	19.0-27.0
Cellulose propionate	Burns, drips	1.3-3.0	18.0-21.0
Cellulose acetate butyrate	Burns, drips	2.5-5.1	17.5-18.0
ABS (general purpose)	Burns	2.5-5.1	17.5-18.0
Styrene acrylonitrile	Melts, chars, bubbles	1.0-4.0	19.1
Polystyrene	Soften, bubbles, black smoke	1.3-6.3	18.3-19.0
Acrylic	Burns slowly, drips	1.4-4.0	16.6-18.2
Nylons	Burns, drips, froths	Self-extinguishing	25.0-31.8
Phenylene oxide		Self-extinguishing	28.0-29.0
Polysulfone		Self-extinguishing	30.0-32.0
Chlorinated polyether		Self-extinguishing	23.2
Polyimide		Self-extinguishing	27.0

2.4.4 Flame Retardant Chemistry

Polymer combustion occurs in a continuous cycle (Figures 2.17-2.18). Heat generated in the flame is transferred back to the polymer surface producing volatile polymer fragments, or fuel. These fragments diffuse into the flame zone where they react with oxygen by free-radical chain process (Nelson, 1995). This in turn produces more heat and continuous the cycle. Flame retardancy is achieved by interrupting this cycle.

There are two ways to interrupt the cycle. One method, solid phase inhibition, involves changes in the polymer substrate. Systems that promote extensive polymer crosslink at the surface, form a carbonaceous char upon heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning (Nelson, 1995).

The second way of interrupting the flame cycle, vapor phase inhibition, involves changes in the flame chemistry. Reactive species are built into the polymer which are transformed into volatile free-radical inhibitors during burning. These materials diffuse into the flame and inhibit the branching radical reaction (Nelson, 1995). As a result, increased energy is required to maintain the flame and the cycle is interrupted. Of course, for many materials both solid and vapor phase inhibition are involved.

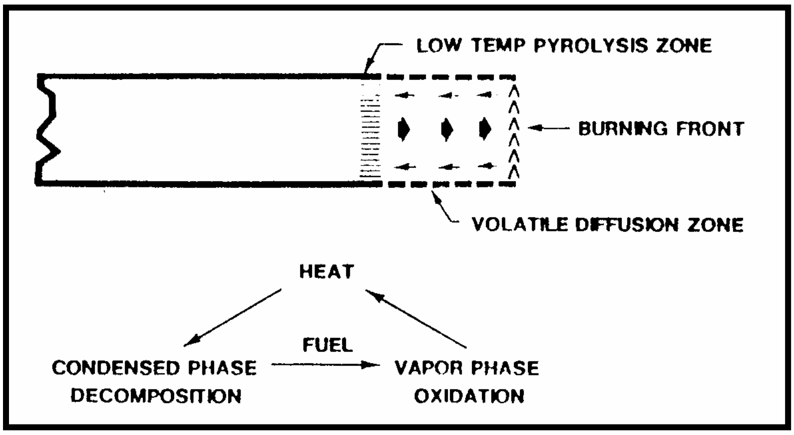


Figure 2.17 : Polymer combustion process cycle

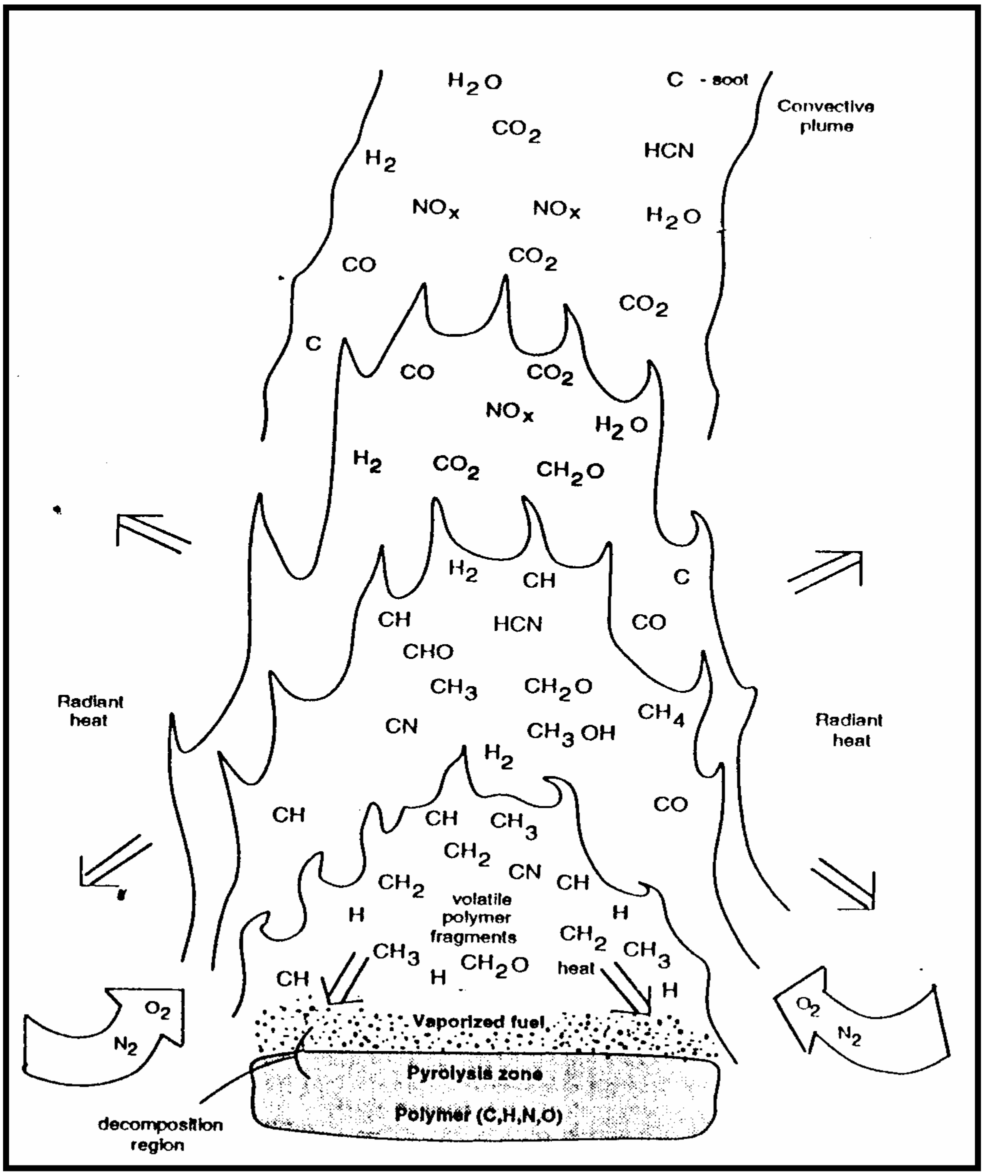


Figure 2.18 : A typical flame involving organic fuel showing decomposition region where volatilized fuel decomposes before combustion

Flame retardant additives used with synthetic polymers include organic phosphorus compounds, organic halogen compounds, and combinations of organic halogen compounds with antimony oxide. Inorganic flame retardants include hydrated alumina, magnesium hydroxide, borates to mention only a few. Not all retardants function well in all polymers. Component may interact (component such as fillers, stabilizers and processing aids must be considered). To be effective, the flame retardant must be decompose near the decomposition temperature of the polymer in order to do the appropriate chemistry as the polymer decomposes, yet be stable at processing temperatures (Nelson, 1995).

2.4.5 Effect of Halogen Compounds

During combustion of thermoplastics, free radicals are formed by pyrolysis. The radicals combine with oxygen in a radical chain reaction. Heat release and further decomposition of the plastics material is caused thereby (Jenkner and Köln. 1983). For continued combustion it is necessary to have sufficient oxygen as well as combustible gaseous compounds. It is presumed that the following reactions take place, when flame-retarded thermoplastics containing organobromine compounds as flame retardants are used (Jenkner and Köln. 1983).

$HO^* + CO = CO_2 + H^*$ (1) propagation, highly exothermic
$H^* + O_2 = HO^* + O^*$ (2) chain branching
$O^* + HBr = HO^* + Br^*$ (3) chain transfer
$HO^* + HBr = H_2O + Br^*$ (4) chain termination

The radical chain reaction is interrupted when the highly reactive HO^* radical, which occupies a key position within the combustion process, is replaced by the less reactive Br^* radical (reaction 4) (Jenkner and Köln. 1983).

2.4.6 Flame Retardant Thermoplastics

ABS resins have greater impact resistance than impact grades of polystyrene but are very sensitive to pigment fillers. For example, the conventional flame retardant system used for impact polystyrene, decabromodiphenyl oxide/antimony oxide, reduces the Izod impact strength from about 2.8 ft-lb/in. for the virgin impact polystyrene to about 2.0. In ABS this flame retardant system reduces the Izod values to about a third of the virgin resin. The effect of antimony oxide on Izod impact strength is shown graphically in Figure 2.19.

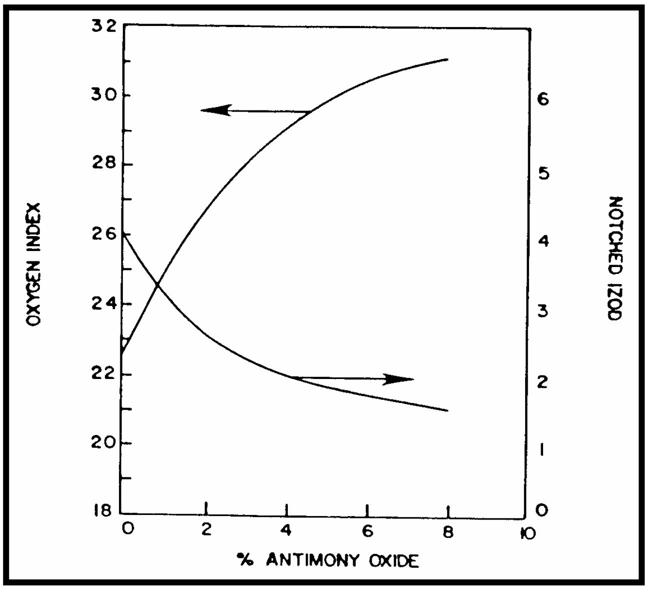


Figure 2.19 : Effect of antimony oxide concentration on the properties of ABS containing 13 wt% flame retardant

The three additives used commercially in ABS are bis(tribromophenoxy)ethane (FF-680), octabromodiphenyl oxide, and tetrabromobisphenol A. Small amounts of antimony oxide may be used for synergism. Also available is an ABS/PVC alloy in which the polyvinyl chloride is the flame retardant (Frank, 1991). Properties of commercial resin are shown in Table 2.7 and are compared with other commercial grades. Cycovin resins exhibit very high impact resistance, with notched Izod strength values of 10.5 ft-lb/in.

Table 2.7 : Properties of flame retardant ABS resin

Property	Commercial Grades ABS Cycovin KAF	 Cycolac KJT	 Cycolac KJB
Specific gravity (g/cm^3)	1.21	1.20	1.20
Izod impact strength, Notched, ½ in. bar (ft-lb/in)	10.5	3.5	3.5
Heat distortion temperature (^{o}F)[a] at 264 psi	-	205	210
Processing temperature (^{o}F)			
Range	370-400	400-440	400-440
Maximum	400	-	-
Flame retardant	PVC	Bromine	Bromine
UL-94 rating/thickness (in.)	**V-1/0.058**	V-0/0.120	V-0/0.120
Oxygen index	30	29	29

[a] Plastics, 8th ed. Desk-top Data Bank, D.A.T.A., Inc., San Diego, California.

Source: Data sheets, Borg-Warner, Parkersburg, West Virginia.

Owen and Harper, 1998 in their study revealed that the LOI values increased as the brominated material loading into ABS is increased. The synergist effect of adding a halogen source and antimony oxide together was observed as expected. The effect of adding antimony trioxide with different particle size was focused. As the average particle size increased, the impact energy absorbed during failure decreased. When antimony oxide and brominated materials were used, the impact energy absorbed by the ABS was reduced further.

Polyvinyl chloride contains 57% chlorine and is inherently flame retardant. Rigid PVC products require stabilizers and processing aids but do not need additional flame retardants to meet flammability specifications. Rigid PVC has a chlorine content of 57% and an oxygen index of about 37. When plasticized with 60 parts of an organic plasticizer such as dioctyl phthalate, the chlorine content drops to 36% and the oxygen index to about 22 (Green, 1989).

Polyvinyl chloride will burn when exposed to an external flame but self-extinguishes when the flame is removed. The flash ignition and self-ignition temperature of PVC are 391 and 454 °C respectively (Grossman, 1989). The effect of stabilizers on the flammability of PVC homopolymer is shown in Table 2.8. In these experiments all the stabilizers chosen increased the oxygen index of PVC.

Table 2.8 : Oxygen index of various metal-stabilized PVC samples[a]

Compound	Metal[b]	Oxygen index
A	**None**	42.4
B	Lead	47.7
C	Tin	43.7
D	Barium, cadmium	45.3

[a] Data from International Wool Secretariat, British Pat. Appl. Sample thickness: about 100 mils.

[b] as salt.

The addition of other additives might also be expected to alter the flammability of PVC. Pure organic materials would decrease the flame retardancy of PVC since the fuel content in the polymer would be increased. In a similar way the flammability of rigid PVC can be further suppressed by the addition of nonorganic fillers to the polymer. This provides a simple dilution effect for the solid fuels. Aside from these effects of additives, rigid PVC is a self-extinguish polymer that will not support combustion, but will burn when exposed to an external flame source.

2.5 Mechanisms of Impact Modification

Three basic mechanisms of energy adsorption are available within a single material: shear yielding, crazing and crack formation. The deformation associated with the particular mechanism occurs irreversibly on the time scale of the deformation process. It is entirely possible that crazing or shear yielding can be reversed by heating the deformed sample to the glass transition or crystalline melting temperature of the polymer, but on the time scales of most mechanical processes the deformation is essentially fixed (Svec *et al.*, 1990).

Shear yielding is the irreversible change of shape of the materials under stress. It may occur over the entire stressed region of material or it may occur in localized portions of the stress region, in which case refer to the response as shear “banding”.

Crazing is a localized irreversible volume expansion. It is often seen in tensile experiments as optical discontinuities that resemble cracks. The craze is not a crack however, as can be shown by microscopic examination. Crack formation is the total separation of matter along a surface. The surface may encompass the entire cross-sectional area of specimen or it may form locally without causing complete failure.

Of the three, shear yielding and crazing offer much higher energy adsorption potential and are consequently to be preferred. The higher potential arises because large numbers of shear bands or crazes can be activated underload, while only a few crack planes are normally found at failure.

2.5.1 Implementing the Mechanism

2.5.1.1 Crazing

Crazing is a highly successful mechanism for toughening some polymers especially for vinyl polymers. In order for the mechanism to be successful, however, a very large number of crazes must be generated. Basically, a craze consists of highly drawn threads of polymer associated with empty space to a net density of approximately 0.5. This means that the craze occupies roughly double the volume of the undrawn polymer and it achieves this by doubling only one dimension. The result is that we have energy absorption via a thread-drawing process (Rosík and Večerka, 1985).

A few crazes cannot contribute significantly to energy absorption. This is why we turn to rubber modification. The addition of small, well-dispersed rubber particles can increase the number of crazes generated by many orders of magnitude. The rubber phase acts as a craze multiplier. The mechanism of initiation is simply for the rubber particles to act as a stress concentrator (Bucknall, 1977). As stress concentrators, the rubber particles cause crazes to nucleate in the elevated stress zones in the vicinity of the particles (Figure 2.20). The crazes then grow into lower-stress regions and stabilize, thus permitting many crazes to be generated (Charles, 1996).

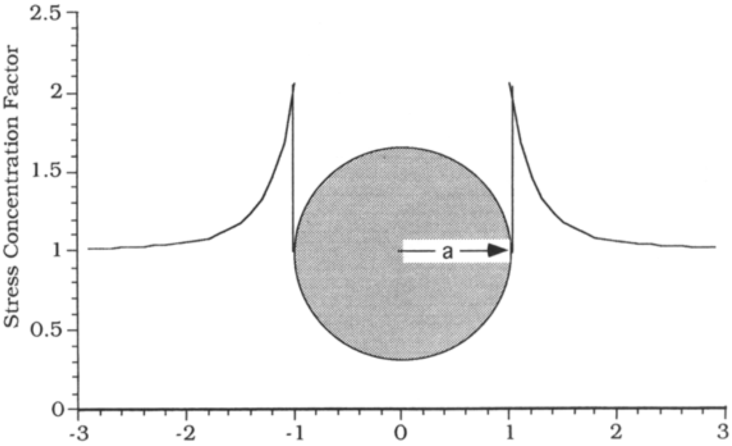


Figure 2.20 : Stress concentration around a hole (Charles, 1996)

A typical ABS will utilize smaller particles than HIPS by factors of 4 to 10. Consequently, up to 1000 times the number of particles may be available. Even though the fracture energy for polystyrene can be six times that of SAN, the superior number of particles in ABS more than makes up for it. The choice of particle size is based on the sizes that maximize performance and is different for each base polymer. Test rate, the incorporation of plasticizers, interface effectiveness, average particle size, as well as size distribution all contribute to the efficiency of craze generation and must be considered when designing a craze-based impact-resistant plastic (Rosík and Večerka, 1985).

2.5.1.2 Crack Multiplication

Just as a fine dispersion of rubber particles can use to nucleate crazes, the rubber particles can also use to nucleate crack initiation sites. The rubber particles once again provide stress concentration sites above and below the growing crack plane and form local cracks that in turn absorb energy. Even though the number of planes that can be activated is small by comparison with the number of crazes that can be generated in a thermoplastic, this technique is still viable for improving toughness (Chanda and Roy, 1993). As an illustration of the technique a series of rubber-modified thermosets were prepared and fractured. The surface roughness of each was measured and compared with fracture energy (G_{1C}). The results are plotted in Figure 2.21 and indicate a definite correlation between the two (Charles, 1996). Incidentally, fracture energies in the rubber-modified samples were approximately 2.5 times the value for a neat sample of the matrix. In other rubber-modified thermosetting systems, fracture energies of from 1.1 to 7 times the neat matrix energies have been observed. Higher toughening efficiencies are usually observed for intrinsically tougher matrices (Rosík and Večerka, 1985).

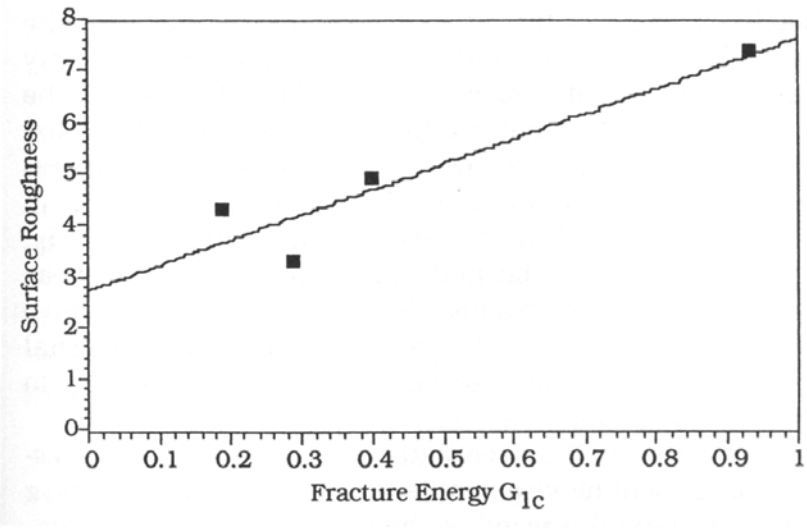


Figure 2.21 : Surface roughness versus fracture energy for several cured epoxies

2.5.1.3 Shear Banding

Normally, shear bands developed in conjuction with rubber particles. As before, the rubber particles provide stress field perturbations, but the rubber itself adds an extra feature, compression of the matrix (Bucknall, 1977). In order to understand this effect we need to realize that the thermal expansion coefficients of glassy plastics are only about one-third that of rubbery plastics. Therefore, when the multiphase material is cooled after processing, a thermal expansion mismatch occurs below the glass transition temperature of the matrix. This causes the rubber phase to be in hydrostatic tension and the matrix to be in compression (Fig. 2.22). This in turn biases the material response toward shear banding and away from crazing (Charles, 1996).

Referring to Fig. 2.23 we see that the addition of a compressive component will move a simple tensile stress field off the *x* axis into the (biaxial) second or fourth quadrant. If the compressive stress is high enough, response can be shifted from crazing to shear yielding (Bucknall, 1977). For example, in unmodified polystyrene the ratio of tensile stresses needed to generate shear banding to the stresses needed to cause crazing has been calculated to be 1.2. Compression resulting from thermal expansion mismatch can reduce the tensile stresses needed to generate shearing while increasing the stresses needed to bring about crazing. It has been predicted that the transition from crazing to shear banding in rubber-modified polystyrene will occur (at slow strain rates) when the rubber content reaches 25%. This agrees well with the occurrence of accelerated increase in impact resistance as rubber content increases above 25%.

When considering the competition between crazing and shearing, it is important to remember that the yield envelope for a given polymer is temperature and rate dependent. It is actually possible to have crazing at high strain rates and shear banding at low strain rates in the same plastic (Rosík and Večerka, 1985).

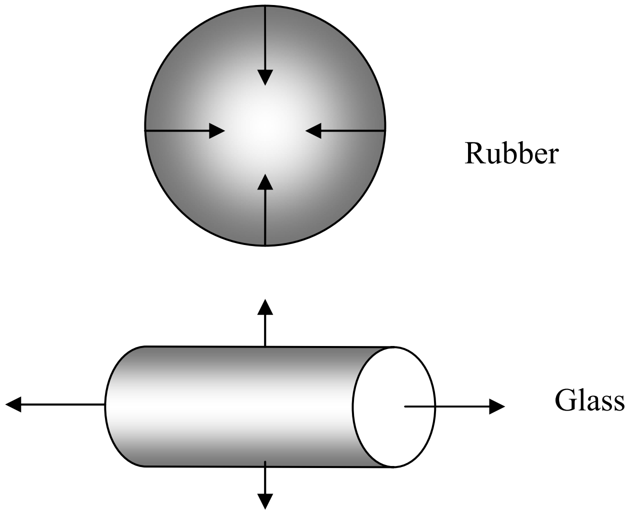


Figure 2.22 : Thermal shrinkage stress directions developed by differential contraction in rubber and glass during cooling

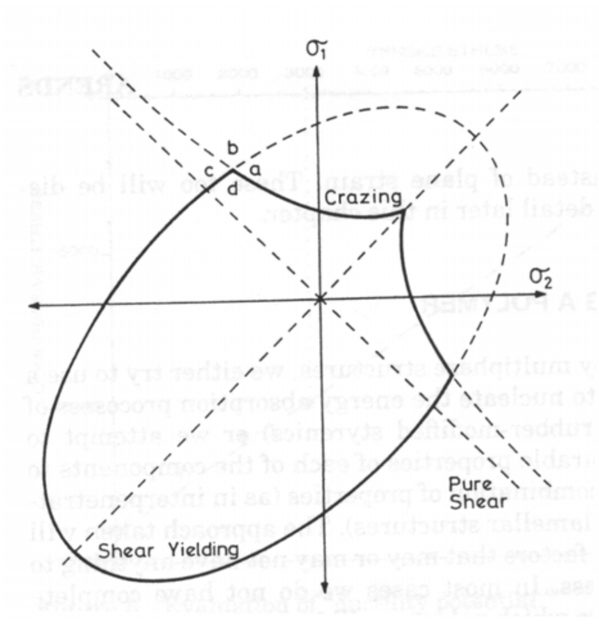


Figure 2.23 : Crazing cusp for PMMA

2.6 Compatibility of Polymer Blends

The variation of properties with the polymer/polymer ratio in a polyblend is shown schematically in Figure 2.24 (Chanda and Roy, 1993). For two polymers to be completely miscible, optimum requirement are: similar polarity, low molecular weight, and hydrogen-bonding or other strong intermolecular attraction.

Most polymer pairs do not meet the above requirements for complete theoretical miscibility. If they are slightly immiscible, each phase will be a solid solution of minor polymer in major polymer, and the phases will separate into submicroscopic domain with the polymer present in major amount forming the continuous matrix phase and contributing most towards its properties. Plots of properties versus the ratio of the two polymers in the blend will be S-shaped showing an intermediate transition region where there is a phase inversion from one continuous phase to the other (Fig. 2.24b). Most commercial polyblends are of this type, with the major polymer forming the continuous phase and retaining most of its useful properties, while the minor polymer forms small discrete domains, which contribute synergistically to certain specific properties.

When the polymer components in a blend are less miscible, phase separation will form larger domains with weaker interfacial bonding between them. The interfaces will therefore fail under stress and properties of polyblends are thus likely to be poorer than for either of the polymers in the blend. U-shaped properties curves (Fig. 2.24c) thus provide a strong indication of immiscibility. In most cases they also signify practical incompatibility, and hence lack of practical utility.

A fourth type of curve for properties versus polyblend ratio representing synergistic behavior (Fig. 2.24d) has been obtained in a few cases. This is synergistic improvement of properties, beyond what would be expected from simple monotonic proportionality, and sometimes far exceeding the value for either polymer alone. Discovery of practical synergistic polyblends is difficult and not predictable with the present state of understanding.

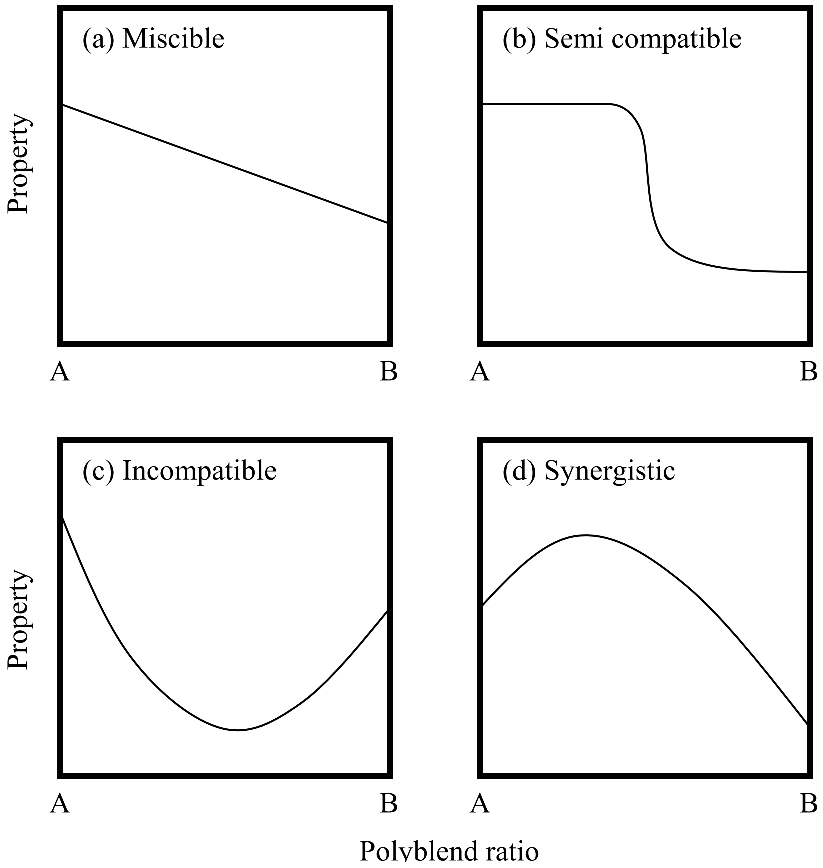
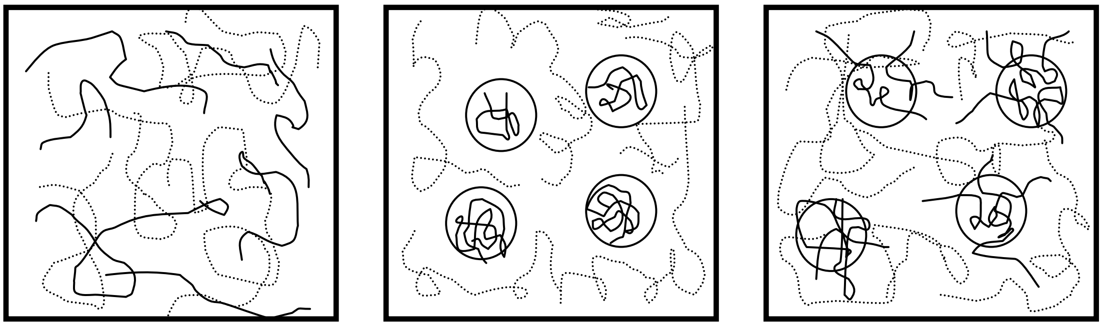


Figure 2.24 : Properties versus polymer/polymer ratio in a polyblend

Under microscopic inspection, a miscible polymer blend consists of a single phase; on a molecular level, polymer A molecules intermingle with polymer B molecules as shown in Figure 2.25a. A second possible morphology for polymer blends is shown in Figure 2.25b, where polymer A forms a separate phase from polymer B. This is the morphology of an immiscible blend, which is far more common than the one phase miscible blend. Frequently, a blend of two polymers is neither totally miscible nor totally immiscible, but falls somewhere in between. A blend of type is partially miscible and is depicted in Figure 2.25c (Fox and Allen, 1985).



(a) (b) (c)

Figure 2.25 : Morphologies of a blend of polymer A (solid line) and polymer B (dashed line) (a) miscible; (b) immiscible; (c) partially miscible (Fox and Allen, 1985)

2.6.1 Methods for Determining Compatibility

When the polymers under consideration have glass transition temperatures sufficiently different from each other, the observation of a single intermediate glass transition temperature generally implies mixing on a submolecular scale, thus compatibility. Whether the glass transitions are observed by DSC, DTA, dynamic mechanical, dilatometric or other methods, it often happens that the glass transition region of a polymer-polymer mixture is broader than of a homopolymer. When this has been observed, some workers have concluded that the polymers were not completely miscible, even though only a single intermediate glass transition was observed for the mixture (Krause, 1989).

When two polymers have glass transition temperatures that are so close together that two glass transitions cannot be observed even for an incompatible, phase-separated mixture, the criterion of sample or film clarity has often been used to indicate compatibility. Some phase-separated samples may however, be clear: (1) if the polymers have almost equal refractive indices, or (2) if the phases are very large, as in layered films (Murayama, 1990). Alternatively, some polymer-polymer mixtures that are considered compatible, the semicrystal-line ones will almost always look turbid because of the refractive index difference between the crystallites and the amorphous phase. In the case of semicrystalline mixtures of two polymers with glass transition temperatures that are very close together, some workers have used the melting point depression of the crystallites by the miscible amorphous polymer phase as a criterion for compatibility.

2.6.1 Dynamic Mechanical Properties

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. The dynamic modulus, the loss modulus, and a mechanical damping or internal friction expresses these properties. The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. It may be a shear, a tensile, or a flexural modulus, depending on the investigating technique (Murayama, 1990).

The dynamic mechanical properties of polymer blends (qv) are determined primarily by the mutual solubility of the two polymers. If two polymers are compatible and soluble in one another. the properties of the blend are nearly the same as those of a random copolymer of the same composition. However, many polymer mixtures form two phases due to the insolubility of the components. In this case, the damping temperature curve shows two peaks: each peak is characteristic of the glass transition temperature of one of the components (Moore, 1989). The two steps in the dynamic modulus temperature curves are characteristic of an immiscible two-phase system.

The dynamic mechanical properties of copolymers are strongly influenced by the characteristics of the homopolymer and the copolymer composition. In a homogeneous copolymer all molecules have the same chemical composition, and hence should have a single sharp α-transition (T_g). On the other hand, the damping curves of the dynamic properties of heterogeneous copolymers reflect the broadening of the transition region caused by the increase in heterogeneity (Murayama, 1990).

The dynamic mechanical properties of an ABS resin is shown in Figure 2.26, where polybutadiene particles are dispersed in a phase of styrene acrylonitrile copolymer (SAN) with the formation of graft bonds on its boundary.

The dependence of dynamic mechanical properties on the amount of components is shown in Figure 2.27 (Moore, 1989). The samples of different compositions were prepared by using PVC and butadiene-acrylonitrile rubber (NBR). The dynamic modulus and loss modulus are shifted on the temperature scale in proportion to the relative concentration of two polymers.

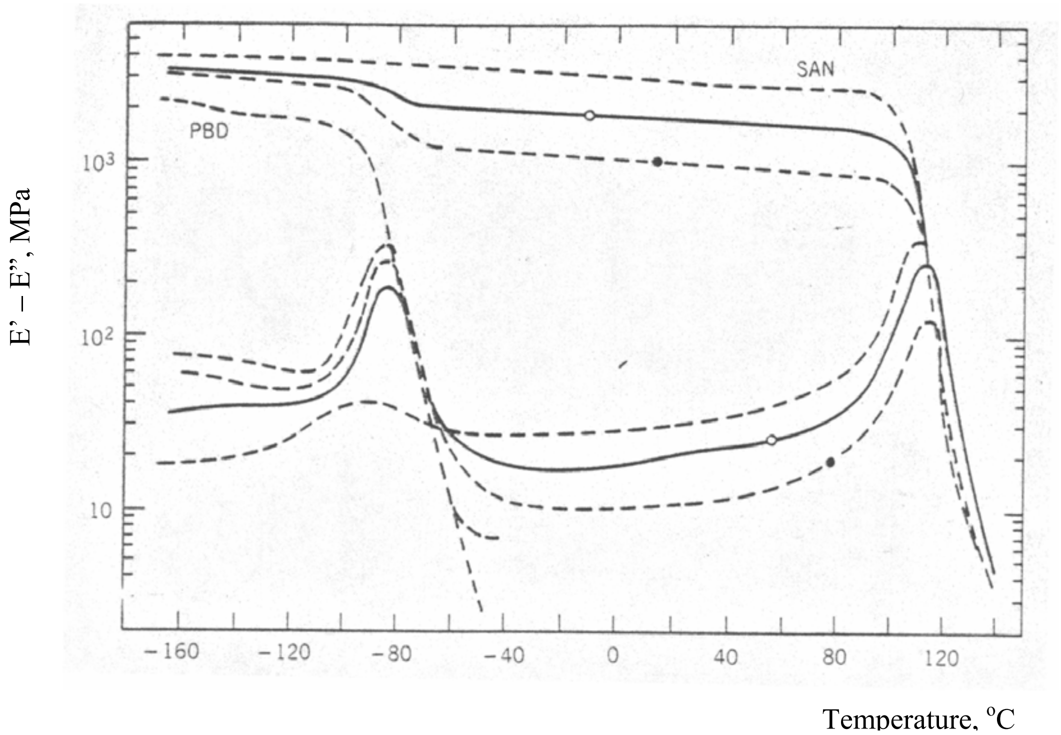


Figure 2.26 : E' – E" versus temperature for polybutadiene in styrene acrylonitrile copolymer (SAN); -------- experimental; and ——— calculated: (SAN)/PBD: ○, 77/23; and ●, 56/44 (Moore, 1989)

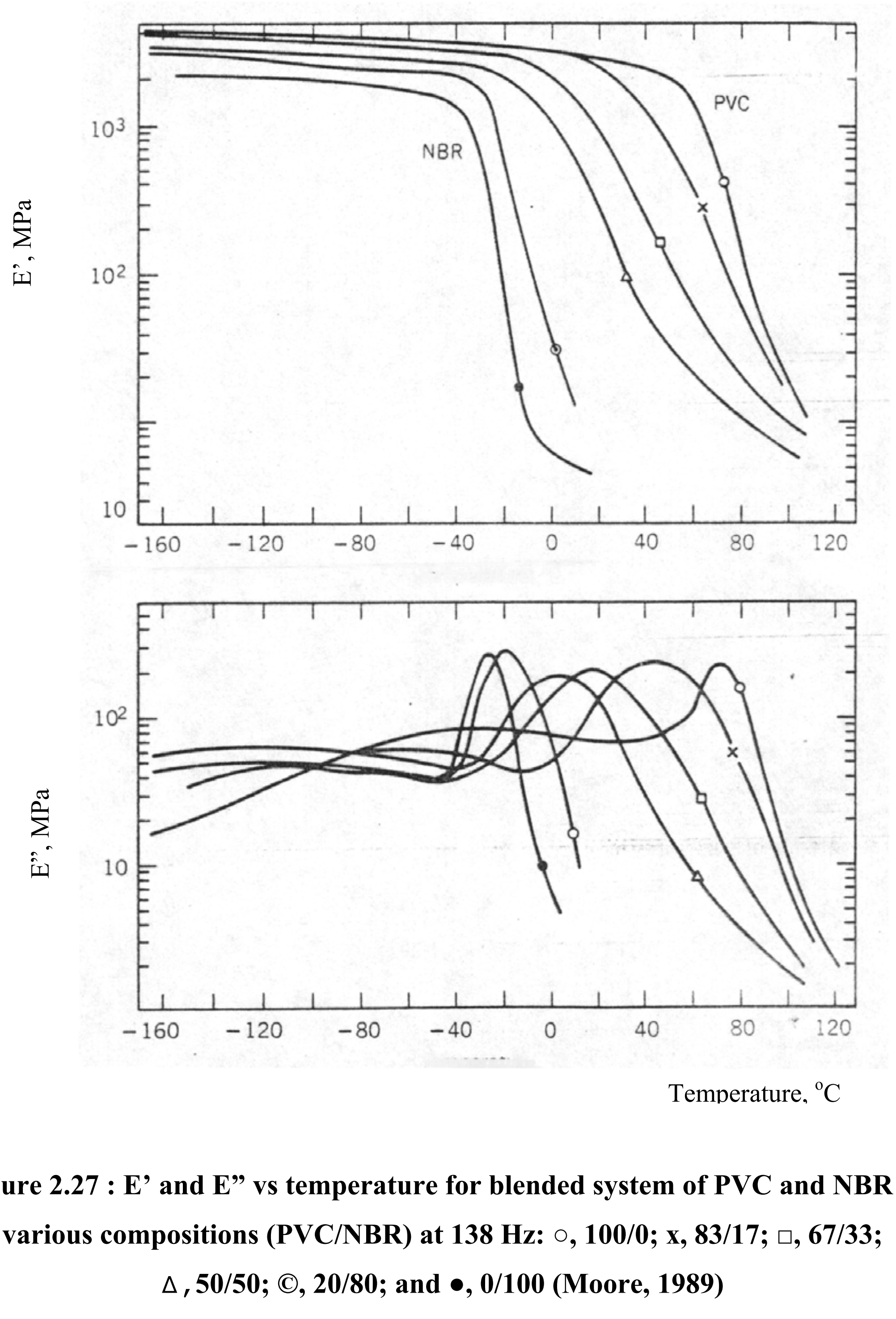


Figure 2.27 : E’ and E” vs temperature for blended system of PVC and NBR of various compositions (PVC/NBR) at 138 Hz: ○, 100/0; x, 83/17; □, 67/33; ∆ , 50/50; ©, 20/80; and •, 0/100 (Moore, 1989)

CHAPTER II

LITERATURE REVIEW

2.1 Acrylonitrile Butadiene Styrene (ABS Polymers)

2.1.1 General Introduction and Historical Background

The name ABS polymer is derived from the initial letters of three main monomers – acrylonitrile, butadiene and styrene, used in its preparation. ABS is not a random terpolymer of acrylonitrile, butadiene and styrene. Industrially important ABS polymers are two-phase polymer systems that consist of dispersed polybutadiene (or a butadiene copolymer) rubber particles and a matrix of styrene-acrylonitrile copolymer (SAN). The rubber particle is grafted with styrene and acrylonitrile to enhance their compatibility with the matrix.

The fraction of rubber content in ABS is varies from 10-25% for common commercial grades and special grades, e.g. for blending with poly(vinyl chloride) can even contain over 45% rubber. The higher rubber content and the different type of polymer forming the continuous phase result in the ABS polymers having a number of properties better than common grades of high-impact polystyrenes.

Introduced commercially in the 1940s, ABS is a polymer whose sales have grown over the years to become the largest engineering thermoplastic in the world. In 1982, the consumption of ABS polymer in the individual Western countries varied from 0.3 to1.5kg per person (Svec *et al.,* 1990). In the U.S. alone, sales in 1989 exceeded 1.2 billion pounds (Brisimitzakis, 1994). Demand in the U.S. for engineered plastic is projected to advance four percent per year through 2006 to 1.6 billion pounds, valued at $3.11 billion. The demand for engineering thermoplastics in the year of 2001 is shown at Figure 2.1, with ABS has the largest consumption rate (28.8%) compare with the others (Freedonia Industry Study, 2002).

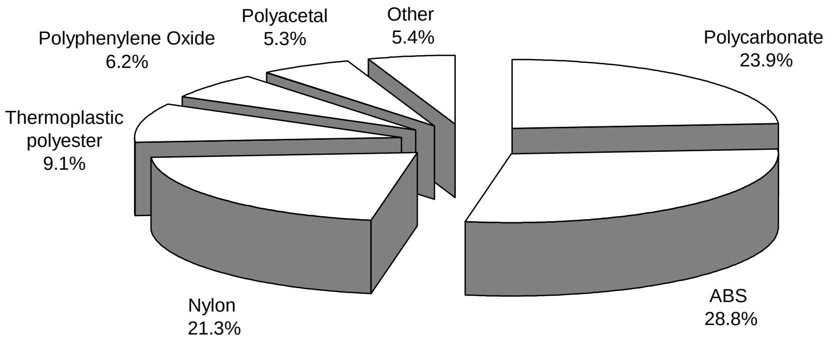


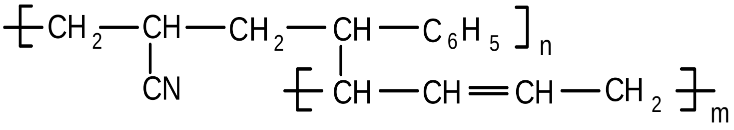
Figure 2.1 : Engineered plastics demand, 2001 (Freedonia Industry Study, 2002)

2.1.2 Chemistry and Manufacturing

ABS consists of two phases, a continuous phase of styrene-acrylonitrile (SAN) copolymer, and a dispersed phase of grafted polybutadiene particles. Each of these phases contributes unique characteristics to the polymer.

2.1.2.1 Chemistry

Each of the three monomers, acrylonitrile, butadiene, and styrene, is important component of ABS. The fundamental repeating unit of the ABS chain is:



$$\left[CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2-\underset{\displaystyle \left[CH-CH=CH-CH_2 \right]_m}{\underset{|}{CH}}-C_6H_5 \right]_n$$

Common types of ABS polymers have an average composition of 21 to 27% acrylonitrile, 12 to 25% butadiene and 54 to 63% styrene. Acrylonitrile primarily offers chemical resistance and heat stability; butadiene delivers toughness and impact strength; and the styrene component provides ABS with balance of clarity, rigidity, and ease of processing (Svec *et al.,* 1990).

Styrene and acrylonitrile can be copolymerized to form SAN copolymers, typically at a 70/30 ratio of S/AN. Like polystyrene, SAN is a clear copolymer, but with the additional characteristics of higher chemical resistance, better surface hardness, and improved toughness (Pillichody and Kelly, 1990). This copolymer is a commercially significant product, with major applications in markets such as battery cases, disposable cigarette lighters, and house wares.

ABS polymer systems typically contain between 70 and 90% SAN. In forming the continuous phases of the ABS, the SAN contributes its characteristics of easy processing, high strength, and rigidity, chemical resistance, and good surface hardness and appearance. The second phase of the two-phase ABS system is composed of dispersed polybutadiene (rubber) particles, which are grafted on their surface with a layer of SAN. The layer of SAN at the interface forms a strong bond between the two phases, which allows the polybutadiene rubber to add toughness to the ABS system, forming a rigid, impact-resistant product. The rubber phase is typically present in the range of 10-30% (Glenn and Cathleen, 1985).

Manipulations of the two phases produce the range of polymer characteristics seen in the different ABS products. The major variables of the SAN phase are the acrylonitrile level and molecular weight. The rubber level can be varied to adjust the impact strength of the polymer. Resin properties are also strongly affected by the rubber particle size distribution, the molecular weight, and cross-link density of the rubber as well as by the molecular weight, composition, and level of the SAN graft on the rubber particle surface. Normally, ABS with high rigidity has higher styrene content. Super high impact ABS possesses higher composition of butadiene if compare to medium impact ABS.

2.1.2.2 Manufacturing

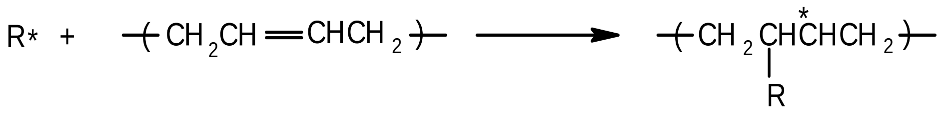
ABS polymers can be prepared by mechanical blending of the individual components or by grafted polymerization of a mixture of styrene with acrylonitrile in the presence of suitable rubber component. There are three commercial polymerization processes for manufacturing ABS: emulsion, suspension and bulk. The most common technique for producing the grafted polybutadiene phase is emulsion polymerization.

2.1.2.2.1 Mechanism of Grafting

Grafting of the styrene-acrylonitrile copolymers onto an elastomer is achieved by copolymerization in the presence of the elastomer. Possible mechanisms include radical abstraction from the polybutadiene (Bach and Knorr, 1989):

$$\mathrm{R{*}} + \;-\!\!\left(\mathrm{CH_2CH{=}CHCH_2}\right)\!\!- \longrightarrow \mathrm{RH} + \;-\!\!\left(\overset{*}{\mathrm{C}}\mathrm{HCH{=}CHCH_2}\right)\!\!-$$

or radical addition to polybutadiene:



$$R^* + -\!\left(CH_2CH{=}CHCH_2 \right)\!- \longrightarrow -\!\left(CH_2\underset{\substack{|\\ R}}{CH}\overset{*}{C}HCH_2 \right)\!-$$

R^* is an initiator radical from a growing copolymer chain. Radical attack on the substrate polybutadiene competes with formation of styrene-acrylonitrile copolymer

$$R^* + nM \longrightarrow RM_n^*$$

with M = Styrene or acrylonitrile monomer.

M_n^* = linear styrene-acrylonitrile polymer radical.

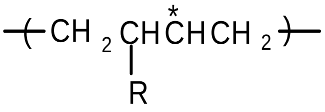
$L^* + nM \longrightarrow LM_n^*$ (grafting by addition)

$L^* + M_n^* \longrightarrow LM_n$ (grafting by termination)

$L^* + L \longrightarrow L - L^*$ (cross-linking)

$L^* + RSH \longrightarrow LH + RS^*$ (chain transfer)

where L^* = $-\!\left(\overset{*}{C}HCH{=}CHCH_2 \right)\!-$ or



$$-\!\left(CH_2\underset{\substack{|\\ R}}{CH}\overset{*}{C}HCH_2 \right)\!-$$

RSH = chain-transfer agent.

2.1.2.2.2 Emulsion Technology

It is possible to produce the final product in a single step by grafting in emulsion. A typical commercial emulsion process is shown in Figure 2.2. It involves five steps: rubber polymerization, agglomeration, grafted polymerization, polymer recovery and compounding (Chang *et al.*, 1997).

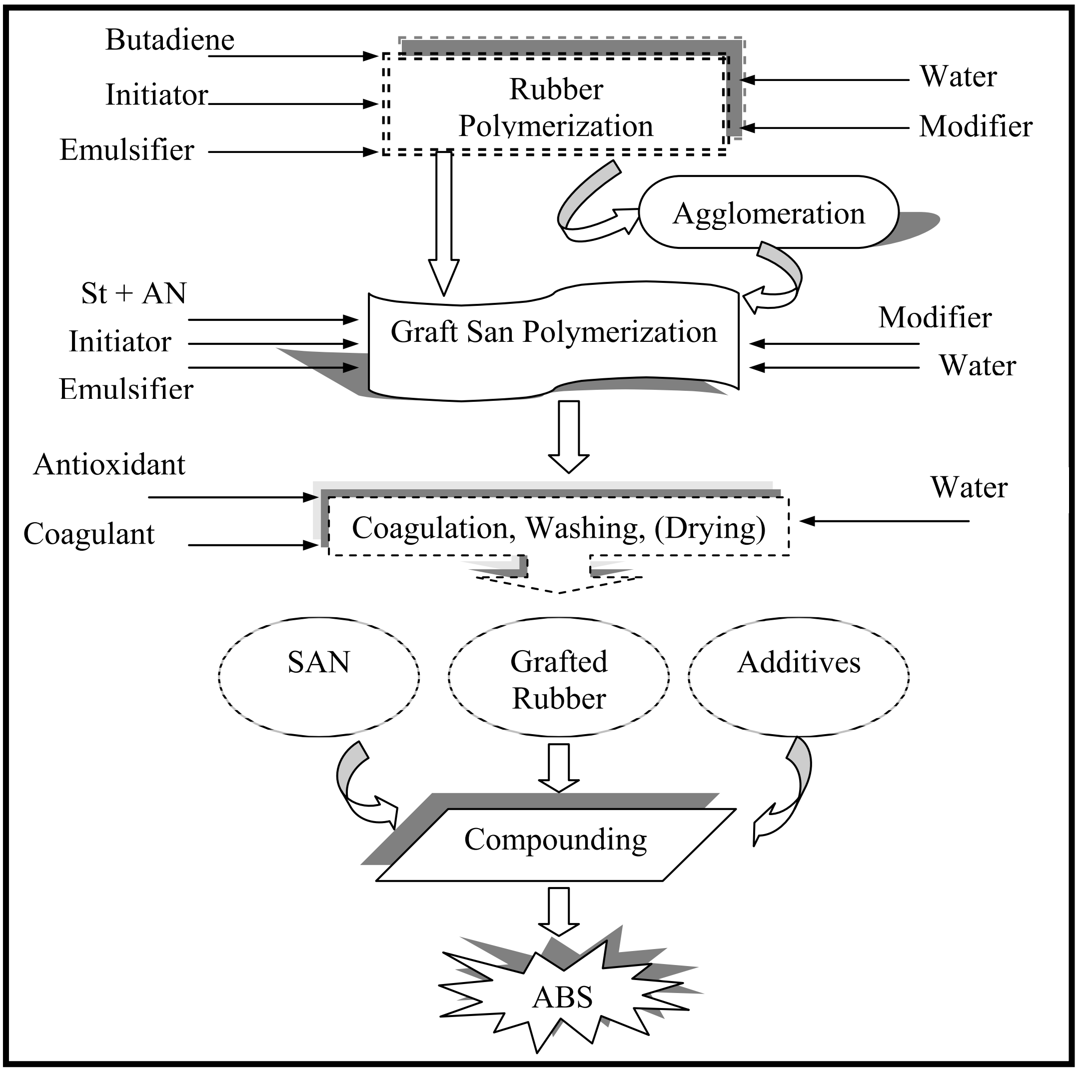


Figure 2.2 : Emulsion ABS polymerization process

The emulsion-mass procedure is used by Toray Industries to prepare ABS polymer. First, part of the styrene and acrylonitrile are grafted onto the polybutadiene in emulsion. The latex particles are then extracted into a newly added monomer mixture in the presence of a coagulant. After separation of the aqueous phase, the partially grafted polybutadiene forms a stable dispersion in the styrene-acrylonitrile mixture. Further polymerization is a continuous mass process; the first stage (up to conversion of 40 to 70%) is carried out in a stirred autoclave and the next stage in a tower plug-flow reactor. The heat of reaction is removed by a cooling jacket. The polymerization is maintained at the boiling point. The unreacted monomers are removed in the evacuated zone of the extruder. A schematic diagram is shown in Appendix A.

2.1.3 Properties

The properties of ABS polymers are strongly affected by the molecular characteristics of both the elastomers phase and the SAN copolymer forming the matrix. Table 2.1 summarized the effects, which will occur under some situations. The properties of this multi-phase system are also affected by conditions at the interface between the rubber and the thermoplastic matrix (Svec *et al.*, 1990). The effect of rubber level is extremely important, and the major trade-offs from increased rubber level are shown in Figure 2.3.

ABS polymer has low density (1020 to 1060 kgm^{-3}) and the bulk density of the pellets is also low, usually 500 to 600 kgm^{-3}(Pillichody and Kelly, 1990). The material is opaque as a result of the different refractive indices of the two phases. The presence of the polar nitrile group results in certain affinity of the ABS polymer for water or water vapour. An increase in the humidity content will lead to complications in processing and to deterioration in some properties.

Table 2.1 : Effect of molecular characteristics of the elastomer phase and SAN copolymer forming the matrix (Svec *et al.*, 1990)

Increase molecular weight of the SAN	Narrow molecular weight distribution	Broad molecular weight distribution	Increase the content of elastomers
Increase resistance to surface-active substances	Improve dimensional stability	Increase heat and pressure sensitivity of the melt	Decrease heat deformation resistance
Impact strength increase	Decrease in shrinkage	Improve flow properties	Increase melt viscosity
Suppression of creep	Increase creep resistance		Improve the impact strength
Tensile strength increase	Tensile strength increase		Ageing resistance decrease
Fluidity decrease			Stiffness increase

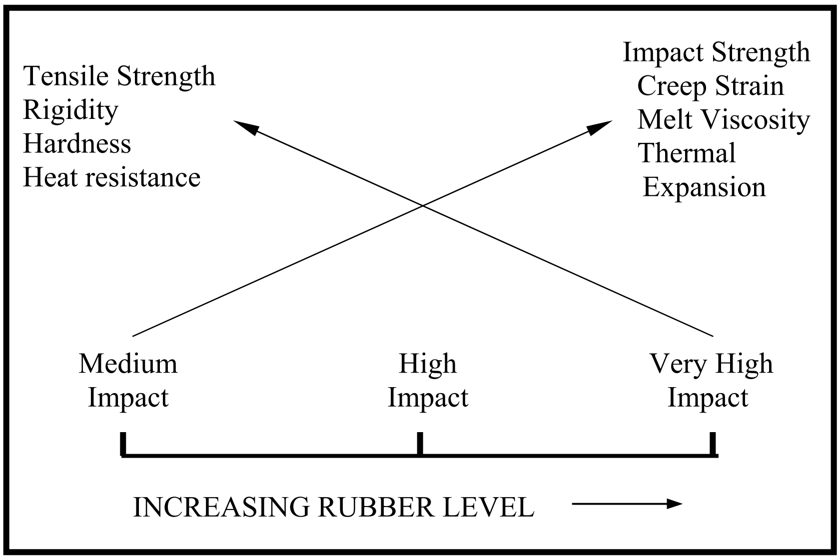


Figure 2.3 : Major property trade-offs for ABS with increasing rubber level. (Glenn and Cathleen, 1985)

2.1.3.1 Mechanical Properties

The overall toughness offered by ABS materials is the prime mechanical property that prompts most users to select ABS for their applications. The standard measure of impact strength used for ABS is notched Izod impact strength, as measured by ASTM D256A. Depending on its impact strength, material is classified as very high-, high- or medium-impact polymer. As pointed out previously, its value determines in which class of standard product a material belongs. Although ABS is notch sensitive, it is much less so than many other polymers, including polycarbonate and nylon. In addition to good impact strength at room temperature, ABS retains significant impact strength at very low temperatures (Svec *et al.,* 1990). This has led to the use of ABS in critical low-temperature applications. ABS materials can deform in a ductile manner over a broad temperature range and at high strain rates. This deformation is accompanied by a significant whitening of the specimen resulting from craze formation and separation of the rubber phase from the matrix polymer.

Another important characteristic of engineering thermoplastics is their stress-strain behavior in flexure. Such measurements are usually made using a simple supported beam test specimen loaded at mid-span according to ASTM D790. As with tensile properties, the flexural strength at yield and flexural modulus can be used to determine the resistance of a product to short-term loadings (Norbert, 1971). They are also useful in comparing the strength and rigidity of the many ABS products.

For many applications, multiaxial impact strength, typically measured using a falling or driven dart, is as important as Izod impact strength. Reporting of multiaxial impact strength is not yet common practice; however, data is now available from manufacturers for many products. Although the two types of tests do not directly correlate, products demonstrating high Izod impact strength in general demonstrate high multiaxial impact strength. Neither of these impact tests produce in- formation that is mathematically applicable to design. The anticipated level of abuse a product will see in a particular application, combined with the designer's experience, will determine the impact class selected (Bucknall, 1977).

The Rockwell hardness (RH) of products is useful in comparing the ability of the surface of a part molded from different products to resist becoming blemished by intermittent loads (Norbert, 1971). The specific gravity of different standard ABS products does not vary much. However, it does vary significantly for many of the specialty grades and alloys.

2.1.3.2 Thermal Properties

The critical thermal properties for ABS are heat distortion, coefficient of linear thermal expansion, thermal endurance, thermal conductivity, and specific heat.

The most common measure of heat distortion is the deflection temperature under load as measured by ASTM D648. High-heat ABS, ABS/polycarbonate (PC) alloys, and ABS/styrene-maleic anhydride (SMA) alloys all extend applications of ABS into the temperature up to 110°C at 1.8 MPa for short-term exposures (Jenker and Köln, 1983).

In general, plastics have significantly higher thermal expansion co-efficients than metals. Consequently, in applications where parts are constrained, thermal stresses must be accommodated in part design or expansion may induce failure in the part. This property is especially important in ABS products designed for electroplating (Moh *et al.*, 1997).

The thermal properties of ABS polymers are characterized mainly by the glass transition temperature, Tg. An increase in temperature of the material leads to a decrease in the tensile strength and an increase in the ductility and toughness. However the modulus of elasticity in tension decreases (Svec *et al.*, 1990).

2.1.3.3 Flammability

Basically, ABS has a low LOI index with a range of 17-18 % (Pál and Macskásy, 1991). ABS materials without flame retardant are easily burned with a luminous yellow flame, smoking strongly and continue to burn after removal of the ignition source. The high impact ABS will has a smell of burnt rubber (Troitzsch, 1980).

ABS grades that meet various standards for flammability performance are available. The non-flame retardant (FR) general-purpose grades are generally classified as 94HB according to Underwriters' Laboratories Test Method UL94, and also meet Motor Vehicle Safety Standard 302. These grades are used in applications having a reduced fire risk. For applications requiring higher degrees of flame retardancy, ABS grades have been developed based on alloys with PVC or through an additive approach using halogen in combination with antimony oxide. Included among the FR grades are materials that meet the Underwriters' UL94 VO requirements beginning at a minimum thickness of 1.47 mm (Bach and Knorr, 1989).

2.1.3.4 Rheology

Factors influencing melt flow behavior of ABS include (Moh *et al.*, 1997):

(1} The presence of the grafted rubber domains, their weight fraction, graft to rubber ratio, particle size and distribution;
(2) The composition, molecular weight and molecular-weight distribution of the matrix;
(3) Additives, ie, lubricants, stabilizers, fillers, pigments, etc;
(4) Residual components from the polymerization process; and
(5) Water.

The presence of the grafted rubber increases viscosity; the viscosity effect increases with decreasing shear rates and increasing rubber content. Residual volatile components and lubricants can function as diluents to reduce viscosity. It has been suggested that their influence on viscosity may depend on whether such materials preferentially reside in the rubber or matrix phase (Glenn *et al.*, 1985).

2.1.3.5 Ultraviolet Resistance

Exposure to ultraviolet (UV) radiation will induce irreversible chemical changes in most organic polymers, including ABS. The extent of degradation depends on the polymer structure, the influencing of prior processing conditions, the effects of additives, the exposure conditions and the presence of protective coatings. UV degradation results in appearance changes characterized by increasing yellowness and an initial embrittlement of the plastic’s outer surface.

ABS is used successfully in many products that are subjected to outdoor exposure for brief periods of time. However, for extended outdoor exposure, measures must be taken to minimize property reduction and changes in appearance. Protection is afforded by UV stabilizer, pigments, paints and film laminates (Glenn *et al.*, 1985).

2.1.3.6 Chemical Resistance

ABS products show very good resistance to chemical attack and most products have good environmental stress-cracking resistance (Svec *et al.*, 1990). ABS is resistant to acids (except concentrated oxidizing acids), alkalis, salts and essential oils. It is, however, attacked by many solvents including ketones and esters.

2.1.4 Processing

2.1.4.1 General Processing

ABS material can be processed by injection molding, extrusion, blow molding or calendaring. However, injection molding and extrusion account for more than 93 % of all ABS material usage. ABS polymers process very easily and can be fabricated into very complex parts. ABS requires significantly lower processing temperatures and is less sensitive to processing conditions (Brisimitzakis, 1994).

2.1.6.2 Preheating and Predrying

ABS materials are hygroscopic, and have an equilibrium moisture content of 0.3-0.4 % at 23 °C and 50 % relative humidity. While mechanical properties in the finished part are not greatly affected by this moisture, its presence during processing can affect the part appearance greatly. Maximum moisture levels of 0.2 % are suitable for injection molding and maximum levels of 0.03 % are suitable for extrusion of ABS materials. These moisture levels can be reached by drying the material prior to processing in a dehumidified air drier (Glenn and Cathleen, 1985).

2.1.5.3 Extrusion

An extruder with a minimum L/D ratio of 24:1 is recommended to ensure a uniform mixing and melt temperature over the die. A screen pack consisting of a 20-40 mesh combination is recommended. Single or two-stage screws are suitable. However, the latter part is preferred since it also aids in devolatilization and results in an improved extrudate quality (Pillichodyand Kelly, 1990).

2.1.5.4 Injection Moulding

ABS polymers can be processed in all types of injection molding equipment, but optimum results are obtained with reciprocating screw machines since it provides more uniform melt and higher available pressure. Processing temperatures range from 177 to 288 ^{o}C, depending on the specific grade. Injection pressure of 69-138 MPa and clamp pressure of 281-422 kg/cm^2 of projected part surface are usually sufficient. Screw having a length to diameter (L/D) ratio of 20:1 are recommended (Glenn and Cathleen, 1985).

2.1.5 Advantages and Disadvantages

ABS, being copolymerized from three different monomers, has high impact strength and competes well with polypropylene, although it is more expensive. Its dimensional stability is good; it replaces die-cast metal components and can be electroplated. ABS is excellent for vacuum-forming and blow-moulding for the production of articles such as fire extinguishers, bus wheel arches, industrial containers, refrigerator shells and protective helmets. Basically, ABS is preferred for its favorable balance of strength, toughness, high gloss, colorability, processability and price.

The balances of properties which are exhibited by ABS are not found in any other plastics material. Specialist applications can be tailor-made by adjustment of the proportions and arrangement of the three parts of the copolymer, thus emphasizing the character of the components.

Besides the advantages, the material has also a number of limitations. The disadvantages are as follows:

1) Limited chemical resistance to hydrocarbon and concentrated acids and alkalis.
2) It is mostly opaque.
3) Electrical properties are not outstanding; however, they are adequate for most purpose.
4) It is easily burn with high flammability value.

2.1.6 Specialty Grades

High Heat Grades. High-heat grades of ABS are produced by increasing the molecular weight, and the acrylonitrile content, while reducing the total rubber present. Most recent work has employed an additive approach (Adam *et al.,* 1993). These products have property balances similar to those of standard ABS except for significantly improved heat resistance. They are somewhat more difficult to process because of the higher melt viscosity, and they are relatively expensive. Alloys of ABS with styrene-maleic anhydride (ABS/SMA) offer similar property balances with a lower melt viscosity at a similar cost (Glenn and Cathleen, 1985).

Chemical Resistance. One of the advantages of ABS relative to reinforced polyolefins and high impact polystyrene is its chemical resistance. The polar nitrite groups make ABS quite resistant to a variety of solvents and uptake of water is relatively low (<1 %) (Adam *et al.,* 1993). This chemical resistance has allowed ABS entry into a wide variety of home appliances and some automotive areas.

Flame Retardant Grades. Standard grades of ABS are considered slow burning polymers, and most meet Underwriters Laboratories requirements for a UL94 HB rating. ABS can be modified using halogenated additives to meet more stringent flammability requirements. These flame-retardant grades offer a balance of properties similar to medium-impact standard ABS grades (Glenn and Cathleen, 1985). Grades with high flexural modulus or with improved light stability are also offered. Many ABS/PVC alloys also meet these flammability requirements. These grades are important for electrical housing applications and contribute to a significant fraction of ABS usage. Halogenated and phosphorus additives are generally used as flame retardants, though halogenated styrene can be copolymerised into the ABS (Uhlmann, 1993).

Clear ABS. Clear ABS is a transparent ABS material, which the basis is the matching of the refractive indices of each of the rubber core, graft and matrix phases (Adam *et al.,* 1993). Clear ABS grades use methyl methacrylate as a fourth monomer to match the refractive indices of the other monomers (Glenn and Cathleen, 1985). The process is complicated by the fact that the refractive indices have to match over the temperature range of use, so that the change in refractive index with temperature must also match (Jalbert, 1991). Properties are similar to those of medium-impact standard ABS grades.

Plating Grades. ABS can be electroplated in the same process used for metals after being prepared via a preplate system, which etches the surface using chromic acid and deposits an electroless layer of copper or nickel, rendering the surface conductive. ABS also lends itself to plating (Glenn and Cathleen, 1985). Such grades are commonly used in car mirrors, headlight bezels and faucets (taps). Chrome plated ABS faucets can be made in styles that cannot be made in metal (Adam *et.al,* 1993). These products also offer a relatively low coefficient of linear thermal expansion which reduces stresses between the metal plate and the ABS during exposure to extremes in temperature.

Filled ABS. A filled ABS has a higher strength, rigidity, modulus and high temperature dimensional stability by adding glass fiber and is suitable for stressed structural applications (Adam *et al.*, 1993). This filled ABS is commonly used is in skis and applications in the automotive industry such as car dashboard supports. Stainless steel filled ABS can be used when more effective shielding from electromagnetic interference is required.

2.1.6 Application

Their broad property envelope, wide processing latitude, and favorable price and performance balance has allowed ABS based products to participate in a wide variety of markets.

Transportation is the largest market for ABS in U.S. Automotive uses are many and include interior and exterior applications. For interior injection molded application, high heat, general purpose, and low-gloss grade have been developed for application. A unibody plastic trailer was designed by using coextruded sheets of Bayer's Lustran ABS is shown in Figure 2.4. This prototype design won in an Automotive Award and People's Choice Award (Molinaro, 1999a). Besides, ABS resin is thermoformed to produce an electric motorbike called the Lectra VR24 (see Figure 2.5) (Molinaro, 1999b).

In the U.S., about 250 million lb. of resin were consumed in appliance market in 1989 (Brisimitzakis, 1994). Most of this consumption was for major appliances with extruded/thermoformed door and tank liners leading the way. Other applications include injection molded housings for kitchen appliances, power tools, vacuum sweepers and hair dryers.

Business machine is a large "value added" market for ABS. Flame-retardant grades have found strong market fits in computer housings and consoles. Closely related is the telecommunication market where by virtue of its exceptional esthetics and good flow/impact balance, ABS resin is enjoying healthy growth in applications such as telephones and modems. A new invented printer/embosser enclosure for a tabletop card personalization system which made by flame retardant ABS had won an Industrial Enclosure Award (Johnson, 1998) (see Figure 2.6).

ABS is used widely in building and construction industry, particularly in extruded drain, waste and vent pipe and injection fittings applications. Consumer and industrial markets contain numerous ABS applications crossing many market segments. These include toys, medical devices, furniture, cosmetic packaging and luggage (Brisimitzakis, 1994). The manufacturers of ABS polymers are constantly introducing new types, with better technical, application and aesthetic characteristics.

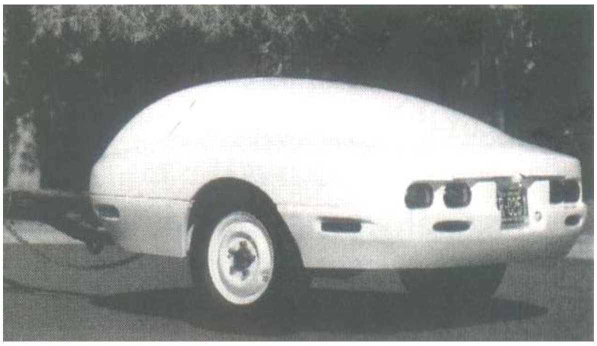


Figure 2.4 : Automotive Award and People's Choice Award : Unibody plastic trailer

Figure 2.5 : ABS resin speeds motorbike to market

Figure 2.6 : Industrial Enclosure Award: Printer/embosser enclosure for a tabletop card personalization system

2.2 Poly(vinyl chloride) (PVC)

2.2.1 What is PVC ?

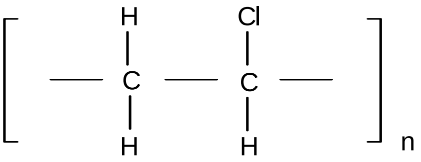
According to Titow, the abbreviation ‘ PVC ’ has one of two meanings, depending on the context in which it appears, viz.

(a) ‘ Poly(vinyl chloride) ’, i.e. the homopolymer of vinyl chloride, or

(b) *as a noun* : a member (or, collectively, the whole) of the large family of plastics materials based on poly(vinyl chloride) and /or vinyl chloride copolymers;
as an adjective : of the nature of, or pertaining to, such member or family.

PVC is the second most widely used thermoplastic polymer. The resin produced in 1999 (15 billion pounds) translates into over 100 billion pounds of compound worldwide. As an amorphous polymer, PVC resin is extensively formulated to produce an extremely large variety of compounds (Blanco, 2000).

The fundamental repeating unit of the PVC chain is:



$$\left[-CH_2-CHCl- \right]_n$$

Where “n” denotes the degree of polymerization. In general, the higher the molecular weight, the greater the difficulty in processing and the higher the physical properties. In commercial resins, the number average molecular weight is in the range of 50,000 to 100,000[6].

2.2.2 Historical Background

The early development of PVC is highlighted in Table 2.2 (Titow, 1990).

Table 2.2 : Historical background of PVC

Year	History
1835	VCM was first prepared by Regnault.
1872	Baumann discussed the reaction of vinyl halides and acetylene in a sealed tube.
1921	Plausen discovered how to polymerize PVC from dry acetylene which made PVC more than a laboratory curiosity.
1928-1930	Patent disclosures of VC/VAC copolymers and polyvinyl halides. Introducing of emulsion polymerization to prepared vinyl chloride.
1930	Plasticisation of PVC by phthalate ester. Introduction in non-rigid vinyl chloride plastics. Suspension polymerization of vinyl chloride in England and Germany. Technical production of chlorinated PVC polymer and fibres. Commercial production of PVC polymers in Germany and USA.
1942-1943	Commercial production of PVC polymers in England.

The outbreak of the world II was a boost to the PVC industry. It was during this period that PVC substituted highly costly rubber in some important applications, notably as insulation and covering for electrical wires and cables (Titow, 1990). Now, PVC has been used extensively to become one of the worlds leading synthetic polymers since it is relatively cheap and versatile.

2.2.3 Chemistry and Manufacturing

2.2.3.1 Vinyl Chloride Monomer (VCM)

Acetylene, ethylene, chlorine and oxygen feedstocks are necessary to manufacture vinyl chloride monomer. The process by which feedstock is converted to VCM is shown in Figure 2.7. In the early days of VCM production, acetylene was the dominant method; today, only 7 % of the VCM is so manufactured. The remainder is produced by oxychlorination (Figure 2.8) (Titow, 1990).

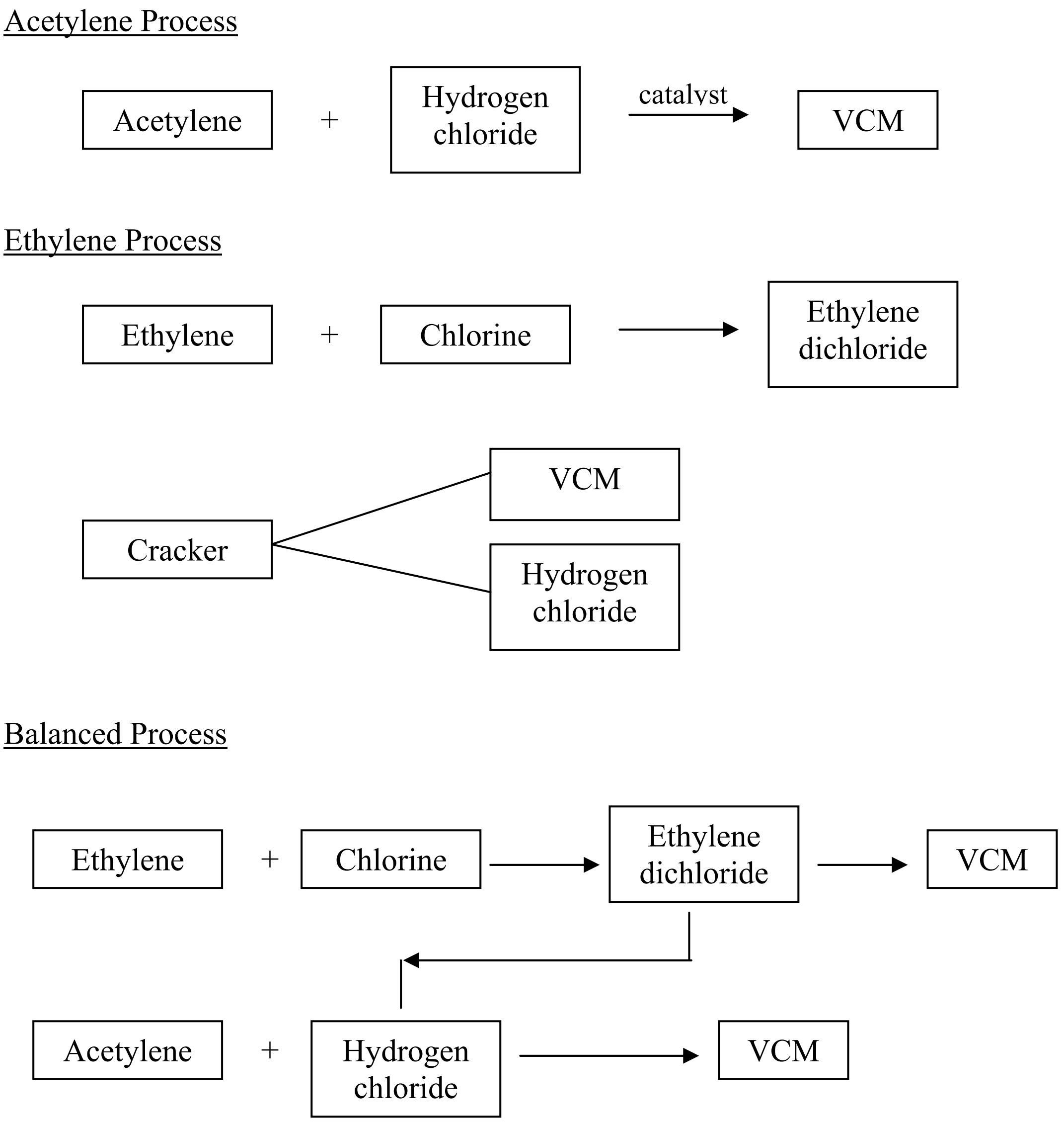


Figure 2.7 : Feedstock conversion to vinyl chloride

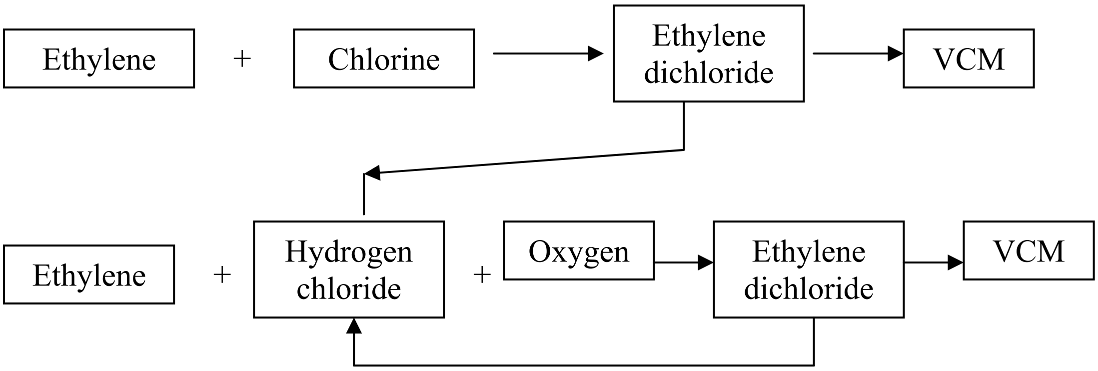


Figure 2.8 : Oxychlorination process

At normal temperature and pressure, VCM is a colorless, dense, pleasantly sweet-smelling gas. VCM is soluble in aliphatic and aromatic hydrocarbons and insoluble in water. Since 56.7 % of the monomer is chlorine, neither VCM nor PVC prices is dominated by oil and gas prices (Gobstein, 1990).

2.2.3.2 Polymerization Process

The polymerization techniques used to produce PVC polymers are suspension, mass (bulk) and emulsion routes. Due to technological and economic advantages, the suspension polymerization process dominates 76% share of the market (Kunststoffe, 1989). The difference between the three types of polymerization process is shown in Appendix B.

Commercial PVC materials are often classified according to the polymerization method, and the molecular weight of the materials. The molecular weight of the polymer is often quoted in terms of a K-value. It is a measurement of the viscosity of dilute solution. The molecular weight of PVC is controlled by the polymerization temperature (Coaker and Wypart, 1993). Block diagram of each method is stated at the Appendix C-G.

The PVC resin used in this research is suspension grade. The suspension polymerization process is sometimes referred to as pearl, bead, or granular processing. PVC so produced has relatively large particles (40 to 200 mesh), low levels of impurities and resembles in particle form (Gobstein, 1990).

2.2.4. Morphology and Properties

Commercial PVC polymers is a "head to tail", essentially amorphous in nature (Katz, Shkolnik, & Ron, 1976) with low degree of crystallinity (8-10% as determined by X-ray diffraction). The crystallinity is associated with the stereo regular (syndiatactic) polymer fraction: high syndiotactic polymer has a higher crystallinity (De Coste, & Hansen, 1962). It contains 0.4 to 1.1 branches per 100 carbon atom chain.

The PVC resin particle is unusual in structure. After polymerization, PVC possesses a specific morphology as illustrated in Figure 2.9. Powder particles which are visible to the naked eye are known as grains. Its glass transitional temperature (T_g) of about 80-84 ^oC varies with the polymerization temperature. The melting point varies with molecular weight, molecular weight distribution and polymerization temperature (Gobstein, 1990).

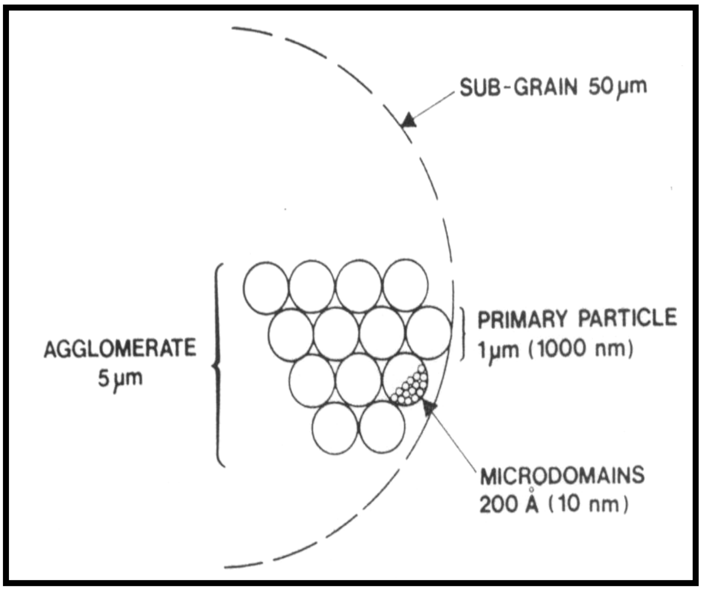


Figure 2.9 : PVC particle morphology

2.2.4.1 Mechanical Properties

The general relationship of physical properties to molecular weight can be represented as in Figure 2.10. As the molecular weight is increased, the mechanical properties (strength) increase. The effect is generally most pronounced for low molecular weight, where properties such as tensile strength, elastic modulus, and impact strength are all low or perhaps even essentially nonexistant. As molecular weight increases, almost all useful mechanical properties are increased but with sequentially diminishing returns. The only useful property lost with increasing molecular weight is melt flow, as described in the preceding section. Thus chosing the right molecular weight is an optimization between mechanical properties and process ability.

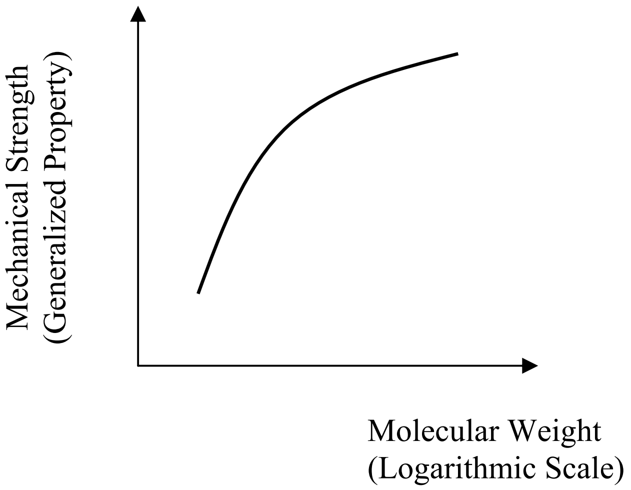


Figure 2.10 : Schematic curve showing the effect of molecular weight on most mechanical properties of PVC. The exact nature of the plot will depend on the mechanical property selected (Donald, 1986)

According to Donald (1986), a great variables ranging from the degree of crystallinity and the state of the glass to the detailed morphology of the specimen, as determined by the compounding ingredients, the starting particles morphology, and the degree of fusion (processing conditions), can all play an important role for the mechanical properties of PVC particles. Small changes can and do make substantial and sometimes quite surprising difference in the outcome.

2.2.4.2 Thermal Properties

The thermal degradation of PVC is considered by most experts to be a major disadvantage of this material. Upon exposure to temperature as low as 100 to 120 °C or upon exposure to ultraviolet radiation, PVC undergoes a degradation reaction that releases hydrochloric acid and forms long polyene sequences of conjugated double bonds.

The longer polyene sequences are intensely colored and only small amount of them can make the PVC appear black. The following values have also been quoted for *Welvic* (ICI, UK) rigid PVC moulding materials (Titow, 1990):

Specific heat at 20 °C	110 Jkg^{-1} °C^{-1}
Thermal conductivity at 20 °C	0.17 Wm^{-1} °C^{-1}
Appproximate total heat (moulding)	270 X 10^{6} Jm^{-3}

2.2.4.3 Melt Viscosity

Melt flow of PVC is a complex situation. At low melt temperature (probably below 200 °C and high syndiotactic polymer), a model of tiny elastic balls that might be lubricated to flow past one another if lubricant is present in the compound might be a more accurate flow model than melt. At higher melt temperatures and low syndiotacticity, and without lubricant, the PVC melt might be more like a true melt.

Basically, molecular weight and shear rate both can change the melt viscosity. PVC with lower molecular weight can reduced the melt viscosity and shear heat generation in the melt significantly (Titow, 1990).

2.2.4.4 Flammability Properties

The flammability of PVC (resin and solid uPVC composition) as determined in standard test is one of the lowest among those of the common plastics. The low flammability is due to the large chlorine content: like the other halogens. Chlorine acts as a retardant in the process of combustion. However, the smoke emission is relatively high and the smoke is irritant and toxic. The smoke evolution can be limited by adding smoke suppressants such as $CaCO_3$ and $MgCO_3$ (Troitzsch, 1980).

The performance of PVC compositions in flammability test falls with increasing dilution of the polymer by the other formulation components (which decrease the overall chlorine content). This is the well known fact that plasticisation increases flammability.

2.2.5 Processing

PVC, in its predominantly dry compound form, is processed mainly by extrusion, calendering and injection moulding. It can also be blow molded into bottles and other parts or made into film on a blown film line. In the extrusion process, PVC compound is fused in an extruder by heat and pressure. The melt is forced through a die to produce a continuous flow. Whereas the injection moulding process develops melt in a method similar to the extrusion process. The melt is injected into a mold cavity by the forward movement of the screw, filling the mold to form the part. After cooling, the mold opens to remove the finished part (Bramfitt and Heap, 1962).

2.2.6 Advantages and Disadvantages

PVC, in all its forms and compounds, is the second largest volume plastic in the world. PVC exists as rigid PVC (RPVC), which is stiff, hard and sometime brittle. It also exists as flexible PVC (FPVC), which is soft and pliable. Basically, PVC can be compounded to posses any degree of rigidity or flexibility between these two extreme, depending on the required properties of the final product. As noted, 56.7 % of the molecular is chlorine. This means that the polymer's availability and pricing are not wholly related to oil or gas feedstock.

Other advantages of PVC are:

1) Relatively cheap and versatile
2) Excellent physical, chemical, electrical and weathering properties
3) Processability by a variety of techniques
4) Nonburning
5) Low water absorption
6) Good surface appearance

The disadvantages are:

1) Poor thermal stability makes processing difficult
2) Low heat deflection temperature (low rise temperature)
3) Poor creep at elevated temperature

2.2.7 Additives

Additives are incorporated into PVC to overcome the limitation of the polymer. The final properties of PVC product are highly dependant on the type and amount of additives presents in the compound. For example, depending on the amount of plasticizer added, PVC can either rigid or extremely flexible. The typical additives used in PVC product are (Gobstein, 1990):

1) Processing aids
2) Lubricants
3) Stabilizers
4) Fillers
5) Impact modifiers

The additives used in this research are lubricant and stabilizer. Further discussion will be based on these two additives.

2.2.7.1 Lubricant

A lubricant is a substance that, when added in small quantities, provides a disproportionate decrease in resistance to movement of chains or segments of polymer of at least partly amorphous structure, without disproportionate change in observable properties (Grossman, 1989).

The two major classes of lubricants are designated “internal” and “external”. It is important to obtain a balance between the external and internal lubricant. Lubricants perform several functions (Titow, 1990):

- Reduce frictional forces between resin chains (internal).
- Reduce frictional forces between the resin chains and the metal surface (external).
- Promote melt flow by reducing melt viscosity.

Calcium stearate act as an internal lubricant in PVC, to promote fusion and modify melt viscosity during extrusion processing. It also act as a co-stabilizer in many PVC applications when combined with a number of primary heat stabilizers (Mesch, 1994).Fatty acids are particularly effective as external lubricants in PVC when used in small amounts. These acids are compatible with PVC, making them particularly useful in applications where clarity is important (Mesch, 1994).

2.2.7.2 Stabilizer

PVC resin is heat sensitive and will degrade if it is exposed to a source of energy such as heat, light, pressure, and shear forces. It tends to cause chemical changes in the polymers that result in noticeable unwanted changes in their properties. Such changes include loss of mechanical strength, fluctuations in melt viscosity and lubricity that make processing more difficult.

The indication of PVC degradation is a dehydrochlorination. Dehydrochlorination is often detected in a compound through discolouration, for example, as the degree of chain unsaturation increases: white, cream, yellow, orange, red, light brown, brown, and finally black. Degradation leads to chain scission and cross linking; hence a loss in physical properties. More changes can occur during the service life of the finished article. Stabilizers, then, are chemical additives that prevent, arrest, or at least minimize such changes, and so “stabilize” the polymer (Kauder, 1989).

The thermal stabilizers commonly available in the market can be divided into 3 main groups. There are (Rabinovitch, Lacatus, and Summers, 1984):

- lead salts, soap, and other metal soaps or salts (Cd, Ca, Zn, Ba)
- organo-tin compounds, organic and miscellaneous stabilizers
- mixed stabilizers (synergistic mixture)

Organo-tin compounds with at least one tin sulfur bond are generally called organo-tin mercaptides. Stabilizers on the basis of these compounds are also called sulfur containing tin stabilizers or thiotins (Andreas, 1984).

2.2.8 PVC Industries and Their Products

The Freedonia Group forecasted that U.S. demand for PVC would increase by 3.4%/yr to 14.4 billion lbs in the year 2002, valued at $6.2 billion (Molinaro, 1999f). This would be driven by PVC’s cost and performance advantages over wood and metal, improvements in production and processing technologies, and the development of improved resin grades with enhanced properties.

Construction constitutes the largest market for PVC, according for 72% of the total demand in 1997 (Molinaro, 1999f). Despite declining housing starts, vinyl products will increasingly be used in remodeling and renovation projects, in which installation ease and low maintenance are highly desirable. Outside of construction, the largest volume PVC markets are insulated wire and cable; and packaging, including film, sheet, and bottles.

Three PVC compounds have been developed by the Geon Co. for a drum and pail pump in fluid-handling applications involving exposure to strong chemical and tough use (Molinaro, 1999g) (refer figure 2.11). A boots manufacturer used ultra-high molecular weight (UHMW) PVC polymer, which are said to offer increased strength, abrasion-resistance, and elasticity to manufacture the Flex3 footwear as shown in Figure 2.12 (Molinaro, 2000). Another example is a robust cash box moulded in PVC material (GAM Report, 2000).

An electric fencing consists of extruded PVC decorative fencing that is affixed with two aluminum conductive rails, is tasked with providing a psychological as well as a physical barrier for large animal (Molinaro, 1999h) (see Figure 2.13). Package for medical components which made of clear PVC had won a Critical Barrier Packaging Award (Johnson, 1998) (see Figure 2.14).

It is not surprising that PVC is currently one of the world’s most important plastics and the second largest after polypropylene in consumption, despite fierce pressure in recent years from environmental group concerning the controversial issue of chlorine chemicals. The release of chlorinated dioxins from the VCM during incineration, as well as the use of health hazardous additives in PVC compounds do not favour the profile of the industry. Issue centers around phthalate plasticizers in PVC intended for food-contact products, medical supplies and toys, but this concern has not yet affected the broad-based PVC market. So far, bans and limitations have been instituted only in the toy industry (Johnson, 1999). The industry itself regards PVC as an environmentally friendly material, given its use in high performance, long-life and maintenance free products and its very low energy demands (making it in fact the most energy efficient of all plastics). In spite of some negative attitude, the market has grown. (see Figure 2.15) (Blanco, 2000).

Figure 2.12 :
Vinyl outsoles resist
Harsh chemicals and oils

Figure 2.11 :
PVC pumps stand up
to chemicals, rough use

Figure 2.13 : **High impact PVC sparks electric fence**

Figure 2.14 : Critical Barrier Packaging Award: Package for medical components

Figure 2.15 : Thermoplastic worldwide forecast (Blanco, 2000)

2.3 Polymer Blends

The concept of physically blending two or more existing polymers to obtain new products (polymer blends) or for problem solving is now attracting widespread interest and commercial utilization. Polymer blends are often referred to by the contraction “polyblends” and sometimes as “alloys” to borrow a term from metallurgy (Modern Plastic Magazine, 1994). The need for improved balance of properties and the potential ability of polymer blends to satisfy this need have converged in the development of polymer blending as a major area for rigorous growth in the past several years. Properties of plastics that have most often been improved by polymer blending include processability, tensile strength, ductility, impact strength, abrasion resistance, heat deflection temperature, low-temperature flexibility, flame retardancy, and environmental stress-crack resistance.

2.3.1 ABS Blends

ABS is itself a blend of PB and SAN, but can be further blended with other materials and thus the scope of possible applications is broadened. Commercial blends with ABS are given in Table 2.3 (Adam *et al.*, 1993) and some of these will be discussed in more detail below.

Table 2.3 Blends with ABS (Adam *et al.*, 1993)

Blend	Key Properties	Application	Growth Rate[a]
PC/ABS	heat resistance, low temperature impact, processability, ease of flame retarding	automotive, computer housing, lawn and garden, power tools, recreational vehicles	9 %
PVC/ABS	impact strength and toughness, flame retardance, UV stability, processability	electrical components, applicances, business machine housings, housewares	12-18 %
Nylon/ABS	high impact, chemical resistance, heat resistance, low moisture sensitivity	Automotive body panels and underhood components, vacuum cleaner housing	7 %
TPU/ABS	Chemical and abrasion resistance, low temperature toughness	Auto bumper fascia	
PBT/ABS	Processability, impact strength, heat and chemical resistance	Lawn and garden equipment, small appliances, fluid engineering industry	8 %
Polysulphone/ABS	Processability, low cost, heat resistance, ccan be plated	Appliances, auto window handles, faucets, food trays	
Miscellaneous*			

[a] U.S. annual consumption growth rate 1990-96. Source: ref. (CEH, 1992)

* miscellaneous blends: ABS/PVC/polyester, ABS/Acrylic acid ester, ABS/EVA, ABS/CPE, ABS/EPDM, ABS/SMA

2.3.2 PVC/ABS Blends

The low price of PVC renders its use desirable in many applications. When blended with ABS, the result is a materials which provide high impact strength, toughness and flame retardance, PVC provides the inherent flame retardance with UV stability, whereas ABS provides the impact strength and process ability (Manson and Sperling, 1976). PVC/ABS is used in a wide variety of applications which include electrical components, appliances, business machine housings and automotive parts. The inherent flame retardance of PVC makes it suitable for applications where the more expensive FR ABS could be employed.

Compatibilized blends of PVC and ABS have been demonstrated by Lindner and Ott, 1989. The compatibility occurred due to the similarity of the solubility parameters of the SAN matrix of ABS and PVC. The effect of this compatibilization was the improvement in the impact strength of the PVC blends. In particular, the data in Table 2.4 showed that the impact strength of PVC blends containing a minor amount of ABS increased with the total amount of polybutadiene in the blend (Datta and Lohse, 1996). These blends were made by melt blending the components at 200 ^{o}C on a mill.

Table 2.4 : Impact strength data for various PVC/ABS blends (Datta and Lohse, 1996)

Wt % PBD	ABS wt % SAN	Phr	PVC phr	Impact Strength NI-A (J/m) 20 ^{o}C	0 ^{o}C
75	25	7	93	491	400
50	50	7	93	357	290
75	25	15	85	2160	800
50	50	15	85	1330	673

Meredith and Ferguson, 1988 have extended the idea of the compatibility of PVC and SAN to form essentially transparent blends of PVC and ABS by closely matching the refractive indices of the ABS and the PVC phases by either changing the composition (S/AN ratio) or by inclusion of minor amounts of comonomers in the rubber phase. Thus, the refractive index of the rubber phase could be altered by adding minor amounts of styrene or AN without significant effect on the elastomeric properties. This procedure reflects the versatility of the synthetic process for ABS since the free radical procedure could accommodate a large variety of monomers.

In the data shown in Table 2.5, the ABS polymers were made with slightly different composition and blended with PVC by milling the mixture on a two roll mill at 173 °C for 8 min with a thermal stabilizer. The data compared the impact strength of blends containing 100 phr of PVC and 14 phr of ABS-type polymers. It illustrated the significant improvement in the impact strength with rather small increases in the amount of the rubber (PBD and copolymers of butadiene) phase of the blends (Datta and Lohse, 1996). All of the ABS polymers in this collection of the data contained 65% of an elastomer phase, 28% styrene and 7% AN.

Doak, 1984 had suggested the formation of compatibilized blends of PVC and ABS type polymers from styrene copolymers such as SMA, SAN and (S, MA, MMA). There were no definite results available to indicate the mechanical properties of the blends which were believed to be compatibilized because of the similarity in the solubility parameters of PVC and the styrene copolymers.

Table 2.5 : Impact strength data for various ABS compositions blended with PVC (Datta and Lohse, 1996)

ABS-type		PVC	Impact Strength NI_A
% PBD	Phr	phr	J/m (@ 23 °C)
69	80	20	110
74	80	20	480
79	80	20	480
84	80	20	450
89	80	20	490
94	80	20	560

2.3.3 Polycarbonate/ABS Blends

The second class of alloys is produced through blends made with polycarbonate (PC). Nearly all PC/ABS is used in automotive and business machine applications, with a small amount in lawn and garden equipment, power tools and recreational vehicles. PC/ABS properties and price are intermediate between those of the more expensive PC and the less expensive ABS; thus it is a good choice for customers who would like better performance than is available with ABS but do not wish to pay the high price for PC. The blends/alloys of PC/ABS provide heat resistance as well as low temperature impact strength and process ability. ABS improve the processibility and reduced cost whereas the PC provides the heat resistance and toughness and impact, higher tensile properties and improved ease of flame retarding (Bonner and Hope, 1993). These alloys exhibit excellent toughness, good heat distortion and high rigidity (Glenn and Cathleen, 1985).

PC/ABS are processed mainly via injection moulding, and because of their relatively high-melt viscosity, they are somewhat more difficult to process than standard ABS. Care must be taken not to exceed temperatures that will result in degradation of the rubber, but a sufficiently high temperature is required so that the PC is not too viscous (Glenn and Cathleen, 1985).

2.3.4 Nylon /ABS Blends

Nylon/ABS alloys provide high impact at both low and high temperatures as well as reduce moisture sensitivity and chemical resistance. The nylon contributes to the key thermal and chemical resistance properties, whereas ABS provides the impact strength and low moisture absorption. Nylon/ABS alloys are used in automotive interior, vacuum cleaner and power tool housings (Bucknall, 1977). Nylon and ABS or SAN are not compatible and simple blends of nylon and ABS display poorer properties than either component. The addition of some maleic anhydride (MA) copolymerised in the SAN matrix for example acts as some sort of compatibilisation (Triacca, 1991).

2.4.1 Flame Retardant

The burning and non-burning characteristics of plastics have been given great deal of attention by the scientific community in the last twenty years (Landrock, 1983). A flame retardant is used to inhibit or even suppress the burning process. (Troitzsch, 1980). In this study, ABS is a highly flammable material. Whereas PVC itself does not burn easily, and act as flame retardant.

2.4.2 Fire and Polymers: An Overview

Our environment is largely one of polymers and all polymers burn whether natural or synthetic. The issue is not whether polymers burn but rather if a given polymer has a proper profile appropriate to provide for an acceptable level of risk in a given application. Here, we should know that hazard is the potential for harm, with the probability of the event (fire), P_{ev} equal to one and the probability of exposure (e.g. people), P_{ex} equal to one. Risk is the product of the probability of the event times the probability of exposure, times the potential for harm, μ_h (Nelson, 1995).

$$\text{Risk} = P_{ev} \text{ x } P_{ex} \text{ x } \mu_h$$

$$\text{Risk} = \text{Hazard, when } P_{ev} = P_{ex} = 1$$

$$\therefore \text{ Risk} = \text{Hazard} = \mu_h$$

2.4.3 Combustion of Plastics

The burning of a solid polymer or polymer composition involves four stages:

1. Heating of the polymer
2. Decomposition
3. Ignition
4. Combustion

Heating the polymer. During this initial stage, thermoplastic materials soften or melt and begin to flow. The amorphous or crystalline linear polymers begin to lose their rigidity at the glass transition temperature and a continuous decrease in the viscosity of the melt takes place up to the decomposition point (Landrock, 1983).

Decomposition of the plastic occurs, with the elimination of volatile gases or chemically degraded polymer fragments, as shown in Figure 2.16 (Landrock, 1983). The temperature and the rate at which this occurs depend upon the thermal stability of the polymer and the chemical decomposition reaction occurring under the existing conditions (Pál, and Macskásy, 1991).

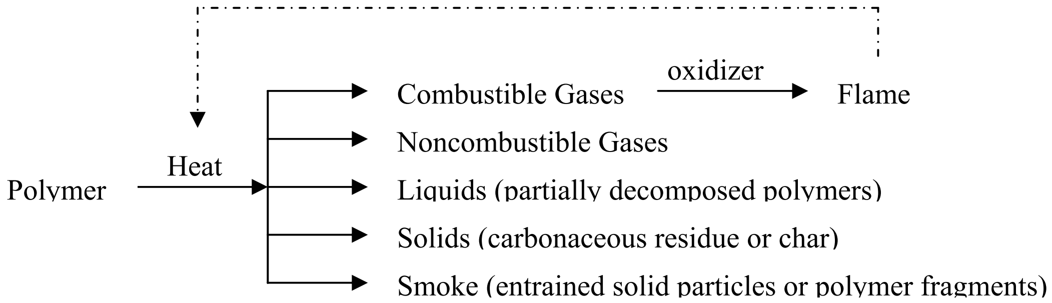


Figure 2.16 : Schematic representation of polymer degradation.

Ignition. The combustible gases and vapours evolved in the coarse of thermal decomposition are mixed with oxygen and ignited with or without the mediation of an external ignition source (Landrock, 1983). Ignition is influenced by the ignition temperature, which is generally lower in the presence of an igniting flame as compared to the self-ignition temperature (Pál, and Macskásy, 1991).

Combustion. After the ignition, the rapid heat generation raises the temperature both of the combustion products and of the environment, including the materials still not burning (Pál, and Macskásy, 1991). If this latter part of heat is sufficient for attaining the ignition temperature of the material, a self-supporting combustion will take place. Otherwise, burning can only be maintained by a continuously acting external heat source (Landrock, 1983).

The burning characteristics of some polymers are summarized in Table 2.6 (Chanda and Roy, 1993; Landrock, 1983).

Table 2.6 : Burning characteristics, burn rates and LOI index of polymers

Polymer	**Burning characteristics**	**Burn rate (cm/min)**	**LOI index (%)**
Polyethylene	Melts, drips	0.8-3.0	17.4
Polypropylene	Melts, drips	1.8-4.0	17.5-18.0
Poly(vinyl chloride)	Difficult to ignite, white smoke	Self-extinguishing	37.0-42.0
Poly(tetrafluoroethylene)	Melts, chars, bubbles	Nonburning	30.0
Fluorinated ethylene propylene copolymer	Does not ignite	Nonburning	> 95.0
Polybutylene	Burns	2.5	18
Acetal	Burns, bluish flame	1.3-2.8	14.8-15.0
Cellulose acetate	Burns, yellow flame, sooty smoke	1.3-7.6	19.0-27.0
Cellulose propionate	Burns, drips	1.3-3.0	18.0-21.0
Cellulose acetate butyrate	Burns, drips	2.5-5.1	17.5-18.0
ABS (general purpose)	Burns	2.5-5.1	17.5-18.0
Styrene acrylonitrile	Melts, chars, bubbles	1.0-4.0	19.1
Polystyrene	Soften, bubbles, black smoke	1.3-6.3	18.3-19.0
Acrylic	Burns slowly, drips	1.4-4.0	16.6-18.2
Nylons	Burns, drips, froths	Self-extinguishing	25.0-31.8
Phenylene oxide		Self-extinguishing	28.0-29.0
Polysulfone		Self-extinguishing	30.0-32.0
Chlorinated polyether		Self-extinguishing	23.2
Polyimide		Self-extinguishing	27.0

2.4.4 Flame Retardant Chemistry

Polymer combustion occurs in a continuous cycle (Figures 2.17-2.18). Heat generated in the flame is transferred back to the polymer surface producing volatile polymer fragments, or fuel. These fragments diffuse into the flame zone where they react with oxygen by free-radical chain process (Nelson, 1995). This in turn produces more heat and continuous the cycle. Flame retardancy is achieved by interrupting this cycle.

There are two ways to interrupt the cycle. One method, solid phase inhibition, involves changes in the polymer substrate. Systems that promote extensive polymer crosslink at the surface, form a carbonaceous char upon heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning (Nelson, 1995).

The second way of interrupting the flame cycle, vapor phase inhibition, involves changes in the flame chemistry. Reactive species are built into the polymer which are transformed into volatile free-radical inhibitors during burning. These materials diffuse into the flame and inhibit the branching radical reaction (Nelson, 1995). As a result, increased energy is required to maintain the flame and the cycle is interrupted. Of course, for many materials both solid and vapor phase inhibition are involved.

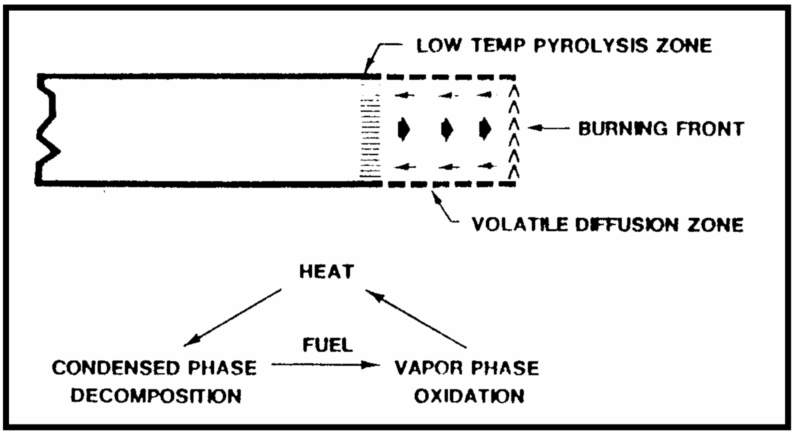


Figure 2.17 : Polymer combustion process cycle

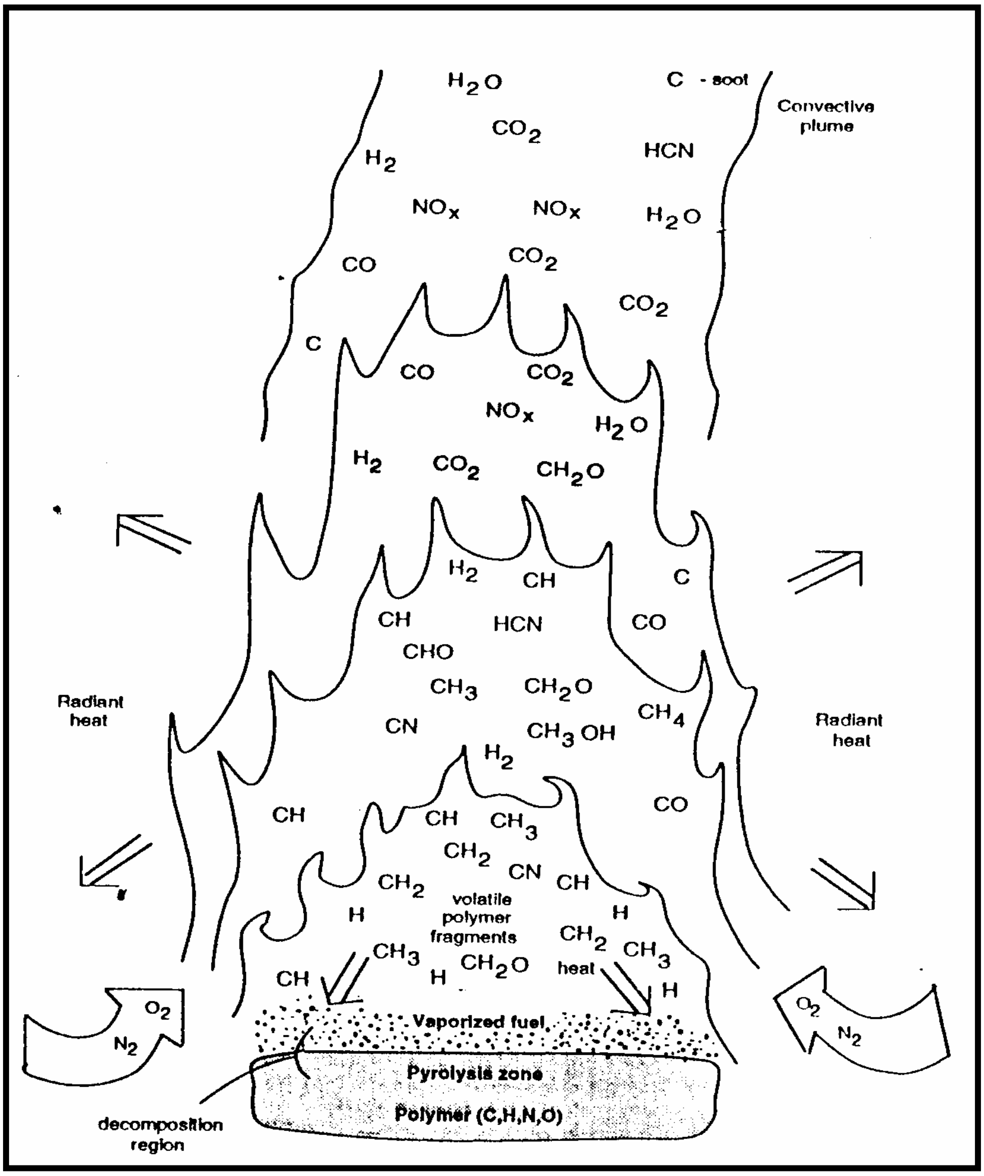


Figure 2.18 : A typical flame involving organic fuel showing decomposition region where volatilized fuel decomposes before combustion

Flame retardant additives used with synthetic polymers include organic phosphorus compounds, organic halogen compounds, and combinations of organic halogen compounds with antimony oxide. Inorganic flame retardants include hydrated alumina, magnesium hydroxide, borates to mention only a few. Not all retardants function well in all polymers. Component may interact (component such as fillers, stabilizers and processing aids must be considered). To be effective, the flame retardant must be decompose near the decomposition temperature of the polymer in order to do the appropriate chemistry as the polymer decomposes, yet be stable at processing temperatures (Nelson, 1995).

2.4.5 Effect of Halogen Compounds

During combustion of thermoplastics, free radicals are formed by pyrolysis. The radicals combine with oxygen in a radical chain reaction. Heat release and further decomposition of the plastics material is caused thereby (Jenkner and Köln. 1983). For continued combustion it is necessary to have sufficient oxygen as well as combustible gaseous compounds. It is presumed that the following reactions take place, when flame-retarded thermoplastics containing organobromine compounds as flame retardants are used (Jenkner and Köln. 1983).

$HO^* + CO = CO_2 + H^*$	(1)	propagation, highly exothermic
$H^* + O_2 = HO^* + O^*$	(2)	chain branching
$O^* + HBr = HO^* + Br^*$	(3)	chain transfer
$HO^* + HBr = H_2O + Br^*$	(4)	chain termination

The radical chain reaction is interrupted when the highly reactive HO^* radical, which occupies a key position within the combustion process, is replaced by the less reactive Br^* radical (reaction 4) (Jenkner and Köln. 1983).

2.4.6 Flame Retardant Thermoplastics

ABS resins have greater impact resistance than impact grades of polystyrene but are very sensitive to pigment fillers. For example, the conventional flame retardant system used for impact polystyrene, decabromodiphenyl oxide/antimony oxide, reduces the Izod impact strength from about 2.8 ft-lb/in. for the virgin impact polystyrene to about 2.0. In ABS this flame retardant system reduces the Izod values to about a third of the virgin resin. The effect of antimony oxide on Izod impact strength is shown graphically in Figure 2.19.

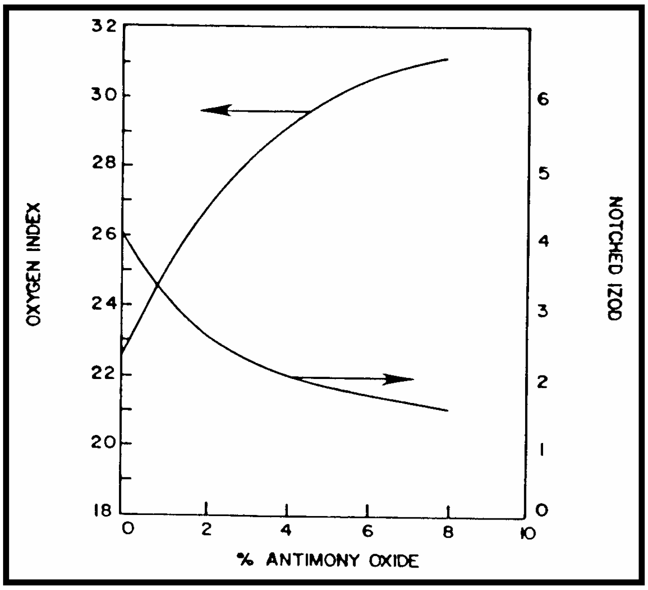


Figure 2.19 : Effect of antimony oxide concentration on the properties of ABS containing 13 wt% flame retardant

The three additives used commercially in ABS are bis(tribromophenoxy)ethane (FF-680), octabromodiphenyl oxide, and tetrabromobisphenol A. Small amounts of antimony oxide may be used for synergism. Also available is an ABS/PVC alloy in which the polyvinyl chloride is the flame retardant (Frank, 1991). Properties of commercial resin are shown in Table 2.7 and are compared with other commercial grades. Cycovin resins exhibit very high impact resistance, with notched Izod strength values of 10.5 ft-lb/in.

Table 2.7 : Properties of flame retardant ABS resin

Property	Commercial Grades ABS		
	Cycovin KAF	Cycolac KJT	Cycolac KJB
Specific gravity (g/cm^3)	1.21	1.20	1.20
Izod impact strength, Notched, ½ in. bar (ft-lb/in)	10.5	3.5	3.5
Heat distortion temperature (^{o}F)[a] at 264 psi	-	205	210
Processing temperature (^{o}F)			
Range	370-400	400-440	400-440
Maximum	400	-	-
Flame retardant	PVC	Bromine	Bromine
UL-94 rating/thickness (in.)	**V-1/0.058**	V-0/0.120	V-0/0.120
Oxygen index	30	29	29

[a] Plastics, 8th ed. Desk-top Data Bank, D.A.T.A., Inc., San Diego, California.

Source: Data sheets, Borg-Warner, Parkersburg, West Virginia.

Owen and Harper, 1998 in their study revealed that the LOI values increased as the brominated material loading into ABS is increased. The synergist effect of adding a halogen source and antimony oxide together was observed as expected. The effect of adding antimony trioxide with different particle size was focused. As the average particle size increased, the impact energy absorbed during failure decreased. When antimony oxide and brominated materials were used, the impact energy absorbed by the ABS was reduced further.

Polyvinyl chloride contains 57% chlorine and is inherently flame retardant. Rigid PVC products require stabilizers and processing aids but do not need additional flame retardants to meet flammability specifications. Rigid PVC has a chlorine content of 57% and an oxygen index of about 37. When plasticized with 60 parts of an organic plasticizer such as dioctyl phthalate, the chlorine content drops to 36% and the oxygen index to about 22 (Green, 1989).

Polyvinyl chloride will burn when exposed to an external flame but self-extinguishes when the flame is removed. The flash ignition and self-ignition temperature of PVC are 391 and 454 °C respectively (Grossman, 1989). The effect of stabilizers on the flammability of PVC homopolymer is shown in Table 2.8. In these experiments all the stabilizers chosen increased the oxygen index of PVC.

Table 2.8 : Oxygen index of various metal-stabilized PVC samples[a]

Compound	Metal[b]	Oxygen index
A	**None**	42.4
B	Lead	47.7
C	Tin	43.7
D	Barium, cadmium	45.3

[a] Data from International Wool Secretariat, British Pat. Appl. Sample thickness: about 100 mils.

[b] as salt.

The addition of other additives might also be expected to alter the flammability of PVC. Pure organic materials would decrease the flame retardancy of PVC since the fuel content in the polymer would be increased. In a similar way the flammability of rigid PVC can be further suppressed by the addition of nonorganic fillers to the polymer. This provides a simple dilution effect for the solid fuels. Aside from these effects of additives, rigid PVC is a self-extinguish polymer that will not support combustion, but will burn when exposed to an external flame source.

2.5 Mechanisms of Impact Modification

Three basic mechanisms of energy adsorption are available within a single material: shear yielding, crazing and crack formation. The deformation associated with the particular mechanism occurs irreversibly on the time scale of the deformation process. It is entirely possible that crazing or shear yielding can be reversed by heating the deformed sample to the glass transition or crystalline melting temperature of the polymer, but on the time scales of most mechanical processes the deformation is essentially fixed (Svec *et al.*, 1990).

Shear yielding is the irreversible change of shape of the materials under stress. It may occur over the entire stressed region of material or it may occur in localized portions of the stress region, in which case refer to the response as shear "banding".

Crazing is a localized irreversible volume expansion. It is often seen in tensile experiments as optical discontinuities that resemble cracks. The craze is not a crack however, as can be shown by microscopic examination. Crack formation is the total separation of matter along a surface. The surface may encompass the entire cross-sectional area of specimen or it may form locally without causing complete failure.

Of the three, shear yielding and crazing offer much higher energy adsorption potential and are consequently to be preferred. The higher potential arises because large numbers of shear bands or crazes can be activated underload, while only a few crack planes are normally found at failure.

2.5.1 Implementing the Mechanism

2.5.1.1 Crazing

Crazing is a highly successful mechanism for toughening some polymers especially for vinyl polymers. In order for the mechanism to be successful, however, a very large number of crazes must be generated. Basically, a craze consists of highly drawn threads of polymer associated with empty space to a net density of approximately 0.5. This means that the craze occupies roughly double the volume of the undrawn polymer and it achieves this by doubling only one dimension. The result is that we have energy absorption via a thread-drawing process (Rosík and Večerka, 1985).

A few crazes cannot contribute significantly to energy absorption. This is why we turn to rubber modification. The addition of small, well-dispersed rubber particles can increase the number of crazes generated by many orders of magnitude. The rubber phase acts as a craze multiplier. The mechanism of initiation is simply for the rubber particles to act as a stress concentrator (Bucknall, 1977). As stress concentrators, the rubber particles cause crazes to nucleate in the elevated stress zones in the vicinity of the particles (Figure 2.20). The crazes then grow into lower-stress regions and stabilize, thus permitting many crazes to be generated (Charles, 1996).

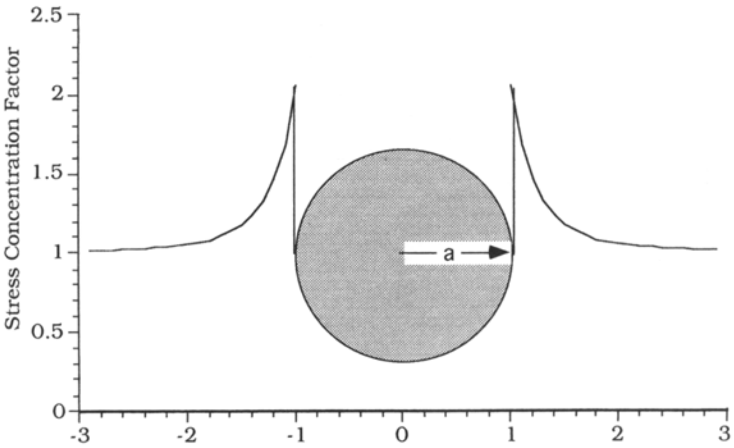


Figure 2.20 : Stress concentration around a hole (Charles, 1996)

A typical ABS will utilize smaller particles than HIPS by factors of 4 to 10. Consequently, up to 1000 times the number of particles may be available. Even though the fracture energy for polystyrene can be six times that of SAN, the superior number of particles in ABS more than makes up for it. The choice of particle size is based on the sizes that maximize performance and is different for each base polymer. Test rate, the incorporation of plasticizers, interface effectiveness, average particle size, as well as size distribution all contribute to the efficiency of craze generation and must be considered when designing a craze-based impact-resistant plastic (Rosík and Večerka, 1985).

2.5.1.2 Crack Multiplication

Just as a fine dispersion of rubber particles can use to nucleate crazes, the rubber particles can also use to nucleate crack initiation sites. The rubber particles once again provide stress concentration sites above and below the growing crack plane and form local cracks that in turn absorb energy. Even though the number of planes that can be activated is small by comparison with the number of crazes that can be generated in a thermoplastic, this technique is still viable for improving toughness (Chanda and Roy, 1993). As an illustration of the technique a series of rubber-modified thermosets were prepared and fractured. The surface roughness of each was measured and compared with fracture energy (G_{1C}). The results are plotted in Figure 2.21 and indicate a definite correlation between the two (Charles, 1996). Incidentally, fracture energies in the rubber-modified samples were approximately 2.5 times the value for a neat sample of the matrix. In other rubber-modified thermosetting systems, fracture energies of from 1.1 to 7 times the neat matrix energies have been observed. Higher toughening efficiencies are usually observed for intrinsically tougher matrices (Rosík and Večerka, 1985).

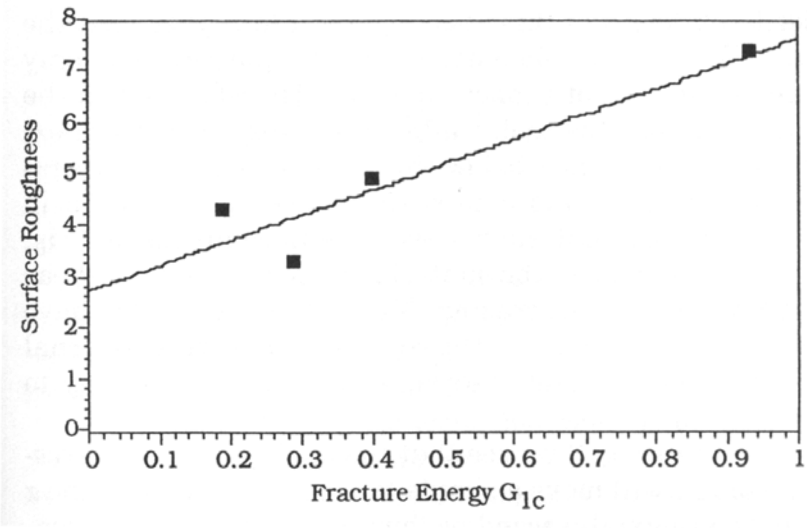


Figure 2.21 : Surface roughness versus fracture energy for several cured epoxies

2.5.1.3 Shear Banding

Normally, shear bands developed in conjuction with rubber particles. As before, the rubber particles provide stress field perturbations, but the rubber itself adds an extra feature, compression of the matrix (Bucknall, 1977). In order to understand this effect we need to realize that the thermal expansion coefficients of glassy plastics are only about one-third that of rubbery plastics. Therefore, when the multiphase material is cooled after processing, a thermal expansion mismatch occurs below the glass transition temperature of the matrix. This causes the rubber phase to be in hydrostatic tension and the matrix to be in compression (Fig. 2.22). This in turn biases the material response toward shear banding and away from crazing (Charles, 1996).

Referring to Fig. 2.23 we see that the addition of a compressive component will move a simple tensile stress field off the *x* axis into the (biaxial) second or fourth quadrant. If the compressive stress is high enough, response can be shifted from crazing to shear yielding (Bucknall, 1977). For example, in unmodified polystyrene the ratio of tensile stresses needed to generate shear banding to the stresses needed to cause crazing has been calculated to be 1.2. Compression resulting from thermal expansion mismatch can reduce the tensile stresses needed to generate shearing while increasing the stresses needed to bring about crazing. It has been predicted that the transition from crazing to shear banding in rubber-modified polystyrene will occur (at slow strain rates) when the rubber content reaches 25%. This agrees well with the occurrence of accelerated increase in impact resistance as rubber content increases above 25%.

When considering the competition between crazing and shearing, it is important to remember that the yield envelope for a given polymer is temperature and rate dependent. It is actually possible to have crazing at high strain rates and shear banding at low strain rates in the same plastic (Rosík and Večerka, 1985).

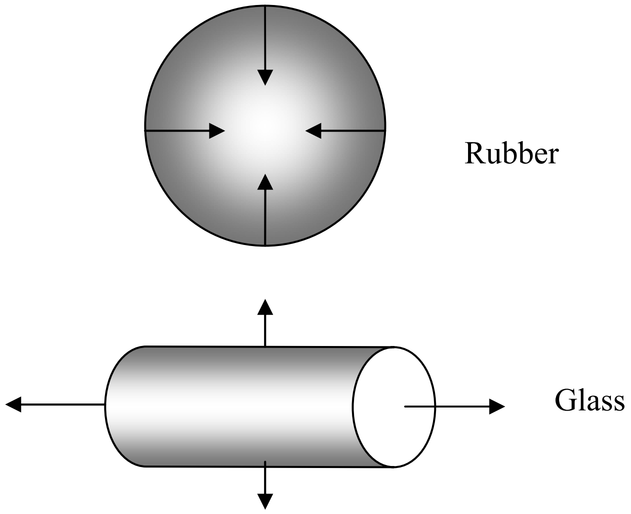


Figure 2.22 : Thermal shrinkage stress directions developed by differential contraction in rubber and glass during cooling

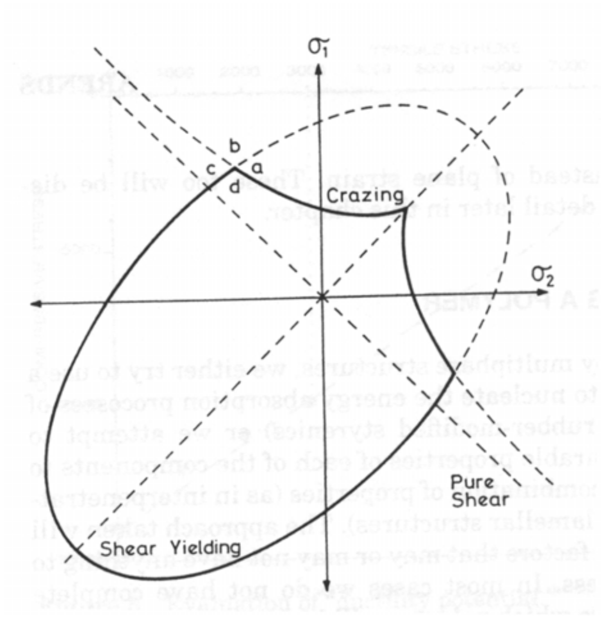


Figure 2.23 : Crazing cusp for PMMA

2.6 Compatibility of Polymer Blends

The variation of properties with the polymer/polymer ratio in a polyblend is shown schematically in Figure 2.24 (Chanda and Roy, 1993). For two polymers to be completely miscible, optimum requirement are: similar polarity, low molecular weight, and hydrogen-bonding or other strong intermolecular attraction.

Most polymer pairs do not meet the above requirements for complete theoretical miscibility. If they are slightly immiscible, each phase will be a solid solution of minor polymer in major polymer, and the phases will separate into submicroscopic domain with the polymer present in major amount forming the continuous matrix phase and contributing most towards its properties. Plots of properties versus the ratio of the two polymers in the blend will be S-shaped showing an intermediate transition region where there is a phase inversion from one continuous phase to the other (Fig. 2.24b). Most commercial polyblends are of this type, with the major polymer forming the continuous phase and retaining most of its useful properties, while the minor polymer forms small discrete domains, which contribute synergistically to certain specific properties.

When the polymer components in a blend are less miscible, phase separation will form larger domains with weaker interfacial bonding between them. The interfaces will therefore fail under stress and properties of polyblends are thus likely to be poorer than for either of the polymers in the blend. U-shaped properties curves (Fig. 2.24c) thus provide a strong indication of immiscibility. In most cases they also signify practical incompatibility, and hence lack of practical utility.

A fourth type of curve for properties versus polyblend ratio representing synergistic behavior (Fig. 2.24d) has been obtained in a few cases. This is synergistic improvement of properties, beyond what would be expected from simple monotonic proportionality, and sometimes far exceeding the value for either polymer alone. Discovery of practical synergistic polyblends is difficult and not predictable with the present state of understanding.

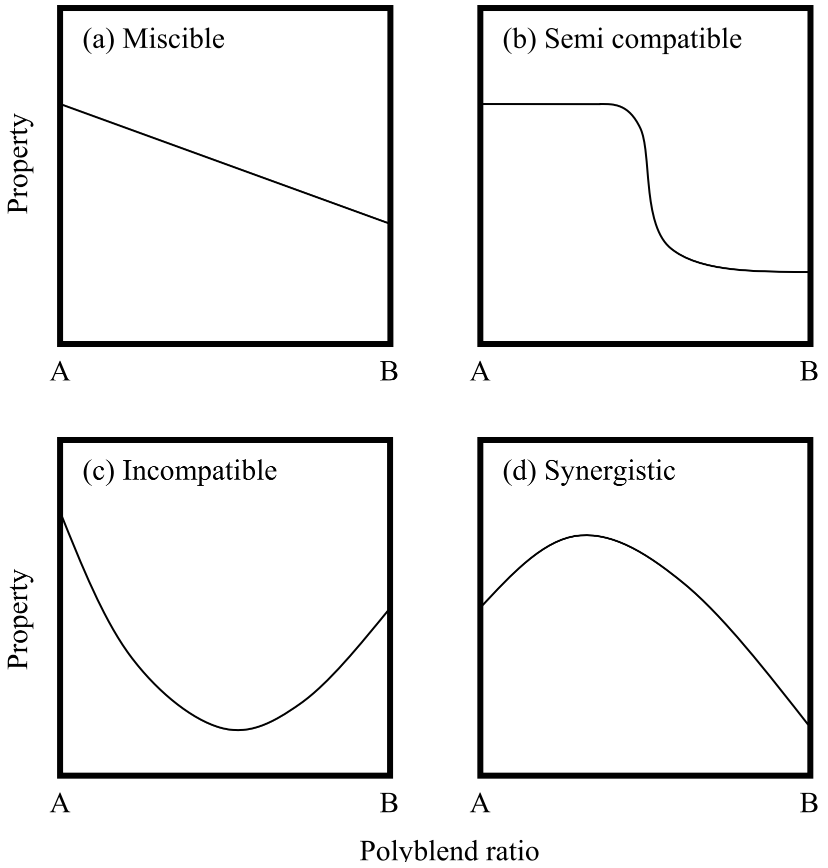


Figure 2.24 : Properties versus polymer/polymer ratio in a polyblend

Under microscopic inspection, a miscible polymer blend consists of a single phase; on a molecular level, polymer A molecules intermingle with polymer B molecules as shown in Figure 2.25a. A second possible morphology for polymer blends is shown in Figure 2.25b, where polymer A forms a separate phase from polymer B. This is the morphology of an immiscible blend, which is far more common than the one phase miscible blend. Frequently, a blend of two polymers is neither totally miscible nor totally immiscible, but falls somewhere in between. A blend of type is partially miscible and is depicted in Figure 2.25c (Fox and Allen, 1985).

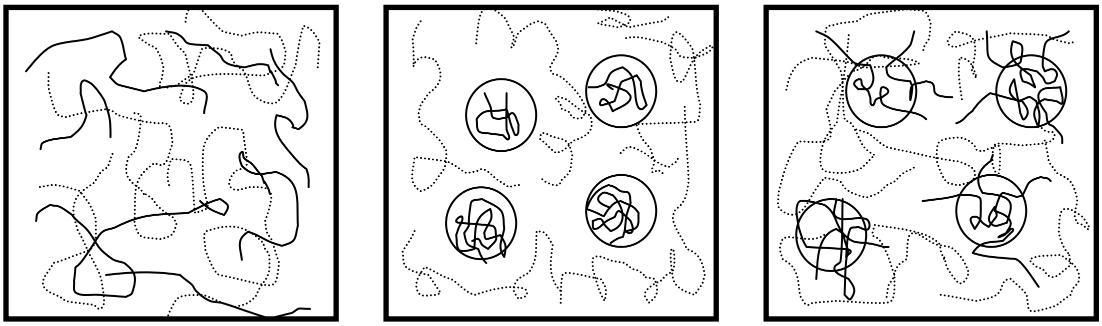

(a) (b) (c)

Figure 2.25 : Morphologies of a blend of polymer A (solid line) and polymer B (dashed line) (a) miscible; (b) immiscible; (c) partially miscible (Fox and Allen, 1985)

2.6.1 Methods for Determining Compatibility

When the polymers under consideration have glass transition temperatures sufficiently different from each other, the observation of a single intermediate glass transition temperature generally implies mixing on a submolecular scale, thus compatibility. Whether the glass transitions are observed by DSC, DTA, dynamic mechanical, dilatometric or other methods, it often happens that the glass transition region of a polymer-polymer mixture is broader than of a homopolymer. When this has been observed, some workers have concluded that the polymers were not compatible, even though only a single intermediate glass transition was observed for the mixture (Krause, 1989).

When two polymers have glass transition temperatures that are so close together that two glass transitions cannot be observed even for an incompatible, phase-separated mixture, the criterion of sample or film clarity has often been used to indicate compatibility. Some phase-separated samples may however, be clear: (1) if the polymers have almost equal refractive indices, or (2) if the phases are very large, as in layered films (Murayama, 1990). Alternatively, some polymer-polymer mixtures that are considered compatible, the semicrystal-line ones will almost always look turbid because of the refractive index difference between the crystallites and the amorphous phase. In the case of semicrystalline mixtures of two polymers with glass transition temperatures that are very close together, some workers have used the melting point depression of the crystallites by the miscible amorphous polymer phase as a criterion for compatibility.

2.6.1 Dynamic Mechanical Properties

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. The dynamic modulus, the loss modulus, and a mechanical damping or internal friction expresses these properties. The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. It may be a shear, a tensile, or a flexural modulus, depending on the investigating technique (Murayama, 1990).

The dynamic mechanical properties of polymer blends (qv) are determined primarily by the mutual solubility of the two polymers. If two polymers are compatible and soluble in one another. the properties of the blend are nearly the same as those of a random copolymer of the same composition. However, many polymer mixtures form two phases due to the insolubility of the components. In this case, the damping temperature curve shows two peaks: each peak is characteristic of the glass transition temperature of one of the components (Moore, 1989). The two steps in the dynamic modulus temperature curves are characteristic of an immiscible two-phase system.

The dynamic mechanical properties of copolymers are strongly influenced by the characteristics of the homopolymer and the copolymer composition. In a homogeneous copolymer all molecules have the same chemical composition, and hence should have a single sharp α-transition (T_g). On the other hand, the damping curves of the dynamic properties of heterogeneous copolymers reflect the broadening of the transition region caused by the increase in heterogeneity (Murayama, 1990).

The dynamic mechanical properties of an ABS resin is shown in Figure 2.26, where polybutadiene particles are dispersed in a phase of styrene acrylonitrile copolymer (SAN) with the formation of graft bonds on its boundary.

The dependence of dynamic mechanical properties on the amount of components is shown in Figure 2.27 (Moore, 1989). The samples of different compositions were prepared by using PVC and butadiene-acrylonitrile rubber (NBR). The dynamic modulus and loss modulus are shifted on the temperature scale in proportion to the relative concentration of two polymers.

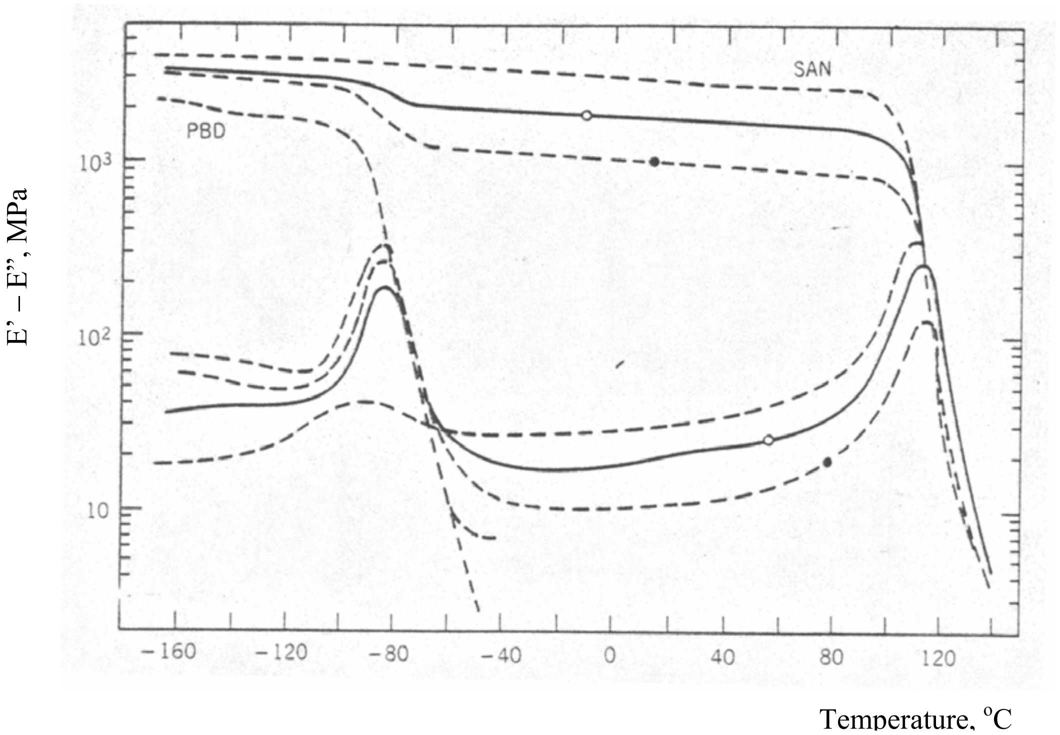


Figure 2.26 : E' – E" versus temperature for polybutadiene in styrene acrylonitrile copolymer (SAN); -------- experimental; and ——— calculated: (SAN)/PBD: ○, 77/23; and ●, 56/44 (Moore, 1989)

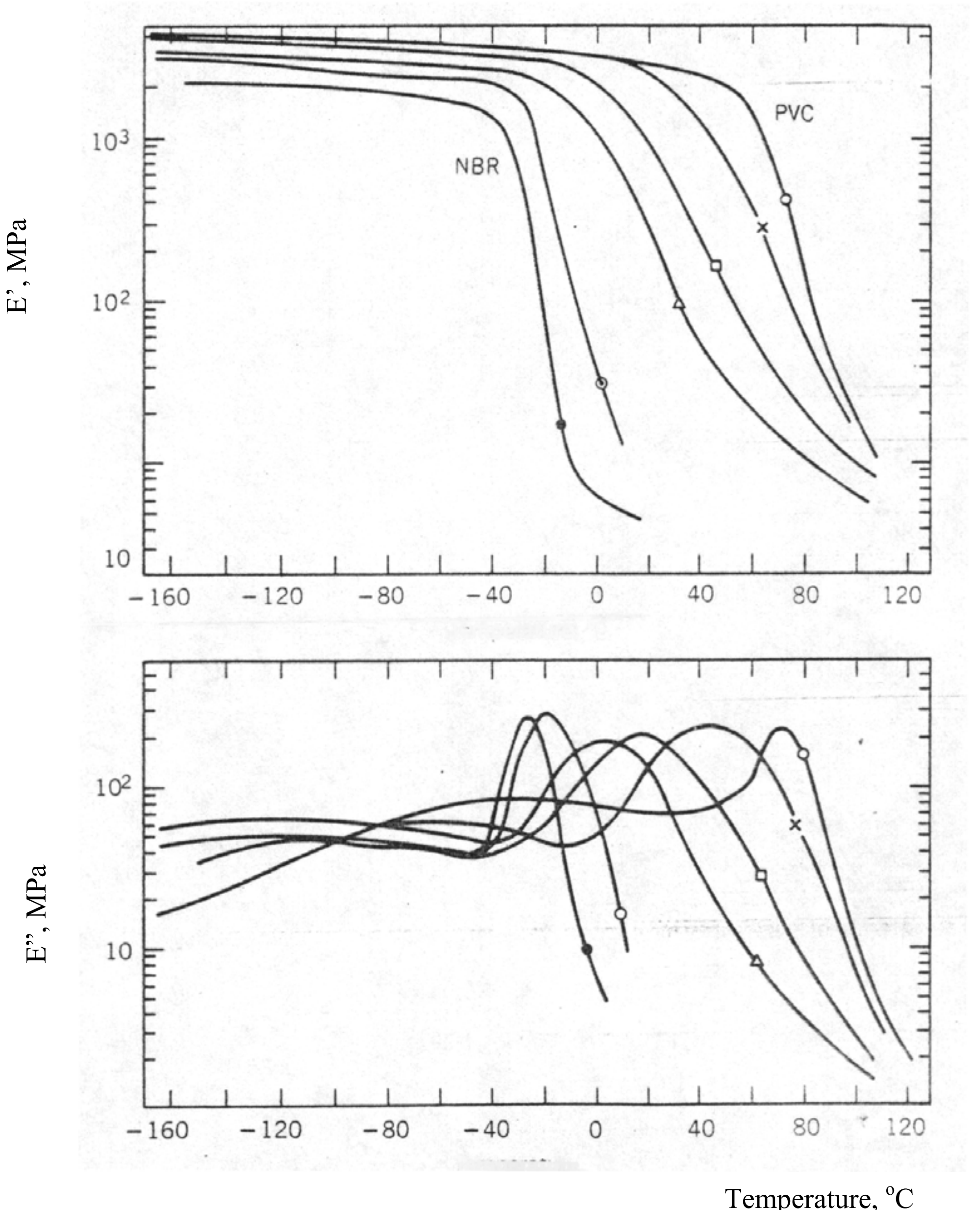
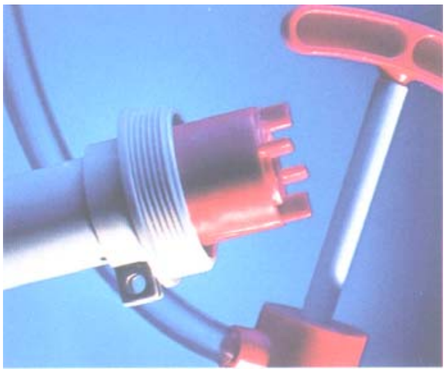
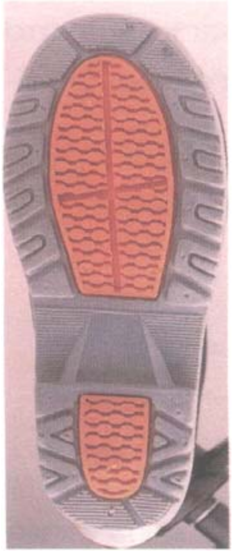
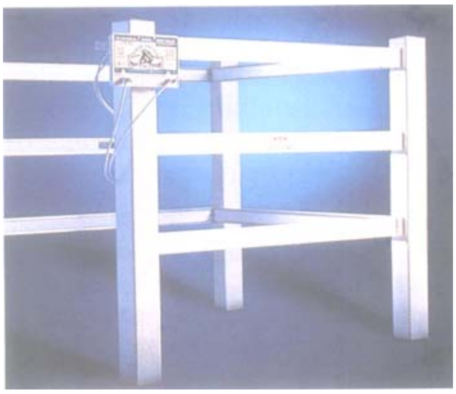


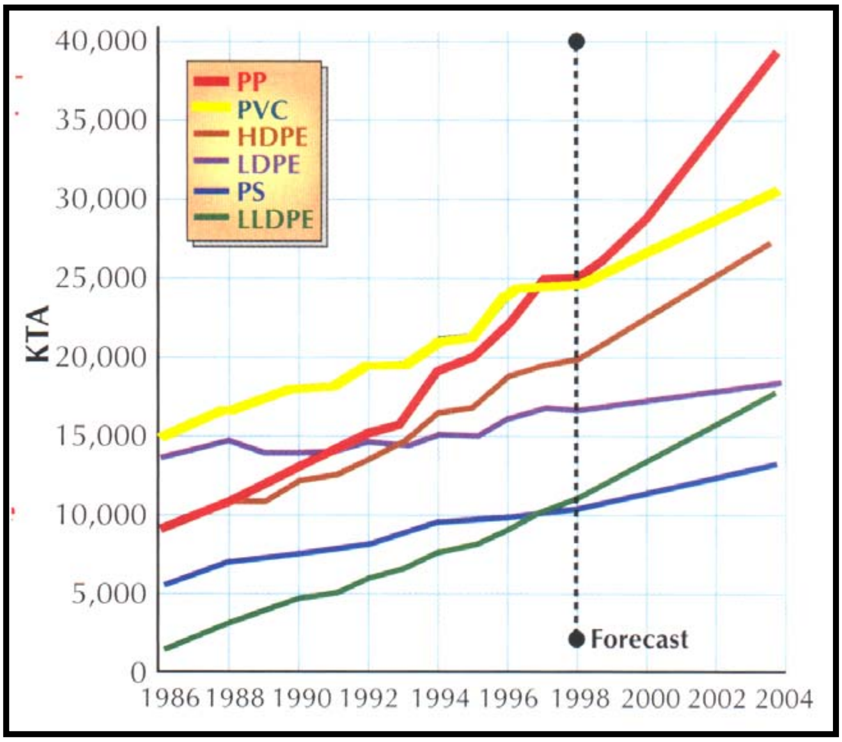
Figure 2.27 : E' and E" vs temperature for blended system of PVC and NBR of various compositions (PVC/NBR) at 138 Hz: ○, 100/0; x, 83/17; □, 67/33; △, 50/50; ©, 20/80; and ●, 0/100 (Moore, 1989)


LECTRA








PP
PVC
HDPE
LDPE
PS
LLDPE
KTA
40,000
35,000
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25,000
20,000
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0
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
Forecast

CHAPTER III

METHODOLOGY

3.1 Materials

High rigidity, medium impact and super high impact ABS were used for this study. They were supplied by Toray Plastics (Malaysia) Sdn. Bhd. in the form of extruded pellets. Typical ABS properties are summarized in Table 3.1. The manufacturer has the proprietary right on the ratio of ABS monomer. Based on information given by the manufacturer, ABS consists of 60% styrene, 25% acrylonitrile and 15% butadiene approximately.

The PVC used in this study was a suspension type homopolymer with solution viscosity of K-58 and 66. They were supplied by Industrial Resins Malaysia Sdn. Bhd. Acrylic grafted PVC with a trade name of Vinidur 464SZ was supplied by SolVin. Types, trade name, manufacturer and purpose of materials for ABS and PVC are presented in Table 3.2.

Three types of additives were used in this study. There are tin, calcium stearate, and stearic acid. The trade name, manufacturer and purpose of materials are stated in Table 3.3.

Table 3.1 : Typical properties of Toyolac ABS

Properties	Test Method	Metric Units (SI)	Test Condition	High Rigidity 500 -322	Medium Impact 700 -314	Super High Impact 100 -X01
Specific gravity	ASTM D792	-	23 ^{0}C	1.05	1.05	1.04
Melt flow rate	ISO 1133	$\frac{G}{10min}$	220 ^{0}C 10 kg	20	23	14
Tensile strength at yield	ASTM D638	MPa	23 ^{0}C	54	50	42
Tensile elongation at break	ASTM D638	%	23 ^{0}C	37	35	>50
Flexural modulus	ASTM D790	MPa	23 ^{0}C	2600	2450	1960
Izod impact strength	ASTM D256	J/m	23 ^{0}C	137	186	274

Table 3.2 : Types, trade name, manufacturer and purpose of materials for ABS and PVC

Types	Trade Name	Manufacturer	Purpose
High Rigidity ABS	Toyolac 500-322	Toray Plastics	Audio & Video Cassette Cases, Remote Controller Cases, Air Cleaner Parts, Buttons & Handles of Audio Products, Calculator Cases, Toys, Typewriter & Printer Ribbon Cartridges, Parts of Camera Body.
Medium Impact ABS	Toyolac 700-314	Toray Plastics	Telephone Cases, Printer Parts, Headphone Stereo Body, Key Board, Vacuum Cleaner Parts, Interior Parts of Refrigerator, Exterior Parts of Room Air-Conditioner, Calculator Cases, Toilet Parts.
Super High Impact ABS	Toyolac 100-X01	Toray Plastics	Toys, Suitcase, Parts of Miscellaneous Goods, etc.
PVC K-58	MH 58	IRM	*Blow extrusion* : opaque or crystal-clear bottles *Injection moulding* : rigid articles *Calendering* : opaque or crystal-clear rigid sheets *Extrusion* : rigid profiles and films
PVC K-66	MH 66	IRM	*Extrusion* : - pressure piping for cold water supply - waste pipe - electrical conduit - rigid profiles
Acrylic Grafted PVC	Vinidur 464SZ	SolVin	Finished products offering high impact strength without adding modifiers.

Table 3.3 : Types, trade name, manufacturer and purpose of materials for additives

Tin	Thermolite T890	Elf Atochem	Stabilizer for PVC
Calcium Stearate (Cast)	Sak-Cs	Sun Ace Kakoh	Internal Lubricant
Stearic Acid (Hst)	-	-	External lubricant
Paraffin Oil	Primol 382	Exxon Mobil	Wetting agent

3.1.1 Blend Formulation

The ABS/PVC blend formulations are shown in Table 3.4. The content of the PVC and ABS were varied to search for the best formulation. Based on PVC content, 3 phr of tin stabilizer, 0.5 phr of calcium stearate and 0.6 phr of stearic acid were used for each blend.

Table 3.4 : Blend formulation

	High Rigidity ABS	Medium Impact ABS	Super High Impact ABS	PVC K-58	PVC K-66	Acrylic Grafted PVC
1	100					
2	90			10		
3	90				10	
4	90		90			10
5	85			15		
6	85				15	
7	85					15
8	80			20		
9	80				20	
10	80					20
11		100				
12		90		10		
13		90			10	
14		90				10
15		85		15		
16		85			15	
17		85				15
18		80		20		
19		80			20	
20		80				20
21			100			
22			90	10		
23			90		10	
24			90			10
25			85	15		
26			85		15	
27			85			15
28			80	20		
29			80		20	
30			80			20

3.2 Preparation of Blends

3.2.1 Dry Blending

The correct proportion of the resin and the additives had to be weighed by using Electronic Balance ER-120A. A Hopper Dryer Type: THD-12E TEW Electronic Equipment Co. Ltd. was used to dry the ABS resins since ABS is a hygroscopic material which can absorb moisture up to 0.3% within 24 hours. PVC was dried by using oven.

To homogenize the formulation of PVC with other additives, a laboratory mixer, National Blender MX-491N was operated. The duration for dry blending process was 14 minutes (Yee, 2001).

3.2.2 Single Screw Extrusion

Primol 382, paraffin oil, acting as a wetting agent was added before melt blending. This was to ensure the PVC to be incorporated later would adhere to the ABS pellets and consequently be evenly distributed. The wetting agent was tumble-mixed with the pellets in a tumbler mixer for 10 minutes. To produce moulded sample, the dry blends of ABS/PVC formulation were melt blending by using 40mm Tanabe single screw extruder. A standard mesh was used to run the extrusion. The operating conditions are shown in Table 3.5.

Table 3.5 : Extrusion operating conditions

Extrusion temperature	185^{o}C
Screw speed	110 rpm

3.2.3 Injection Moulding

Impact bars were injection moulded by using Chen Hsong Jet Master JM 4 MKII. The mould for injecting the test specimens is shown in Figure 3.1. The parameter of the setting is shown in Table 3.6.

Table 3.6 : Injection moulding operation condition

Setting	Unit	Value
Temperature at zone 1	^{o}C	170
Temperature at zone 2	^{o}C	180
Nozzle temperature	^{o}C	185
Back pressure	psi	60

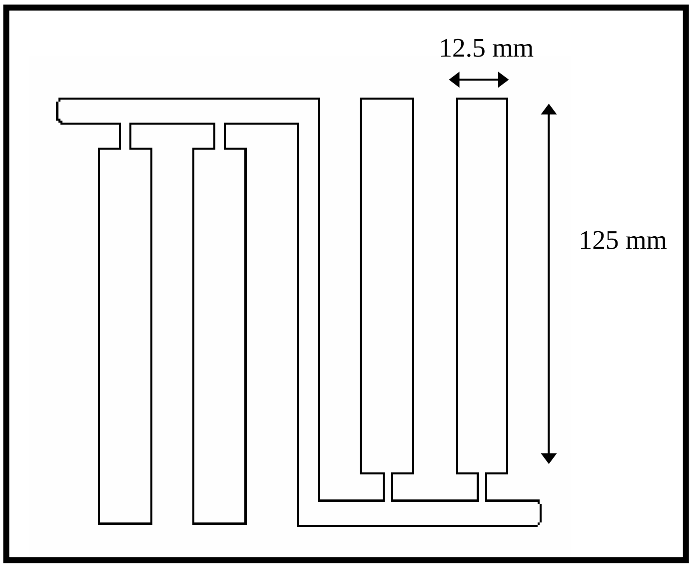

Figure 3.1 : Mould for Injection moulding specimen

3.3 Testing and Analysis Procedure

3.3.1 Pendulum Impact Test

The impact test was done according to ASTM D 256A by using Izod impact tester, pendulum type model (the maker is Toyoseiki) as shown in Figure 3.2. The test specimen obtained from the injection moulding, with dimension stated in Table 3.7 and illustrates in Figure 3.3 was then notched using a notching machine. The notching machine used is made by Atlas with ASN model. The notch depth fixed at 2.5 ± 0.05 mm. The impact strength is calculated by dividing the indicator reading (energy) by the cross sectional area of the specimen. The results were reported in kJ/m^2 of notch for notched specimens. Ten specimen values test were carried out for each blend sample. This test was measured at room temperature (25 ± 2^oC) and 50 ± 5% relative humidity.

Figure 3.2 : Izod Impact Tester

Table 3.7 : Dimension measurement for Izod type test specimen

Dimension	Measurement (mm)
X_k : Notch depth	2.5 ± 0.1
X : Width of specimen	12.5 ± 0.1
Y : thickness of specimen	3.0 ± 0.1
l : length of specimen	125 ± 1.0

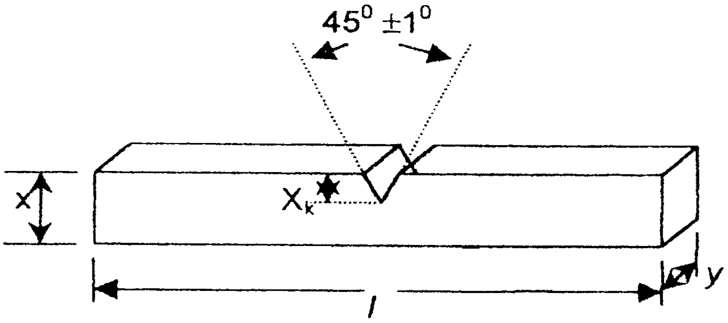

Figure 3.3 : Dimension for Izod type test specimen

3.3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements are carried out on Perkin Elmer DMA-7e which consisting a temperature programmer and controller. Figure 3.4 illustrates the schematic diagram of DMA-7e. It measures dynamic modulus (both storage and loss modulus) and damping of a specimen under oscillatory load as a function of temperature. The measurements are carried out in accordance to MS 1473 (1999) using three point bending.

The samples were mounted on the three point blending stainless steel measuring system as shown in Figure 3.5. The advantage of using this fixture on a vertical DMA becomes obvious as the sample do not require heat absorbing clamping fixture. The experiment was conducted from 30 °C to 200 °C at a frequency of 1 Hz with a programmed heating rate of 5 °C /min. Liquid nitrogen was used to achieve modulus (E\ E") temperature. The mechanical loss factor tan and dynamic modulus (E\ E") were calculated with a microcomputer.

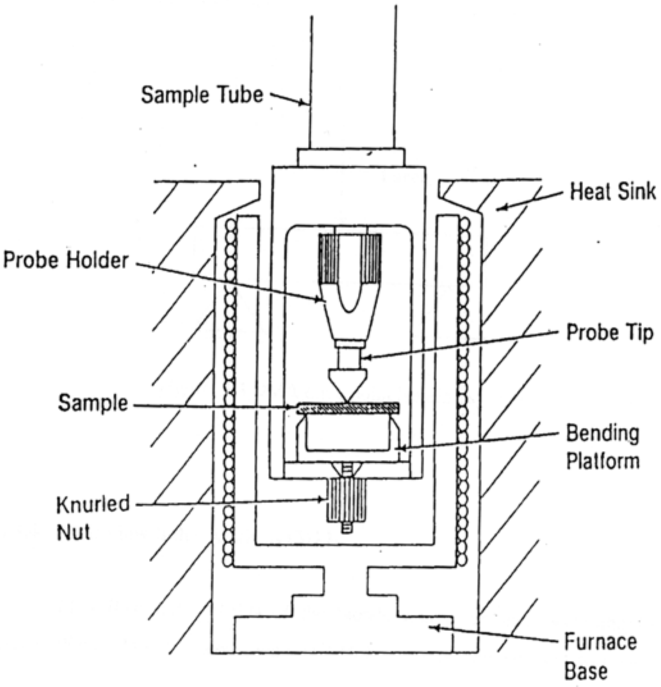

Figure 3.4 : A schematic diagram of a DMA used to determine the compatibility of the blends (Perkin-Elmer Instrument)

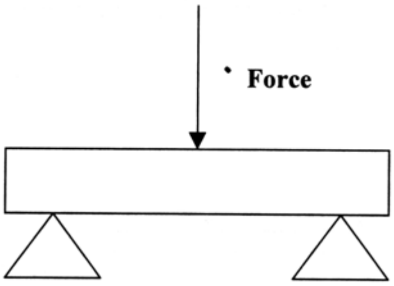

Figure 3.5 : DMA three point bending system

3.3.3 Scanning Electron Microscopy (SEM)

SEM JEOL JSM 5610 (as shown in Figure 3.6) was used to obtain the surface behaviour of the different blends. The samples to be examined was chosen after the impact test and then cut into smaller pieces. It was placed on double-sided sticky tape on a specimen stub. The specimen to be scanned was mounted on a stub and accommodated in the specimen chamber. The fracture surface prepared for SEM examination by sputter coating with a layer of gold on biotech machine (JFC-1600 auto fine coater) to facilitate examination under the SEM. SEM picture were taken at different magnifications (x200 and x2000).

Figure 3.6 : Photograph of SEM JSM 5610

3.3.4 Flexural Properties

Flexural test was carried out according to ASTM D 790. The test procedure used is Test Method 1, Procedure A, i.e., three-point loading utilizing center loading. Since the modulus was determined between small initial deflections, to ensure good accuracy, a low force load cell (100N) was used. Flexural test was carried out a simple supported beam. The distance between the spans was 4.96 cm and the strain rate (compression speed) was 3 mm/min. The flexural properties were measured at room temperature (25 ± 2 ^{o}C) on an Instron Universal Tester (model 5567) as shown in Figure 3.7. Five samples were tested for each composition and average values were recorded.

Figure 3.7 : Photograph of Instron universal tester

3.3.5 Oxygen Index Test (LOI)

Oxygen index is the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under the set condition.

The test determines the minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that will just support combustion. This process was carried out under equilibrium conditions of candlelike burning. Figure 3.8 illustrates a typical equipment layout of LOI and the maker is Fire Test Technology, UK.

The test specimen used in the experiment must be dry since the moisture content will alter the oxygen index. The samples were moulded according to ASTM D 2863, 125 x 10 x 3 mm. The oxygen index was calculated as follows:

$$\boxed{\text{Oxygen index percent} = (100 \times O_2) / (O_2 + N_2)}$$

where O_2 = volumetric flow of oxygen at the concentration determined;

N_2 = volumetric flow of nitrogen.

Figure 3.8 : Typical equipment layout for oxygen index test

3.3.6 Heat Defection Temperature (HDT)

Heat deflection temperature is defined as the temperature at which a standard test bar (127 x 12.5 x 3 mm) deflects 0.25 mm. under a stated load of 1820 kPa. This test can distinguish between those materials that lose their rigidity over a narrow temperature range and those that are able to sustain light at high temperature.

HDT test was carried out following ASTM D 648, with HDT Tester S-3 machine (Maker: Toyoseiki) as illustrated in Figure 3.9. The apparatus for measuring HDT consists of an enclose oil bath fitted with a heating chamber and automatic heating control. A cooling system is also incorporated. The specimens were supported on steel supports that are 4 in. apart, with the load applied on top of the specimen vertically and midway between the supports. A dial indicator was used to measure deflection.

The specimen was positioned in the apparatus and was submerged into the oil bath kept at room temperature. The load was applied to a 1820 kPa. Five minutes later, the pointer was adjusted to zero and the oil was heated at the rate of 2 ± 0.2^{o}C/min. The temperature of the oil at which the bar had deflected 0.25 mm was recorded as the heat deflection temperature at the specified fiber stress.

Figure 3.9 : Heat distortion tester S-3 machine

3.3.7 Melt Flow Index (MFI)

Melt flow index (MFI) of the blends was determined according to ASTM D1238-90b at 200 °C under a load of 2.16 kg. The equipment used was Toyoseiki thermo controller. About 3 g of sample was introduced into the barrel, at 200°C and was allowed to melt and achieve thermal equilibrium for 4 minutes. Load of 2.16 kg was applied on the melt and material was extruded through the die. The extrudates were cut at regular interval, usually at 10 minutes interval. The cut-off extrudates were weighed and the value was converted to the unit of g/min. The average of four extrudates was taken for the MFI value.

CHAPTER III

METHODOLOGY

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Table 3.1 : Typical properties of Toyolac ABS

Properties	Test Method	Metric Units (SI)	Test Condition	High Rigidity 500 -322	Medium Impact 700 -314	Super High Impact 100 -X01
Specific gravity	ASTM D792	-	23 ^{0}C	1.05	1.05	1.04
Melt flow rate	ISO 1133	$\frac{G}{10min}$	220 ^{0}C 10 kg	20	23	14
Tensile strength at yield	ASTM D638	MPa	23 ^{0}C	54	50	42
Tensile elongation at break	ASTM D638	%	23 ^{0}C	37	35	>50
Flexural modulus	ASTM D790	MPa	23 ^{0}C	2600	2450	1960
Izod impact strength	ASTM D256	J/m	23 ^{0}C	137	186	274

Table 3.2 : Types, trade name, manufacturer and purpose of materials for ABS and PVC

Types	Trade Name	Manufacturer	Purpose
High Rigidity ABS	Toyolac 500-322	Toray Plastics	Audio & Video Cassette Cases, Remote Controller Cases, Air Cleaner Parts, Buttons & Handles of Audio Products, Calculator Cases, Toys, Typewriter & Printer Ribbon Cartridges, Parts of Camera Body.
Medium Impact ABS	Toyolac 700-314	Toray Plastics	Telephone Cases, Printer Parts, Headphone Stereo Body, Key Board, Vacuum Cleaner Parts, Interior Parts of Refrigerator, Exterior Parts of Room Air-Conditioner, Calculator Cases, Toilet Parts.
Super High Impact ABS	Toyolac 100-X01	Toray Plastics	Toys, Suitcase, Parts of Miscellaneous Goods, etc.
PVC K-58	MH 58	IRM	*Blow extrusion* : opaque or crystal-clear bottles *Injection moulding* : rigid articles *Calendering* : opaque or crystal-clear rigid sheets *Extrusion* : rigid profiles and films
PVC K-66	MH 66	IRM	*Extrusion* : - pressure piping for cold water supply - waste pipe - electrical conduit - rigid profiles
Acrylic Grafted PVC	Vinidur 464SZ	SolVin	Finished products offering high impact strength without adding modifiers.

Table 3.3 : Types, trade name, manufacturer and purpose of materials for additives

Tin	Thermolite T890	Elf Atochem	Stabilizer for PVC
Calcium Stearate (Cast)	Sak-Cs	Sun Ace Kakoh	Internal Lubricant
Stearic Acid (Hst)	-	-	External lubricant
Paraffin Oil	Primol 382	Exxon Mobil	Wetting agent

3.1.1 Blend Formulation

The ABS/PVC blend formulations are shown in Table 3.4. The content of the PVC and ABS were varied to search for the best formulation. Based on PVC content, 3 phr of tin stabilizer, 0.5 phr of calcium stearate and 0.6 phr of stearic acid were used for each blend.

Table 3.4 : Blend formulation

	High Rigidity ABS	Medium Impact ABS	Super High Impact ABS	PVC K-58	PVC K-66	Acrylic Grafted PVC
1	100					
2	90			10		
3	90				10	
4	90		90			10
5	85			15		
6	85				15	
7	85					15
8	80			20		
9	80				20	
10	80					20
11		100				
12		90		10		
13		90			10	
14		90				10
15		85		15		
16		85			15	
17		85				15
18		80		20		
19		80			20	
20		80				20
21			100			
22			90	10		
23			90		10	
24			90			10
25			85	15		
26			85		15	
27			85			15
28			80	20		
29			80		20	
30			80			20

3.2 Preparation of Blends

3.2.1 Dry Blending

The correct proportion of the resin and the additives had to be weighed by using Electronic Balance ER-120A. A Hopper Dryer Type: THD-12E TEW Electronic Equipment Co. Ltd. was used to dry the ABS resins since ABS is a hygroscopic material which can absorb moisture up to 0.3% within 24 hours. PVC was dried by using oven.

To homogenize the formulation of PVC with other additives, a laboratory mixer, National Blender MX-491N was operated. The duration for dry blending process was 14 minutes (Yee, 2001).

3.2.2 Single Screw Extrusion

Primol 382, paraffin oil, acting as a wetting agent was added before melt blending. This was to ensure the PVC to be incorporated later would adhere to the ABS pellets and consequently be evenly distributed. The wetting agent was tumble-mixed with the pellets in a tumbler mixer for 10 minutes. To produce moulded sample, the dry blends of ABS/PVC formulation were melt blending by using 40mm Tanabe single screw extruder. A standard mesh was used to run the extrusion. The operating conditions are shown in Table 3.5.

Table 3.5 : Extrusion operating conditions

Extrusion temperature	185^{o}C
Screw speed	110 rpm

3.2.3 Injection Moulding

Impact bars were injection moulded by using Chen Hsong Jet Master JM 4 MKII. The mould for injecting the test specimens is shown in Figure 3.1. The parameter of the setting is shown in Table 3.6.

Table 3.6 : Injection moulding operation condition

Setting	Unit	Value
Temperature at zone 1	^{o}C	170
Temperature at zone 2	^{o}C	180
Nozzle temperature	^{o}C	185
Back pressure	psi	60

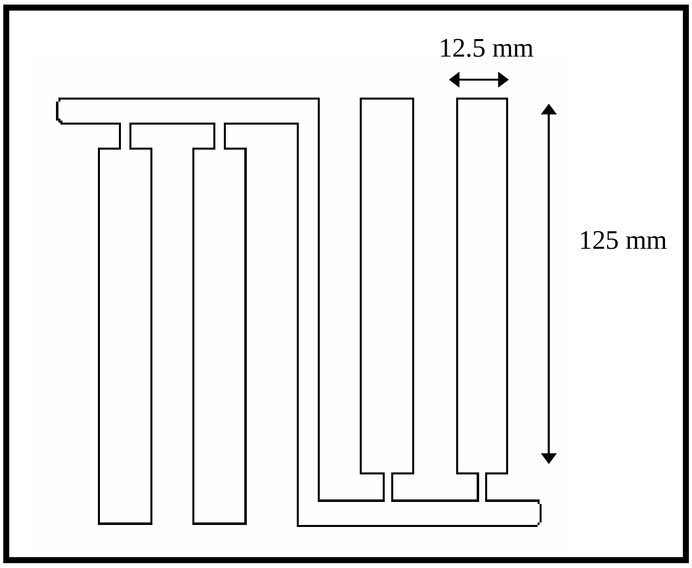

Figure 3.1 : Mould for Injection moulding specimen

3.3 Testing and Analysis Procedure

3.3.1 Pendulum Impact Test

The impact test was done according to ASTM D 256A by using Izod impact tester, pendulum type model (the maker is Toyoseiki) as shown in Figure 3.2. The test specimen obtained from the injection moulding, with dimension stated in Table 3.7 and illustrates in Figure 3.3 was then notched using a notching machine. The notching machine used is made by Atlas with ASN model. The notch depth fixed at 2.5 ± 0.05 mm. The impact strength is calculated by dividing the indicator reading (energy) by the cross sectional area of the specimen. The results were reported in kJ/m^2 of notch for notched specimens. Ten specimen values test were carried out for each blend sample. This test was measured at room temperature (25 ± 2°C) and 50 ± 5% relative humidity.

Figure 3.2 : Izod Impact Tester

Table 3.7 : Dimension measurement for Izod type test specimen

Dimension	Measurement (mm)
X_k : Notch depth	2.5 ± 0.1
X : Width of specimen	12.5 ± 0.1
Y : thickness of specimen	3.0 ± 0.1
l : length of specimen	125 ± 1.0

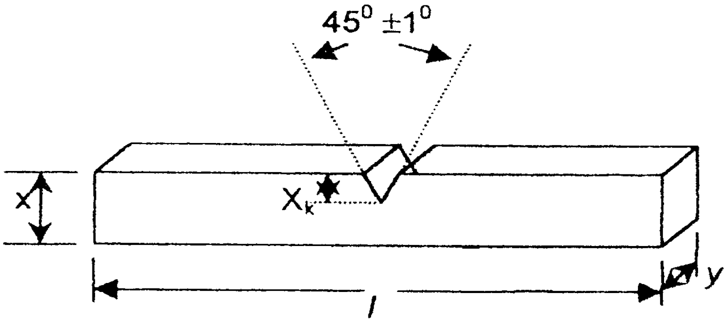

Figure 3.3 : Dimension for Izod type test specimen

3.3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements are carried out on Perkin Elmer DMA-7e which consisting a temperature programmer and controller. Figure 3.4 illustrates the schematic diagram of DMA-7e. It measures dynamic modulus (both storage and loss modulus) and damping of a specimen under oscillatory load as a function of temperature. The measurements are carried out in accordance to MS 1473 (1999) using three point bending.

The samples were mounted on the three point blending stainless steel measuring system as shown in Figure 3.5. The advantage of using this fixture on a vertical DMA becomes obvious as the sample do not require heat absorbing clamping fixture. The experiment was conducted from 30 °C to 200 °C at a frequency of 1 Hz with a programmed heating rate of 5 °C /min. Liquid nitrogen was used to achieve modulus (E\ E") temperature. The mechanical loss factor tan and dynamic modulus (E\ E") were calculated with a microcomputer.

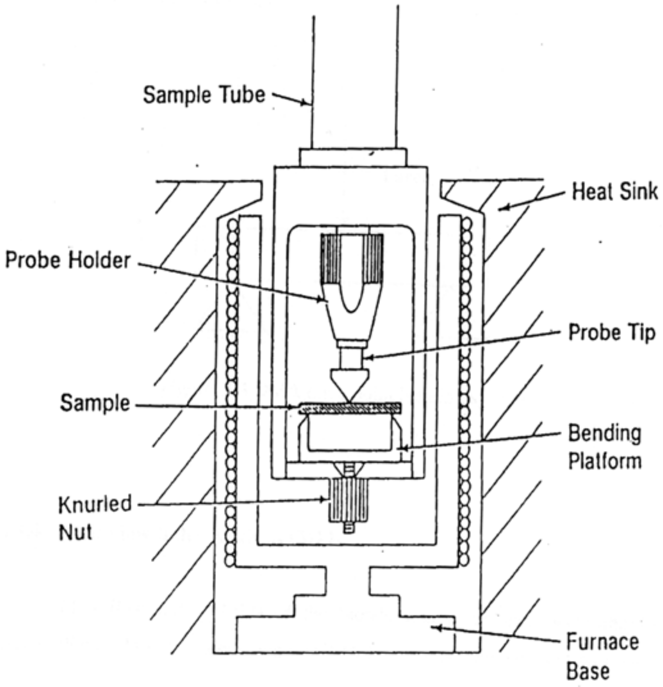

Figure 3.4 : A schematic diagram of a DMA used to determine the compatibility of the blends (Perkin-Elmer Instrument)

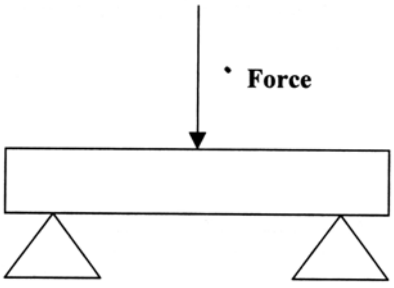

Figure 3.5 : DMA three point bending system

3.3.3 Scanning Electron Microscopy (SEM)

SEM JEOL JSM 5610 (as shown in Figure 3.6) was used to obtain the surface behaviour of the different blends. The samples to be examined was chosen after the impact test and then cut into smaller pieces. It was placed on double-sided sticky tape on a specimen stub. The specimen to be scanned was mounted on a stub and accommodated in the specimen chamber. The fracture surface prepared for SEM examination by sputter coating with a layer of gold on biotech machine (JFC-1600 auto fine coater) to facilitate examination under the SEM. SEM picture were taken at different magnifications (x200 and x2000).

Figure 3.6 : Photograph of SEM JSM 5610

3.3.4 Flexural Properties

Flexural test was carried out according to ASTM D 790. The test procedure used is Test Method 1, Procedure A, i.e., three-point loading utilizing center loading. Since the modulus was determined between small initial deflections, to ensure good accuracy, a low force load cell (100N) was used. Flexural test was carried out a simple supported beam. The distance between the spans was 4.96 cm and the strain rate (compression speed) was 3 mm/min. The flexural properties were measured at room temperature (25 ± 2 ^{o}C) on an Instron Universal Tester (model 5567) as shown in Figure 3.7. Five samples were tested for each composition and average values were recorded.

Figure 3.7 : Photograph of Instron universal tester

3.3.5 Oxygen Index Test (LOI)

Oxygen index is the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under the set condition.

The test determines the minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that will just support combustion. This process was carried out under equilibrium conditions of candlelike burning. Figure 3.8 illustrates a typical equipment layout of LOI and the maker is Fire Test Technology, UK.

The test specimen used in the experiment must be dry since the moisture content will alter the oxygen index. The samples were moulded according to ASTM D 2863, 125 x 10 x 3 mm. The oxygen index was calculated as follows:

$$\boxed{\text{Oxygen index percent} = (100 \times O_2) / (O_2 + N_2)}$$

where O_2 = volumetric flow of oxygen at the concentration determined;
N_2 = volumetric flow of nitrogen.

Figure 3.8 : Typical equipment layout for oxygen index test

3.3.6 Heat Defection Temperature (HDT)

Heat deflection temperature is defined as the temperature at which a standard test bar (127 x 12.5 x 3 mm) deflects 0.25 mm. under a stated load of 1820 kPa. This test can distinguish between those materials that lose their rigidity over a narrow temperature range and those that are able to sustain light at high temperature.

HDT test was carried out following ASTM D 648, with HDT Tester S-3 machine (Maker: Toyoseiki) as illustrated in Figure 3.9. The apparatus for measuring HDT consists of an enclose oil bath fitted with a heating chamber and automatic heating control. A cooling system is also incorporated. The specimens were supported on steel supports that are 4 in. apart, with the load applied on top of the specimen vertically and midway between the supports. A dial indicator was used to measure deflection.

The specimen was positioned in the apparatus and was submerged into the oil bath kept at room temperature. The load was applied to a 1820 kPa. Five minutes later, the pointer was adjusted to zero and the oil was heated at the rate of 2 ± 0.2^{o}C/min. The temperature of the oil at which the bar had deflected 0.25 mm was recorded as the heat deflection temperature at the specified fiber stress.

Figure 3.9 : Heat distortion tester S-3 machine

3.3.7 Melt Flow Index (MFI)

Melt flow index (MFI) of the blends was determined according to ASTM D1238-90b at 200 °C under a load of 2.16 kg. The equipment used was Toyoseiki thermo controller. About 3 g of sample was introduced into the barrel, at 200°C and was allowed to melt and achieve thermal equilibrium for 4 minutes. Load of 2.16 kg was applied on the melt and material was extruded through the die. The extrudates were cut at regular interval, usually at 10 minutes interval. The cut-off extrudates were weighed and the value was converted to the unit of g/min. The average of four extrudates was taken for the MFI value.


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CHAPTER IV

RESULT AND DISCUSSION

The findings of ABS/PVC blends are discussed through Izod impact testing, dynamic mechanical analysis, scanning electron microscopic, flexural modulus, limiting oxygen index, heat distortion temperature and melt flow index test.

4.1 Izod Impact Testing

The ability of a material to absorb the energy of a high-speed blow without breaking is a property of great technological importance. Izod impact test is one of the empirical methods of measuring impact strength in current use in the plastics industry. A pendulum striker hits the specimen horizontally at a point above the notch. After the specimen has been fractured, the pendulum continues on its and the energy remaining is measured by the extent of the excess swing.

Factors contributing to the total breaking energy as measured by the Izod test are: (a) energy to initiate fracture of the specimen; (b) energy to propagate fracture across the specimen; (c) energy for plastic deformation of the specimen; (d) energy to throw the broken end of the test piece; and (e) energy lost through vibration of the apparatus and its base and through friction (Cogdell and Hardesty, 1958).

The results for impact testing will be divided into two parts. The first part is to study the effect of different PVC molecular weight on high rigidity, medium impact and super high impact ABS. The second part will focus on the effect of different ABS grades on PVC K-58, K-66 and acrylic grafted PVC.

4.1.1 Effect of PVC Molecular Weight on Different Grades of ABS

4.1.1.1 High Rigidity ABS

In this section, the effect of different PVC molecular weight (K-58 and K-66) and acrylic grafted PVC on ABS will be presented. The ABS loading level of 80, 85, 90 and 100 phr were used. As shown in Figure 4.1, impact strength increases with increasing PVC content in the ABS/PVC blends. The use of PVC K-66 shows higher impact strength when compared with PVC K-58. This shows that the higher the molecular weight the greater the impact strength. The explanation will be given in section 4.1.3. However when PVC is grafted with acrylic rubber, with the K-value of 64 has better properties than PVC K-66. The result shows that acrylic grafted PVC is the most effective in enhancing the impact strength. The reason is the presence of the acrylic rubber which is an effective impact modifier for PVC. The addition of 20phr acrylic grafted PVC increased the impact strength at 38 %.

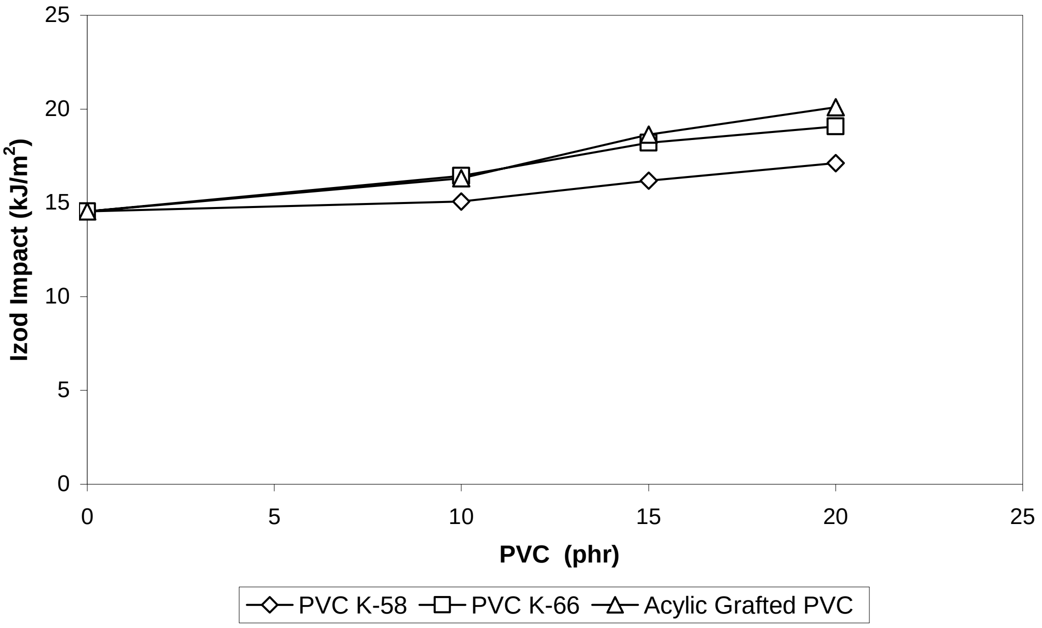


Figure 4.1 : Effect of different PVC molecular weight and content on Izod impact strength of high rigidity ABS

4.1.1.2 Medium Impact ABS

Figure 4.2 illustrates that as the PVC content increases from 0 phr (virgin ABS) to 20 phr, the average impact strength values increases. The trend is similar to the high rigidity ABS. The results indicate that 20 phr acrylic grafted PVC shows the best enhanced properties, with the highest increment of 60 % compared to virgin ABS. When the blends with PVC K-58 and K-66 are compared, PVC K-66 shows higher impact value. This shows that the higher the molecular weight, the more effective it is in enhancing the impact strength of ABS.

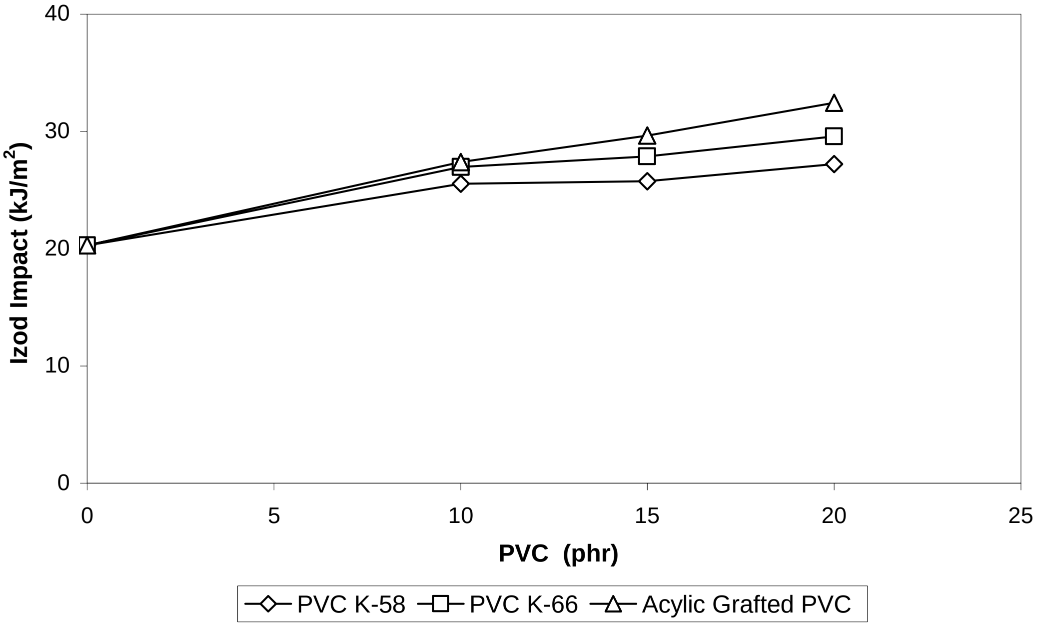


Figure 4.2 : Effect of different PVC molecular weight and content on Izod impact strength of medium impact ABS

4.1.1.3 Super High Impact ABS

A clear trend is apparent in Figure 4.3, as the loading level of PVC increased, the impact energy absorbed during failure increase. At the PVC content of 10 phr, PVC K-58 and PVC K-66 have the similar impact strength around 43 kJ/m^2. At the blends composition of 15 and 20 phr of PVC content, PVC K-66 has a significant effect, which has the similar impact strength with acrylic grafted PVC. Acrylic grafted PVC posses a slightly higher increment of impact strength, which is around 65 % if compared with PVC K-66 (63 %) at the optimum loading level of PVC (20 phr).

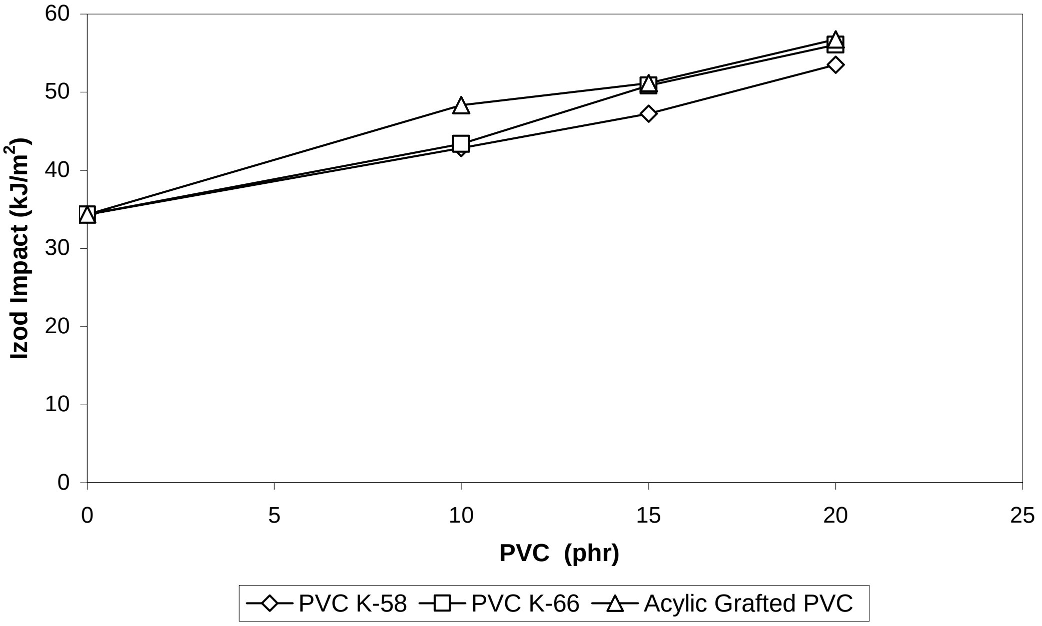


Figure 4.3 : Effect of different PVC molecular weight and content on Izod impact strength of super high impact ABS

4.1.2 Effect of ABS Grades on Different PVC Molecular Weight

The results in this section is obtained from the same data as in section 4.1.1 but are presented to demonstrate the effect of different ABS grades..

4.1.2.1 PVC K-58

In this section, the results of PVC K-58 blended with different grades of ABS are given. From Figure 4.4, it is observed that as the loading level of PVC K-58 increases from 0 phr to 20 phr, the average impact strength values increase. The results also shows that for pure ABS, the super high impact grade has the highest impact strength values as expected since it has the highest butadiene rubber content. This is followed by the medium impact grade and the high rigidity grade is the lowest. It is interesting to observe that as the PVC content increases, the super high impact grades shows the highest increment, around 56 % increment in 80 phr ABS/20 phr PVC K-58 blends. High rigidity ABS has the lowest increment of impact strength, which is about 18 %. This shows that the butadiene rubber content influence the enhancement of impact strength.

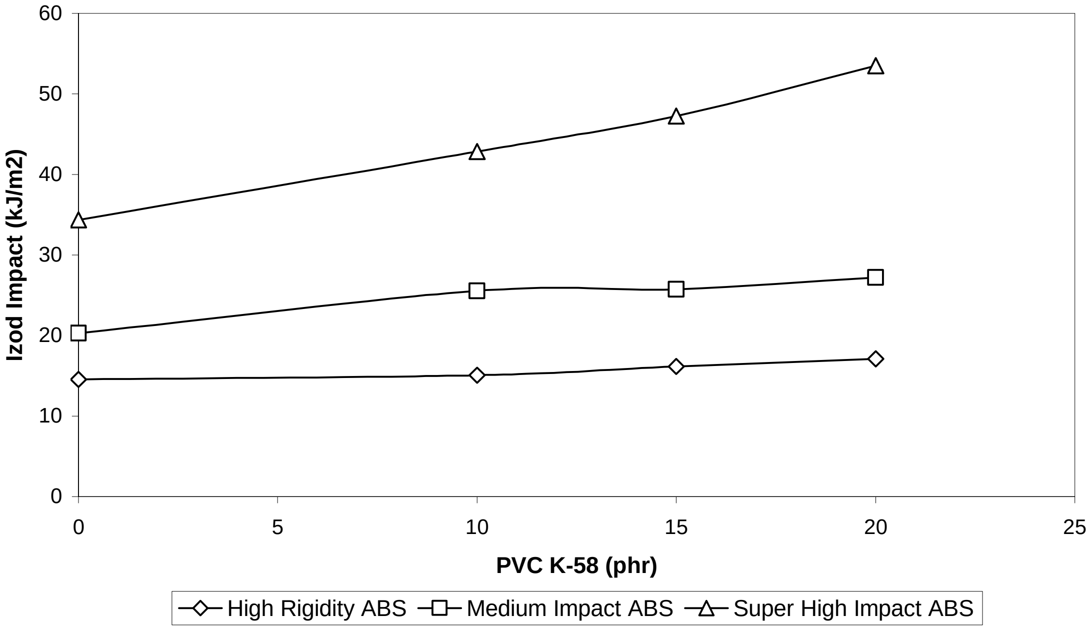


Figure 4.4 : Effect of ABS grades and PVC content on Impact strength of PVC K-58

4.1.2.2 PVC K-66

Figure 4.5 illustrates that the incorporation of PVC K-66 into ABS results in a considerable increase in the impact strength of pure ABS, similar with the trend observed in PVC K-58. Super high impact ABS shows a sharp increase of impact strength (63 %) as compared to 31 % for high rigidity ABS.

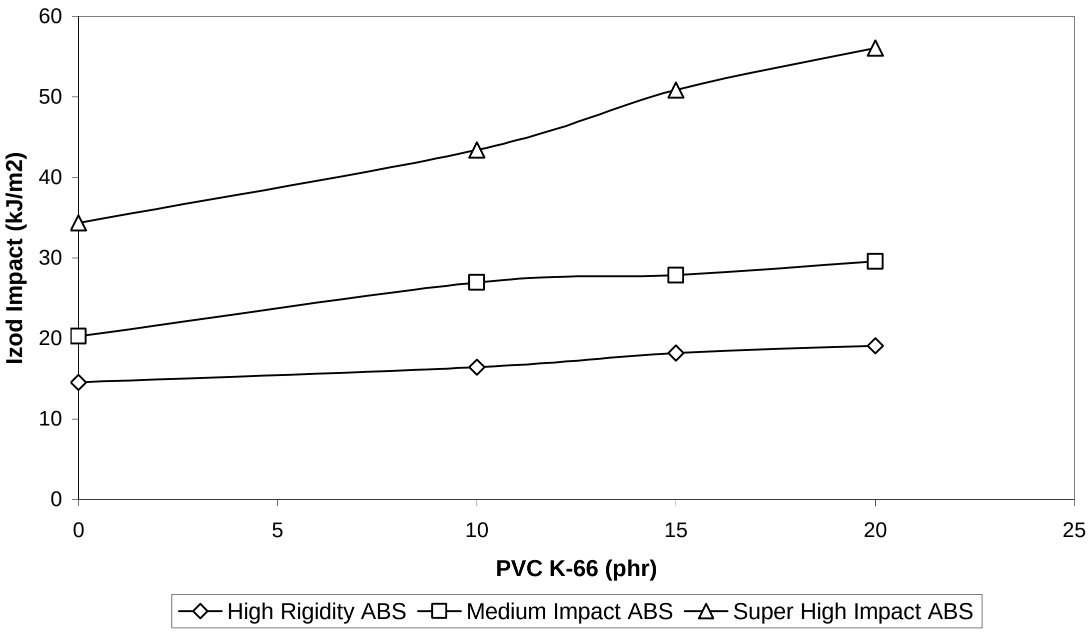


Figure 4.5 : Effect of ABS grades and PVC content on Impact strength of PVC K-66

4.1.2.3 Acrylic Grafted PVC

Enhancement of impact strength is observed as the content of acrylic grafted PVC are increased as illustrated in Figure 4.3. The trend of impact strength variation with the blend composition is similar to the previous report as shown in Figure 4.4 and 4.5. The super high impact ABS has sharp improvement in notch impact strengths upon the addition of 10 phr acrylic grafted PVC. It then rises rather slowly from 10 to 20 phr with an increment of 65 %. Apparently, both medium impact and high rigidity ABS have a marginal effect in failure mode when blended with acrylic grafted PVC.

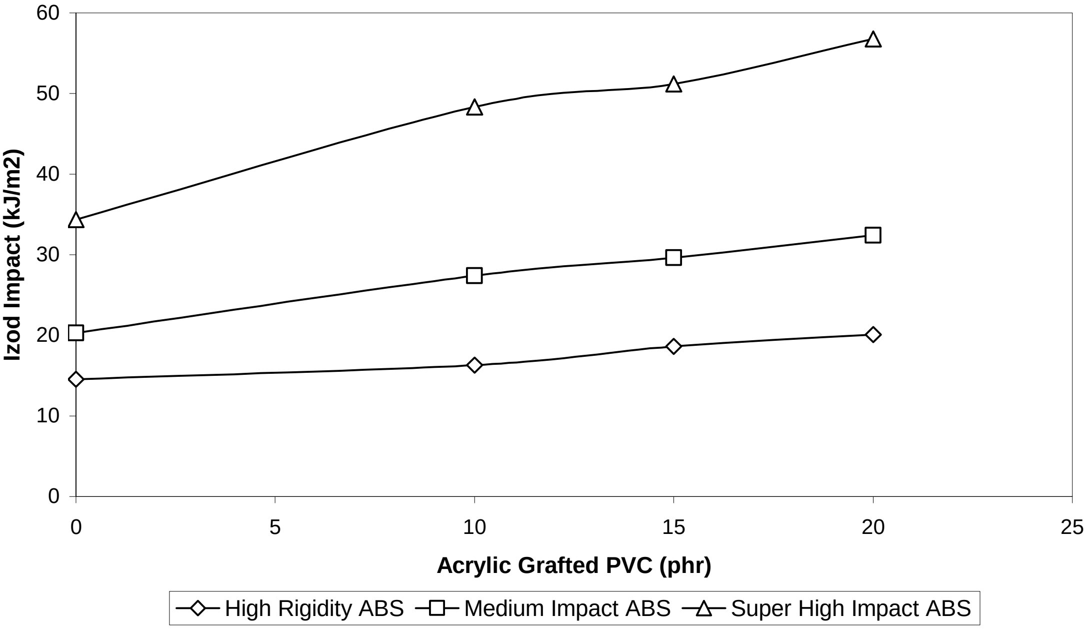


Figure 4.6 : Effect of ABS grades and PVC content on Impact strength of acrylic grafted PVC

4.1.3 Overall Discussion on Impact Test

The addition of PVC into ABS has produced a very interesting result. A synergistic effect is the impact strength of the ABS/PVC blends is found to be higher than pure ABS and PVC. Impact testing for PVC was not done in this study but the value is based on study by other researches. The impact strength for unfilled PVC obtained by Sivaneswaran (2002) is 9 kJ/m^2. Other researchers also supported that PVC has a lower impact strength compared with ABS (Gobstein, 1990). The possible reason for this synergistic effect is that the addition of PVC into ABS enhanced the ductility of the matrix thus increasing the amount energy being absorbed. The result is in good agreement with the finding of Deanin and Moshar (1974). The effect of matrix ductility upon impact strength are illustrated in Figure 4.7, which presents data obtained by Deanin and Moshar (1974) in notch Izod impact strength tests on PVC/ABS blends. From the figure, it can be observed that the impact strength rises as the PVC concentration increase ranging from 0 to 100% and reach the maximum at 75% PVC. This confirms that adding PVC into ABS increase the ductility of the ABS matrix as stated in the study of Bucknall (1977).

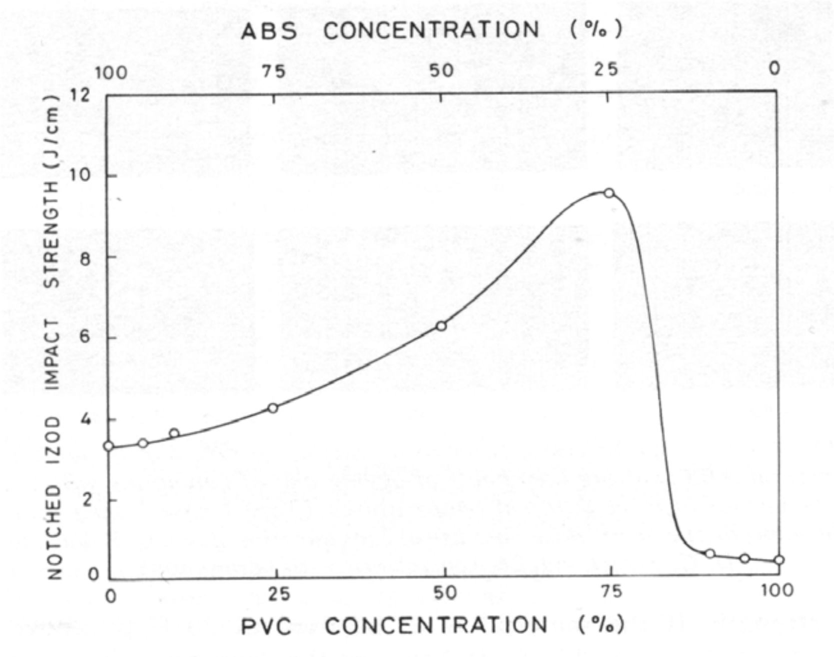


Figure 4.7 : Notch Izod impact strength of PVC/ABS blends at 23°C showing the toughness achieved by balancing matrix ductility against PVC content (Deanin and Moshar, 1974)

In ABS polymer, SAN forms the matrix phase and butadiene is the discrete phase which acts as a stress concentrator. The yielding in the SAN matrix phase is relatively difficult due to the presence of benzene molecule. The addition of PVC will modify the matrix phase since PVC is believed to be nearly miscible with SAN (Manson, 1986).

The miscibility between PVC and SAN may be explained in terms of solubility parameter of both polymers. The solubility parameter δ, a measure of attractive forces between molecules, may be used to determine the miscibility. According to data given by Bramfitt and Heaps (1962), SAN has a solubility parameter of 19.6 $MPa^{1/2}$ whereas solubility parameter for PVC is 19.4 $MPa^{1/2}$. The difference of these two polymers is 0.2. According to Rosík (1985), the difference in solubility of two polymer must be lesser than 0.4 if the polymers are miscible. Therefore, SAN/PVC fulfilled the criteria. Hence, addition of PVC into SAN matrix will form a new matrix phase which is a combination of PVC and SAN.

The presence of PVC will promote shear yielding for the blend and thus increase the impact strength. The strong interfacial adhesion of the SAN matrix with PVC results in the increase in impact strength and toughness.

The small difference in solubility parameter can be explained due to the secondary valences forces present in PVC and SAN, which will result in the dipole-dipole intermolecular forces in these molecules. As shown in Figure 4.8, these stronger secondary valences forces and the entanglement of polymer chain will increase the strength and toughness of hydrocarbon polymer (Seymour, 1975). The charges of dipole-dipole intermolecular force are labeled as δ^+ and δ^-.

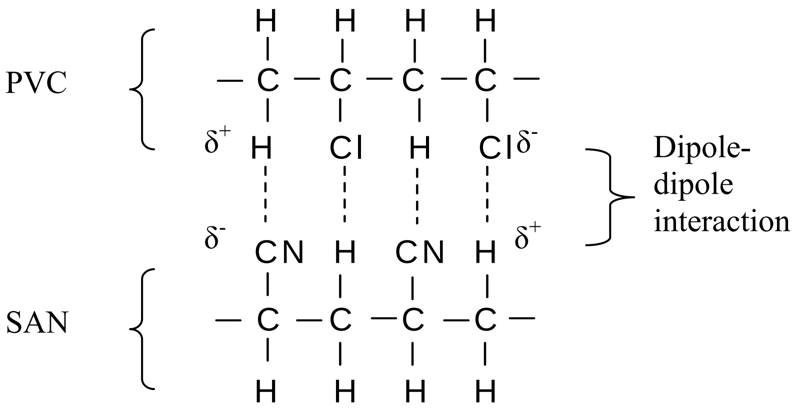


Figure 4.8 : Typical dipole-dipole interaction and segments of chains between molecules of PVC and SAN (Seymour, 1975)

Based on the results presented, acrylic grafted PVC gives the highest impact strength enhancement on all grades of ABS, followed by PVC K-66 and PVC K-58. Basically, the molecular weight (K value) of the PVC has a substantial influence on the mechanical properties of the polymer.

The acrylic grafted PVC are obtained by vinyl chloride (VC) polymerisation and grafting polyacrylic elastomer onto the PVC backbone, make it possible to produce finished products offering high impact strength without adding modifiers. With the good condition offered and K value of 64, acrylic grafted PVC will provide excellent impact strength if blends with ABS. The reason for the highest increment of impact strength values of acrylic grafted PVC/ABS blends is the extra elastomer content in the acrylic grafted PVC.

According to Donald (1986), the higher the molecular weight, the higher the mechanical properties of PVC. PVC K-66 has a degree of polymerization of 1000 ± 50 which give higher molecular weight compare to PVC K-58. The higher impact strength of PVC K-66 compared to k-58 is that the higher the molecular weight, the more effective it is in enhancing the yielding and thus improves the ductility. As mentioned earlier, the yielding in the SAN matrix phase is relatively difficult due to the presence of benzene molecule. The longer the PVC molecular chain, the more effective it is in reducing the effect of brittleness due to the benzene molecule which is a bulky group. Therefore its increment of impact strength is higher.

Although the K value for PVC K-66 is higher than acrylic grafted PVC, the impact strength of acrylic grafted PVC is higher than PVC K-66. This means, the presence of acrylic elastomer has greater influence than the K value in determining the impact strength of the blends.

From the graph observed in figure 4.1 - 4.6, impact strength of the blends significantly influenced by the types of ABS, which is dependant on the monomer ratio. Super high impact ABS has the highest impact values compare to medium impact, whereas high rigidity ABS shows the lowest impact energy absorbed during failure. The higher content of rubber (or butadiene), which forms droplets in a continuous glassy SAN, plays an important role of enhanced toughness in super high impact ABS (Bucknall, 1977).

The toughening effect is associated with the crazing behaviour (Bucknall, 1977). Rubber particle has the ability to modify the deformation behaviour of the matrix polymer. Triaxial tension due to the presence of a notch, a high strain rate and a low temperature all combine to raise the shear yield stress relative to the crazing and fracture stress. The energy absorbed in crack growth consequently falls.

The results obtained is supported by the finding of Dear *et al.* (1997), the present of many well distributed voids or rubber particles creates a multiple of stress paths, provide point of local stress concentration. The equatorial zones of the dispersed rubber particles has the ability to increase the number of microcrazes occurred under a stress, and they are observed as a whitening phenomenon (Mitsuru *et al.*, 1983). These are not true cracks with a continuous free surface capable of further opening, but rather small, localized inhomogeneties transformed zones, localized perpendicular to the main stress. The presence of many crazes is considered to distribute stresses which would otherwise be concentrated at the tip of a few growing crack, thus results in great toughening effect.

After craze formation, the rubber particle shares the stress with the SAN matrix and the originally spherical particles are deformed and become ellipsoidal in shape. Part of the energy can also be consumed in scission of grafts between the SAN and rubber particles (Manson and Sperling, 1976).

The mechanism of craze termination is also important for attaining optimal toughness. If brittle fracture is to be avoided, growth of the crazes into macroscopic cracks must be prevented. Craze growth terminates when the stress at the tip of the craze decreases below a critical value, necessary for the growth or if it encounters an obstacle, such as the nearest sufficiently large rubber particle. Thus, the presence of rubber particles in the material not only initiates crazing but also limits craze growth. A further mode of craze termination is interaction with shear bands (Bucknall, 1977).

For ABS, the more dominant toughening effect is the increased shear yielding in the reduced cross-section of the matrix between the rubber particles (Dear *et al.*, 1997). Localized shear yielding leads to the formation of shear bands at an angle of about 45^{o} to the main stress direction, observable as a birefringent region. Their presence indicates that shear of the macromolecules occurred in a narrow region, with strong polymer orientation. The present of shear bands is to act as obstacles to craze propagation and control craze size, thus help to increase toughness: in fracture mechanics terms, the intrinsic flaw size of the blends is reduced (Bucknall, 1977).

Cavitation of the rubber particles, particularly the large ones, adds to this shear yielding process. Crack blunting and arrest by the rubber particle cavities is another factor more attributable to larger particles. These toughening effects play a large part in determining the resistance offered by ABS material to a propagating crack normal to the applied unidirectional load (Dear *et al.*, 1997). Here again, the presence of rubber particles is considered to be responsible for the initiation of these phenomena. Shear yielding is probably an even more efficient mechanism than multiple crazing for the dissipation of the applied energy (Manson and Sperling, 1976).

4.2 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) technique was employed in this study. DMA is able to characterize the blend miscibility on a molecular level by studying their glass transition behaviour (Wetton and Corish, 1988/9; Scobbo, 1991). DMA have been widely used in the study of polymer miscibility by UTM researchers (Wan Aizan Wan Abdul Rahman, 1996; Ching Yern Chee, 2001; Sani Amril, 2003). DMA has the advantages of a thousand fold greater sensitivity when studying glass transition phenomena than differential scanning calorimeter (DSC) (Wetton and Corish, 1988/9).

T_g is the reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from a viscous or rubbery condition to relatively brittle one. At T_g, micro-Brownian motion of molecular segments begins where short range diffusion can take place. At temperature less than T_g, energy is insufficient to cause rotational and translational motions of segments (Ferry, 1980).

The temperature at which this T_g occurs is characterized in DMA by a peak in the loss modulus (E”) and loss tangent (Tan δ) and a decrease in the storage modulus (E’). Storage modulus is a quantitative measurement of the stiffness or rigidity of a material. Loss modulus is the ability of a material to dissipate mechanical energy by converting it through molecular motion. The absorption of mechanical energy is often related to the movement of molecular segments within the materials, such as polymeric side chains or specific molecular groups within the main chain. While the storage modulus decreases about three orders of magnitude, the loss modulus and Tan δ go through maxima at T_g. They are related to Tan δ (damping factor) as shown in Equation below:

$$Tan\ \delta = \frac{E''}{E'}$$

In this section, selected ABS/PVC blends were chosen and comparisons were made between different grades of ABS with PVC K-66. Glass transition temperature (T_g) are determined as the temperature is at maximum of Tan δ. Table 4.1 shows the temperature dependence of loss tangent delta for selective blends.

From the data obtained, 100% high rigidity ABS has a main transition temperature at 111.3 ^oC. This transition belongs to SAN and is in good agreement with literature (Moore, 1989). The polybutadiene content in ABS is not shown in the figures because it has a peak at -82 ^oC. The noticeable effect of the addition of PVC K-66 in ABS is observed in the decrease in temperature transition of SAN from 111.3 ^oC to 108.7 ^oC. The broadening of the peak occurred from 25 to 26 ^oC (as shown in Table 4.1). In addition, a virgin high rigidity ABS has a higher peak height value (around 1.49 Pa) compared to high rigidity ABS/PVC K66 blend with the value of 1.25 Pa. The comparison for pure high rigidity ABS and addition of PVC K-66 is presented in DMA curve as shown in Figure 4.9 and 4.10.

Figure 4.11 represents the DMA curves for virgin medium impact ABS. The same effect is observed, where the temperature transition of SAN is shifted from higher temperature (110.1 ^oC) to lower temperature (107.1 ^oC) when PVC is added into ABS (Figure 4.12). From the table, it is shown that the peak height of ABS decrease by around 0.24 Pa (from 1.53 to 1.30 Pa) upon addition of 20 phr PVC to form a blend. A widening of the peak is also observed when PVC is incorporated into ABS.

As for super high impact ABS, a decrease in peak height value is observed by incorporation of PVC. The temperature transition of SAN is shifted from 110.7 ^oC to 107.7 ^oC when PVC is added into ABS. The peak height also reduced from 1.36 to 1.13 Pa when PVC is incorporated into ABS. Again, a broader glass transition region is observed with addition of PVC into ABS.

Table 4.1 : Transition temperature of loss tan delta for selected materials

Selective Blends	**T_g (^oC)**	**Peak Height (Pa)**	**$W_{1/2}$[a] (^oC)**
High Rigidity ABS	111.3	1.49	25
High Rigidity ABS + PVC K66 (80:20)	108.7	1.25	26
Medium Impact ABS	110.1	1.53	24
Medium Impact ABS + PVC K66 (80:20)	107.1	1.30	28
Super High Impact ABS	110.7	1.36	25
Super High Impact ABS + PVC K66 (80:20)	107.7	1.13	27

[a] Width of the peak at half height

Lian *et al.* (2001) reported that PVC has a T_g at 85 ^oC. A miscible blend will exhibit a sharp single T_g. The T_g values in partially miscible blends are expected to shift towards each other (Macknight *et al.*, 1978; Wetton and Corish, 1988/9). According to Dayal *et al.* (1998), the widening of the peak at T_g and the reduction of peak height indicates that a heterogeneous copolymer is produced. This statement is in agreement with Murayama (1990) that a sharp single T_g is observed if the blends is homogeneous copolymer since all molecules have the same chemical composition.

In this study, the T_g for the three ABS/PVC blends are shifted toward the T_g of PVC. A single T_g with a slightly broadening and lower peak height is produced. This fairly indicates there is good interaction between the phases of SAN and PVC due to the same polarity produced. It is proposed that a nearly miscible SAN/PVC blend has been produced. Jin *et al.* (1998) supported that PVC and SAN formed a mixed phase and enhanced the miscibility of the blends. The nearly miscible of the SAN phase with PVC is strongly supported by Cheng and Mantell (1989). In fact, PVC is miscible with structurally different homopolymers and copolymers (Olabisi, 1982).

The miscibility between SAN component of ABS has improved the interfacial adhesion between PVC and ABS. There is no distinct interfacial boundary between PVC and SAN. The highly miscible SAN/PVC blend has a reduced interfacial tension and hence, is expected to increase the degree of dispersion in blends and results in stronger impact strength and toughness (Liang and Li, 2000).

In general, the marked increase in the mechanical characteristics for the ABS/PVC blends suggested that an enhancement of interaction and well-developed interlayer formed by the SAN/PVC is essential for good impact properties of this multiphase polymeric system.

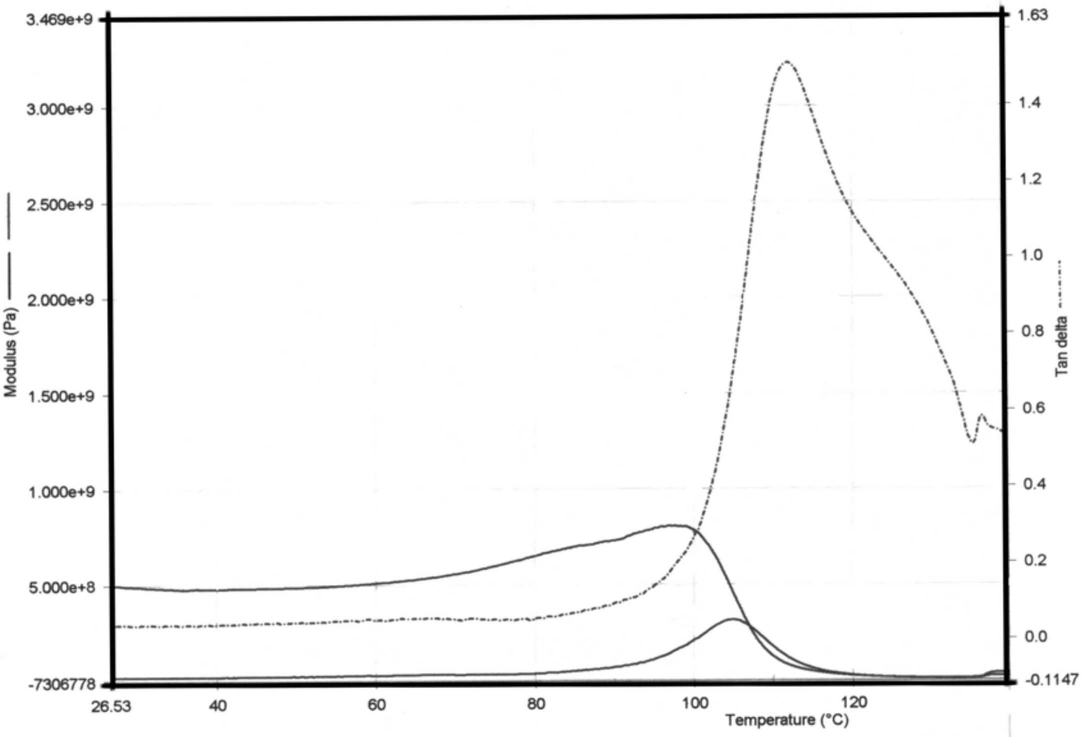


Figure 4.9 : DMA curves for high rigidity ABS as a function of E"/E' and tan δ

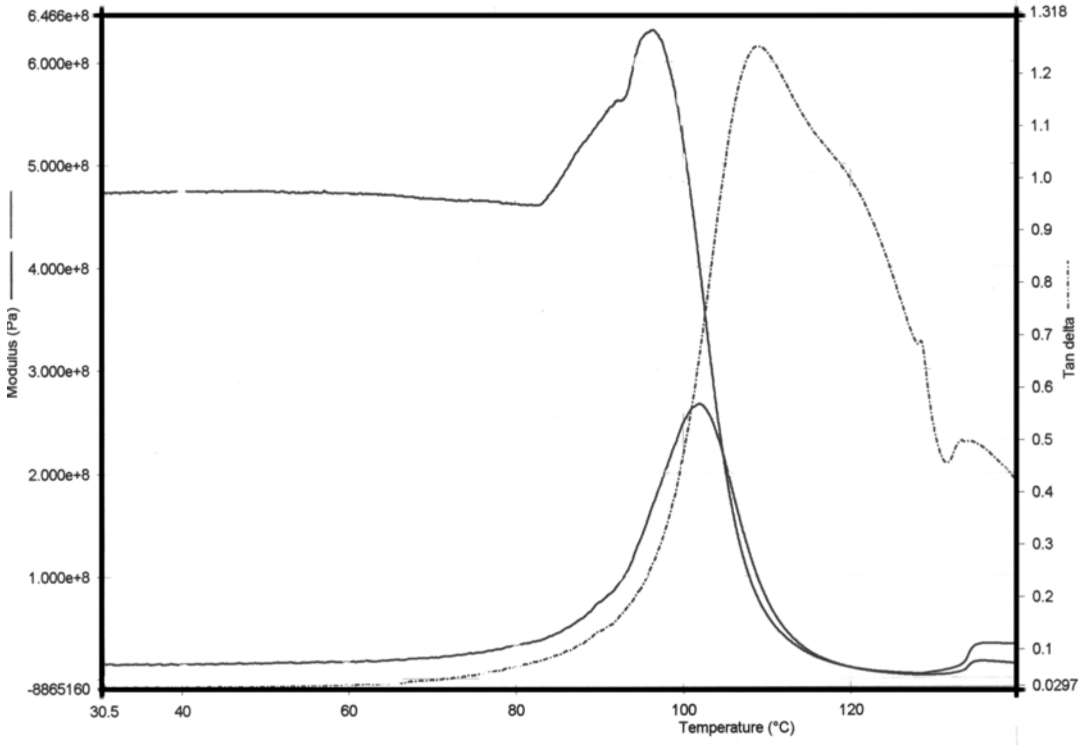


Figure 4.10 : DMA curves for high rigidity ABS – PVC K66 as a function of E"/E' and tan δ

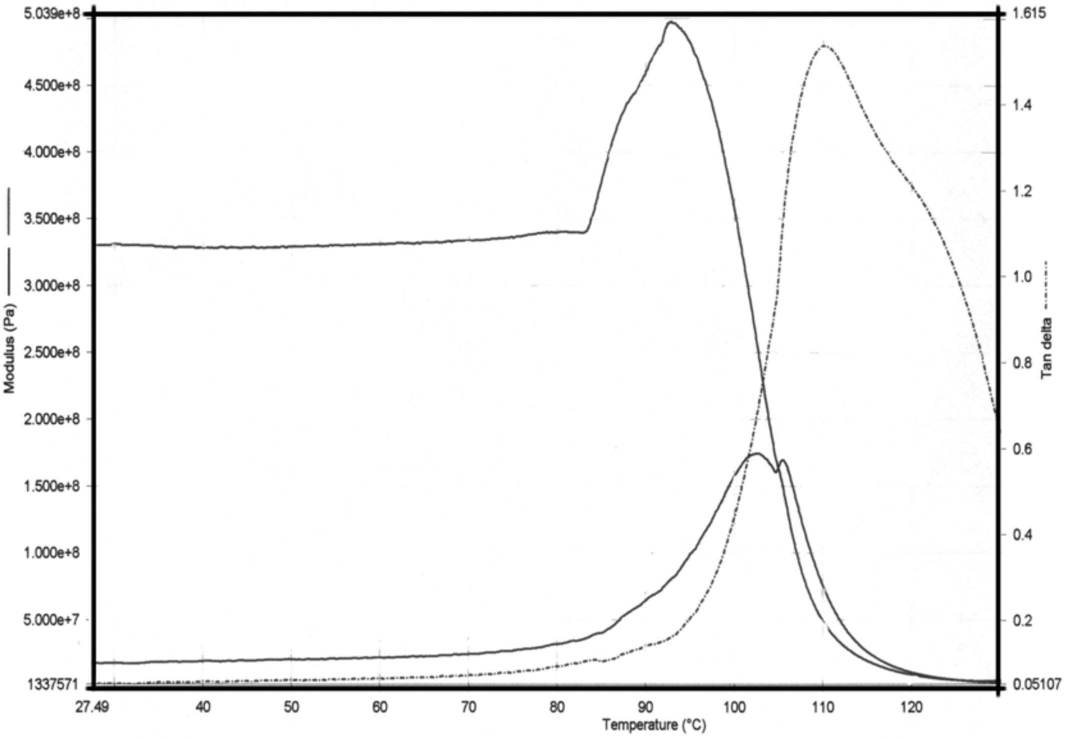


Figure 4.11 : DMA curves for medium impact ABS as a function of E"/E' and tan δ

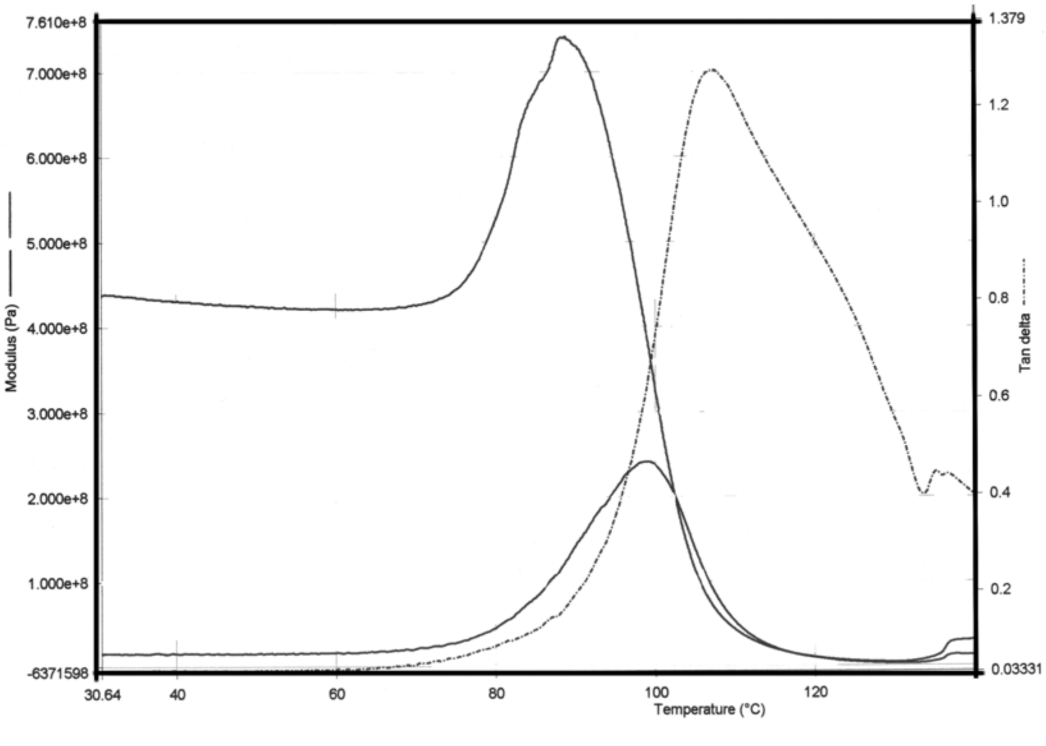


Figure 4.12 : DMA curves for medium impact ABS – PVC K66 as a function of E"/E' and tan δ

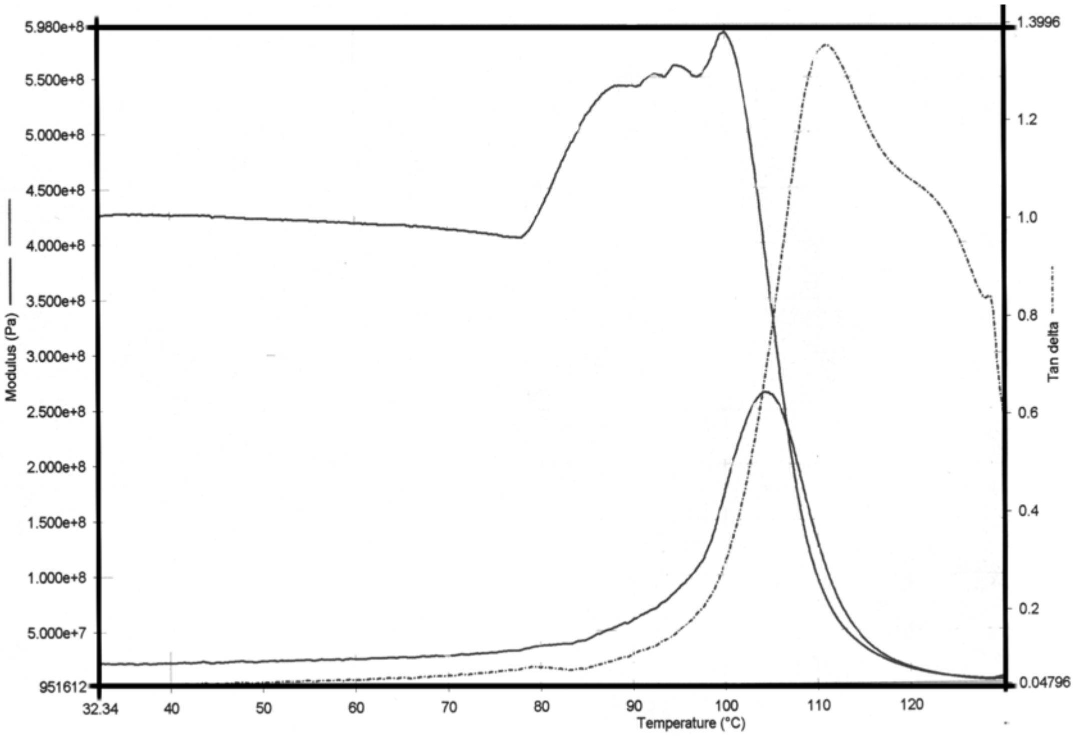


Figure 4.13 : DMA curves for super high impact ABS as a function of E”/E’ and tan δ

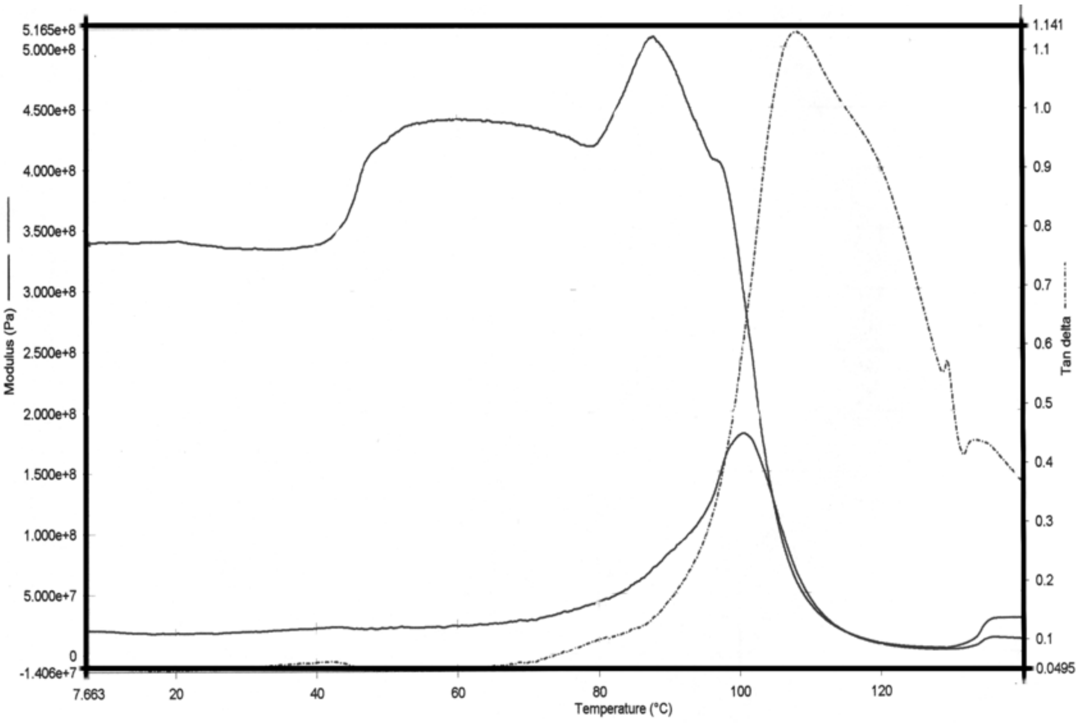


Figure 4.14 : DMA curves for super high impact ABS - PVC K66 as a function of E”/E’ and tan δ

4.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) method has been used to study the fracture surfaces at a higher magnification and to relate the fracture mechanism with the impact strength. This study is not intended to compare the fracture surface with the types of ABS and PVC.

Azman Hassan (1996) in his study on the fracture behaviour of the acrylate-modified PVC samples classified the fracture surface into three types based on fracture mode (brittle/ductile) and whitening degree. The three types are:

Type I : Ductile fracture with formation of elliptical shaped stress-whitening zone near the edge and on the fracture surface.
Type II : Brittle fracture with whitening on the fracture surface
Type III : Brittle fracture without whitening

Based upon the above study, the fracture behaviour of ABS/PVC samples from the Izod impact testing in the present study can also be classified into three different types. The three types are:

Type 1. : Brittle fracture with whitening on the surface
Type 2 : Ductile fracture with whitening on the surface
Type 3 : Ductile fracture with formation of elliptical shaped stress-whitening zone near the edge and on the fracture surface (refer Figure 4.15).

This classification will be used as the basis for the analyzing the results from SEM. The scanning electron micrographs of the fracture surface are taken at the midway point between the notch and the hinge of the specimens.

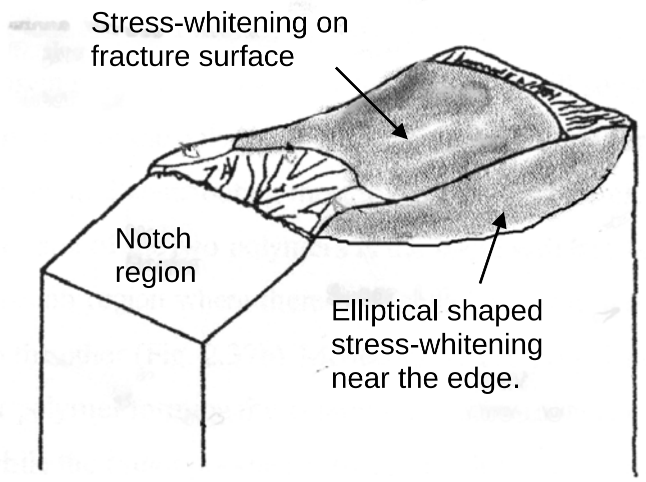


Figure 4.15 : Schematic stress-whitening zone of Izod impact specimen, near the edge and on the fracture surface region

Firstly, let us look at the sample which exhibited as type 1 fracture. Two samples from type 1 fracture with different impact strength are observed. The first sample is from virgin high rigidity ABS with impact strength of 14 kJ/m^2. As shown in Figure 4.16A, at low magnification (X200) a scaly and typical flat surface with the micro characteristics typical of rigid and glassy surface is observed. Figure 4.16B show a zoom of this fracture surface with higher magnification (X2000).

The second sample from type 1 fracture observed under SEM is 90 high rigidity ABS/10 PVC K-66 with impact strength of 16 kJ/m^2 as shown in Figure 4.17A and B. The fracture surface shows a jagged appearance with no evidence of fibrils or yielding. The overall evidence suggests the fracture mechanism is a brittle failure.

When PVC k-66 is added into high rigidity ABS, the scanning electron micrographs of fracture surface is relatively rough and coarse (refer Figure 4.17A and B), whereas virgin ABS is relatively smooth (refer Figure 4.16A and B). This is probably due to plastic deformation and tearing during fracture process.

This statement is in good agreement the findings of Kim (1990). The roughness surface for different grades of ABS is increased when the loading level of

PVC K-66 increase and is related to the ductility of the materials. The surface roughness can be related to fracture energy. A higher toughening efficiency is observed for intrinsically tougher matrices (Charles, 1996). Figure 2.32 in chapter II indicates a definite correlation between the surface roughness and fracture energy of rubber modified thermosets.

The next thing is to study the sample which exhibited hinge break phenomenon caused by plastic deformation and crack deceleration during the impact test. In our earlier classification, it is categorized as type 3 in which the samples fracture in ductile mode with the formation of an elliptical shape whitening zone on the fracture surface.

Figure 4.18 A and B shows the scanning electron micrograph of the typical type 3 fracture surface taken from 80 super high impact ABS/20 PVC K-66 with impact strength of 56 kJ/m^2. The appearance of the surface is identified as sphaghetti-like, long and elongated structure. Looking at X200 magnification, the micrograph shows a parabolic multiple fracture surfaces with furrows and is considered an additional energy adsorption mechanism because it can be seen in tough plastics (Riew *et al.*, 1979). The micrograph clearly shows the ductile yielding and fibrillation associated with crack blunting and termination. Localized yielding has resulted in the formation of voids, suggesting high impact energy has been absorbed as shown in Figure 4.18B.

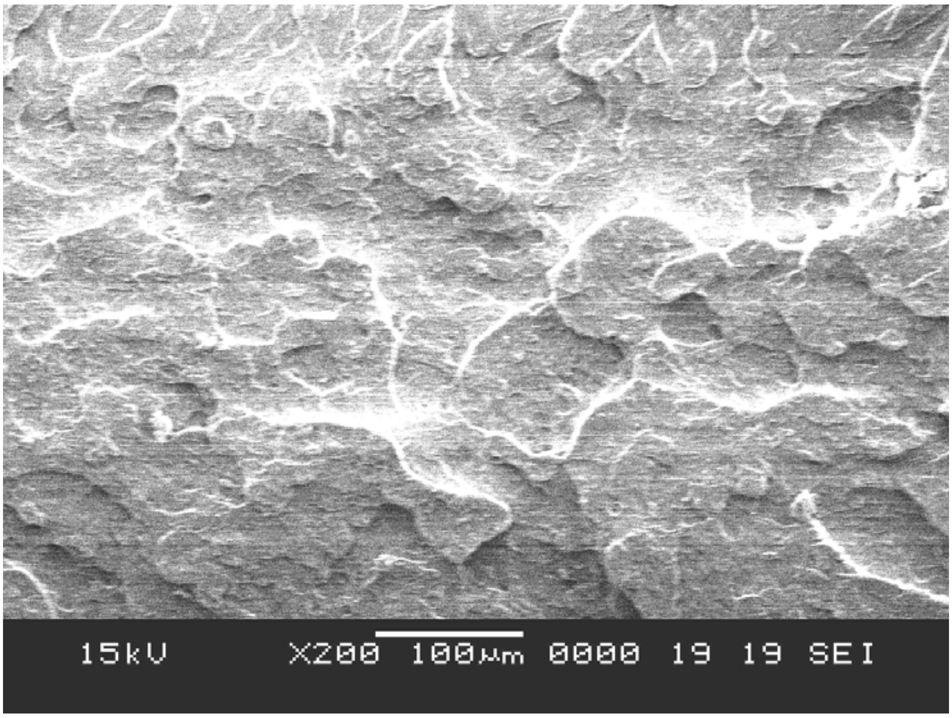


Figure 4.16 A : SEM micrographs of the fractured surfaces of the virgin high rigidity ABS (Magnification X200)

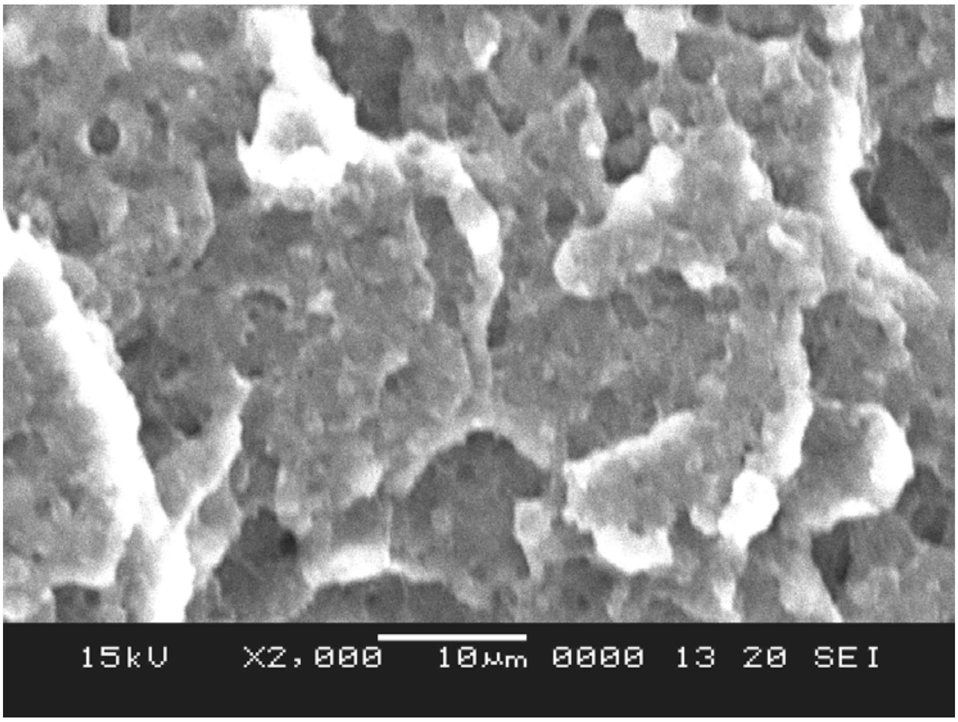


Figure 4.16 B : SEM micrographs of the fractured surfaces of the virgin high rigidity ABS (Magnification X2000)

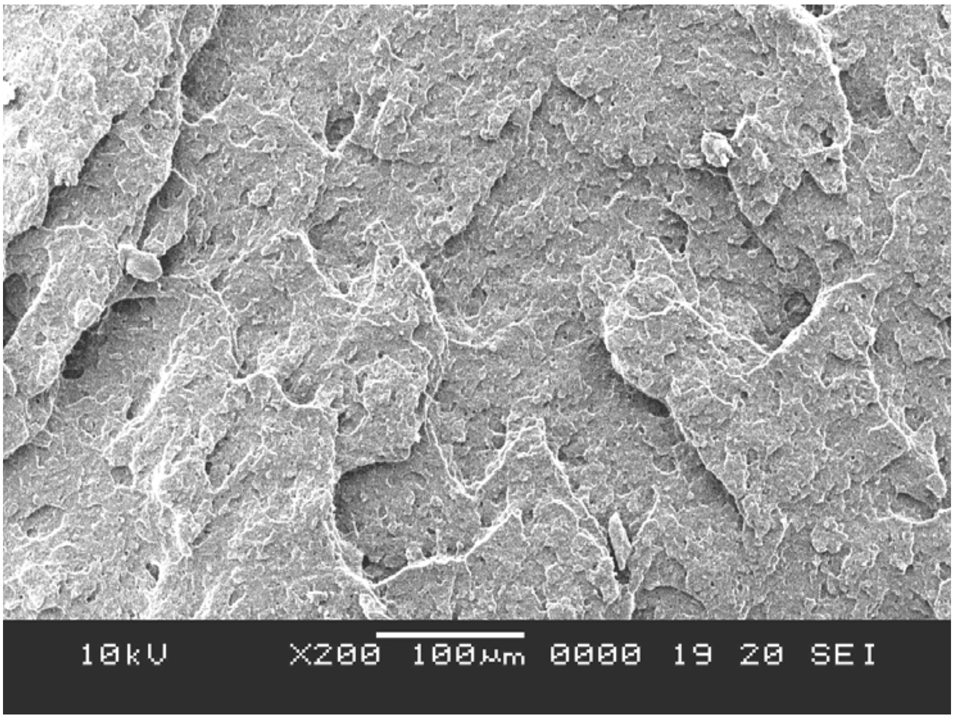


Figure 4.17 A : SEM micrographs of the fractured surfaces of the high rigidity ABS/PVC K-66 (90/10 phr/phr) (Magnification X200)

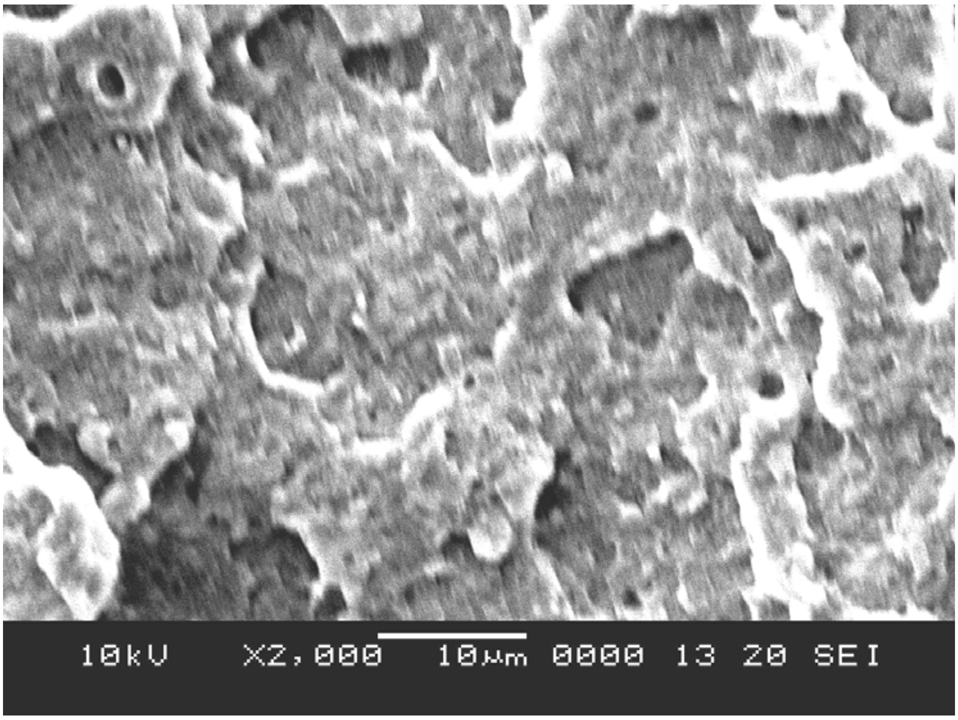


Figure 4.17 B : SEM micrographs of the fractured surfaces of the high rigidity ABS/PVC K-66 (90/10 phr/phr) (Magnification X2000)

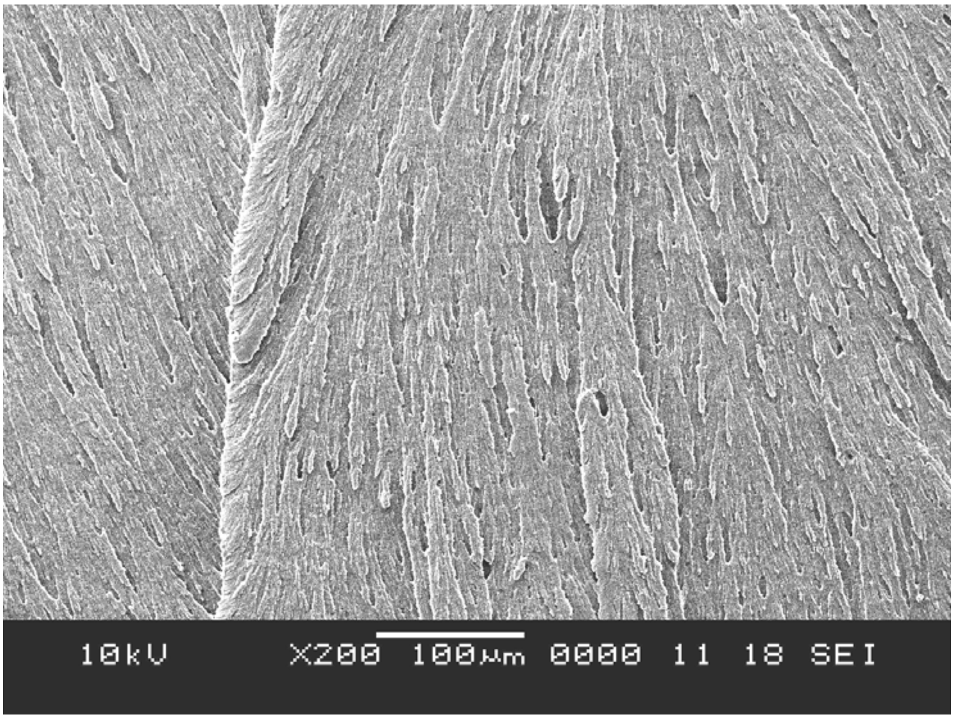


Figure 4.18 A : SEM micrographs of the fractured surfaces of the super high impact ABS/PVC K-66 (80/20 phr/phr) (Magnification X200)

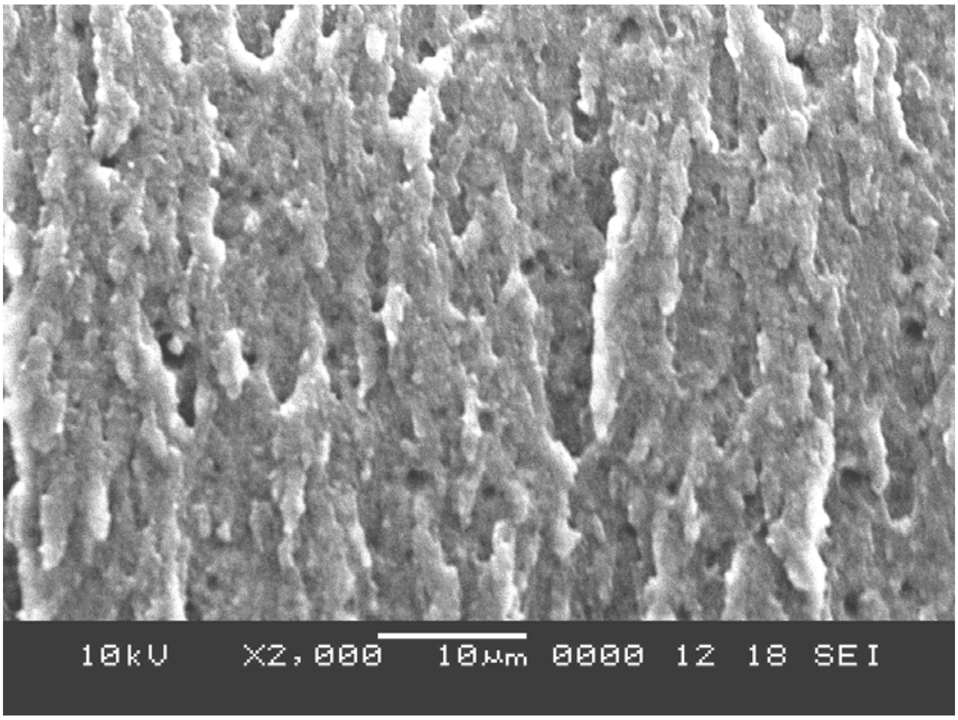


Figure 4.18 B : SEM micrographs of the fractured surfaces of the super high impact ABS/PVC K-66 (80/20 phr/phr) (Magnification X2000)

Having characterized the extreme of fracture and failure spectrum for type 1 and type 3 fractures, the next step is to examine the sample classified as type 2 fracture.

85 medium impact ABS/15 acrylic grafted PVC is taken as type 2 fracture with the impact strength of 29 kJ/m^2. Although the sample failed in ductile manner, the impact strength values is lower than type 3 sample. There is no elliptical shaped stress-whitening zone appears on the surface near the edge of the sample.

Generally, the appearance of the surface is in between type 1 and type 3 (refer Figure 4.19A). There is a small scale jagged and cratered appearance which can be clearly observed at higher magnification (X2000). As shown in Figure 4.19B. At this stage, an indication of fibrillar microstructure is observed. However, the structure of yielding and fibrillation is not as long-elongated as types 3 fracture.

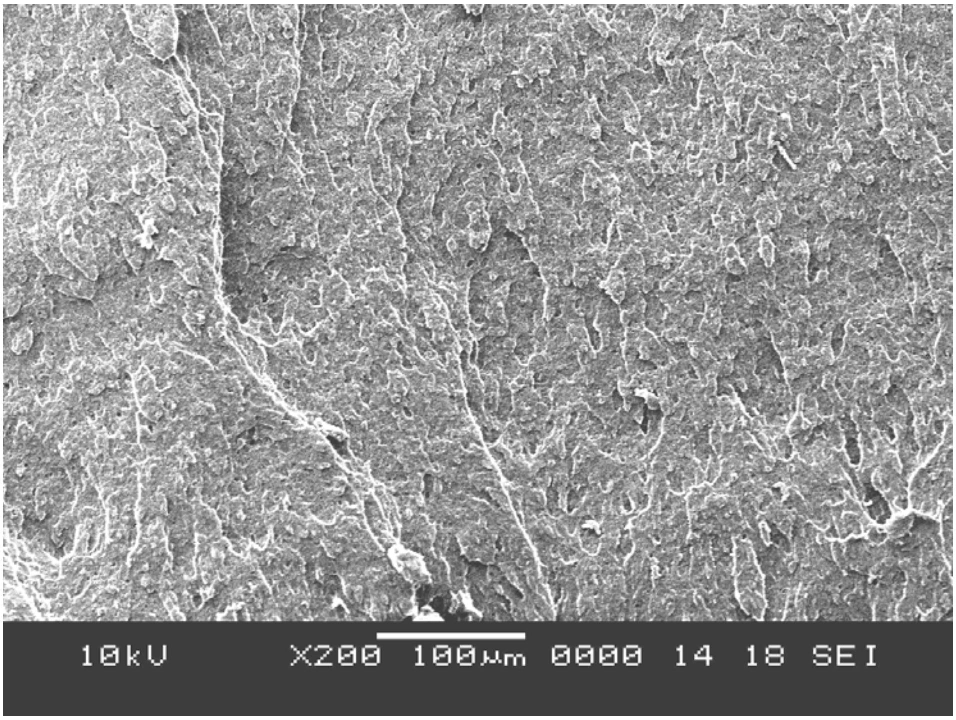


Figure 4.19 A : SEM micrographs of the fractured surfaces of the medium impact ABS/acrylic grafted PVC (85/15 phr/phr) (Magnification X200)

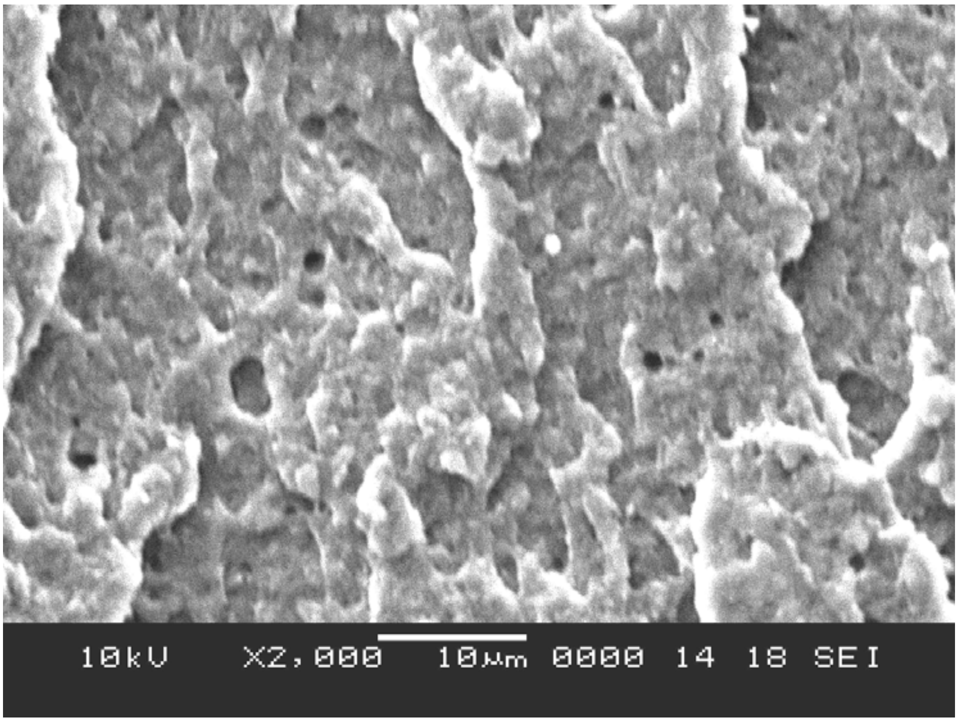


Figure 4.19 B : SEM micrographs of the fractured surfaces of the medium impact ABS/acrylic grafted PVC (85/15 phr/phr) (Magnification X2000)

Observation on the fractured surface of Izod impact test specimen shows that stress whitening occurs on all samples. A good correlation between impact strength and degree of whitening is established. Several researchers have also reported similar results (Azman Hassan, 1996; Yee Joon Wee, 2001; Sivaneswaran, 2002).

In this study, some microvoids and cavities occur in the blends. They absorb deformation or fracture energy to produce the brittle-ductile transition in addition to shear yielding of crazing of the matrix (Liand and Li, 2000). The presence of many well-distributed voids in a matrix material creates a multitude of stress pains through the matrix material of different cross-section. Each of these paths can have points of local stress concentration.

In the case of rubber particles which are well bonded to the matrix, these rubber particles can support some stresses and in so doing produce triaxial stresses in the matrix material (Bucknall, 1977). For ABS. the more dominant toughening effect is the increased shear yielding in the reduced cross-section of the matrix material between the rubber particles. The suggestion that rubber toughening might be due to shear yielding in the matrix was made by Newman and Strella (1965). Cavitation of the rubber particles, particularly the large ones add to this shear yielding process (Dear *et al.*, 1998)

As mentioned by Dear *et al.* (1998), crack blunting and arrest by the rubber particle cavities is another factor more attributable to larger particles. These toughening effects play a large part in determining the resistance offered by ABS material to a propagating crack normal to the applied unidirectional load. This seems to be the cause of uniform stress whitening at the fracture surface.

The subject of toughening mechanism in rubber-toughened polymers has attracted many researchers (Bucknall and Smith, 1965; Mertz, *et al.*, 1959; Newman and Strella 1965; Bucknall, 1977; Partridge, 1992; Liand and Li, 2000).

4.4 Flexural Properties

The flexural properties of materials are of considerable technical importance since deformations involving flexure are most frequent. Usually a molded article must be designed to maintain its shape under flexure. Therefore, flexural stiffness or modulus of flexure is a property of considerable technical importance. Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced by the flexural load are a combination of compressive and tensile stresses. This effect illustrated in Figure 4.20.

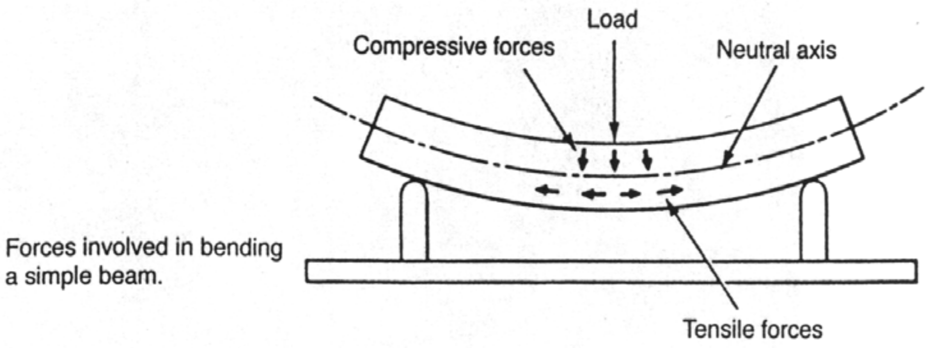


Figure 4.20 : Forces involved in bending a simple beam (Vishu, 1998)

In this section, the evaluation will be based on the effect of PVC molecular weight (K-58 and K-66) and acrylic grafted PVC on the flexural modulus (stiffness) of the different grades of ABS blends. Flexural modulus values are presented in Table 4.2.

Table 4.2 : Flexural modulus for ABS/PVC blends

(a)

High Rigidity ABS (phr)	PVC (phr) K-58	K-66	Grafted	Flexural Modulus (MPa)	Percent Decrease (%)
100	-	-	-	3300	-
90	10	-	-	3294	0.2
85	15	-	-	3279	0.6
80	20	-	-	3271	0.9
90	-	10	-	3273	0.8
85	-	15	-	3232	2.1
80	-	20	-	3229	2.1
90	-	-	10	3274	0.8
85	-	-	15	3249	1.6
80	-	-	20	3198	3.1

Table 4.2 (b)

Medium Impact ABS (phr)	PVC (phr)			Flexural Modulus (MPa)	Percent Decrease (%)
	K-58	K-66	Grafted		
100	-	-	-	3237	-
90	10	-	-	3143	2.9
85	15	-	-	3182	1.7
80	20	-	-	3105	4.1
90	-	10	-	3103	4.2
85	-	15	-	3081	4.8
80	-	20	-	3075	5.0
90	-	-	10	3082	4.8
85	-	-	15	3028	6.4
80	-	-	20	3000	7.3

Table 4.2 (C)

Super High Impact ABS (phr)	PVC (phr)			Flexural Modulus (MPa)	Percent Decrement (%)
	K-58	K-66	Grafted		
100	-	-	-	2939	-
90	10	-	-	2833	3.6
85	15	-	-	2708	7.8
80	20	-	-	2652	9.8
90	-	10	-	2929	0.3
85	-	15	-	2676	8.9
80	-	20	-	2612	11.1
90	-	-	10	2707	7.9
85	-	-	15	2665	9.3
80	-	-	20	2608	11.2

In Table 4.2 (a), it is observed that when PVC is incorporated into high rigidity ABS, there is a slight decrease in the flexural modulus. This shows that upon addition of PVC, the blend has become less stiff. The decrease of flexural modulus due to the addition of PVC K-58 is lower than the decrease due to PVC K-66. Acrylic grafted PVC blend has the lowest flexural modulus with a drop of 102 MPa or 3.1 % as the content increases from 10 to 20 phr. From the study conducted by Sivaneswaran (2002), PVC K-66 (without impact modifier and filler) was found to have a flexural modulus of 3000 MPa. The flexural modulus values obtained for high rigidity ABS/PVC blends in this study are in between the values of high rigidity ABS and PVC.

Table 4.2 (b) shows the flexural modulus of the medium impact ABS filled compound. Again, acrylic grafted PVC at the loading level of 20 phr shows the lowest value of flexural modulus (3000 MPa). Flexural modulus values for the medium impact ABS/PVC blends do not show much variation with varying the PVC content.

A similar trend is presented in Table 4.2 (c) for super high impact ABS, where the addition of PVC K-58, K-66 and acrylic grafted PVC also slightly decrease the flexural modulus of the blends. However, the decrease is relatively greater than high rigidity and medium impact ABS.

The studies has also shown that when pure ABS are compared, high rigidity ABS has the highest flexural modulus followed by medium impact and super high impact. This result is similar to the trend shown in the technical brochure of Toyolac general purpose ABS (refer Table 3.2). The results mentioned above show that different grades of ABS have major effect on flexural modulus. The observation confirmed that the flexural modulus is dependant on the content level of elastomer (Svec *et al.*, 1989). It is expected that super high impact ABS, which has the highest content of polybutadiene has the lowest flexural modulus. Polybutadiene is an elastomer with low rigidity and therefore, it is expected that the higher the PVC content, the lower the rigidity.

The molecular weight of PVC generally has a minimal effect on flexural modulus. PVC K-66 blend has a lower flexural modulus due to the longer chain compared with PVC K-58 blend. When PVC K-66 is incorporated into ABS, the benzene molecule (which is a bulky group) attached to the SAN molecule (which is the matrix) will be further apart since PVC K-66 with a longer chain has the ability to separate the benzene molecule more than PVC K-58. Thus, the flow of the matrix for ABS/ PVC K-66 blends become easier and the matrix become less rigid and results in low flexural modulus.

The above results also show that the effect of acrylic grafted PVC in decreasing the stiffness of the blends is greater than the PVC K-58 and K-66. This is due to the higher elastomer content in acrylic grafted PVC. High rigidity ABS/PVC K-58 blend shows the highest flexural modulus, whereas super high impact ABS/acrylic grafted PVC blend shows the lowest flexural modulus. The flexural modulus relates well with impact strength where acrylic grafted PVC, with the lowest modulus of elasticity has the highest impact strength. PVC K-58 which has the least decrease of modulus elasticity shows the lowest increment in impact strength. This study is supported by Svec *et al.* (1990), Kumbhani and Kent (1981) who indicated that an increase in the ductility and toughness will decrease the modulus of elasticity in tension. Crawford (1987) also mentioned that the inherent nature of plastics is such that low modulus tends to be associated with high ductility and steps that are taken to improve the one cause the other to deteriote. There is an almost inescapable rule by which increased ductility is accompanied by decreased modulus and vice versa.

The study on the flexural modulus of PC/ABS and PC/MABS blends by Balakrishnan and Neelakantan (1998) shows that the values do not have much variation upon increasing the PC content. This is due to the similar flexural modulus values of the feedstock materials (ABS: 2321 MPa; MABS: 2372 MPa and PC: 2333 MPa). There is a slight negative blending effect occurred in the blend composition of 65, 75 and 90 wt % of PC in PC/ABS blends and 25, 35 and 50 wt % of PC in PC/MABS blends.

Basically, the flexural modulus in this ABS/PVC blends did not have much difference upon adding the PVC since the largest reduction is only 11.2 %.

4.5 Flammability Properties

Thermoplastic materials are more or less easily combustible. Efforts to develop flame-retarding plastic materials have been going along with the increasing use of thermoplastics. As a result, flame retarding formulations are available today for all thermoplastics which strongly reduce the probability of their burning in the initiating phase of fire. The possibility to make plastic flame retardant secures the scope of utilization for thermoplastics and, in fact increases their range of application.

In this section, the significant flammability properties of LOI from burning blends of different grades of ABS and varies PVC molecular weight is discussed. Flammability was measured using standard oxygen index technique (LOI). Blends of ABS and PVC containing up to 20 phr of PVC in the blends were examined. Results from the LOI test are tabulated in Table 4.2 to 4.3.

Table 4.3 shows that high rigidity ABS has the highest LOI value followed by medium impact and super high impact ABS. The results are similar to the finding of Pál and Macskásy (1991) where ABS has a LOI value in a range of 17 to 18 %. Therefore, ABS is a flammable polymer since the LOI value for self-extinguishing polymer is often taken as 27 % and above (Chanda and Roy, 1993). Due to the flammability behavior of ABS, it is necessary to produce flame retardant blends.

Table 4.3 : LOI index for ABS

Formulation	phr	LOI Index (%)
High Rigidity ABS	100	18
Medium Impact ABS	100	17
Super High Impact ABS	100	17

The effects of flame retardancy of adding PVC into high rigidity ABS are shown in Table 4.4(a). Basically, the LOI value increased as the loading level of PVC increased. At the blend compositions of 90 ABS/10 PVC and 85 ABS/15 PVC, the LOI is raised by 1 unit (1 unit = 1 %). When 20 phr PVC is added, the LOI value is 20 %, which indicate a raise of 2 units from 100phr high rigidity ABS. Obviously, there is no difference in LOI value for different PVC molecular weight (K-58 and K-66) and acrylic grafted PVC.

Table 4.4(b) shows the effect of different PVC molecular weight into medium impact ABS. The trend of the results is similar to high rigidity ABS. At the blend composition of 90 ABS/10 PVC and 85 ABS/15 PVC, the oxygen index obtained is 19 %, which is raised by 2 units. High LOI values (20 %) can be obtained when 20 phr PVC is incorporated into medium impact ABS. It is clearly indicated that the increment of oxygen index is higher when PVC is added into medium impact ABS. Again, the effect of blending different PVC molecular weight and acrylic grafted PVC did not show any difference.

From Table 4.4 (a) and (b), the results indicated that the highest LOI value obtained is 20 %, when 20phr of PVC is incorporated into high rigidity and medium impact ABS. It is surprising how well the medium impact ABS performed when blended with 20 phr PVC. The LOI is raised by 3 units for medium impacts ABS.

A similar trend is observed when compared the oxygen index of ABS/PVC blends with the finding of Carty and White (1994). LOI value increases as the loading level of PVC increased. In their paper, at a blend composition of 80 ABS/20 PVC the LOI value is 21.1 % and is raised by 2.9 units when compared with 100 % ABS (LOI value: 18.3 %).

Blends of ABS and PVC containing up to 20 phr PVC in the blend were presented in Table 4.4(c) The LOI value is similar for 10, 15 and 20 phr loading level of PVC. The oxygen index obtained is 19 % with the increment of 2 units when compared with virgin super high impact ABS.

Table 4.4 : LOI index for ABS/PVC blends

(a)

High Rigidity ABS (phr)	PVC (phr)			LOI Index (%)	δ LOI
	K-58	K-66	Grafted		
90	10	-	-	19	+ 1
85	15	-	-	19	+ 1
80	20	-	-	20	+ 2
90	-	10	-	19	+ 1
85	-	15	-	19	+ 1
80	-	20	-	20	+ 2
90	-	-	10	19	+ 1
85	-	-	15	19	+ 1
80	-	-	20	20	+ 2

Table 4.4 (b)

Medium Impact ABS (phr)	PVC (phr)			LOI Index (%)	δ LOI
	K-58	K-66	Grafted		
90	10	-	-	19	+ 2
85	15	-	-	19	+ 2
80	20	-	-	20	+ 3
90	-	10	-	19	+ 2
85	-	15	-	19	+ 2
80	-	20	-	20	+ 3
90	-	-	10	19	+ 2
85	-	-	15	19	+ 2
80	-	-	20	20	+ 3

Table 4.4 (C)

Super High Impact	PVC (phr)			LOI Index	
ABS (phr)	K-58	K-66	Grafted	(%)	δ LOI
90	10	-	-	19	+ 2
85	15	-	-	19	+ 2
80	20	-	-	19	+ 2
90	-	10	-	19	+ 2
85	-	15	-	19	+ 2
80	-	20	-	19	+ 2
90	-	-	10	19	+ 2
85	-	-	15	19	+ 2
80	-	-	20	19	+ 2

The flammability studies reveal that different types of ABS influence the LOI value more than different molecular weight of PVC. Interestingly, the higher the content of polybutadiene, the lesser the effectiveness of PVC as flame retardant. Super high impact ABS is not as effective as medium impact ABS. Conversely, the higher styrene content (high rigidity ABS) will have a better flame retardancy property.

According to Kuryla and Papa (1973), the burning characteristics of polystyrene are soft, bubbles and black smoke with the burning rate of 1.3 - 6.3 cm/min. Where as, polybutylene burns easily with the burning rate of 2.5 cm/min. Polybutadiene contain one double bond per repeating unit which favor crosslinking (Hirschler, 2000). According to Landrock (1983), the rubber backbone (C=C structure) conferred by the butadiene comonomer in ABS, is a highly flammable material. This higher rubber (butadiene) content in super high impact ABS will deteriote most rapidly (Bair *et al.*, 1980). As a group, the polybutadiene will burn hotter than the other comonomer, very much like rubber compounds and producing large quantities of carbon (and thus, heavy black smoke) and carbon monoxide. There is always the possibility that other short-chain hydrocarbons and hydrocarbon derivatives will be formed, but they are all combustible (Frank, 1991).

The incorporation of some PVC into a range of ABS considerably changes the burning characteristic of the polymer blends. It is believe that the chlorine content of PVC, which usually has 56 % chlorine is difficult to ignite and has self-extinguishing property (Chanda and Roy, 1993).

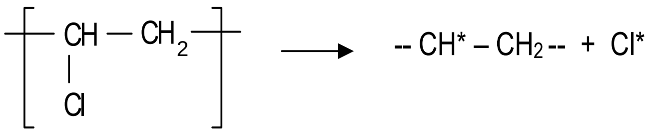
Here, the chemical role of PVC in reducing the flammability is considered. During combustion, free radicals are formed by pyrolysis. The radicals combine with oxygen in a radical chain reaction. Heat release and further decomposition of the plastics material is caused thereby (Titow, 1990). For continued combustion it is necessary to have sufficient oxygen as well as combustible gaseous compounds. It is presumed that the following reactions take place, when flame-retarded thermoplastics containing chlorinated compounds as flame retardants are used (Frank, 1991).

PVC acts by interfering with the radical chain mechanism taking place in the gas phase. The high-energy OH and H radicals formed by chain branching:

$$H^* + O_2 \rightarrow OH^* + O^*$$

$$O^* + H_2 \rightarrow OH^* + H^*$$

are removed by the PVC. At first, the flame retardant (PVC) breaks down to



$$\left[\underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2 \right] \longrightarrow \text{-- } CH^* - CH_2 \text{ --} + Cl^*$$

the Cl* radical react to form the hydrogen chloride:

$$\text{-- } CH^* - CH_2 \text{ --} + HCl \rightarrow Cl^* + \text{-- } CH_2 - CH_2 \text{ --}$$

which in turn interferes with the radical chain mechanism:

$$HCl + H^* \rightarrow H_2 + Cl^*$$
$$HCl + OH^* \rightarrow H_2O + Cl^*$$

The high-energy H and OH radicals are removed by reaction with HCl and replaced with low-energy Cl* radicals. The actual flame retardant effect is thus produced by HCl. The HCl consumed is regenerated by reaction with hydrocarbon:

$$Cl^* + \text{--}\,CH_2 - CH_2\,\text{--} \rightarrow \text{--}\,CH^* - CH_2\,\text{--} + HCl$$

Thus HCl ultimately acts as a catalyst. HCl is non-flammable gases and they are not only dilute the flammable gases but also form a non-combustible protective layer on the condensed phase interfering with or halting the combustion process (Troitzsch, 1980).

There are a lot of studies based on flame retardant ABS has been done. The study of Carty and White (1994) in the flammability and smoke generated from burning blends of ABS and PVC revealed simply blending the ABS and PVC is insufficient to reduce the flammability significantly.

High LOI value (>28 %) can be obtained with a minimum of 10phr of PVC in the ABS with only 2.5 phr FeOOH. At higher levels of PVC in the ABS, even less iron is required to achieve high LOI value. For example, the 90 ABS/10 PVC/1 FeOOH formulation has a LOI value of 27.2 %, the 85 ABS/15 PVC/1 FeOOH formulation has a LOI value of 30.4 % and the 80 ABS/20 PVC/1 FeOOH formulation has a LOI value of 30.4 %. The difference between ABS/PVC blends with ABS/PVC/FeOOH blends is around 10 units. Increasing the FeOOH content to 10phr in a ABS/PVC blends had marginal effect on the LOI value. This is shown by

80 ABS/20 PVC/10 FeOOH formulation with LOI value of 30.9 %. Interestingly, blends of ABS and FeOOH containing up to 5phr FeOOH (without adding PVC) have little effect on flammability.

According to Carty and White (1994), different types of iron compound were used as a synergist to replace FeOOH, there are iron (III) molybdate, iron oxide Fe_3O_4 and iron (III) oxychloride (FeOCl) The study revealed that iron (III) molybdate is rather ineffective. The 80 ABS/20 PVC/5 iron (III) molybdate formulation has a LOI value of 24.4. Whereas 80 ABS/20 PVC/5 FeOOH formulation has a LOI value of 30.7 %. Adding iron oxide Fe_3O_4 into the blends did not show much increment in LOI value. The 80 ABS/20 PVC/5 Fe_3O_4 formulation has a LOI value of 24.4. FeOCl is an effective flame retardant in 100% ABS. At a 5phr FeOCl in 100% ABS the LOI value was raised to quite a high value of 29.3 % (an increase of 11 units when compared with pure ABS without PVC). The 70 ABS/30 PVC/10 FeOCl formulation has a LOI value of 32.2 %. This compound is not as effective as FeOOH. A 70 ABS/30 PVC/10 FeOOH formulation gave on LOI value of 33.8 %.

Adding iron containing compounds, especially the materials based on Lepidocrocite (FeOOH) as synergist into the blends significantly increase the polymer’s resistance to ignition and burning. It is therefore obvious from these results obtained (refer Table 4.4), it can concluded that simply blending the two polymers is insufficient to reduce flammability. Essentially, a synergist is required to improve the flame resistance.

4.6 Heat Distortion Temperature

To function as structural material, plastic is expected to maintain its shape under load, and hence heat distortion temperature (HDT) represent s an upper limiting point at which a plastic may be used. So far not much studies has yet been reported in determining the effect of PVC molecular weight (K-58 and K-66) and acrylic grafted PVC in ABS upon HDT. In this section, the evaluation on the effect of PVC content and types of PVC upon HDT of different grades of ABS samples are presented.

Figure 4.21 illustrates the effect of PVC molecular weight and acrylic grafted PVC on high rigidity ABS upon HDT. Comparison will be based on samples with PVC content of 10, 15 and 20 phr. The result shows that HDT decreases upon adding the PVC. At 10 phr PVC, there is no significant difference in HDT for PVC K-58, K-66 and acrylic grafted PVC. A reduction is observed as the loading level increases from 10 to 15 phr for all samples. PVC K-66 has the highest temperature, followed by acrylic grafted PVC and PVC K-58. Again, at the loading level of 20 phr, no significance difference between the types of PVC was observed.

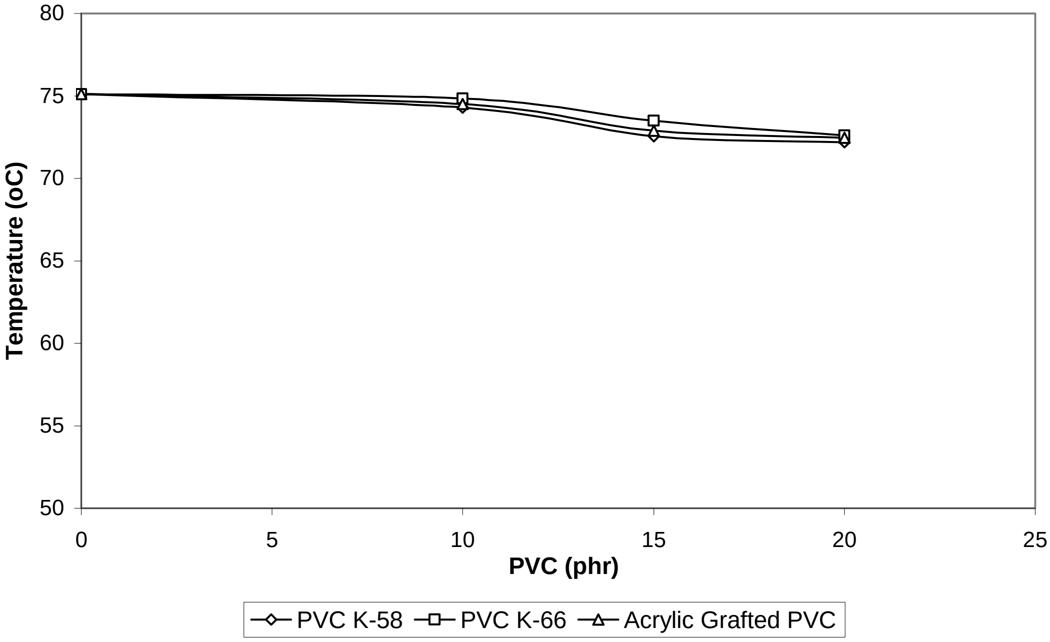


Figure 4.21 : Effect of PVC molecular weight on heat distortion temperature of high rigidity ABS

A similar trend is observed in Figure 4.22, where HDT for medium impact ABS reduces with increasing PVC content. PVC K-66 and acrylic grafted PVC does not show a significance reduction of HDT value as the loading level of PVC increases. Along the trend line of PVC K-58, at a blend composition of 20 phr PVC, the HDT value is drastic dropped by 2.9 units. Again, at 20 phr, PVC K-58 has the lowest value followed by PVC K-66 and acrylic grafted PVC.

The effect of PVC molecular weight (K-58 and K-66) and acrylic grafted PVC on super high impact ABS upon HDT were also investigated. As shown in Figure 4.23, adding PVC into ABS results in a decreased in HDT and similar to the trend show in Figure 4.24 and 4.25. Although PVC K-58 has the highest value at 10 and 15 phr, the value drops quite drastically from 72°C to 69°C at 20 phr. The result shows that there is not much difference at the loading level of 20 phr for different molecular weight of PVC and acrylic grafted PVC.

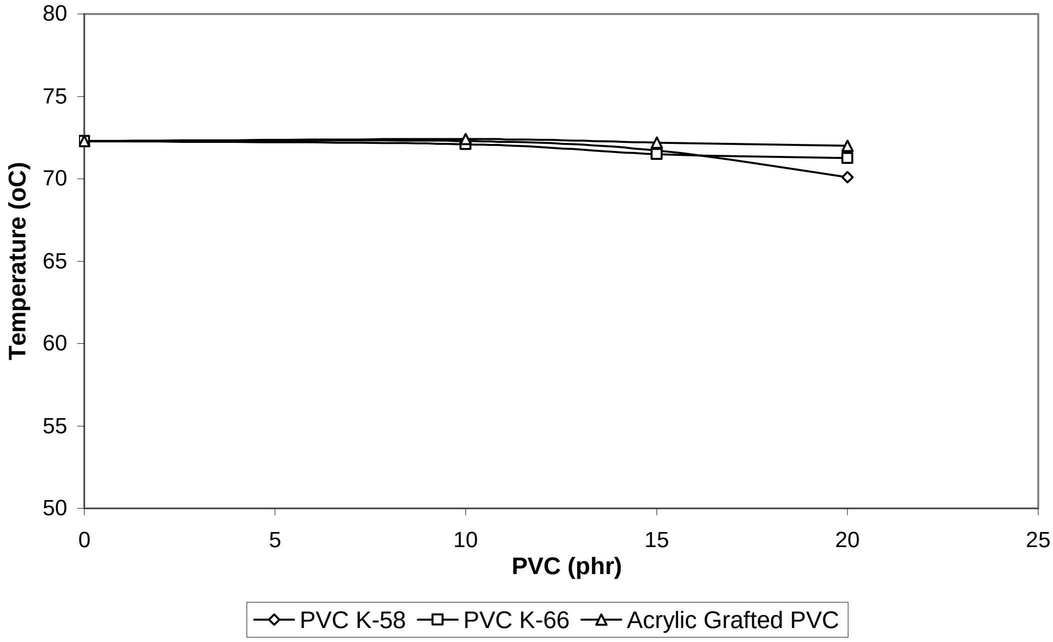


Figure 4.22 : Effect of PVC molecular weight on heat distortion temperature of medium impact ABS

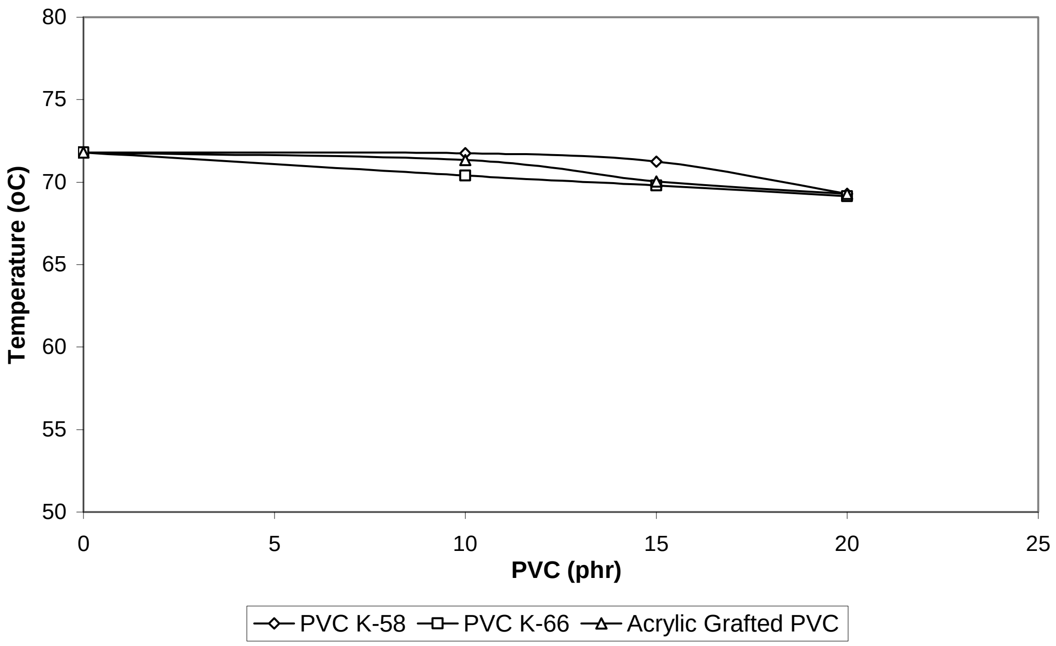


Figure 4.23 : Effect of PVC molecular weight on heat distortion temperature of super high impact ABS

Not unexpectedly, the results from the HDT experiments confirm that by incorporating PVC into ABS, the temperature decrease with increasing loading level of PVC. It can be noted that adding of PVC into ABS has only a marginal effect on HDT, and the maximum reduction of the temperature is only 3 ^{o}C. The trend line from the graph reveals that the blends are following a simple rule of mixture. Virgin PVC has a lower HDT value (68 ^{o}C) compared with virgin ABS. The higher the PVC content, the lower the HDT value.

As shown in the figure 4.21 - 4.23, when PVC K-58 is incorporated into different grades of ABS, it shows the poorest performance upon HDT. This is explained by PVC molecular weight, where PVC K-58 has a lower molecular weight than PVC K-66 and acrylic grafted PVC (K-64). It has been reported that lower molecular weight of PVC displays lower heat distortion than the higher molecular weight ones (Perry, 1997). So for this reason, the HDT for PVC K-58 is lower than PVC K-66 and acrylic grafted PVC.

The results from the HDT studies also revealed that different grades of ABS have different HDT values. The results obtained are similar to data presented by Toray, where a virgin high rigidity ABS has the highest HDT value followed by medium impact and super high impact ABS. The reason is due to the higher content of acrylonitrile (AN) at high rigidity ABS results in higher HDT value (Lee *et al.*, 1999). Besides, super high impact ABS has the highest content of elastomer (butadiene) phase compare with medium impact and high rigidity ABS. This elastomer rich phase will decrease the heat resistance of the blends (Svec *et al.*, 1990) and hence, virgin super high impact ABS has the lowest value of 72 ^{o}C compared with the others.

The overall results show that the drop due to incorporation of PVC into ABS is relatively small and therefore it would be no effect on the application of ABS as a structural material.

4.7 Melt Flow Index

The melt flow index shows relative flowability of plastic resins in the melt form. It is one of the most basic critical tests used as an incoming quality control check to assure that the resin furnished meets specifications, and as a post-processing check of molded plastics parts. The MFI of polymer is related to polymer’s viscosity. It is an inverse function of viscosity and could be used to qualitatively assess the interaction between the phases. An increased in viscosity suggest a substantial reduction in processability.

MFI data for different grades of ABS are shown in Table 4.5. The MFI experiment was done at 200 ^{o}C and shows similar trend with the result obtained by Toray Plastics as shown in Table 4.6. From the table, medium impact ABS shows the highest MFI value which means it is the easiest polymer to be processed. The possible reason is that medium impact ABS has a broader molecular weight distribution compared with high rigidity ABS. Svec *et al.* (1990) reported that ABS with a broader molecular weight distribution of the SAN has good flow properties.

Table 4.5 : MFI data for ABS

Sample	MFI (g/10min) 200 °C , 5kg
High rigidity ABS	2.20
Medium impact ABS	2.90
Super high impact ABS	1.69

Table 4.6 : MFI data for ABS obtained from Toray Plastics

Sample	MFI (g/10min) 220 °C, 10kg
High rigidity ABS	20
Medium impact ABS	23
Super high impact ABS	14

Super high impact ABS with the lowest value of MFI indicates that its melt viscosity is the highest and results in process difficulty. The decrease of MFI with higher polybutadiene content in super high impact ABS is expected since the viscosity of polybutadiene is much higher (Schwarz and Bley, 1988). Kuriakose and De (1985) had also reported that the addition of polybutadiene to the polypropylene matrix caused an increased in the viscosity. The relatively high MFI for the high rigidity ABS (MFI value: 2.20) is due to the higher content of styrene and acrylonitrile. Gao *et al.* (2000) explained that a high content of styrene and acrylonitrile can decrease the melt flow viscosity and reduce the processing temperature.

Table 4.7 shows the influence of the addition of PVC into different grades of ABS. Interestingly, PVC K-58 decrease the melt viscosity of the blends as shown in Table 4.7(a). PVC has a lower melt viscosity and the addition of PVC to ABS decreases the melt viscosity of the blend as observed in PVC/ABS/polyester blend (Khanna and Congdon, 1983) and PVC/EPR blend (Severini *et al.*, 1971). This observation is likely due to the ease processing properties of PVC K-58. As we know, in industrial practice, dilute-solution viscosity of PVC polymers is normally determined as an index of the molecular weight. The results are commonly expressed in terms of K value. PVC K-58 has a lower K value compare with PVC K-66 and acrylic grafted PVC. An increase in molecular weight of PVC leads to a very large increase in melt viscosity had been observed in PVC/NBR blend (Schwarz and Bley, 1988). So, lower molecular weight of PVC K-58 resins have lower melt viscosity as illustrated by the corresponding high melt flow indices and the easier in processing.

The melt viscosity of ABS/PVC blends at 200°C was higher than that of pure ABS (refer Table 4.7 (b) and (c)). Though not significant, the higher content level of PVC, the lower the values of melt index. The decreased of MFI with increasing PVC content may be due to the entanglement of molecules, and there is likely to be a contribution from the van der Waals forces (Billmeyer, 1984). An increase in the polymer molecular mass increase the melt viscosity, because each molecule is entangled with more of its neighbours (Mills, 1986).

Table 4.7 : Melt flow index for ABS/PVC blends

(a)

PVC K-58 (phr)	ABS (phr)			MFI (g/10min)
	High Rigidity	Medium Impact	Super High Impact	
10	90	-	-	2.49
15	85	-	-	2.49
20	80	-	-	2.55
10	-	90	-	2.82
15	-	85	-	3.08
20	-	80	-	3.31
10	-	-	90	1.89
15	-	-	85	1.92
20	-	-	80	1.92

Table 4.7 (b)

PVC K-66	ABS (phr)			MFI
(phr)	High Rigidity	Medium Impact	Super High Impact	(g/10min)
10	90	-	-	2.18
15	85	-	-	2.12
20	80	-	-	1.90
10	-	90	-	2.79
15	-	85	-	2.63
20	-	80	-	2.39
10	-	-	90	1.54
15	-	-	85	1.50
20	-	-	80	1.37

Table 4.7 (C)

Acrylic Grafted	ABS (phr)			MFI
PVC(phr)	High Rigidity	Medium Impact	Super High Impact	(g/10min)
10	90	-	-	2.13
15	85	-	-	2.08
20	80	-	-	1.88
10	-	90	-	2.76
15	-	85	-	2.63
20	-	80	-	2.46
10	-	-	90	1.61
15	-	-	85	1.52
20	-	-	80	1.39

Higher melt flow properties will be preferred for injection moulding compounds. For extrusion grades, high melt viscosity or low MFI is desirable in order to maintain dimensional stability after the melt leaves the die. Although the melt flow rate is decreased when PVC K-66 and acrylic grafted PVC are incorporated into different grades of ABS, they still meet the requirement of processing for injection moulding. According to Van Krevelen and Hoftyzer (1976), the melt flow index required for the injection moulding process is from 1 to 6 g/10min (at 200 ^{o}C, 5 kg). So, the blends could still be injection moulded without difficulty.

4.8 Costing

Another important factor in designing materials is to evaluate the economic value of the formulation prepared. The selection of appropriate ABS and PVC is expected to lower the formulation cost. In this section, each material is compared on the basis of unit volume of resin Since ABS are sold on per-kg basis, it is economic value comes from the volume of resin they replace. Table 4.8 shows the calculation of cost per unit volume of pure ABS and ABS/PVC blends. Method of calculating the cost per unit volume is shown in Appendix H.

The calculation indicate that super high impact ABS has the higher cost per volume followed by medium impact and high rigidity ABS. Acrylic grafted PVC has the higher cost per volume, followed by PVC K-58 and PVC K-66. A same value is observed for each high rigidity and medium impact ABS blends. Interestingly, ABS/PVC K-66 blends are much cheaper than the pure ABS. However, there is a slight increment of cost per unit volume (around 3 %) by adding PVC K-58 and acrylic grafted PVC into high rigidity and medium impact ABS. This increment is due to the expensive tin stabilizer (3 phr), which must be added into PVC to avoid PVC degradation during processing. For super high impact ABS, with the exception of acrylic grafted PVC, the incorporation of both PVC K-58 and K-66 tend to lower down the cost of the ABS/PVC blends.

Table 4.8 : Calculation of cost per unit volume of pure ABS and ABS/PVC blends

(a)

High Rigidity ABS (phr)	PVC (phr)			Cost per Unit Volume (RM/m^3)
	K-58	K-66	Grafted	
100	-	-	-	4.9350
90	10	-	-	4.9368
85	15	-	-	4.9378
80	20	-	-	4.9388
90	-	10	-	4.8986
85	-	15	-	4.8798
80	-	20	-	4.8605
90	-	-	10	5.0197
85	-	-	15	5.0644
80	-	-	20	5.1107

Table 4.8 (b)

Medium Impact ABS (phr)	PVC (phr)			Cost per Unit Volume (RM/m^3)
	K-58	K-66	Grafted	
100	-	-	-	4.9350
90	10	-	-	4.9368
85	15	-	-	4.9378
80	20	-	-	4.9388
90	-	10	-	4.8986
85	-	15	-	4.8798
80	-	20	-	4.8605
90	-	-	10	5.0197
85	-	-	15	5.0644
80	-	-	20	5.1107

Table 4.8 (C)

Super High Impact ABS (phr)	PVC (phr)			Cost per Unit Volume (RM/m^3)
	K-58	K-66	Grafted	
100	-	-	-	4.9920
90	10	-	-	4.9895
85	15	-	-	4.9883
80	20	-	-	4.9869
90	-	10	-	4.9513
85	-	15	-	4.9303
80	-	20	-	4.9088
90	-	-	10	5.0721
85	-	-	15	5.1144
80	-	-	20	5.1583

4.9 General Discussion

To quantify the most appropriate combination mechanical properties, correlation between impact strength and flexural modulus has been done as shown in Figure 4.24-4.26. Normally, increased ductility is accompanied by decreased modulus (Crawford, 1987). The most optimum blend is the one which shows the highest values for both properties.

From Figure 4.24, when high rigidity ABS is taken into account, the optimum blend is 80 ABS/20 acrylic grafted PVC, followed by 80 ABS/20 PVC K-66 and 85 ABS/15 acrylic grafted PVC. As for medium impact ABS (refer Figure 4.25), the optimum blend is obtained when 80 phr medium impact ABS is blended with 20 phr acrylic grafted PVC. This is followed by 80 ABS/20 PVC K-66 and 85 ABS/15 acrylic grafted PVC. A similar trend is observed in super high impact, where 80 ABS/20 acrylic grafted PVC is the optimum blend, followed by 80 ABS/20 PVC K-66 and 85 ABS/15 acrylic grafted PVC. These results show that the optimum blend properties were obtained when the 20 phr acrylic grafted PVC is used. From the three figures, flexural modulus did not show much variation as the impact strength increased.

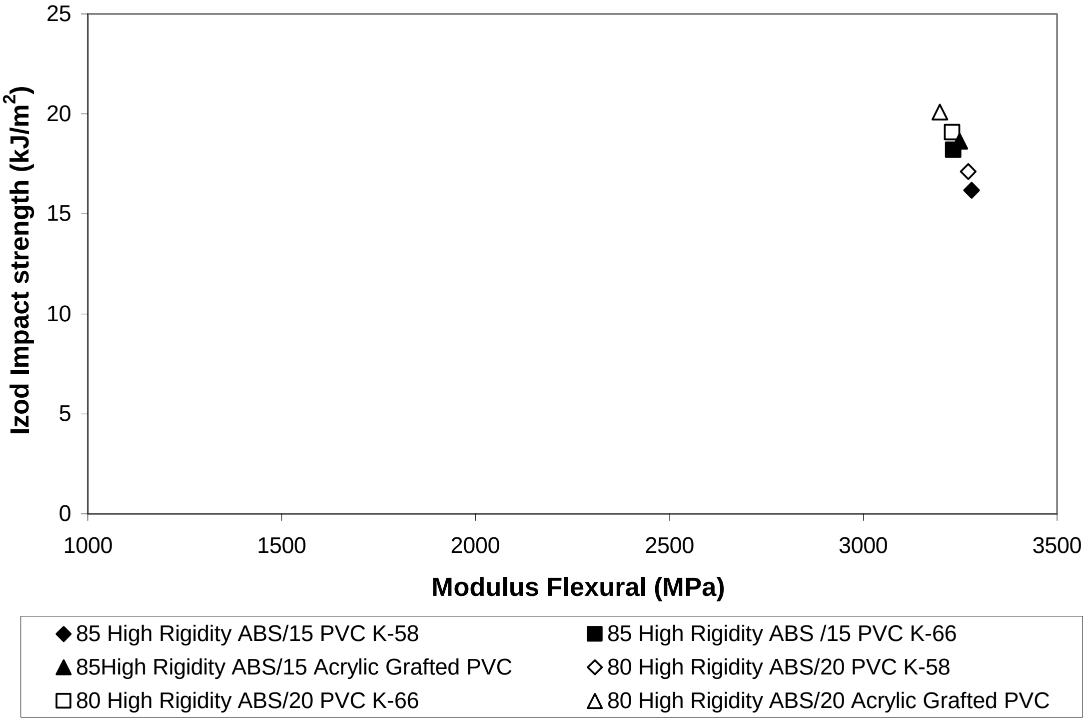


Figure 4.24 : Determination of balance properties based on impact strength and flexural modulus of high rigidity ABS blends

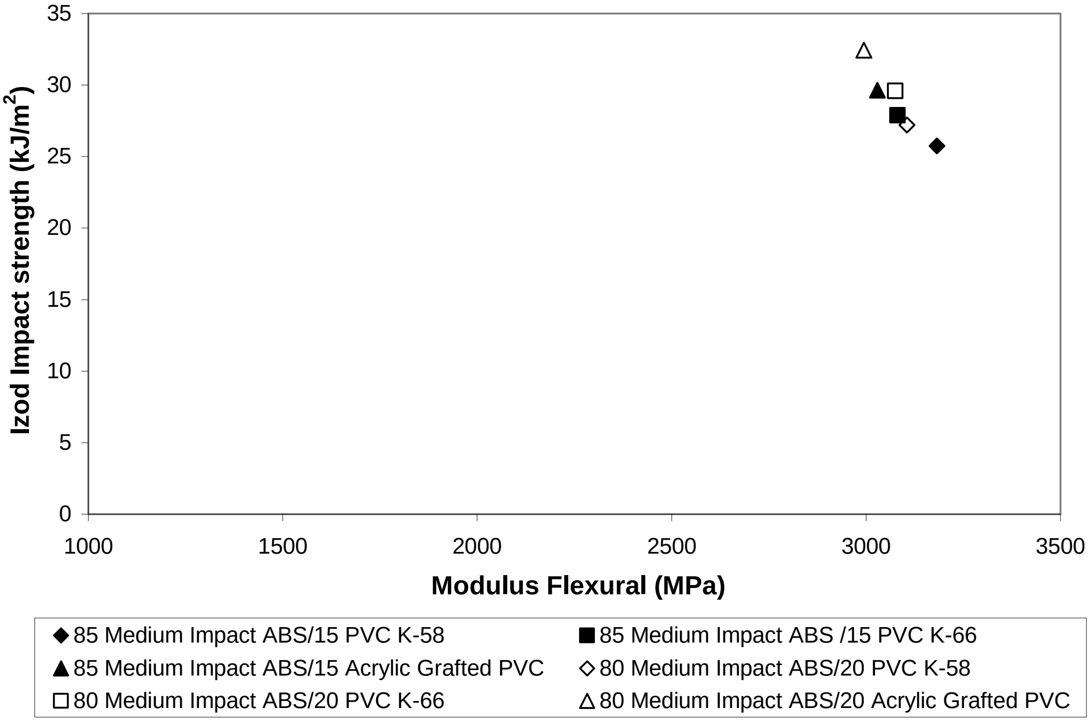


Figure 4.25 : Determination of balance properties based on impact strength and flexural modulus of medium impact ABS

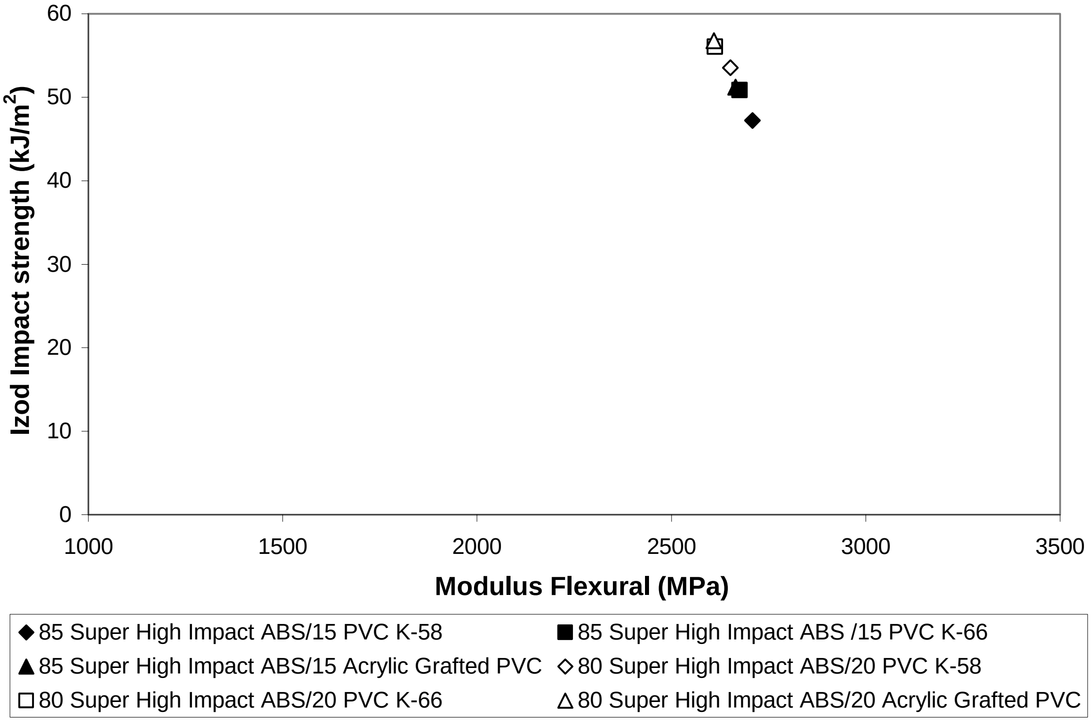


Figure 4.26 : Determination of balance properties based on impact strength and flexural modulus of super high impact ABS

The three optimum blends from different grades of ABS are then plotted in Figure 4.27 to search for the most optimum formulation in terms of mechanical properties. From the figure, the most optimum blend is 80 super high impact ABS/20 acrylic grafted PVC, followed by 80 super high impact ABS/20 PVC K-66 and 80 super high impact ABS/20 PVC K-58.

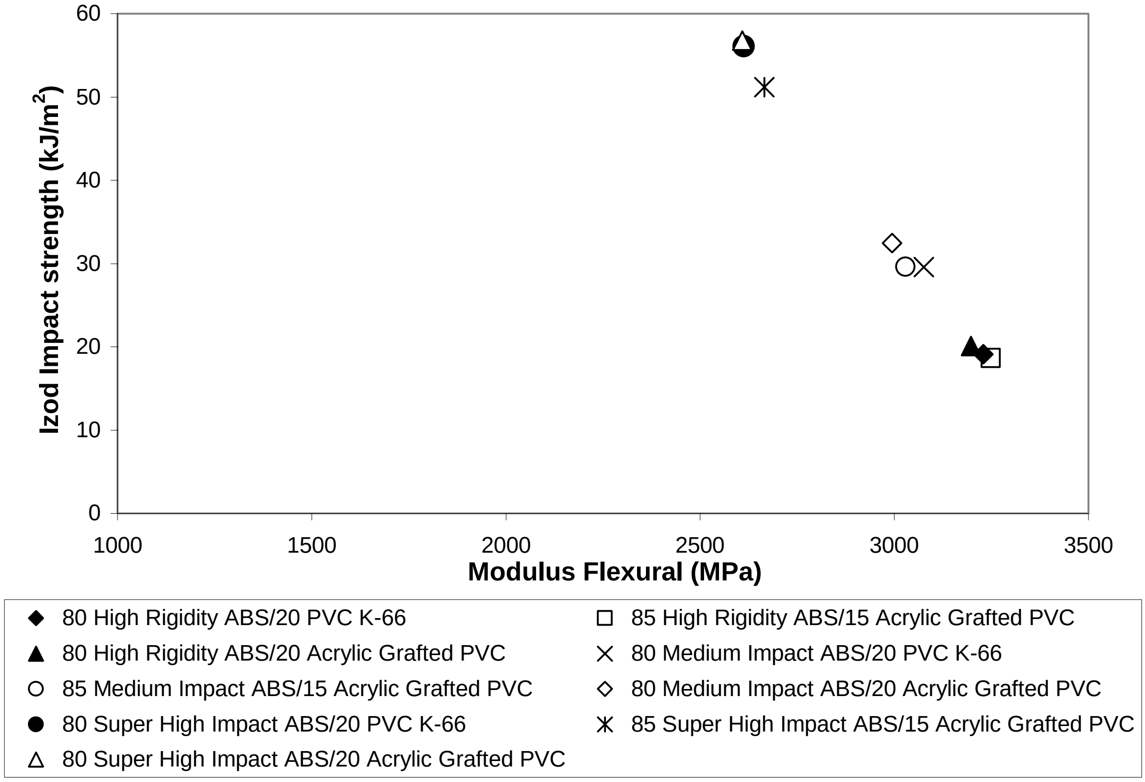


Figure 4.27 : Determination of balance properties based on impact strength and flexural modulus of selected ABS/PVC blends

Based on flame retardancy, 80 medium impact ABS/20 acrylic grafted PVC and 80 medium impact ABS/20 PVC K-66 are better choice. On the other hand, 80 high rigidity ABS/20 PVC K-66 and 80 medium impact ABS/20 PVC K-66 are better in term of cost. The selection of the ABS/PVC formulation is very much depends on their application. As a conclusion, 80 super high impact ABS/20 PVC K-66 is found to be the most optimum formulation in terms of mechanical properties and cost. Whereas, 80 medium impact ABS/20 PVC K-66 is being selected to be the most appropriate formulation in terms of flame retarded polymer.

Table 4.9 : Relationship between impact properties, flexural modulus, cost per unit volume and flame retardancy of selected ABS/PVC blends

Sample	Impact Strength kJ/m^2	Difference %	Flexural Modulus MPa	Difference %
100 Super high impact ABS	34	-	2939	-
80 super high impact ABS/ 20 acrylic grafted PVC	57	67.65	2608	-11.26
80 super high impact ABS/ 20 PVC K-66	56	64.71	2612	-11.13
80 super high impact ABS/ 20 PVC K-58	54	58.82	2652	-9.77
80 medium impact ABS/ 20 acrylic grafted PVC	32	-5.88	3000	2.08
80 medium impact ABS/ 20 PVC K-66	30	-11.76	3075	4.63
80 high rigidity ABS/ 20 PVC K-66	19	-44.12	3229	9.87

Sample	Cost/Volume Rm/kg	Differences %	LOI %
100 Super high impact ABS	4.99		17
80 super high impact ABS/ 20 acrylic grafted PVC	5.16	3.33	19
80 super high impact ABS/ 20 PVC K-66	4.91	-1.67	19
80 super high impact ABS/ 20 PVC K-58	4.99	-0.10	19
80 medium impact ABS/ 20 acrylic grafted PVC	5.11	2.38	20
80 medium impact ABS/ 20 PVC K-66	4.86	-2.63	20
80 high rigidity ABS/ 20 PVC K-66	4.86	-2.63	20

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The main objective of this research is to study the effect of different molecular weight of PVC (K-58 and K-66) and acrylic grafted PVC on different grades of ABS in terms of mechanical properties and flame retardancy. Besides that, the morphology, thermal and rheological properties of the blends were investigated.

In this chapter, an overall conclusion and suggestions for possible future work in this area will be recommended.

5.1 Overall Conclusions

The study has indicated that the addition of PVC into ABS has produced a very interesting result. A synergistic effect in which the impact strength of the ABS/PVC blends is found to be higher than pure ABS and PVC. The data for ABS was obtained from this study whereas the impact strength value of PVC was referred to previous study (Sivaneswaran, 2002; Gobstein, 1990). With increasing content of PVC, the impact strength of the blends increased. The impact strength was also found to be dependant upon PVC molecular weight, with the higher K value, the higher the impact strength value. PVC with higher molecular weight has a longer molecular chain and results in enhancing the yielding and thus improves the ductility. Acrylic grafted PVC is more effective in increasing the impact strength than the non-grafted PVC. This is due to the elastomer content in acrylic grafted

PVC, which provides excellent impact strength. The study also indicated that the impact properties of ABS/PVC blends are dependent on polybutadiene content. High rigidity ABS is relatively brittle whereas medium and super high impact ABS are relatively ductile. The higher content of polybutadiene in super high impact ABS, which forms droplets in a continuous glassy SAN, has the ability to increase the number of microcrazes, distribute the stress and increased shear yielding of the matrix, thus plays an important role of enhanced toughness. The result also shows that the highest impact strength occurs when acrylic grafted PVC was added into super high impact ABS. The enhanced impact strength upon addition of PVC into ABS can be explained in terms of solubility parameter of both polymers. It is proposed that PVC is highly miscible with SAN in ABS matrix and formed mixed matrix, which successfully increase the shear yielding of the blends.

However, it was observed that when PVC is incorporated into ABS, there is a marginal decrease on flexural modulus. The flexural modulus of the blends was also found to be dependant upon PVC molecular weight, with the lower K-value the higher the flexural modulus. The reason for the higher impact strength of PVC K-66 blends compared to K-58 blends is that the higher the molecular weight, the more effective it is in enhancing the yielding and thus improve the ductility. Higher molecular weight is more effective in reducing the brittleness due to the bulky benzene molecule. With increasing the content of PVC, the flexural modulus of the blends decreased. Flexural study also revealed that ABS with higher polybutadiene content or higher impact strength results in lower flexural modulus and vice versa. The impact improvement is usually accompanied by a sacrifice in flexural modulus. The highest flexural modulus occurred when PVC K-58 is added into high rigidity ABS (least decrease in flexural modulus).

Study on DMA confirmed that ABS is thermodynamically compatible with PVC. This is due to the single T_g observed with a slightly broadening peak and reduction of the peak height in ABS/PVC blends. Besides, the T_g for SAN in virgin ABS is shifted to lower temperature when PVC is added. The miscibility between SAN component of ABS has improved the interfacial adhesion between PVC and ABS. The highly miscible SAN/PVC blend has a reduced interfacial tension and hence, is expected to increase the degree of dispersion in blends. As a result, the marked increase in mechanical properties (impact strength) for the ABS/PVC blends shows some enhancement of interaction and interlayer formed by the SAN/PVC is essential for good impact properties.

The fracture behaviour of ABS/PVC samples from the Izod impact testing can also be classified into three different types, from the standpoint of fracture mode and whitening degree.

Type 1. : Brittle fracture with whitening on the surface
Type 2 : Ductile fracture with whitening on the surface
Type 3 : Ductile fracture with formation of elliptical shaped stress-whitening zone near the edge and on me fracture surface.

Evidence from SEM micrographs taken from the fracture samples correlate well with the impact strength values. The SEM analysis shows that high rigidity ABS with impact strength of 14 kJ/m^2 has a scaly and typical flat surface with the micro characteristics typical of rigid and glassy surface. The micrograph which shows ductile yielding and fibrillation (Type 3) has high impact strength values compared to the micrograph which shows jagged appearance (Type 1). Sample with Type 2 fracture exhibits smaller jagged and shorter yielding structure on the fracture surface. As the loading level of PVC increased, the specimen displays a coarser surface which indicated that an increase in ductility of the material.

Another important finding in this study is that the incorporation of PVC into different grades of ABS results in increasing LOI index or flame retardancy. The flame retardancy of ABS is relatively poor with super high impact deteriote the most rapidly. The polybutadiene in ABS with the double bond structure is a highly flammable material. From the result obtained, the effect of PVC on medium impact ABS shows the highest increment of LOI index. An 80/20 medium impact ABS/PVC has a LOI index of 20% which is 3 units higher than pure medium impact ABS. The effect of PVC on LOI index of super high impact ABS is the least due to the highest rubber content. The PVC molecular weight is found that not influence the flammability of the ABS/PVC blends.

The HDT analysis shows that the temperature at which the materials loss rigidity decrease slightly as the loading level of PVC into ABS increased. The effect of molecular weight of PVC into different grades of ABS is minimal. The 80/20 medium impact ABS/PVC K-58 shows the maximum reduction of HDT and the decrease is only 3 ^{o}C for

The viscosity of the blends increased as PVC K-66 and acrylic grafted PVC is incorporated into different grades of ABS. However, the blends could still be injection moulded without difficulty. Interestingly, PVC K-58 shows a decrease in viscosity when blended with different grades of ABS. This observation is due to the ease processing properties of PVC K-58.

The most optimum formulation in terms of cost and mechanical properties is 80 super high impact ABS/20 PVC K-66. From the properties obtained, it is proposed that this material is suitable to produce suitcase and parts of miscellaneous goods. 80 medium impact ABS/20 PVC K-66 is selected to be the flame retardant grade ABS. According to the properties obtained, it is suggested that 80 medium impact ABS/20 PVC K-66 blend is suitable to use as computer monitor, photocopier parts, fax machine parts, and parts of camera and printer.

5.2 Recommendations

i) Studies have shown that PVC acted as flame retardant polymer has the ability to increase the flame retardancy of the blends. However, the LOI value is much lower than the requirement proposed. It would be interesting to investigate the following in order to increase the flame retardancy of the blends.

  a) Using higher content of PVC
  b) Incorporation of different types of flame retardant (not more than 10 phr) into ABS/PVC blends such as:

Iron compounds	1) FeOOH – Bayferrox yellow 3905 (Bayer) 2) Fe_3O_4 – ferrosoferric (magnetic) black iron oxide (BDH) 3) FeOCl – iron (III) oxychloride 4) Iron (III0 molybdate
Brominated materials	1) Octabromodiphenyl oxide 2) 1,2 – bistribromophenoxy ethane 3) Tetrabromobisphenol A 4) Poly-dibromostyrene

c) Incorporation of Sb_2O_3 as synergist in flame retardant ABS/PVC polymer.
d) Varies the particles size of Sb_2O_3.

ii) The initial work on flammability properties has given interesting results. This method can be further investigated by developed a correlation between LOI and smoke density (smoke production). Char determination can also be carried out by using DTA/TGA technique to record accurately heat and mass change.

iii) Incorporation of flame retardant will reduce the mechanical properties of the blends. In order to minimize the reduction, compatibilizer should be added to study the effect of coupling agents in flame retarded ABS/PVC blends.

iv) To investigate the effects of compatibilizer on flame retarded ABS/PVC blends.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABS - Acrylonitrile-butadiene-styrene
AN - Acrylonitrile
ASTM - American Standard Test Method
$CaCO_3$ - Calcium carbonate
Cast - Calcium stearate
DMA - Dynamic mechanical analysis
DSC - Differential scanning calorimetry
E’ - Storage modulus
E” - Loss modulus
EPDM - Ethylene-propylene-diene terpolymer
EPM - Ethylene-propylene copolymer
FeOOH Ferum trioxide
FR - Flame retardant
FRSS - Flame retardant smoke suppressants
HDT - Heat deflection temperature
H_f - Heats of fusion
Hst - Stearic acid
L/D - Length to diameter
LOI - Limiting oxygen index
MFI - Melt flow index
$MgCO_3$ - Magnesium carbonate
min - Minutes
MPa - Mega pascal
NBR - Butadiene-acrylonitrile rubber

PBD	-	Polybutadiene
PC	-	Polycarbonate
phr	-	Part per hundred
PMMA	-	Poly(methyl methacrylate)
PVC-U	-	Unplasticised Poly(vinyl Chloride)
r.p.m.	-	Revolutions per minit
RH	-	Rockwell hardness
SAN	-	Styrene-acrylonitrile copolymer
SEM	-	Scanning electron microscopy
SMA	-	Styrene maleic anhydride
Tan δ	-	Tangent delta
T_g	-	Glass transition temperature
TGA	-	Thermogravimetric analysis
T_m	-	Melting temperature
T_p	-	Crystallization peak
TPU	-	Thermoplastic polyurathane
UF	-	Urea formaldehyde
VCM	-	Vinyl chloride monomer
$W_{½}$	-	Width of the peak at half height
ΔH	-	Heat of crystallization

SHAHRIR HASHIM

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