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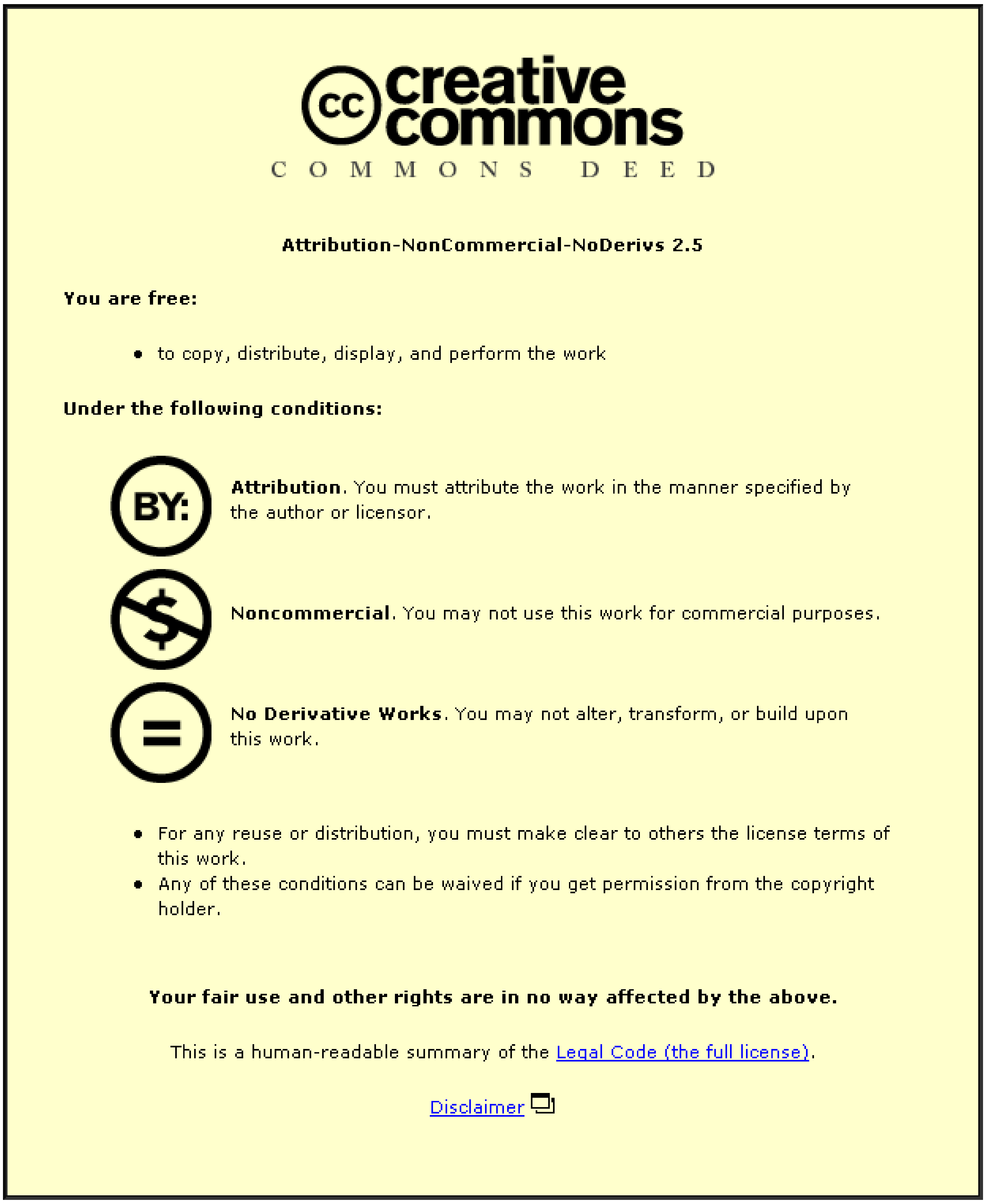

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THE CHEMISTRY AND TECHNOLOGY OF TRANSPARENT FLEXIBLE POLYURETHANES

by

SYED EJAZ AHMED
BSc (Honours), MSc

A doctoral thesis submitted in
partial fulfilment of the requirements
for the award of Doctor of Philosophy

May 1982

Supervisor: Claude Hepburn, BSc, MSc (Cantab),
ANCRT, FRSC, FPRI

Institute of Polymer Technology

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Dedication

I am indebted to my parents, brother and sisters for their patience and continuous encouragement. Their perseverance and prayers aided the transformation of my ambition into a reality.

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I am indebted to Mr C Hepburn for his invaluable guidance and advice and not least for his encouragement during the course of the work. His constructive criticism, encouragement and willingness to unselfishly sacrifice time greatly facilitated the completion of this thesis.

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Finally my thanks are due to Mrs J Smith for her patience and immaculate typing of the script.

ABSTRACT

Thermoset and thermoplastic polyurethanes have been prepared which are transparent and flexible. A synthesis technique and reaction and curing conditions were investigated to establish a reproducible method of obtaining these transparent urethanes: this is based on a polycaprolactone diol/4,4'-methylene biscyclohexyl diisocyanate (H_{12}MDI) prepolymer system. Only certain chain extenders will give transparent polyurethanes and these are aliphatic diols, cycloaliphatic diols and triols. Their relative reactivities with diisocyanates were studied.

The way in which the various chemical constituents control light transmission characteristics in polyurethane elastomers has been investigated by studyingthe morphology using differential scanning calorimetry (DSC), infrared spectroscopy and dynamic mechanical thermal analysis techniques.

Physical and mechanical properties of the prepared materials were used as the criteria of their quality and measurementswere made of modulus, ultimate tensile strength, elongation at break, hardness, tear strength, tension set and compression set.

The stability of these materials toward thermooxidative degradation, UV exposure, hydrolysis and gamma radiation have been quantfied. In Northern Australia outdoor weathering trials for retention of transparency in these polyurethanes have been organised and these are still progressing, but no firm conclusions can be drawn at this date.

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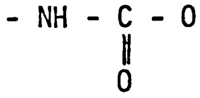
CHAPTER 1

POLYURETHANES

1.1 Chemistry and Properties

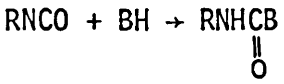
1.1.1 Introduction

Polyurethanes, sometimes referred to as "urethanes" are one of the most important class of polymers ranging very widely in their properties and applications. Because of their versatility they have been developed very rapidly during the last 3 decades and as a result urethanes are now being commonly manufactured in various forms including elastomers, plastics, fibres, foams and surface coatings etc. Saunders and Frisch [1] describe polyurethanes as those polymers which contain a significant number of the urethane group,  $-\mathrm{NH}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}$, regardless of the constitution of the rest of the molecule. Urethane groups often make up only the minor part of a typical polyurethane structure which may contain in addition to urethane groups, aliphatic and aromatic hydrocarbon, ester, ether, amide and urea groups.

Polyurethanes are widely prepared by reacting a small excess of diisocyanate with a long chain polyol (hydroxyl terminated polyester or polyether) to give a prepolymer. This prepolymer has terminal reactive isocyanate groups in its chain and these are then further reacted with diol or diamine chain extender to yield a final product. Sometimes catalysts are used to expedite these reactions. If difunctional reactants are employed the resulting polyurethane will be essentially linear. Crosslinked or branched polyurethanes can be obtained by either using trifunctional polyol and chain extenders, or an excess of diisocyanate. Thus urethanes with a wide range of properties can be achieved by varying the nature and ratio of reactants, degree of branching and reaction conditions. These reactions occur during the processing of the polymer from a liquid to a solid state and hence this technology is different from that of most other polymer systems. The history of urethane goes back to 1849 when Wurtz [2] first synthesized an aliphatic isocyanate by reacting organic sulphates with cyanates. A number of isocyanates were prepared following his work, but it was not until the late thirties when a team under the direction of Professor Otto Bayer discovered that the reaction between aliphatic diisocyanates and aliphatic diols (glycols) went smoothly under reflux conditions to build linear polymers of high molecular weight [3]. Although the melting points of these polyurethanes were a little lower than the nylons, the new material could be drawn into high tenacity yarn (Perlon) or used as thermoplastics for injection moulding (Durethan). The investigation was widened in scope and the reactions between aromatic polyisocyanates and alkyd or polyester resins were studied in detail. This research proved very fruitful and in a wartime Germany foamed products, coatings, adhesives, and even an elastomer - 'I rubber' - were discovered and gradually came into industrial use [4]. After recovering from war, the Bayer Company introduced novel machines for the mass production of flexible foamed polyurethane under the name of Moltopren and in many countries firms entered into licence agreements to make such products. Later ICI, Du Pont, Union Carbide, Shell Chemicals Ltd, Dow Chemical and others exploited their knowledge of polyurethanes and as a result of consistent research a wide range of polyurethanes were marketed in the late 1950's. Now they are available in the form of solid elastomers, plastics, fibres, foams and coatings.

1.1.2 Chemistry

The reaction of isocyanates with active hydrogen containing groups form the basis of all methods for polyurethane preparation. It is the carbon-nitrogen double bond of the isocyanate group that undergoes ionic addition reactions with a variety of functional groups which contain an active hydrogen atom, including water, alcohols, phenols, thiols, amines, amides and carboxylic acid to give a stable urethane group [5]

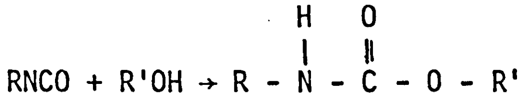


$$\mathrm{RNCO + BH \rightarrow RNH\underset{\underset{\displaystyle O}{\|}}{C}B} \qquad (1.1)$$

The following primary reactions of isocyanates are very important in polyurethane chemistry:

Alcohols:

Isocyanates react with alcohol (ROH) to give urethanes in the following manner:

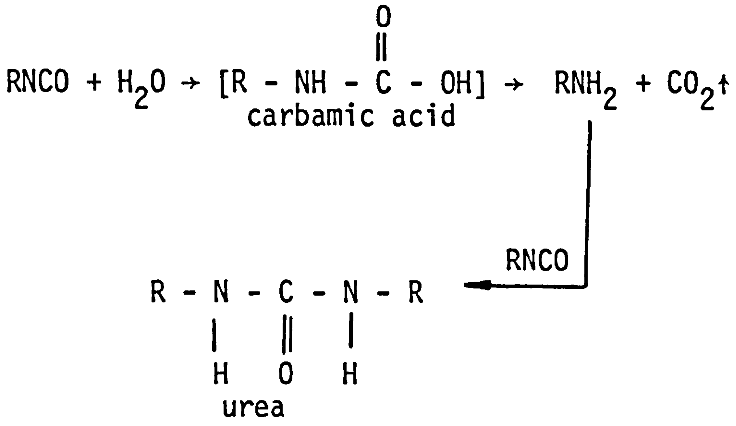


$$RNCO + R'OH \rightarrow R - \overset{\overset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - O - R' \qquad (1.2)$$

This is the most important reaction in polyurethane preparation as the backbone polyols are OH terminated and also the most widely used chain extenders are diols e.g. 1,4-butane diol. The reactivity of primary alcohols is greater than secondary alcohols which in turn are more reactive than tertiary alcohols. Stability of urethane products is inversely proportional to their rate of formation, thus polyurethanes from aliphatic isocyanates are more stable than those from aromatic isocyanates [6].

Water:

The reaction of isocyanates with water is important in urethane foam and moisture curing of one-component isocyanate-terminated coatings. Isocyanates react with water to give an unstable intermediate product of carbamic acid followed by amines and carbon dioxide. The amines are more reactive toward isocyanate than the water and hence form a disubstituted urea:



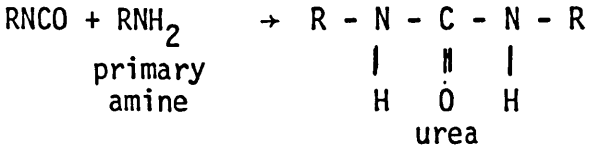
$$RNCO + H_2O \rightarrow \underset{\text{carbamic acid}}{[R - NH - \overset{\overset{O}{\|}}{C} - OH]} \rightarrow RNH_2 + CO_2\uparrow$$

$$RNH_2 \xrightarrow{RNCO} \underset{\text{urea}}{R - \underset{H}{\underset{|}{N}} - \underset{O}{\underset{\|}{C}} - \underset{H}{\underset{|}{N}} - R} \qquad (1.3)$$

This reaction shows the importance of handling urethane raw materials in perfectly dry conditions during the formation of coatings, solid elastomers and sealants, containing free isocyanate group, in order to avoid unwanted bubble formation due to the release of carbon dioxide gas.

Amines:

Isocyanate react with primary and secondary amines to form ureas (equations 1.4 and 1.5):



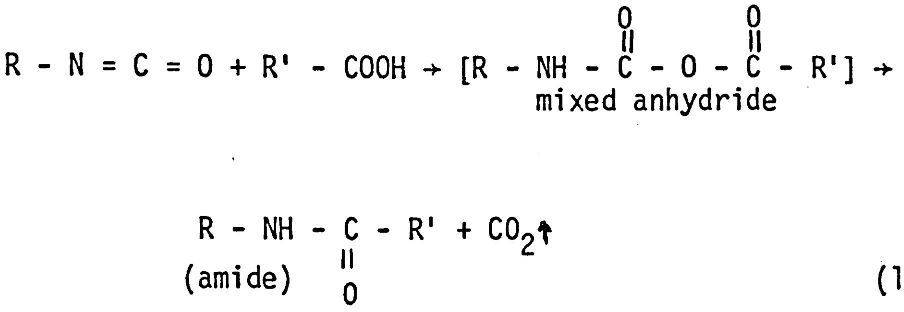
$$RNCO + \underset{\text{primary amine}}{RNH_2} \rightarrow \underset{\text{urea}}{R - \underset{H}{\underset{|}{N}} - \underset{O}{\underset{\|}{C}} - \underset{H}{\underset{|}{N}} - R} \qquad (1.4)$$

$$RNCO + \underset{\text{secondary amine}}{R_2NH} \rightarrow \underset{\text{urethane}}{RNHCONR_2} \qquad (1.5)$$

The reactivity increases as the amine becomes more basic. This reaction is of particular value in chain extension of isocyanate terminated prepolymers, forming urethane-urea elastomers.

Carboxylic acid:

The reaction of isocyanate with carboxylic acid proceeds usually with formation of a mixed anhydride followed by decomposition, yielding the corresponding acid amide with liberation of carbon dioxide [7].



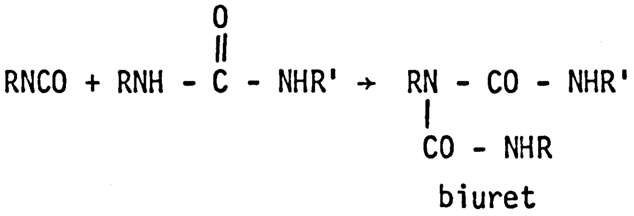
$$R - N = C = O + R' - COOH \rightarrow \underbrace{[R - NH - \overset{\overset{O}{\|}}{C} - O - \overset{\overset{O}{\|}}{C} - R']}_{\text{mixed anhydride}} \rightarrow$$

$$\underbrace{R - NH}_{\text{(amide)}} - \underset{\underset{O}{\|}}{C} - R' + CO_2\uparrow \qquad (1.6)$$

The extent of reaction between isocyanates and carboxylic acids depends on the concentration of acid used.

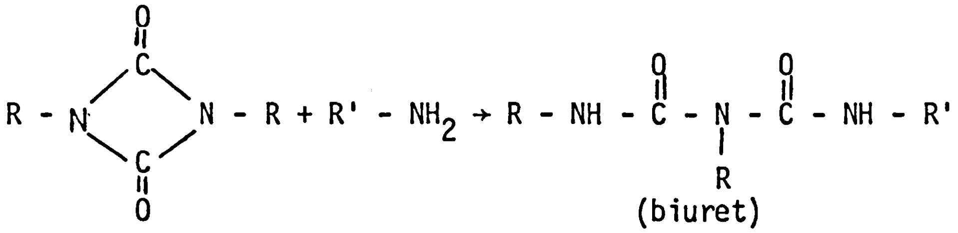
Ureas:

At elevated temperatures, about 100°C, the isocyanates react with ureas to give biuret linkages:



$$RNCO + RNH - \overset{\overset{O}{\|}}{C} - NHR' \rightarrow \underset{\text{biuret}}{\underset{\underset{CO - NHR}{|}}{RN} - CO - NHR'} \qquad (1.7)$$

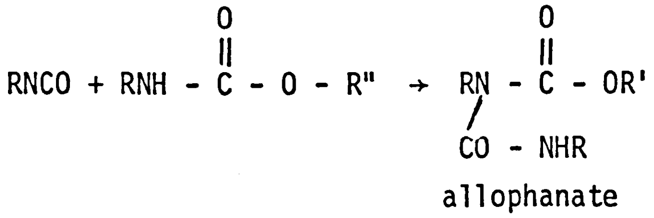
Isocyanate dimers also react with amines to yield the corresponding biurets (equation 1.8)



(1.8)

Urethanes:

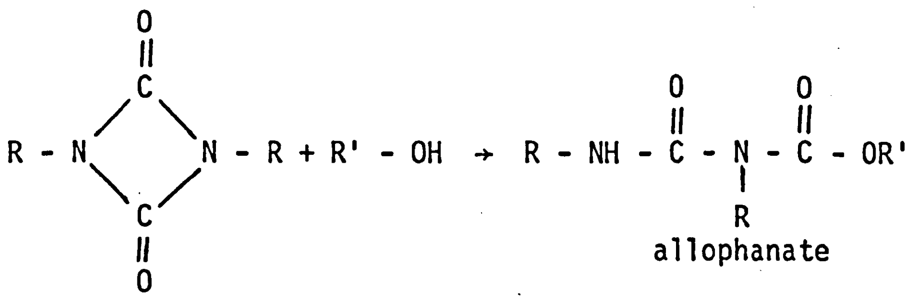
At elevated temperatures (above 100°C) or at lower temperatures in the presence of certain catalysts urethane groups react with isocyanate to form allophanate linkages



$$RNCO + RNH - \overset{\overset{O}{\|}}{C} - O - R'' \rightarrow \underset{\text{allophanate}}{\underset{CO - NHR}{RN} - \overset{\overset{O}{\|}}{C} - OR'}$$

(1.9)

Allophanates can also be formed in a reaction of alcohols with aromatic isocyanate dimers (equation 1.10)



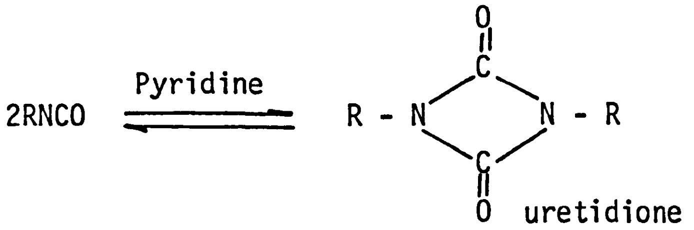
(1.10)

Although this reaction is slow, it can be increased 1000 times by employing a basic catalyst such as triethylamine [7].

Self-addition or self-polymerization reactions:

The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds. However, tertiary amines are effective catalysts for isocyanate self-addition reactions whereas metal compounds generally have less influence; tin compounds are rather poor catalysts in these reactions [8]. The following are the three important self addition reactions of isocyanates.

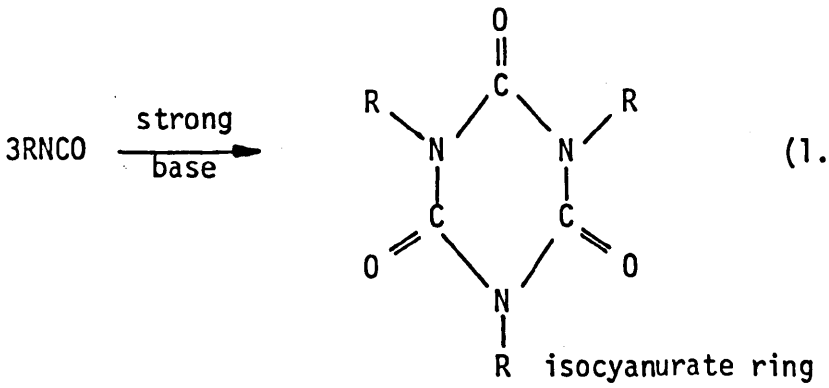
a) Dimerization of isocyanates (equation 1.11) takes place in the presence of pyridine giving rise to uretidione rings.



(1.11)

Dimerization is readily reversible and is capable of breakdown to give two molecules of the original component.

b) Trimerization of isocyanates gives stable isocyanurate rings



(1.12)

These trimer or isocyanurate rings, unlike dimer or uretidione rings, are exceptionally stable. It can be seen that polymerization of polyisocyanates can give isocyanurate polymers which contain many isocyanate groups and therefore can behave as multifunctional isocyanates. Both uretidione and isocyanate formation is important in isocyanate chemistry, but isocyanurate formation is significant in a wider range of 'polyurethane' applications [9].

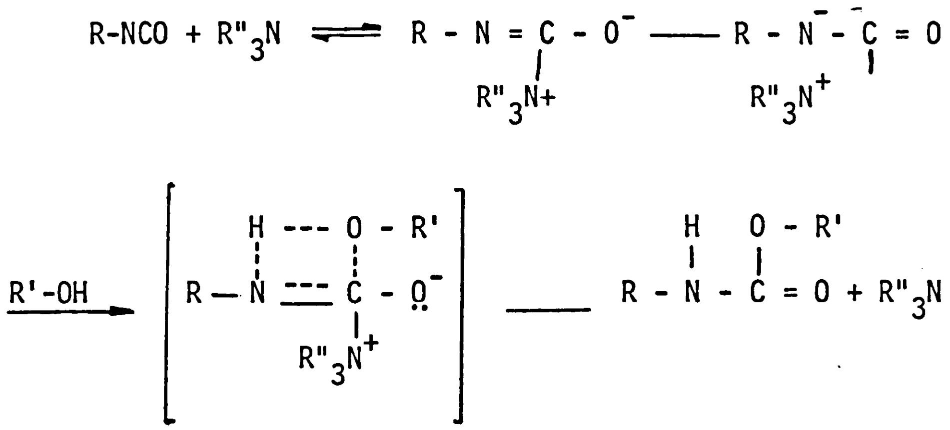
c) Condensation polymerization between isocyanate molecules occurs with the elimination of carbon dioxide. This results in the formation of carbodiimides which are used as hydrolysis inhibitors in certain polyester urethane systems (equation 1.13).

$$2RNCO \xrightarrow[\text{phospholine oxide catalyst}]{\text{High temperature}} \underset{\text{carbodiimide}}{RN = C = NR} + CO_2\uparrow \qquad (1.13)$$

Catalysis:

The use of catalysts in polyurethane chemistry is to accelerate the reaction rate to completion and to reduce reaction time. The other purpose of catalysts is to achieve a balanced reaction rate in the system where the activity of various reactants towards isocyanates differ. In polyurethane synthesis the catalysts employed are usually either bases, acids or certain specific metal compounds.

The basic catalysts used are either inorganic bases or tertiary amines and materials which can generate tertiary amines. The tertiary amine (R''_3N) catalysis is thought to proceed as follows [8]:



(1.14)

In general the catalytic effect of bases increases with increasing strength of the base. Tertiary amines are relatively more powerful catalysts due to the accessibility of their nitrogen atoms and lack of steric hindrance.

Acids have a very mild catalytic effect on polyurethane preparation but retard allophanate and biuret formation. The only reaction strongly catalysed is that with water which ideally should not be present in solid polyurethanes [6]. Acid halides e.g. p-nitrobenzoyl chloride or benzoyl chloride can be used safely as stabilizers (0.05-0.1% of polyol wt) for the prepolymer and to prevent moisture reacting with free isocyanate [10]. An acid may also render inactive a metal which may be present, for example, from the polyether polymerization catalysts or esterification catalysts.

Metal catalysts especially tin catalysts, are also commonly used to expedite isocyanate reactions with the hydrogen containing component. Organotin compounds are extremely effective catalysts and include stannous octoate, stannous oleate, dibutyl tin dilaurate etc.

1.1.3 Raw Materials

The main raw materials used in the preparation of polyurethanes are hydroxyl terminated polyesters or polyethers (polyols, di- or polyisocyanates and chain extension diols or amines of low molecular weights. Some of these raw materials which are widely used commercially will be discussed briefly in this section.

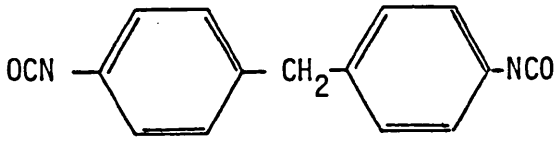
Diisocyanates:

Several reactions are known by which isocyanates are formed. However the only commercially important method used in preparing isocyanates is the reaction between phosgene and amines (equation 1.15)

$$R - NH_2 + COCl_2 \rightarrow R - N = C = O + 2\ HCl \qquad (1.15)$$

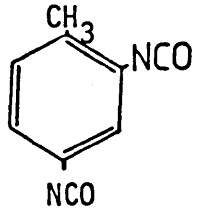
The most widely used diisocyanates are 4,4'-diphenyl methane diisocyanate (MDI), Tolylene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI) and 1,5-naphthalene diisocyanate (NDI). All these isocyanates are prepared by reaction of the corresponding amines with phosgene in an inert solvent like ortho dichlorobenzene at temperatures of 25-100°C.

The preparation of MDI involves the condensation of aniline and formaldehyde in the presence of hydrogen chloride and subsequent phosgenation. The melting point of MDI is around 38°C and it contains two equally reactive isocyanate groups:



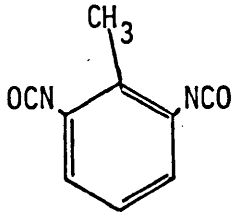
A saturated MDI is a water like liquid at room temperatures and mainly used for surface coatings and transparent urethane articles.

TDI is mostly used as a mixture of the 2,4- and 2,6-isomers, usually the 80:20 mixture, obtained by starting from the total di-nitration products of toluene, although by a different route a 65:35 commercial mixture can also be produced:



2,4-isomer

TDI



2,6-isomer

The NCO group in the 4 position is 8 or 10 times as reactive as that in the 2 position at room temperature ($25^{o}C$). With increase of temperature the activity of the ortho NCO groups increases at a greater rate than that of the para until at $100^{o}C$ the ortho and para NCO groups have similar reactivity. This difference in activity at lower temperatures is advantageous in the preparation of isocyanate terminated prepolymers [7]. The undistilled grades of MDI and TDI commonly referred to as crude isocyanate due to their lower reactivity have found extensive use in the manufacture of one shot rigid foam and adhesives.

The disadvantage of these aromatic diisocyanates is the tendency of their derivative urethanes to turn yellow on prolonged exposure to sunlight. The aliphatic diisocyanates on the other hand leads to urethane polymers with better resistance to discolouration, hydrolysis and heat degradation.

Physiological effects of isocyanates

All isocyanates are potentially hazardous chemicals and because they are used as raw materials on a very large scale in the manufacture of polyurethanes, great care must be taken in handling these materials. Isocyanates are strong lachrymators due to their high vapour pressure and may cause asthma after repeated inhalation [11].

As a result of experiments based on animal and clinical analysis, a threshold limit value (TLV) of each isocyanate has been set by the manufacturer of these materials and different governmental industrial hygienists. The term TLV means the maximum average atmospheric concentration of an isocyanate to which one may be exposed for an eight hour working day. TLV is expressed in concentration as 'parts per million' which is the parts of vapour per million parts of contaminated air by volume at 25^{O}C and 760 mm pressure. The probability of an isocyanate vapour becoming harmful is increased if it is used above its TLV. One should always wear rubber gloves and safety spectacles while handling isocyanates and ensure proper ventilation. In the case of any spillage, a decontaminant should be used to neutralise the reaction of isocyanate. A liquid decontaminant is a mixture of methanol, water and concentrated ammonia solution in the rate of 50:45:5 respectively by weight or volume.

Polyols

The two polyols, polyether and polyester based are widely used as intermediates in the manufacture of all types of polyurethanes and the choice of polyol strongly influences the final properties of urethanes. In general polyesters provide better mechanical properties than the polyethers which yield more hydrolytically stable polyurethanes.

Polyethers

The polyethers are commercially the most important of the polyhydroxy compounds used to prepare polyurethanes. The first polyether designed specifically for preparing polyurethanes was a poly (oxytetramethylene) glycol derived from tetrahydrofurane. At present, most of the polyethers used for the manufacture of foam are derived from propylene oxide and/or ethylene oxide and poly (oxyalkylene) derivatives of polyhydric alcohols such as glycerol, trimethylolpropane and sorbitol. Polyethertriols of relatively high molecular weight (about 3000) are extensively used for the production of flexible foams whilst polyols of low molecular weight (about 500) are used for rigid foams and surface coatings.

Polyethers are generally prepared by catalytic polymerization of the epoxide group in the alkylene oxide with suitable initiators. The catalysts used are Lewis acids and bases and salts. The widely used polyethers in urethane elastomers are polyoxypropylene glycols and polyoxytetramethylene glycols. In general polyether glycols are light coloured viscous liquids. They are non volatile and soluble in common organic solvents. The choice of polyether glycol depends on its hydroxyl content, unsaturation, water content, acidity and molecular weight which have direct influence on the final properties.

Polyesters

The polyesters used in the preparation of polyurethanes generally have molecular weight ranging from 500 to 3000 and are liquid or low melting solids: they are usually saturated. The hydroxyl terminated polyesters are prepared by the reaction of dibasic acid with molar excess of glycols and polyhydric alcohols. The most common monomers used in polyesters for the urethane polymers are adipic acid, phthalic anhydride, ethylene glycol, propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, and diethylene glycol. For the preparation of branched polyesters, triols such as 1,2,6-hexanetriol and trimethylol propane are commonly used. Some lactones such as caprolactone have also been used to prepare polyesters for polyurethanes. For use in elastomers, linear polyesters having molecular weight close to 2000 are preferred, whereas slightly branched ones of similar molecular weight are used for flexible foams and elastic coatings, and highly branched polyesters are used for rigid foam and chemically resistant coatings.

Chain extenders

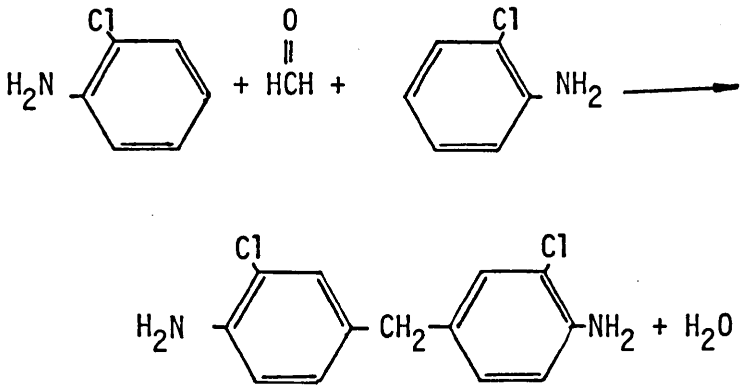
Several glycols and diamines are used as chain extension agents in the manufacture of polyurethanes and typical examples of widely employed chain extenders are 1,4-butanediol and 4,4-methylene bis o-chloroaniline (MOCA).

The manufacture of 1,4-butanediol involves the high pressure hydrogenation of 1,4-butynediol using a nickel-copper-manganese catalyst. The butynediol is obtained by the reaction between acetylene and formaldehyde [6].

$$CH{\equiv}CH + 2HCHO \rightarrow HOCH_2 - C{\equiv}C - CH_2OH$$

$$HOCH_2 - C{\equiv}C - CH_2OH \xrightarrow[H_2]{Ni/Cu/Mn} HOCH_2CH_2CH_2CH_2OH \qquad (1.16)$$

The most widely used diamine so far has been 4,4'-methylene bis (o-chloroaniline) and this can be manufactured by the condensation of o-chloroaniline with formaldehyde in acid medium:



(1.17)

1.1.4 Synthesis

In the synthesis of polyurethanes the terms block ratio or NCO/OH ratio are frequently used as a basis of controlling the synthesis and relating the stoichiometric proportion of starting materials with that of final physical properties. For example a polyurethane based on 1:3:2 ratio signifies the stoichiometric equivalent weight ratio by which the polyol, the diisocyanate and chain extenders are respectively reacted to give the final product. Similarly a polyurethane with NCO/OH = 1.3 is a product obtained by reacting 1.3 equivalent of diisocyanate with 1 equivalent of hydroxyl containing reactant. Another term "isocyanate index" is sometimes used particularly in foam production which is NCO/OH ratio multiplied by 100.

The two techniques commonly employed in the synthesis of polyurethanes are:

1. prepolymer route, and
2. one shot process,

the former sequence is by far being the most widely used and provides better handling, controlled processing and consequently better properties. The prepolymer obtained by reacting a long chain polyol with an excess of diisocyanate are moderate molecular weight liquids or low melting solids and which in the second stage can be chain extended with low molecular weight diol or diamine to yield final cured materials.

Prepolymers can be prepared either by melt polymerization or solution polymerization. In melt polymerization the predried diisocyanate and a polyol at NCO/OH ratio greater than one, are mixed in molten form with vigorous stirring. As the reaction between NCO and OH is exothermic the reaction temperature is controlled to avoid any undesired crosslinking in the case of linear polymer or dimerization of diisocyanate which may take place at elevated temperatures. A typical prepolymer reaction is schematically shown below:

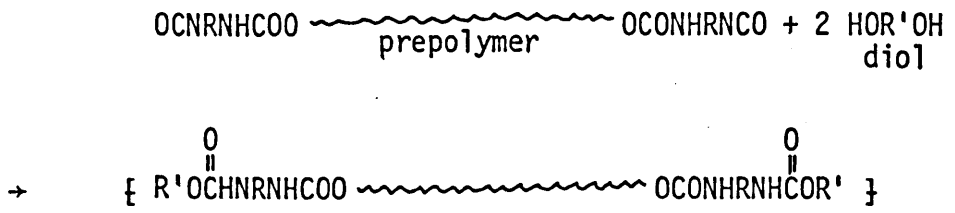
$$\underset{\text{diisocyanate}}{2\ \text{NCO-R-NCO}} + \underset{\text{polyol}}{\text{HO}\sim\sim\sim\sim\sim\sim\sim\sim\text{OH}} \longrightarrow$$

$$\text{OCN - R - NHCOO}\sim\sim\sim\genfrac{}{}{0pt}{}{\text{capped}}{\text{polyol}}\sim\sim\sim\text{OCONH - R - NCO}$$

(isocyanate terminated prepolymer)

The prepolymer when prepared should be stored under an atmosphere of nitrogen to assist shelf stability by preventing moisture coming in contact with NCO groups. Sometimes stabilizers like acid chlorides are mixed with polyol in a very small quantity before reaction to achieve better shelf life stability.

Chain extension reactions proceed by the reaction of prepolymer of low molecular weight diol or diamine in the dried molten or liquid state. Generally the prepolymer is left for a few minutes under vacuum to remove entrapped air bubbles before mixing takes place. Again the chain extension reaction is exothermic and needs temperature control. Diols are comparatively less reactive than diamines and sometimes necessitate the use of catalysts which should be added to the polyol prior to mixing. A typical chain extension reaction is given below:



$$\text{OCNRNHCOO}\underbrace{\sim\sim\sim\sim\sim\sim\sim\sim}_{\text{prepolymer}}\text{OCONHRNCO} + 2\ \underset{\text{diol}}{\text{HOR'OH}}$$

$$\rightarrow \{\ \text{R'O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{HNRNHCOO}\sim\sim\sim\sim\sim\sim\sim\sim\sim\text{OCONHRNH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OR'}\ \}$$

As the pot life of melt polymerized urethanes is short the reacting mix is quickly poured into a mould after mixing. Cure is normally carried out by heating in the temperature range 50-110°C for several hours.

The synthesis technique of solution polymerization is similar to bulk polymerization as discussed above, except that this process is carried out in a common-non reactive solvent. Solution polymerization techniques have the following advantages over bulk polymerization:

a) A much wider range of diisocyanates and chain extension agents can be used including those having high melting points and high reactivity.

b) It gives rapid and efficient dispersion of reactants leading to more uniform reactions throughout the medium.

c) Disadvantages of short pot life are overcome and the final polymer solution can be easily cast to form a thin film by solvent evaporation procedures.

In one shot systems the three materials, viz a diisocyanate, a polyol and chain extender are mixed together whereas in one step prepolymer formation and chain extension reactions take place simultaneously. In practice the polyol and chain extender are first mixed, dried and then added to diisocyanate. The major problem in one shot systems occurs in balancing the reactivities of the polyol and chain extender with isocyanates in order to obtain an acceptable network build-up. No serious problem arises when both polyol and diol materials are used together, but in the case of mixed polyol-diamine systems, catalysts are required to preferentially promote the hydroxyl-isocyanate reaction.

Tin catalysts, e.g. Stannous Octoate are commonly employed which provide a suitable balance of reactivities for the polyol and diamine and leads to a successful method of manufacture for these one-shot elastomers. In solid polyurethanes one shot systems are mostly used due to economical reasons in the production of segmented thermoplastic materials where the three starting ingredients are mixed and extruded in a continuous process.

1.1.5 Categories

Because of its versatility and broad range of properties, polyurethane elastomers fall into many categories:

1. *Castable Polyurethanes*

Castable polyurethanes are by far the largest class and can be manufactured by either prepolymer or one shot route. The fabrication techniques of this class of polyurethanes include open casting, compression and transfer moulding, centrifugal and centrifugal vacuum casting. It is useful to record the various advantages that castable urethane elastomers possess [12] and these are stated below:

i) Curable viscous liquid elastomeric compounds have some physical properties that are unattainable in thermoplastic urethanes which are 20% to 50% higher priced than castables. Simplified liquid compounding makes customized product properties more readily available with greater economies.

ii) Open casting is the simplest method of moulding reactive liquid polymer systems with the lowest capital investment.

iii) Centrifugal casting is very adaptable to short part runs or large products that cannot be handled in injection moulding equipment.

iv) Centrifugal vacuum casting is another way of preparing elastomeric products by an economical, low-cost process, that offers total design freedom, low-cost tooling, lower material cost, rapid investment pay off and shorter start-up times.

v) Centrifugal vacuum casting is capable of making multiple cavity, small parts as well as single cavity, large parts. The process has been limited only by the size of equipment.

2. *Linear or Thermoplastic Polyurethanes*

Linear or thermoplastic polyurethanes are usually prepared by addition reaction between aliphatic difunctional polyols, aliphatic diisocyanates and diols. The NCO/OH ratio is kept at 1.0 so that no crosslinking between the chains occurs or chain branching results. Thermoplastic polyurethanes are defined as materials having elastomeric properties at ambient temperatures but at elevated temperature they are readily fabricated by such melt-processible techniques as injection moulding or extrusion, which are characteristic of plastic materials. The structure, morphology and properties of such segmented materials is discussed in later section. It is now generally known that the excellent mechanical properties associated with thermoplastic polyurethane elastomer is due to their tendency to undergo phase separation. Owing to their excellent mechanical strength, abrasion, oil resistance and ease of processing thermoplastic polyurethanes have found widespread application in sealing, shoe heels, automobile parts, textile equipment parts, transparent tubing, fastening devices and gaskets etc.

3. *Millable Polyurethanes*

Millable polyurethanes are the polymeric materials that can be processed by the conventional techniques of 2-roll mill compounding and vulcanization. The properties of the final product are inferior in strength to those from the castable polyurethanes but have superior compression set and creep. The millable urethanes have mainly been used for products which could not be satisfactorily produced using the cast systems for example, thin walled flexible gaiters, diaphragms and other similar components most easily manufactured by compression and similar moulding techniques [6]. Unlike cast urethane systems, in these a small deficiency of diisocyanate is employed. The diisocyanate is first reacted with a long chain polyol to yield a millable hydroxyl terminated prepolymer. These prepolymers are thermoplastic and in processing character resemble unvulcanized natural rubber. Because the physical properties of such millable prepolymer is poor, it is necessary to introduce crosslinking and thus to obtain a network structure similar to cast urethanes. The established commercial procedure of transforming the millable prepolymer into strong vulcanized elastomer are:

1. Chain extension of the hydroxyl-ended millable prepolymer with a diisocyanate (or blocked diisocyanate).
2. Peroxide crosslinking.
3. Sulphur crosslinking through small amounts of ethylenic unsaturation introduced as lateral groups on the main chain polymer.

The latter two techniques are of special value in obtaining true covalent type crosslinking which results in much improved time-dependent properties like creep and set.

4. *Cellular Polyurethanes*

All polyurethanes can be made into cellular structures which are flexible or rigid depending on the modulus (stiffness) characteristics of the solid polymer. Cells can be interconnecting (open cell) or isolated (closed cell) and the density of such structures varied as desired, although usual ranges found are 0.35-1.0 $\mathrm{gm.ml^{-1}}$. As mentioned earlier the reactants to produce a cellular urethane are usually a diisocyanate, a long chain polyol and water. An isocyanate group reacts with polyol and water to give urethane and urea groups respectively with the evolution of carbon dioxide gas which leads to cellular polymer formation.

Poromeric polyurethanes are a special class of cellular urethane elastomers used mainly in footwear. Their flexibility and abrasion resistance make them excellent surface coating films on artificial and natural rubber. Poromeric polyurethanes also find useful application in the shoe and furnishing industries and some commercial poromerics contain randomly dispersed fibres (e.g. Corfam and Porvair) whereas others have a microporous unreinforced structure.

1.2 Structure, Morphology and Transparency in Polyurethanes

1.2.1 Introduction

Structurally polyurethanes are $\leftarrow$A-B$\rightarrow_n$ type block copolymer and contain alternating segments of flexible chains of low Tg (soft segments) and highly polar, relatively rigid blocks (hard segments). As mentioned earlier the soft segment is derived from a polyol such as hydroxyl terminated polyester or polyether. The hard segment is a result of diisocyanate reaction with either a short chain diol (forming carbamate) or a diamine (forming urea). By varying the relative soft/hard segment ratio and particularly the crosslinking and block molecular weight, the urethanes obtained range in properties from soft, highly extensible materials to hard compositions which superficially resemble conventional thermoplastics more than rubber. Also, a number of additional structural features that influence the final urethane properties are intermolecular forces, the stiffness of chain units, ease of rotation of chain segments and crystallization. The interactions between the polar entities like urethane, urea, ester and other groups are of great importance in determining the properties of polyurethanes of all types, and specially the polyurethane block copolymers where local concentrations of polar groups occur together leading to a supra-molecular organization into aggregated structures, which may be in the form of glassy domains or crystallites. It is notable that crosslinked polyurethane elastomers are not necessarily block copolymers as the crosslinking beyond a certain low level disrupts hard block domain structures and prevents phase separation [14]. Moreover due to restrictive chain mobility the hard segments are evenly dispersed in a soft block matrix yielding mixed polymer structure. The hard segment length in such crosslinked material is smaller than the wavelength of visible light and consequently a higher degree of transparency results.

The transparency in segmented polyurethane (thermoplastics), however, is relatively more complex and these copolymers have recently generated considerable interest in their synthesis, properties and solid state morphology [14-18]. The physics controlling the morphology of the block copolymer is simple to describe. In a material composed of units of types A and B, which have a positive heat of mixing, there is a tendency towards phase separation. The topology (chemical bonds) of the block copolymer molecules impose restrictions on this segregation and leads to microdomain formation. It is now widely accepted that the unusual properties of these copolymers are directly related to their two phase microstructure, with the hard domains acting as a reinforcing filler and multifunctional crosslink. Block copolymers of the type behave as chemically crosslinked elastomers, yet they can be processed by rapid thermoplastic-forming techniques at elevated temperature. Because of the relatively short segment length and its molecular weight distribution microphase separation may be incomplete, suggesting impure domains and interfacial regions comprised of a mixed phase in which there is a gradient of composition.

Microphase structure may be described as the microphase structure that results from a combination of two or more dissimilar polymers or components. The size of microphases is normally in the range of 10μ or less but the most characteristic size range is approximately 0.01 to 1.0μ [19]. A typical example of two phase systems can be seen in high impact polystyrene where the addition of about 10% of rubber gave 10-20 fold increase in impact strength to polystyrene with the least deterioration of its rigidity [20]. In block polyurethane it is the hard block domains which serve as tie points similar to covalent bonds present in a crosslinked elastomer. The microphase separation of the hard segments results in highly dispersed rigid particles which reinforce the elastomeric matrix in a manner similar to carbon block reinforced vulcanisates. If the size of these rigid particles is smaller than the wavelength of visible light, the resultant material will be transparent despite any soft/hard segments incompatibility or difference in their refractive indices. This characteristic (transparency) in urethanes as a result of microphase formation can be clearly understood by considering the following example of SBS copolymer [14,15,18]. As the polystyrene and polybutadiene are incompatible with each other, a block copolymer based on these two homopolymer shows a unique microphase separation. Matsuo [20] et al prepared a series of styrene-butadiene block copolymers with varying styrene and butadiene combinations and compositions. They compared the microphase dispersion and transparency in these prepared copolymers with those of commercial high impact polystyrene and styrene/butadiene polyblends. They found all the prepared copolymers showed heterogeniety as evidenced by the two separate dynamic loss peaks (ε'') in dynamic viscoelastic curves. However these samples exhibited extensive transparency in spite of a large difference in refractive index between polystyrene and polybutadiene. Matsuo and co-workers explained this fact on the basis of microphase dispersion. For instance in an SBS type copolymer the rubber component was found to form very fine discrete particles in electron micrographs which was well recognized by comparing with those of a styrene/butadiene mechanically mixed polyblend. It was concluded that the transparency of the block copolymers, in comparison with the complete opaqueness of the polystyrene/polybutadiene blend is due to the fineness of the particle size. These particles, due to their very fine size, do not scatter light.

It is thought that the main problem in achieving transparent polyurethanes arises from the undesirable tendency of some polyesters to crystallize (cold hardening) on ageing. Flocke [21] has demonstrated that as the polyester molecular weight increases so does the rate of polyester crystallization in the polyurethane elastomer. This soft segment crystallization can be avoided by the use of a co-polyester which possess structural irregularity. For example Poly(ethylene-co-1,2 propylene adipate), containing the glycols in 70/30 ethylene/propylene molar ratio, although crystallizing at room temperature, gives elastomers which do not cold harden but the properties are not usually quite as good as those from poly(ethylene adipate) [14]. The other alternative way of preventing soft segment crystallization to improve transparency is to introduce some crosslink network e.g. by the use of a triol chain extender. The presence of crosslinking beyond a certain low level although giving lower physical properties due to disruption of hard block domain structure increases transparency to a much higher level. A 1/1 blend of diol and triol on equivalent basis has been found to give polyurethanes with a good combination of physical properties and transparency. (See experimental section).

One additional feature of the crystalline transition behaviour is worthy of mention. Segments that are essentially amorphous in the isotropic undeformed state may develop crystallinity, upon deformation. This phenomenon is commonly referred to as "stress induced crystallization" and its result is to produce excellent ultimate tensile strength properties. The fact that some polyurethanes e.g. those based on polycaprolactone exhibit high tensile strength and excellent wear and abrasion resistance is attributed to the ability of the soft segments to stress crystallize. The phenomenon can even be visually observed. High extension normally results in opacity which disappears upon removal of stress.

The extension and subsequent relaxation processes in an elastomeric polyurethane block copolymer probably involves orientation and restructuring of the molecular organization initially present [14,22,23]. Upon a limited elongation, stress induced crystallization of the soft segment may occur. Not all the soft segments in a polyurethane block copolymer are capable of crystallizing, either due to their chemical constitution or to their physical environment in the polymer matrix. Those soft segments which do form crystallites will provide resistance to further extension because of the crystalline forces now present. At this stage of the extension process Bonart [22] suggests that, in some compositions at least, the hard segments will be aligned at different angles to the direction of elongation. On the basis of this model, on further extension some polyester segments will be removed from soft segment crystallites and ultimately sliding of the hard blocks from their aggregates (domains) will occur to accommodate the extension forces. Continuation of this process will result in the restructuring of the hard blocks in new arrangements, a process which will be accelerated by heat treatment.

Stress hysteresis is prominent in segmented copolymers because of the disruption of hard segments with strain. Unlike Young's modulus which depends on the rigidity and morphology of hard-segment domains, stress softening is a function of domain restructuring and ductility and the nature of the mixed hard and soft segment interfacial regions [22]. In segmented polyurethanes hard segment crystallization has been found to increase stress hysteresis, permanent set, and tensile strength. Heat build up in polyurethanes, attributable to their high hysteresis losses, has limited their suitability in applications such as high speed tyres.

With regard to ultimate tensile strength properties, the fracture process can be represented by three steps: initiation of microcracks or cavitation, slow crack propagation, and catastrophic failure [17,19]. Dispersed phases tend to interfere with the crack propagation step, redistributing energy that would otherwise cause the cracks to reach catastrophic size. Thus a two phase morphology is essential to the achievement of high strength in elastomers. The presence of hard-segment domains increases energy dissipation by hysteresis and other viscoelastic mechanisms. Growing cracks can be deflected and bifurcated at phase boundaries. Upon deformation, triaxial stress fields are formed about hard phase particles, tending to inhibit the growth of cavities. Cavities which do form can be limited to small sizes, stabilised by surface energy effects. The high modulus hard phase can also relieve stress concentrations by undergoing deformation or internal structural organization. At lower temperatures, strength can be raised because of the greater domain yield stresses, increasing matrix viscosity, or strain-induced crystallization effects. The relative importance of these and other reinforcement mechanisms in two phase polymer systems depends on the type, size and concentration of the domains or phases [17]. At above room temperature where the soft segments are no longer crystalline, the hard segment domain cannot retard crack growth because of insufficient cohesive strength at these temperatures.

The transparency in polyurethanes is largely dependent on the polymer structure which in turn is influenced by the synthesis method and previous thermal and processing history. One shot processes give rise to random block type copolymers. Crystallinity and melting point for block and random copolymers were studied and compared. The principle was illustrated in polyester block copolymers by Charch and Shivers [24]. In random copolymers where a rapid decrease of melting point (i.e. decrease crystallinity) is observed with comonomer incorporation, they found it to be much less pronounced in block systems because of the presence of long chain sequences. From a theoretical standpoint, Peebles [34] has shown a two-step prepolymer method of block copolymer synthesis should lead to a narrower distribution of hard segment lengths as compared with that for a one step synthesis, providing that reaction of the first isocyanate moiety occurs at a faster rate than that of the remaining moiety. It is notable here that narrow hard segment molecular weight distribution leads to phase segregation and consequently crystallization which is undesired for a transparent urethane [30]. When a solution polymerization technique is employed, depending on solvent system various structures are possible. Wilkes and Samuels [27] reported spherulitic morphology of the segmented piperazine polyurethane cast from chloroform whereas similar series investigated by Cooper et al [35] showed no superstructure when using methylene chloride as solvent. Chang and Thomas [36] studied the morphology of bulk polymerized and solution cast urethanes based on polycaprolactone diol/MDI/BD with varying block ratio from 1:2:1 to 1:6:5. As reacted samples contained a more ordered hard segment phase while solution cast samples contained a more ordered, soft segment phase. The lower ordering of the hard segment phase in solvent (DMF) cast samples indicated poor degree of phase separation, but improved transparency.

There are a number of analytical techniques used in the study of polyurethane morphology and their solid state structure property relationship. These include dynamic mechanical property, thermal analysis, infrared spectroscopy, X-ray diffraction, infrared dicroism, and microscopy. Since the first two techniques have been employed in the present investigation on transparent flexible urethanes, these will be briefly reviewed below.

1.2.2 Dynamic mechanical analysis

The dynamic mechanical behaviour of polyurethanes has been studied by several investigators [25-29] in order to understand polymer morphology and microphase separation. It is generally agreed that the transitions depend on temperature and/or frequency and that they are markedly influenced by such parameters as block length composition and thermal history. Illinger and co-workers [25] studied the low temperature soft segment dynamic mechanical properties of polyether based urethanes with varying diisocyanate content. The Tg of the soft segment was found to be approximately the same as that of a homopolymer up to a minimum diisocyanate level. However when this level was exceeded ~~the soft segment~~ the Tg was significantly raised. This was explained by restrictions in soft segment mobility due to the termination of soft segments by urethane groups and also because of hard segment solubility in a soft segment matrix. Similar increases in soft segment Tg with increased urethane content was observed by Ferguson and co-workers [28]. They attributed this effect to the presence of a spherulitic crystalline interface which constrained molecular motion. Likewise the hard segment melting transition became more marked with increased hard segment length because of better developed crystallites with higher melting points. Using dynamic mechanical techniques Seefried [29] et al investigated the soft segments and hard segment variation effects in thermoplastic polyurethanes based on poly caprolactone diol/MDI/1,4-BD systems and found when the soft segment molecular weight varied a substantial decrease in the respective storage modulus properties for each polymer corresponded to the transitions from the brittle glassy state to the elastic rubbery state. An increase in the molecular weight of the soft segment polycaprolactone diol at a constant hard segment sequence length shifts this modulus decrease to progressively lower temperatures. A similar technique was used to study the variation in hard segment content of two urethane series, each being derived from polycaprolactone diol as soft segment of 830 $\overline{M}n$ and 2100 $\overline{M}n$ respectively.

For the series of urethane polymers containing the 830 $\overline{M}n$ polycaprolactone diol, increasing the relative hard segment concentration, from a block ratio of 1:2:1 to 1:20:19, produces responses typical of compatible copolymers, i.e. an increase in the glass transition temperature corresponding to changes in hard-segment levels. At this soft segment molecular weight, the hard segments exert considerable restrictions on the mobility of the amorphous regions. In contrast, the urethane polymers based on 2100 $\overline{M}n$ polycaprolactone diol as the soft segment exhibited properties at increased hard segment concentration which are similar to those observed for partially crystalline polymers.

It is now generally accepted that the behaviour of copolymers under deformation is a function of both the domain size and the degree of order within the domains. The original morphology may be altered through stretching to high elongations, annealing or annealing under strain (heat setting). The importance of these parameters is apparent because an understanding of morphological features and their variations is fundamental to the development of structure-property relationships. The most important factor in establishing the original morphology is the sample preparation method. It is worth mentioning as an example, Harrell's [30] elegant synthesis procedure to prepare well defined monodisperse amine terminated hard segments that could be coupled with chloroformate-terminated poly (tetrahydrofuran) to yield perfectly alternating $\{A\text{-}B\}_n$ blocks. The dynamic mechanical analysis of this sample exhibited a higher plateau modulus associated with polyurethanes having narrow hard segment molecular weight distribution. This seems to be a particularly important feature for the hard segment. This behaviour can be rationalized on the basis of a more perfect physical network and the enhanced development of crystallization and phase separation.

It is interesting to note that the introduction of chemical crosslinks [31] by reaction of polyurethanes with benzoyl peroxide or low molecular weight triols produces a lower plateau modulus. However, chemical crosslinking by reaction with 4,4'-diphenylmethane diisocyanate (MDI) increased the modulus. These results were explained by the incorporation of MDI into hard segment domains leading to increased hard segment content while crosslinking by peroxide and triols decreased the organization of the hard domains resulting in loss of modulus.

1.2.3 Thermal analysis

Several thermoanalytical techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and thermal expansion measurement have been used in the study of the morphology and intermolecular bonding in polyurethane block copolymers. Three endothermic regions are normally seen by DSC and were attributed by several earlier workers to the break up of intersegmental hydrogen bonds. Specifically, the endotherm in the region of 80°C was ascribed to the dissociation of the urethane soft segment hydrogen bonds while the endotherm near 150-170^{o}C was related to the break up of interurethane hydrogen bonds [39]. The small peak at about 190^{o}C which is more prominent in materials having longer urethane segments, results from melting of microcrystalline hard segment regions. Recent DSC studies of urethane block polymers that have no capability of hydrogen bonding confirm that the DSC endotherms do not result from disruption of specific secondary bond interaction. It rather appears that all three endotherms are morphological in origin. As suggested [32,33], the highest temperature peak may be assigned to relatively well-ordered microcrystalline aromatic polyurethane segments, the numbers and perfection of which are determined by segment length and thermal history. The lower temperature endotherms represent disordering of hard segments with relatively short-range order that may be improved in a continuous manner by annealing. The appearance of two lower temperature peaks is similar to the multiple melting endotherms often observed in semicrystalline polymers. Here it is caused by a continual disordering-reordering process during the DSC experiment. The short range order may be reorganised into a microcrystalline state if the hard segments are of sufficient length and if the annealing time is sufficiently long. Improvement (i.e. better chain regularity) of short range ordering is still possible in materials not capable of microcrystallization.

Van Begart [17] et al reported that in some samples, as many as five transitions can be observed in a DSC thermogram, depending on the nature of the solid state structure of the sample. These include the glass transition temperatures of each phase which appear as base line shifts, a short-range order endotherm of the hard phase attributable to storage or annealing effects, and endotherms associated with the long range order of crystalline portions of either segment. Schollenberger [37] observed multiple endotherm minima above 100°C for TPU based on MDI/BD hard segments. He interpreted these minima (melting temperatures) to segmental melting/disruption of hard segment domains having different degrees of organization which were developed during prior TPU thermal and processing history.

Harrell's [30,38] work is probably the most well characterized study in the entire literature of linear polyurethanes. This work which is briefly mentioned earlier, involves the preparation of urethanes with narrow molecular weight distribution and perfectly alternating $\left(A\text{-}B \right)_n$ structures. They showed unequivocal crystalline transitions without hydrogen bonding, since they were devoid of N-H groups. It is apparent from the thermal analysis of these well defined systems that the thermoplastic elastomeric behaviour of these materials is due to the presence of the soft elastomeric phase and to the reinforcing and physical crosslink characteristics of the microcrystalline and glassy urethane hard blocks. The effect of polyol type on the structural organization of urethanes can be seen in DSC transitions. Schneider [25,39] et al studied structural organization and thermal transitions in several poly(butylene adipate) and poly(tetramethylene glycol) based urethanes. The transitions below room temperature were assigned to the soft block. The transition at 60-80^{o}C which was attributed to urethane-polyol hydrogen bond disruption. This can be better explained to be due to the glass transition of the hard phase for the particular block length employed. A transition at 205^{o}C which occurred in the polyether systems was considered to be the polyurethane crystalline block T_m. Such a transition was not seen in the polyester urethane. The latter material also was much more transparent, in agreement with smaller crystallite and/or a much lower degree of crystallinity.

Seymour et al [40] in their work involving various polyols revealed that polyester based samples have a greater tendency for the hard segment units to be trapped in the soft matrix when compared to polyethers. This was believed to be due to greater polarity of the polyester segment which is considered desirable for transparency.

X-ray Diffraction

X-ray diffraction studies is one of the effective techniques for investigating the ordered arrangements of atoms and molecules present in a solid substance. By using X-rays of known wavelength it is possible to calculate the spacings between atoms that are regularly arrayed in a lattice. This technique is therefore appropriate to determine the geometry of the regularly repeating unit cell and polymer segments in block copolymers.

Bonart [22] was first to study the polyether and mixed polyester urethane-urea copolymers. He found urethane-urea polyether segments formed discrete highly ordered regions about 2.5 nm in width separated by "soft" polyether or polyester domains approximately 10-20 nm in width. Polyether soft segments tended to stress crystallize, whereas polyester soft segments showed only paracrystalline behaviour. When Bonart followed hard segment orientation as a function of strain he noticed the aromatic urethane segments became oriented perpendicular to the stretch direction at elongations below 200%. Further elongation caused hard segments to slip past one another, breaking up the original structure. As elongation continues, hard segments become progressively more oriented into the stretch direction. Bonart suggested that this restructuring of the hard segments during elongation is related to stress hysteresis phenomena characteristic of these polymers.

Clough and Schneider [39,41] et al studied domain structure in both polyether and polyester derived polyurethanes. Light scattering and small angle X-ray scattering (SAXS) indicated separation into domains in both cases, but to a higher degree in polyether-based polymers than in equivalent polyester based polymers.

Wilkes and Yusek [42] investigated diol extended polyether and polyester derived polyurethanes by wide and small angle X-ray diffraction. They found lamellar domains with average centre-to-centre separations of 10 nm to 250 nm. It was suggested that these domains serve as crosslinks which restrict relaxation of the chains, allowing stress crystallization when the polymer is highly extended and therefore, leading to high tensile strength in the bulk polymer. Annealing the extended polymers caused the domains to break up and reform, relieving stress but retaining considerable orientation.

Bonart and co-workers in a series of investigations [22,43-45] studied a polyurethane elastomer based on poly(oxytetramethylene)-MDI and extended with hydrazine. They observed in relaxed samples a broad amorphous halo at .450 nm and a weak interference ring at 1.2 nm in the WAXS photographs indicating the absence of crystallinity. However at 500% elongation the samples showed clear fibre type diagrams having highly oriented crystal reflexes. This was considered due to the crystallization of soft segment polyol on extension. When these elongated samples were treated with warm water the crystallinity disappeared. However, the 1.2 nm interference was found to persist which was attributed to interplanar spacings associated with hydrogen bonded hard segments.

Infrared studies

The polyethers and polyesters from which urethane elastomers can be obtained vary in structure and consequently they can contain different proton-acceptor groups. This fact is also valid for other intermediates like chain extenders. Hence the extent and possible forms of hydrogen bonding (H-bonding) is dependent on many factors including the electron donating ability and relative proportion and spatial arrangement of the proton-acceptor groups in the polymer chains. Functional groups of a molecule possess characteristic vibrational frequencies, and by observing these absorption frequencies, information on the overall molecular structure can be obtained.

There are three regions in an infrared spectra which are important in polyurethane analysis: the NH stretch absorptions (3500-3200 cm^{-1}), the CH_2 stretch absorptions (3000-2700 cm^{-1}) and the carbonyl vibrations (1750-1650 cm^{-1}). Participation in hydrogen bonding decreases the frequency of the NH vibration and increases its intensity, making this absorption very useful in the study of H-bonding effects. The peak found at about 3320 cm^{-1} is a characteristic of hydrogen bonded NH groups. Non-bonded NH absorbs around 3450 cm^{-1} with a significantly smaller absorption coefficient [46]. Changes in hydrogen bonding can thus be followed, in principle, by frequency or intensity measurements.

The carbonyl absorption is also of potential use in hydrogen bond studies. In practice this is limited to polyether-based polyurethanes, because the presence of two types of carbonyl groups in polyester urethanes gives only a broad unresolved peak. Splitting of the carbonyl band (due to H-bonding)has been reported by Seymour and co-workers [47] for a polyether/MDI based elastomer. A band at 1733 cm^{-1} was attributed to free carbonyl groups, while a band at 1703 cm^{-1} was assigned to H-bonded carbonyl groups. Seymour [40] studied hydrogen bonding as a function of strain in segmented polyether and polyester derived polyurethanes, by analysing infrared absorption intensities of the NH and C=0 groups. In several compositions nearly all NH groups were found to be hydrogen bonded, whereas only about 30-60% of the urethane carbonyl was similarly associated. At room temperature neither polyether nor polyester based polyurethanes showed substantial change in the extent of hydrogen bonding at elongations up to 300%. Thus it was suggested that stress softening could not be explained by changes in the extent of hydrogen bonding.

The thermal behaviour of hydrogen bonds in polyurethane elastomers was investigated by Seymour and Cooper [48] who studied the temperature dependence of infrared absorption for the NH vibration. At 25°C all NH groups were hydrogen bonded, giving a single peak at 3320 cm^{-1}. As the temperature was raised, a high frequency shoulder developed and the overall intensity diminished. Since non-bonded NH groups are known to absorb at a higher frequency and with much lower intensity, the latter effect can be used to monitor hydrogen bond disruption. To characterise this dissociation quantitatively, the area of the total NH peak was measured as a function of temperature which decreased with bond disruption. Seymour and Cooper noticed no appreciable decrease in NH bonded peak area up to the Tg of hard segments which is due to the rigidity of the latter that restricts hydrogen bond disruption. As the temperature raises above 80°C (Tg of hard segments) sufficient mobility was attained and secondary bond dissociation occurred more readily. It is important to note, however, that there was still significant hydrogen bonding at 200°C and that the thermal behaviour of the hydrogen bonds is insensitive to the morphological details. No annealing effects were seen in the IR experiments, while large changes could be observed in the DSC response.

Infrared dichroism [49]

Molecular orientation can also be studied spectroscopically, using the technique of infrared dichroism. It is of particular interest in block polymer systems wherethe dichroic behaviour of bands characteristic of the individual blocks can be studied. This is possible if there are infrared active groups peculiar to each segment that absorb in regions free from other bands.

A quantitative description of segmental orientation also requires a reasonably accurate knowledge of the transition-moment directions for the vibration of interest. In polyurethanes the NH group is characteristic solely of the hard segment and may be conveniently used to study hard block orientation. The CH_2 group generally can be used for soft segment orientation, although methylene groups are also normally present at small concentrations in the hard segments. The transition-moment direction for both of these vibrations can be taken as 90^o [50]. Thus infrared dichroism is a powerful technique for following the deformation behaviour of multiphase elastomers because the orientation of specific polymer segments can be monitored while the sample is being progressively strained or relaxed. Quantitative analysis of appropriate infrared absorption bands during deformation yields the average orientation of the separate segments. Infrared vibrations result in a changing dipole moment, which is characterized by a transition-moment vector. If plane polarized radiation is used, maximum absorption occurs when the directions of polarization and the transition moment are parallel, and there will be no absorption when they are perpendicular. Therefore, differences in absorption intensity with polarization direction occur if transition-moment vectors are preferentially oriented. The use of infrared dichroism involves orienting a sample and measuring the absorbance of selected bands with radiation polarized parallel and perpendicular to the stretch direction. If the transition moment of a particular vibration has been preferentially aligned, the two absorbances (A_{11} and A_{1}) will not be equal and the dichroic ratio, A_{11}/A_{1} may be calculated.

Seymour and Cooper [49] referred to the work of Ishihara et al [51,52] who studied hard segment orientation in poly (urea-urethanes) by both infrared dichroism and X-ray diffraction. Infrared dichroism showed transverse hard segment orientation up to 200% elongation with maximum transverse orientation at 100% strain. As elongation increased, the hard segments oriented into the stretch direction and the residual orientation remained parallel when the sample was relaxed. X-ray diffraction confirmed these results and agreed with earlier studies by Bonart [22].

To investigate the connection between strain history and segmental orientation, orientation functions were measured on films prestrained to various elongations [53]. A virgin sample was stretched to 25%, allowed to come to stress equilibrium, and dichroic measurements were made. The load was removed and the sample relaxed for 5 minutes, then stretched to 25%, 50%, relaxed, etc through 250%. These experiments were based on polyether/MDI based films. The results of dichroic measurements showed that the soft segment orientation is essentially independent of strain history. However, the hard segment orientation shows a marked prestrain effect.

Electron microscopy

Electron microscopy is the technique that can provide direct information on the domain structure under favourable conditions, such as when the domains are crystalline [14,54-56]. Koutsky et al were the first to provide direct evidence of a domain structure in polyurethanes using transition electron microscopy [54]. They studied polyester and polyether segmented polyurethanes and used iodine as a staining agent for hard phase. Domain structures were observed for both systems and the hard domains were found to vary from 3 to 10 nm in size.

The domain structure is not as clearly observable as in most styrene-diene-styrene block copolymers, because of difficulties of phase staining and the smaller domain sizes involved.

Chang and Thomas [36] using transmission electron microscopy (TEM) studied the morphology of melt cast and solvent cast polyurethanes based on polycaprolactone diol/MDI/BD. The morphology of pure, soft segment copolymer (PCD/MDI) and pure, hard segment copolymer (MDI/BD) were found to be dependent on the sample preparation technique. For example melt cast films of soft segments and hard segments yielded very large (50 μm diameter) non-banded, positively birefringent (0-90°) spherulites. Solution cast films, on the other hand, sometimes exhibit banded spherulites, but the optical anisotropy of the random copolymer and pure, hard segment spherulites were greatly diminished. The electron micrographs indicated the pure, soft segment spherulites to consist of the familiar branching, radiating lamellae, whereas the pure hard segment spherulites exhibited a radiating, rough fibrous texture.

EXPERIMENTAL

TABLE 2.1.1

List of Raw Materials' Abbreviations

Materials	Abbreviation
Polycaprolactone diol MW=2000	CAPA 2000
Polyoxypropylene diol MW=2000	D2002
4,4'-methylene bis cyclohexyl diisocyanate (Desmodur W)	$H_{12}MDI$
Isophorone diisocyanate	IPDI
1,4-butane diol	1,4-BD
1,3-butane diol	1,3-BD
1,6-hexane diol	1,6-HD
1,2-cyclohexane diol	1,2-CHD
1,4-cyclohexane diol	1,6-CHD
1,3-cyclohexane diol	1,3-CHD
1,5-pentane diol	1,5-PD
Diethylene glycol	DEG
1,4-Cyclo hexane dimethanol	1,4-CHDM
Trimethylol propane	TMP
Polycaprolactone triol MW=540	CAPA 305
Phenyl mercury oleate (catalyst)	PMO

CHAPTER 2

EXPERIMENTAL

2.1 Sample Preparation

2.1.1 Objective

The aim of the research was to prepare flexible, transparent polyurethane elastomers for application as moulded face-pieces or visor inserts for respirators. It was also intended to establish the manner in which the various chemical constituents of segmented urethane elastomers and elastoplastics control light transmission characteristics. The general requirements for the material are outlined in an application specification prepared by the Chemical Defence Establishment (CDE, Porton Down entitled "Provisional Specifications for a Transparent Facepiece Material" (Appendix 1). The research programme objectives are detailed below:

1. Establishment of a reproducible transparent thermoplastic and crosslinked polyurethane preparation method.
2. Determination of the optimum block ratio(s) capable of producing transparent polyurethane elastomers that also possessed the properties of the specification in Appendix 1.
3. Evaluation of different mould surfaces and mould release agents with respect to their effects on transparency.
4. Investigation of novel chain extenders and crosslinkers.
5. Establishment of a large scale synthesis method capable of yielding completely reacted products.

6. Feasibility and optimization, of injection moulding conditions for TPU transparency.

In addition the selected crosslinked and thermoplastic materials were required to be stable and resistant toward thermooxidative degradation, UV light, hydrolysis and discolouration at elevated temperature and high humidity.

2.1.2 Selection of raw materials

Initially various polyurethane systems were assessed in a preliminary investigation (see later text) but the one chosen for detailed study was based on polycaprolactone diol, 4,4'-methylbis cyclohdexyl diisocyanate (Desmodur 'W'(1) (formerly Hylene 'W'(2))) and different diols and triols as chain extenders. Examination of polypropylene glycol and Isophrone diisocyanate was also made for comparison purposes and the results cited where appropriate.

The raw materials employed in the present research are given in Appendix 2 with their suppliers name and other relevant technical information.

Polyols

The CAPA polyols used were ε-Caprolactone derived hydroxyl terminated polyols. ε-Caprolactone, the internal ester of hydroxy caproic acid is produced from cyclohexanone by a novel route based on peroxygen technology developed by Interox Chemicals Ltd, [57]. Polymerization

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1. Trade name of Bayer; 2. Trade name of Du Pont.

is carried out by a ring opening mechanism which allows precise control of molecular weight and functionality. Polycaprolactones are saturated aliphatic polyesters similar in type to adipates. Unlike adipates, however, polycaprolactones contain a single repeating unit. This factor, allied to the complete absence of water, as a reaction product during polymerization, results in polymers of exceptional purity, a prerequisite for void-free transparent polyurethanes. CAPA polyols were found appropriate for the use in transparent urethanes due to their ability to blend with a wide range of chemical constituents yielding mixed and compatible polymer systems. The high polarity in CAPA increases the intermolecular attraction in urethanes and hence improves mechanical properties. The only disadvantage with CAPA with respect to transparency, is its partially crystalline structure which tends to crystallize in final products on ageing if the hard segment content is not sufficient to restrict the mobility or regularity of the soft segment.

Another polyol, D2002*, a noncrystalline polyoxypropylene diol was also selected from the polyether series and is known from the literature to give polyurethanes with much better transparency and resistance to hydrolysis and discolouration. The major disadvantage associated with D2002 is its low reactivity and this necessitates the use of catalysts that may then promote hydrolytic instability and yield urethanes with much reduced long term shelf ageing properties. However because of its noncrystalline nature, D2002 based urethanes exhibit outstanding clarity and show no tendency to stress crystallize or cold harden.

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* Diamond Shamrock

Diisocyanates

It is well known that aliphatic diisocyanates impart superior colour stability to polyurethanes, two of these were selected for the preparation of transparent materials.

The Desmodur W is a 4,4'-methylenebis-cyclohexyl diisocyanate ($H_{12}MDI$) available in clear liquid form with high purity. The low reactivity of Desmodur W was overcome to some extent by using high reaction temperatures. In transparent urethane preparation where thorough mixing is required, the low reactivity of $H_{12}MDI$ was considered as an advantageous factor. This had enabled safe processing and complete removal of entrapped air bubbles during evacuation due to the low viscosity of the polymer mix.

The other diisocyanate used was Isophorone diisocyanate (IPDI). This is a cycloaliphatic diisocyanate chemically derived from isophrone and is a colourless liquid. IPDI is a low viscosity liquid (though higher in viscosity than $H_{12}MDI$) with no tendency to crystallise at low storage temperatures. Due to its relatively high molecular weight the vapour pressure is very low which greatly simplifies handling this isocyanate. IPDI has two differently combined isocyanate groups. The aliphatic isocyanate group is about ten times as reactive as the cycloaliphatic one. This difference in reactivities enabled prepolymers to be produced which have a low diisocyanate monomer content and hence give controlled structure urethanes.

Chain extenders

Various low molecular weight aliphatic and cycloaliphatic diols employed in the preparation of transparent polyurethanes are given in Appendix 2. The selection of diols should be based on the stereo isomer content in diisocyanate. To obtain an optically clear elastomer, it is generally considered necessary that the monomeric diol be symmetrical when the diisocyanate is low in trans, trans isomer content, for example less than about 30 percent [58]. Both symmetrical and unsymmetrical chain extenders were employed to study their effects on transparency and ageing. It is useful to note that since the melting points of 1,4- and 1,2-cyclohexane diol are 98°C and 75°C respectively and also, due to their high volatility, these could not be employed as single chain extender systems as the diols tended to condense on the walls of the reaction vessel. These diols were therefore used as a blend with other liquid diols e.g. 1,4-butane diol (i.e. the 1,4-BD which acted as a solvent for the main diol). In this way they were found to be reasonably reactive and to yield completely reacted products at the curing conditions used.

Crosslinkers

Two types of crosslinkers in the form of triols of different molecular weights were used in chemically crosslinked polyurethanes. Their effects on transparency and flexibility were studied. Trimethylol propane (TMP) and polycaprolactone triol (CAPA 305) of respective molecular weight 134 and 540 were employed. They were expected to give products of varying degrees of hardness and elongation.

2.1.3 Reactivity of raw materials

The reactivity of each reactant was studied before they were employed. All the reactions were carried out in an uncatalysed systems at 128°-130°C and the extent of reaction was followed by an infrared spectroscopic technique which monitored the progressive disappearance of the NCO absorbance peak at 4.4μ (2280 cm^{-1}). The diols and a triol were reacted with $H_{12}MDI$ at a 1/1 equivalent ratio under a nitrogen atmosphere until the reaction was completed. It is to be noted that a solid product (100% hard segment) was obtained at the end of each reaction. Figure 2.1.1 indicates the relative reactivity of aliphatic diols where 1,4-butane diol was found to be the most reactive followed by 1,6-hexane diol and 1,3-butane diol. This is as expected as the methylene pendant group in 1,3-BD tends to interfere in the reaction and lowers reactivity. Similar behaviour was observed in the cycloaliphatic diol system. Figure 2.1.2 shows the relative reactivity of cycloaliphatic diols where symmetrical 1,4-cyclohexane-dimethanol is observed to be more reactive than the unsymmetrical 1,3-cyclohexane diol. Both the aliphatic and cycloaliphatic diols showed similar affinity toward IPDI though the reaction of the first half isocyanate moiety occurs at a much faster rate due to the aliphatic NCO group attached to IPDI* molecule. The reactive time shown in Figures 2.1.1 and 2.1.2 are for 100% hard segment product and it should be noted that the actual chain extension time of prepolymer is delayed by the factor of 8 to 12 times due to dilution effect. The reactivity of IPDI with CAPA 220 and D2002 was also studied. Figure 2.1.3

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* Veba Chemie

indicates relative reactivity and it can be seen that D2002 (polypropylene glycol) has very low reactivity compared to CAPA 220 and the reaction remained incomplete even after 9 hours. This is considered to be due to the pendant methylene group in the PPG and steric hindrance. A problem associated with the IPDI system is that of wrinkles that often appear on the top surface of the cured sample. This phenomena is at present not well understood but it is assumed to occur due to the large differences in the rates of reactivity of the isocyanate groups present in IPDI. Also, it is considered that the wrinkle formation is enhanced by hot air circulation during oven curing.

In general the reactivity data indicates that the process safety time (i.e. pot life) is quite adequate and that chain extenders can be safely mixed with prepolymers, degassed and cast without causing an undue increase in viscosity or gelling.

2.1.4 Synthesis

In the preparation of transparent polyurethanes the term "block ratio" has been used throughout as a basis of indicating the stoichiometric proportion of starting materials. For example a polyurethane based on a 1:3:2 block ratio signifies the stoichiometric equivalent weight ratio by which the polyol, the diisocyanate and chain extenders are respectively reacted to give the final products.

On the basis of preliminary investigations, the following synthesis method was found suitable and used throughout.

The required amount of polyol was placed in a five necked reaction vessel of 500 ml capacity and degassed under vacuum for not less than one hour at 100-105°C. Prewarmed diisocyanate was then added dropwise into the reaction vessel with continuous stirring. To complete the reaction the contents were heated for 1-1½ hours at 130°C while a steady flow of dry nitrogen was passed continuously through the apparatus. After the completion of prepolymer preparation the contents were degassed and cooled to 100°C. The chain extenders which were previously dried under vacuum at 100°C, then added with vigorous stirring until the solution became clear after which the polymer melt was again degassed under vacuum for 5-10 minutes before it was finally cast onto preheated moulds at 120°C. Curing conditions were 16-18 hours at 120°C followed by postcuring at ambient temperatures and humidity for a minimum of one week. A one shot synthesis technique was also used where the polyol and chain extenders were mixed and dried for 1½ hours at 100°C under vacuum. To this the required amount of diisocyanate was added, stirred and degassed under vacuum before cast and cured at 120°C. When catalyst (phenyl mercury oleate) was employed it was added to the polyol/chain extender mixture before the drying process.

2.1.5 Large scale synthesis of thermoplastic polyurethane

A large scale synthesis procedure was also established for thermoplastic polyurethanes; this is a little different from the one mentioned in Section 2.1.4. Using a typical example of a selected, prepared thermoplastic urethane (Sample T1), the large scale synthesis procedure is summarised below:

	Block Ratio	Eq. Wt.	Amount (gms)
CAPA 220 Polycaprolactone diol (MW 2000)	1	1000	2500.0
Desmodur W ($H_{12}MDI$)	3	131	982.0
1,4-butane diol	1	45	112.5
1,4-cyclohexane dimethanol	1	44.5	180.0

Initially the required amount of CAPA 220 was placed in a 5-litre reaction vessel and dried under vacuum in a vacuum oven at 90°C for not less than 2 hours. Similarly the Desmodur W was degassed at 80°C for ½ an hour under vacuum before it was added to CAPA 220 for the prepolymer reaction. The rest of the synthesis condition is similar to that mentioned in Section 2.1.4. This consisted of prepolymer preparation at 130°C under a nitrogen atmosphere followed by chain extension at 100°C before finally being cast at 120°C onto highly polished preheated aluminium trays which were previously treated with DI CILASE 1818* release agent. A schematic diagram of the equipment used for this large scale synthesis is shown in Figure 2.1.4 A semi-electronic temperature controller (Electrothermal) was used in conjunction with a contact thermometer to obtain a precise reaction temperature with a tolerance of ±0.5°C. Moreover an anchor type stainless steel stirrer was used and provided a homogeneous temperature and mixing. The upper half of the reaction vessel was covered with thermal insulation pads to prevent any heat loss which causes a temperature gradient in the reaction

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* Compounding ingredients, Manchester, UK

mixture. It is notable that after the addition of chain extenders to the prepolymer, the mixture could not be degassed completely owing to the large quantity of reactants and also due to the viscosity of reaction mixture which increased with the chain extension reaction. However these entrapped air bubbles are eliminated during the injection moulding process due to the high injection pressures and temperatures used.

2.1.6 Casting and curing

It has been experienced that the casting and curing procedure markedly influence the transparency and haziness in the final cured material. Following are some of the observations made during the course of these investigations.

1. Prolonged evacuation of prepolymer/chain extender mixture, due to its increasing viscosity leaves pour marks in the cast cured materials causing haziness.
2. If the release agent used is a high viscosity type (greasy) as in the case of Contour 1711, it is deposited on the polymer surface and adversely affects optical properties. Even in the case of less viscous (hence less greasy) release agent (DI Cilase 1818), it is generally necessary to wipe off the sprayed droplets with tissue paper still leaving a very thin layer on the mould surface. This gives a good release property and results in haze free material.

3. When the mould is left near the fan during hot air oven curing, a wavy pattern and wrinkles are found to appear on the top surface of cured material.

4. An unlevelled mould gives uneven film thickness. Moreover due to viscous flow on non-horizontal surfaces, the casting mixture entraps air bubbles which persist in the final sheet.

5. In the one shot process void free/non hazy urethanes can conveniently be obtained due to the very low viscosity of the polymer mixture.

6. The polyurethane tends to turn yellow if the curing temperature exceeds 130°C due to oxidation.

7. Any excess of unreacted diol or polyol makes the cooled polymer sheet difficult to remove from the mould.

Considering the above mentioned points, the established specimen preparation method includes casting of degassed polymer mix into a levelled preheated mould and curing at 120°C for about 18 hours. Prolonged evacuation of chain extended liquid polyurethane is to be avoided to keep the viscosity low so that pouring may occur before set-up commences.

2.1.7 Moulds and release agents

Mould surfaces were found to have profound effects on the optical clarity of polyurethanes. Different moulds were examined such as glass, silicone rubber (RTV), polyester (melinex) film lined moulds, polished aluminium trays and polished and unpolished steel moulds.

Glass moulds both with and without release agents showed extremely poor release properties. Resin/glass adhesion was so strong that they were impossible to part. It is commented that the glass/polymer laminate exhibited excellent optical properties.

Silicone moulds yielded clear transparent materials but on repeated use such moulds tended to give materials which were found to craze and crack. This is believed to have resulted from imperfections in the silicone mould surface. It is notable that the craze occurred only at the mould-polymer interface and not on its outer surface.

Melinex sheets of different thickness were also used as mould liners since they are considered to have good release properties. These sheets showed a similar tendency to glass namely that of strong adhesion to polyurethane. Clear laminates resulted from Melinex/polyurethane combinations.

Polished aluminium trays were found to give transparent materials with excellent release properties provided a very thin layer of Cilase 1818 release agent is used as mentioned earlier. The polish, however, diminishes on repeated use and it is impractical to repolish again. Moreover aluminium trays are very susceptible to scratches. The advantages associated with aluminium trays are their low cost, lightweight and good optical and release property. Steel moulds with highly polished surfaces (mirror-like) yielded clear materials while a slight roughening on such mould surfaces caused translucency in the final product. This was further confirmed when suface defects of polymers were eliminated by immersing a specimen in a clear liquid of the same refractive index and carrying out transparency measurements. It is notable that a thin layer of Cilase 1818 release agent was used throughout with all polished moulds to facilitate polymer release. The advantages of steel metal moulds are their high quality polish, relatively less susceptibility to scratch and can be repolished.

2.1.8 Injection moulding of thermoplastic polyurethanes

The cured thermoplastic urethane sheets were either chopped into small pellets by the use of a Vanguard-Dahle guillotine 510 cutter or granulated in a conventional plastic granulator. The latter, however, often gave rise to contamination which was apparent from the reduced optical clarity of the moulded sheets. Injection moulding was carried out in a reciprocating screw injection moulder manufactured by "Bipel" which has the advantage of delivering a homogeneous melt into the mould cavity. The technical data for the machine is given below:

Hopper capacity	9.20 Kg
Screw diameter	66.68 mm
Maximum cylinder heating consumption	2.40 kW
Maximum thrust on screw	7785.0 Kg
Stroke of screw	63.5 mm
Screw speed	Variable up to 220 rpm
Maximum clamping pressure	310 kgf/cm^2 (30.39 MPa)
Cavity of mould used	Rounded corner rectangular cavity of 22 c

Operating procedure

The screw and cylinder were cleaned thoroughly and the TPU pellets were fed into the hopper of the injection moulder. Different parameters were altered and depending on the nature of thermoplastic materials regarding flow property, hardness etc. optimum conditions were empirically achieved for the moulding of flawless transparent sheets. The following is a typical example of the optimum injection moulding conditions of a typical transparent thermoplastic polyurethane (sample T-1, Table 2.1.3).

1. *Barrel Temperatures*

Zone 1	155^oC	Zone 3	180^oC
Zone 2	170^oC	Nozzle	190^oC

2.	Injection pressure (hydraulic)	1300 psi
3.	Injection time	6 secs
4.	Hold on pressure	150 psi
5.	Hold on time	9 secs
6.	Cooling time	40 secs
7.	Mould temperature	Ambient
8.	Screw speed	80 rpm

2.1.9 Specific polyurethane elastomers synthesised in this research programme

All the polyurethanes prepared in the present investigations are divided into two classes, viz. crosslinked and thermoplastic designated by the letters 'C' and 'T' respectively. Table 2.1.2 summarises the crosslinked urethane samples prepared in this research with their designation used in the present work. Similarly the thermoplastic samples synthesised are given in Table 2.1.3 with their chemical composition and designation. At the end column of each table stated comments on individual polymers regarding their transparency and physical appearance which were noted at least one year after their synthesis.

TABLE 2.1.2:

List of prepared crosslinked polyurethanes

Sample No	Block Ratio (equivalent ratio) Capa 220:H_{12}MDI:chain extender(s)	Comments
C-1	1/3/2 (1,4-BD+TMP at 1/1 ratio)	Transparent, flexible, good physical properties. Meets the outlined specification
C-2	1/3/2 (1,3-BD+TMP at 1/1 ratio)	"
C-3	1/3/2 (1,6-HD+TMP at 1/1 ratio)	"
C-4	1/3/2 (1,4-CHDM+TMP at 1/1 ratio)	"
C-5	1/3/2 (1,3-CHD+TMP at 1/1 ratio)	"
C-6	1/3/2 (1,4-BD+TMP at 1.5/0.5 ratio)	" (strong), slightly hazy
C-7	1/3/2 (1,4-BD+TMP at 0.5/1.5 ratio)	" (much weaker than C6)
C-8	1/2.5/1.5 (1,4-BD+TMP at 1/0.5 ratio)	" (hazy)
C-9	1/3.5/2.5 (1,4-BD+TMP at 1.5/1.0 ratio)	" (but harder)
C-10	1/4/3 (1,4-BD+TMP at 1/1 ratio)	" (harder than C-9)
C-11	1/4/3 (1,4-BD+TMP at 2/1 ratio)	"
C-12	1/3.5/2.5 (1,4-CHD+TMP+DEG at 1/0.5/1 ratio)	Opaque, weak, undesirable material
C-13	1/3.2/2.2 (1,4-CHD+TMP+1,4-BD at 0.8/0.2/1.2 ratio)	Transparent, flexible and tough material
C-14	1/3.2/2.2 (1,4-CHD+TMP+1,4-BD at 0.85/0.15/1.2 ratio)	"
C-15	1/3/2 (1,4-CHDM+CAPA 305 at 1/1 ratio)	Transparent, softer and weaker than TMP derived polyurethanes

TABLE 2.1.2: continued

C-16	1/3/2 (1,4-BD+CAPA 305 at 1/1 ratio)	Transparent, softer and weaker than TMP derived polyurethanes
C-17	1/3/2 (1,6-HD+CAPA 305 at 1/1 ratio)	"
C-18	1/3/2 (1,3-BD+CAPA 305 at 1/1 ratio)	"
C-19	1/3/2 (1,3-CHD+CAPA 305 at 1/1 ratio)	"
C-20	1/3/2 (TMP+CAPA 305 at 1/1 ratio)	Highly transparent but weak
C-21	1/3/2 (CAPA 305)	"
C-22	1/3/2 (TMP)	"
C-23	1/3/2 (1,4-CHDM+CAPA 304)	Turned translucent
C-24*	1/3.2/2.2 (1,4-CHDM+TMP at 1/1 ratio)	Transparent but weak
C-25*	1/4/3 (1,4-CHDM+TMP at 1/1 ratio)	Transparent
C-26*	1/5/4 (1,4-CHDM+TMP at 1/1 ratio)	Transparent

* In these samples the H_{12}MDI is replaced by IPDI

TABLE 2.1.3:

List of prepared thermoplastic polyurethanes

Sample No	Block Ratio (equivalent ratio) Capa 220:H_{12}MDI:chain extender(s)	Comments
T1	1/3/2 (1,4-BD+1,4-CHDM at 1/1 ratio)	Transparent, haze free, flexible, very strong, exceptional tear resistance, does not crystallise
T2	1/3/2 (1,4-BD+1,6HD at 1/1 ratio)	"
T3	(1/3/2 (1,4-BD+1,3-BD at 1/1 ratio)	"
T4	1/3/2 (1,4-BD+1,3-CHD at 1/1 ratio)	Same as above but turns hazy on storage
T5	1/3/2 (1,4-CHDM+1,4-BD+TMP at 1/0.9/0.1 ratio)	"
T6	1/3/2 (1,4-CHD+1,4-BD at 0.8/1.2 ratio)	Transparent, flexible and strong
T7	1/3.5/2.5 (1,4-CHD+1,4-BD at 1/1.5 ratio)	"
T8	1/3/2 (1,4-CHD+1,4-BD+TMP at 0.9/1.2/0.1 ratio)	"
T9	1/3/2 (1,4-CHDM+1,3-CHD at 1/1 ratio)	Initially transparent and flexible but turned into hard, strong and opaque plastic. Thermally reversible
T10	1/3/2 (1,4-CHDM+1,6-HD at 1/1 ratio)	"
T11	1/3/2 (1,3-BD+1,6-HD at 1/1 ratio)	"
T12	1/3/2 (1,4-CHDM+1,3-BD at 1/1 ratio)	"
T13	1/3/2 (1,4-CHDM+1,4-CHD+TMP at 1/0.9/0.1 ratio)	Initially transparent but on long storage turned translucent

TABLE 2.1.3: continued

T14	1/3.2/2.2 (1,4-CHDM+1,3-CHD+TMP at 1.2/0.9/0.1 ratio)	Better transparency than T13
T15	1/3.2/2.2 (1,4-CHDM+1,3-CHD+TMP at 0.9/1.2/0.1)	Turned to hard, opaque but strong plastic
T16	1/3/2 (1,4-CHD+DEG at 1/1 ratio)	Weak, opaque, plastic like material
T17	1/4/3 (1,4-CHD+DEG at 1/2 ratio)	Weak, soft, hazy though transparent
T18	1/3/2 (1,4-CHDM+1,4-BD at 1/1 ratio). 1% silicone fluid (12,500 cs) of polyol was also added	Opaque but softer material
T19	1/2.6/1.6 (1,4-BD)	Hard but flexible, wax like opaque material
T20	1/5/4 (1,3-BD)	Strong, hard and translucent
T21	1/6/5 (1,3-BD	Very strong, hard and translucent
T22	1/7/6 (1,3-BD)	Very strong, hard and glass like transparent
T23	1/5/4 (1,6-HD)	Hard and translucent
T24	1/6/5 (1,6-HD)	Strong, hard and transparent
T25	1/7/6 (1,6-HD)	Very strong, hard and clear transparent
T26	1/5/4 (1,5-PD)	Hard, strong, yellow, opaque material
T27	1/5/4 (1,5-PD+1,3-BD at 1/1 ratio)	Strong, flexible, touch transparent material
T28	1/5/4 (1,3-BD+1,6-HD at 1/1 ratio)	"

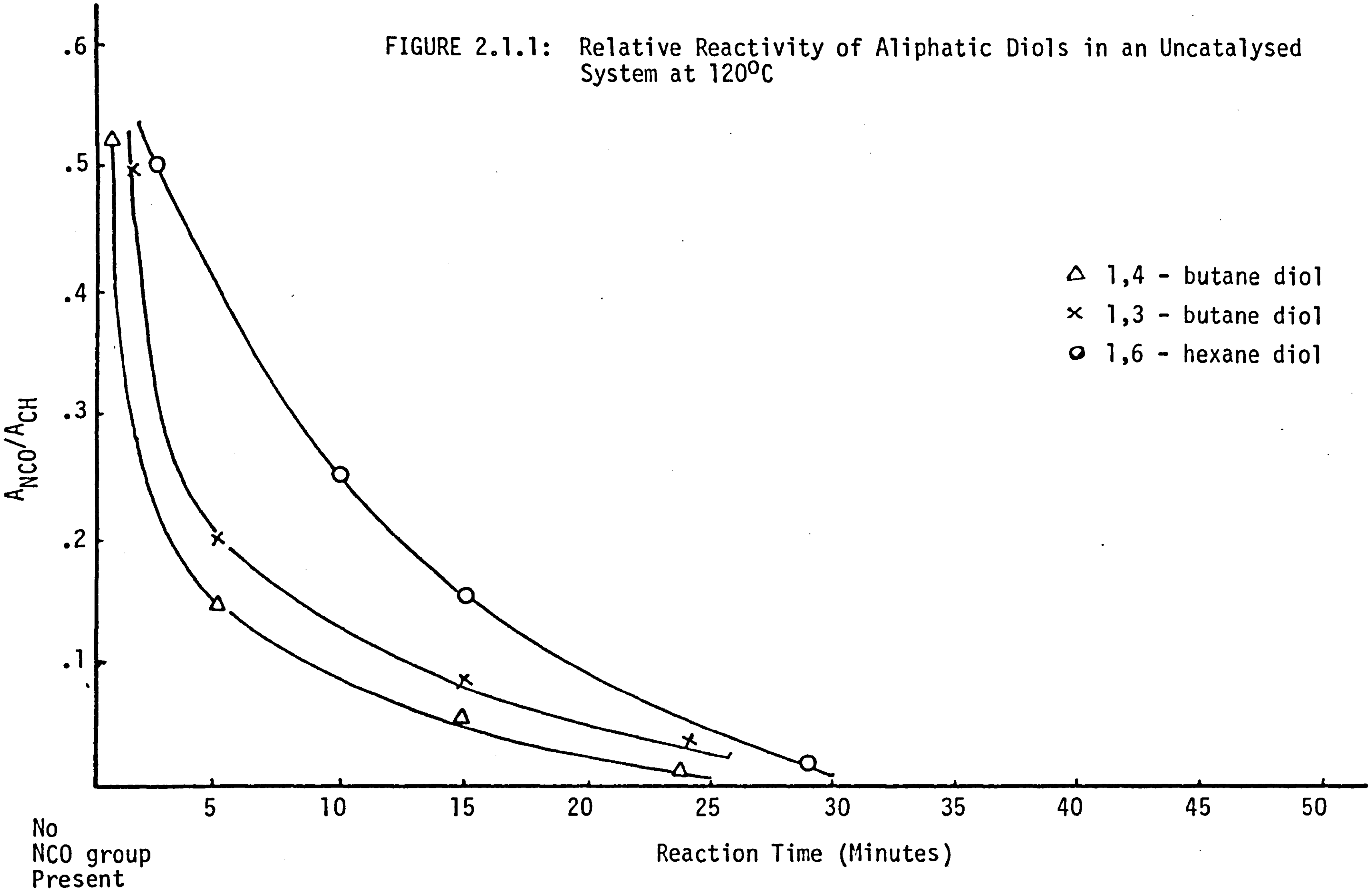


FIGURE 2.1.1: Relative Reactivity of Aliphatic Diols in an Uncatalysed System at 120°C

FIGURE 2.1.2: Relative Reactivity of Cycloaliphatic Diols and Triol in an Uncatalysed System at 120^{o}C

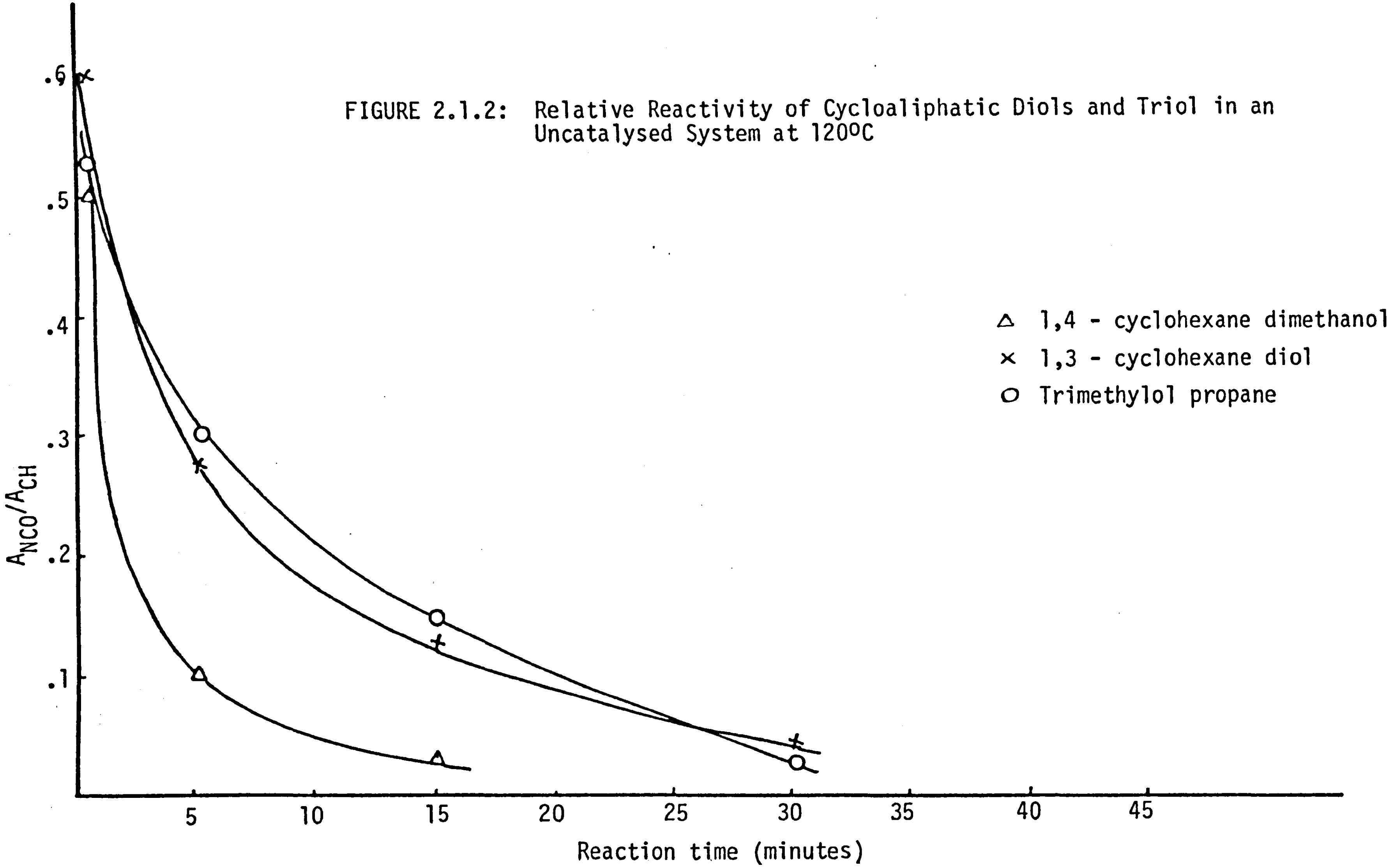
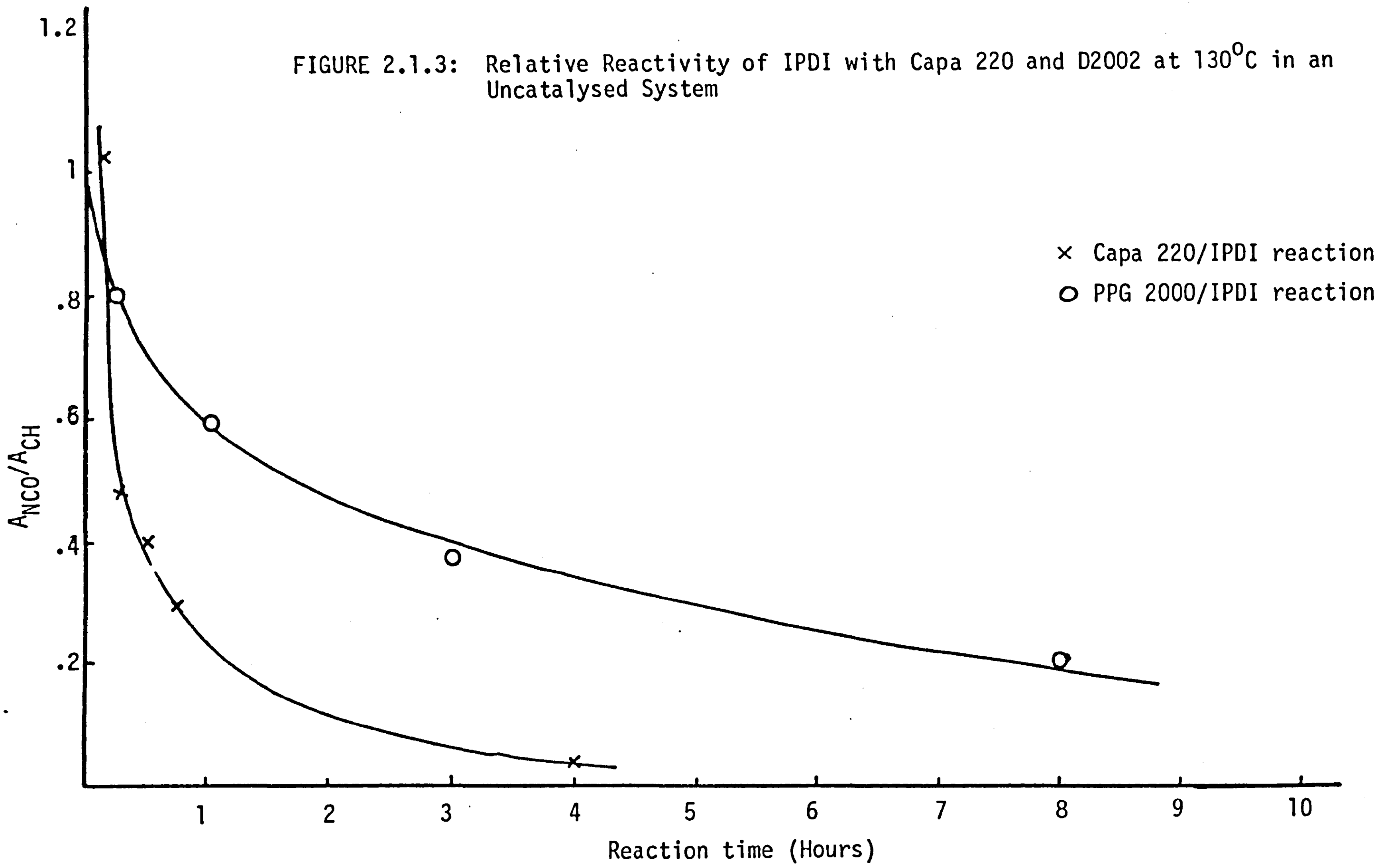


FIGURE 2.1.3: Relative Reactivity of IPDI with Capa 220 and D2002 at 130°C in an Uncatalysed System



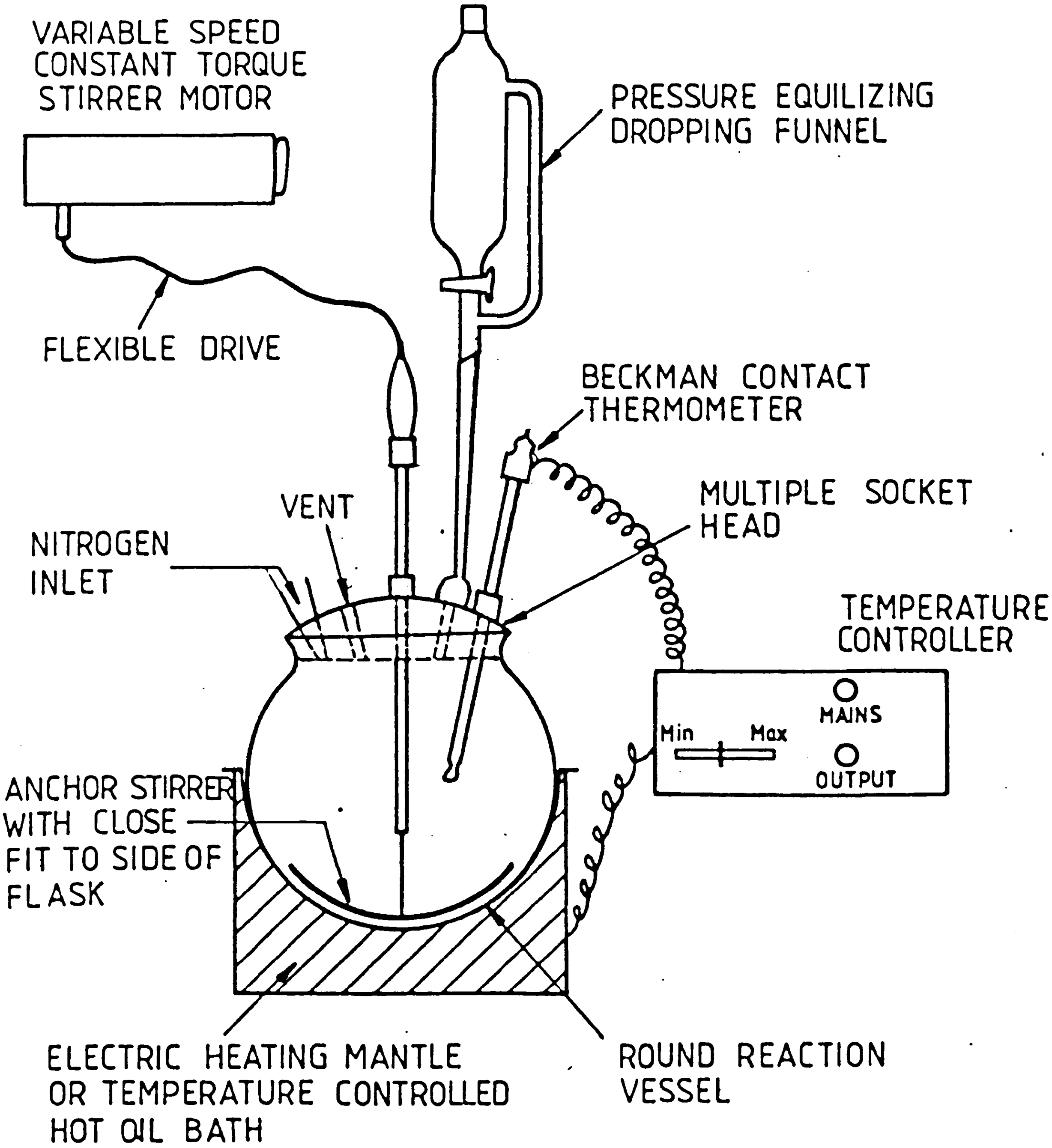


Fig.2.1.4 TYPICAL LABORATORY APPARATUS FOR THE PREPARATION OF A POLYURETHANE ELASTOMER

2.2 POLYMER STRUCTURES

As mentioned earlier it is the tendency of polyurethane segments to undergo phase separation that effects the structure and properties of the final product. Also a number of additional structural features that influence the final urethane properties are intermolecular forces, the stiffness of chain units, stearic hindrance and crystallization. In order to study these factors on transparency, the following techniques were employed.

2.2.1 Infrared spectroscopy

Hydrogen bonding in polar polymers like polyurethanes, which sometimes dominates the crystalline structure, influences physical properties of the amorphous state through relatively strong interchain interactions or through the formation of paracrystalline structure. The polyethers and polyesters from which urethane elastomers can be obtained vary in structure and consequently they can contain different proton-acceptor groups. This fact is also valid for other intermediates like chain extenders. Hence the extent and possible forms of hydrogen bonding (H-bonding) is dependent on many factors including the electron donating ability and relative proportion and spatial arrangement of the proton acceptor groups in the polymer chains. Functional groups of a molecule possess characteristic vibrational frequencies, and by observing these absorption frequencies by IR technique, information on the overall molecular structure can be obtained.

In a typical hydrogen bonded polyurethane the NH group of uretane unit (-NH-COO) serves as proton donor and the proton acceptors can be carbonyl group (C=O) of urethane unit and/or polyester chain. In case of polyether polyols it is the ether oxygen (O<) which acts as a proton acceptor.

Hence it was considered necessary to measure the percentage of hydrogen bonding present in the synthesised polyurethane elastomers.

The H-bonding estimation is based on the resolution of urethane NH and carbonyl band into the bonded and unbonded components. Table 2.2.1 shows the infrared band assignments of polyurethanes. The determination of hard-soft segment mixing through hydrogen bonding in polyether urethanes is simple as the only proton acceptors are the carbonyl group of the urethane hard segment and the ether oxygen of the polyether soft segment which give absorbances at different wavelengths. The measure of NH and C=O absorbances can indicate the extent of phase segregation. In turn, the fraction of NH groups bonded to ether determined by difference, indicates the degree of hard segment-soft segment mixing.

Polyester urethanes, on the other hand, contain two different carbonyl groups, each belong to hard and soft segment units and may have free and bonded components. Thus there are four possible peaks in the polyester spectra. This gives rise to a much broader carbonyl absorption region in polyester urethanes compared to polyether urethanes and make the hydrogen bonding estimation difficult.

The preferential bonding between different donors and acceptors is determined by their equilibrium constants (K) for formation of H-bonds. The value of K is dependent on the free-energy change in the formation of the H-bond complex, higher values corresponding to stronger H-bonds. It has been shown earlier [60-63] that the equilibrium constant of the hydrogen bonding urethane NH···O=C is considerably higher than NH···O and unless the urethane content is very low, the former type of bonding dominates giving phase segregated morphology. However, in polyester based systems the equilibrium constants of NH and both the urethane and ester carbonyl groups are comparable, they behave as similar H-acceptors. Thus the NH hydrogen bonding is scattered all over the system independent of the concentration of urethane groups giving rise to mixed phase polyurethane structure.

Infrared technique

When electromagnetic radiation falls on a material, energy is absorbed due to molecular transitions between quantum states corresponding to different internal energies. Infrared spectra are normally observed using a double beam infrared spectrophotometer. This consists basically of a source of infrared radiation, and a dispersion system to give a spectrum of varied wavelength radiation. Prisms of inorganic salts and diffraction gratings are commonly used as dispersion agents. A beam of monochromatic radiation is split into two beams of equal intensity by means of a system of mirrors. One beam is arranged to pass through the sample, and the other through a suitable reference medium. If the frequency of vibration of the sample molecule falls within the range of the instrument, the molecule will absorb energy at this frequency,

TABLE 2.2.1

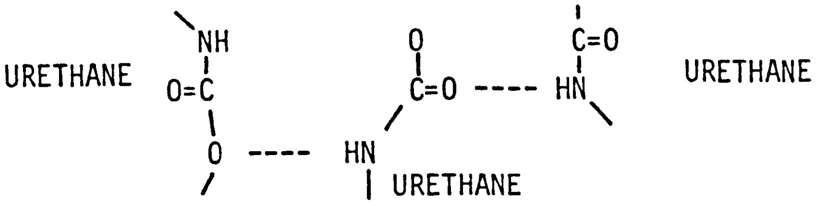
Infrared Band Assignments for Prepared Polyurethanes

Band Location (cm^{-1})	Assignment	Relative Intensity[(a)]
3430	Free NH stretching	w, sh
3330-3340	Hydrogen bonded NH stretching	s
2925	Asymmetric CH_2 stretching	s
2860	Symmetric CH_2 stretching	m, sh
1700-1730	Free and hydrogen bonded carbonyl stretching	s
1520	Amide II band	w
1420	C-C stretching in aromic groups	w
1080	C-O-C stretching	w

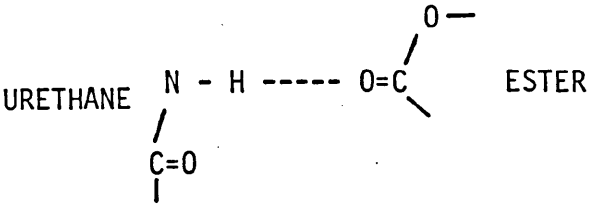
(a) w = weak
s = strong
m = medium
sh = shoulder

FIGURE 2.2.1:

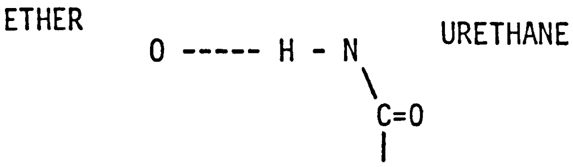
Schematic diagram of the three main types of hydrogen bonds in polyurethanes



I. Hydrogen bonding between urethane units



II. Hydrogen bonding between urethane and ester



III. Hydrogen bonding between urethane and ether.

resulting in a difference in the intensities of the sample and reference beams which is detected by a photocell system. The final spectrum is recorded on a chart recorder which is coupled to the dispersion and detection systems. Spectra show peaks, corresponding to absorption, plotted against wavelength (or frequency). In the system outlined above, absorption of infrared radiation by the sample can be brought about using two techniques.

a) Transmission of radiation through the sample.
b) Reflection of radiation from the sample.

Transmission techniques are most commonly used, in which infrared radiation is passed directly through the sample. Solutions, vapours, liquid films and mulls provide suitable samples for this technique. Solid samples, particularly polymeric films and sheets, can be readily investigated using infrared reflection methods.

Multiple Internal Reflectance (MIR) spectroscopy, also termed Attenuated Total Reflectance (ATR) spectroscopy, is a relatively new technique. The infrared ATR unit consists essentially of a flat crystal (usually thallium iodide), arranged in the sample beam of the spectrophotometer so that infrared radiation can pass through it by total internal reflection (see Figure 2.2.2 overleaf). Samples are clamped firmly on either surface of the crystal. When radiation is totally internally reflected at the surface of the crystal, a small proportion actually passes through the surface of the sample and may be absorbed. On repeated internal reflection along the crystal, the sum intensity of absorption increases. Therefore the emerging radiation has a lower intensity than the reference beam, and a spectrum is obtained in the usual way.

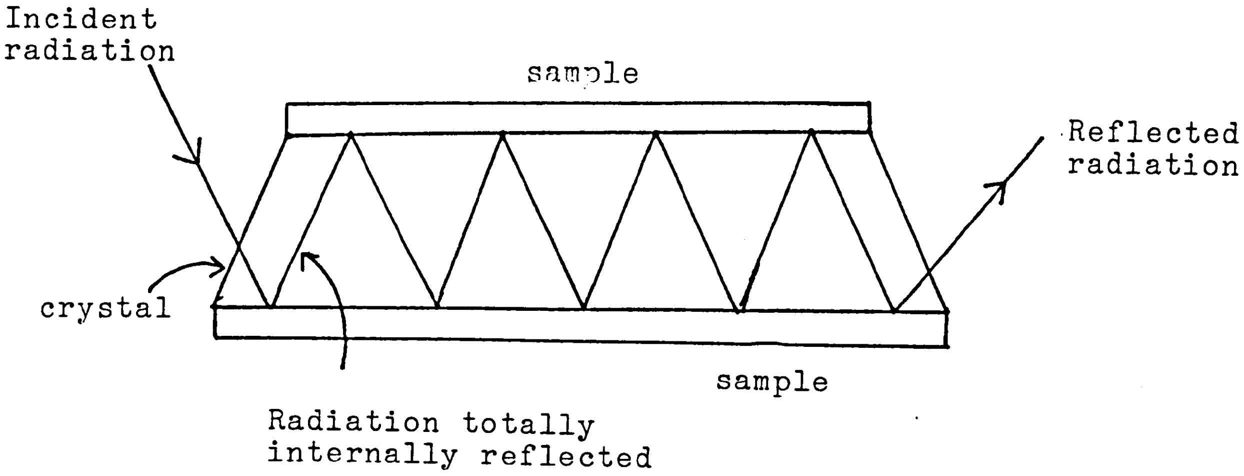


FIGURE 2.2.2: Totally internally reflected infrared radiation

In the present investigation the prepared thermoplastic and crosslinked polyurethanes were studied by infrared technique for their intermolecular interaction and the extent of hydrogen bonding. Figure 2.2.1 shows in a schematic diagram the three main types of hydrogen bonds in polyurethanes explained earlier. Since the prepared polyurethanes are based on polycaprolactone diol (polyester), only the first two types of hydrogen bonding shown in Figure 2.2.1 are expected and considered. Spectra of prepared thermoplastic and crosslinked polyurethane elastomer films were recorded using a Beckman TR-9 ATR unit (giving 9 internal reflections), installed in a Pye-Unicam SP3-200 Grating Infrared Spectrophotometer. Samples of polymer film (approximately 1 mm thick) were cut so as to cover the two surfaces of the crystal. With film samples clamped firmly against the crystal surfaces, spectra were recorded between 600 cm^{-1} and 4000 cm^{-1} (16.5 μm to 2.5 μm), using a medium scanning mode. The 100% adjustment was set at maximum to give zero obscuration of the sample beam. The reference beam was attenuated using an R11C AT-P4 attenuation device, to give a baseline at around 70% transmittance. The ATR infrared technique applied to solid films, essentially gives a spectrum of the molecular structure of the surface layers of the material. It was therefore necessary to observe the transmission spectra of several polymer films for comparison. Transmission spectra were obtained by casting dilute DMF solutions of polymer samples onto sodium chloride discs evaporating of the solvent in vacuo and, after 24 hours, recording the spectra in the usual way. Transmission spectra were found to be identical with ATR infrared spectra of elastomers, indicating that the ATR technique gives rise to absorption spectra representative of the internal structure (as well as the surface layers) of the materials investigated.

Spectra of all the prepared urethanes prepared were found to be very similar to Figures 2.2.3 and 2.2.4 which are respectively the representatives of a typical crosslinked and a thermoplastic material. Assignments of the most pronounced absorption bands in these spectra are given in Table 2.2.1. The spectrum below 1500 cm^{-1} i.e. "finger-print" region is characteristic of the individual molecular structure it represents. Assignment of absorption bands in these regions to particular functional group vibrations can be misleading, especially as combination and overtone bands may be present. Moreover the absorption bands below 1500 cm^{-1} are not useful in measuring the hydrogen bond and phase segregation sought in the present study and hence not considered. It should be noted that only minor variations between spectra of elastomers were found in the finger print region which were due mainly to the variation in structure of the chain extension agent.

However the three major absorption bands which appear between 1600 and 4000 are particularly useful in determining percent hydrogen bonding and hence the interurethane and urethane-soft segment linkages.

Hydrogen bonding

From Figure 2.2.5, the characteristic NH absorption band at around 3330 cm^{-1} is seen to have a shoulder at approximately 3430 cm^{-1}. Similar absorption bands were exhibited by all the prepared polyurethane materials with minor variation in their intensities. The band at 3330 cm^{-1} is assigned to hydrogen bonded NH groups and the shoulder at 3430 cm^{-1} to free NH groups. The splitting of the NH absorption band is affected by chain extenders and hard segment content is illustrated in Figures 2.2.6 and 2.2.7 for crosslinked and thermoplastic polyurethane respectively. A simple estimation of the extent of hydrogen bonded NH interactions was made as follows:

By using a suitable baseline (see Figure 2.2.5), the absorbances, at the absorption maxima were calculated. The absorbance, A_b, of the hydrogen bonded absorption maximum is given by:

$$A_b = E_b \, C_b \, L_b$$

Similarly, for the free NH absorption maximum:

$$A_f = E_f C_f L_f$$

where E_b, E_f = Extinction coefficients of the bonded and free NH absorption maxima respectively

C_b, C_f = Concentration of the bonded and free NH groups respectively.

L_b, L_f = Radiation path length through the bonded and free NH group absorbing medium respectively.

As an approximation, assuming $E_b = E_f$, then:

$$A_b = K C_b$$

and $$A_f = K C_f \quad \text{(where K is a constant)}$$

The proportion of bonded NH groups is then given by

$$\text{Hydrogen bonded (NH)\%} = \frac{(A_b)}{(A_b + A_f)} 100$$

Using this approximation, the values given in Tables 2.2.2 and 2.2.3 were calculated from the spectra of prepared crosslinked and thermoplastic materials respectively.

The absorbances A_b and A_f were calculated according to Beer-Lambert's Law of absorption which states:

$$A = \log_{10} I_o/I$$

where A = absorbance

I_o = intensity of incident radiation

I = intensity of transmitted radiation

$\therefore$ from Figure 2.2.5

$$A_b = \log_{10} \left(\frac{I_o}{I}\right)_{\text{bonded NH}} = \left[\frac{AC}{BC}\right]$$

Similarly

$$A_f = \log_{10} \left(\frac{I_o}{I}\right)_{\text{free NH}} = \left[\frac{DF}{EF}\right]$$

It is apparent from the Tables 2.2.2 and 2.2.3 that all the prepared polyurethanes exhibited H-bonding between 57-65% irrespective of chain extender type used. Although the crosslinked polymers showed relatively lower level of bonding than thermoplastics the difference is not considered big. Since the urethanes in the present study are based on cycloaliphatic diisocyanate (H_{12}MDI), their polarity or proton donating capability is expected to be the same throughout the samples and which actually gave bonding values in the same region (57-65%). This clearly indicates that the extent of H-bonding is largely dependent on the proton donating ability of NH groups which in turn depends on the molecular structure of diisocyanate used and the chemical substituents attached to NCO group. Similarly one of the two carbonyl groups present in prepared samples having proton accepting affinity comes from the polyol employed. In the present study the only type of polyol used was CAPA 220 and this provided similar affinity toward the protons in all the samples. The role of the second type of carbonyl group resulting from the isocyanate-chain extender reaction is considered insignificant due to its very low proportion when compared to the polyol carbonyl. Following is a brief discussion on H-bonding based on infrared results.

1. The lower values of H-bonding in crosslinked polymers can be explained by considering the reduction in intermolecular attractive forces that result from a spatial separation of chains due to increased crosslinking. Samples C1-C5 (Table 2.2.2) exhibited slightly higher bonding due to the short chain TMP triol constituent and should be compared to their counterparts urethanes (C15 to C22) which are based on a relatively high molecular weight triol crosslinker (CAPA 305). The latter is considered to enhance spatial separation and consequently reduce bonding. Since the H-bonding values of both the transparent and opaque urethanes (eg C1 and T12) are comparable, it is deduced that the high degree of transparency found in crosslinked polymers is due to reduced chain segment mobility which prevents aggregation of polar species and crystallisation. It is to be noted that no phase separation (see next section) is observed to have occurred in any of the crosslinked urethanes and the original transparency and flexibility were maintained after 2 years.

2. The thermoplastic polyurethanes showed H-bonding between 60-65% (Table 2.2.3). These values are marginally higher than crosslinked samples which were earlier thought to yield considerably higher values due to increased chain mobility and hard-segment mixing. The fact that both the transparent (T1-T7)

and opaque (T9-T12) thermoplastic samples showed the same level of H-bonding indicates that the transparency is not directly influenced by the bonding. This was further confirmed by warming up an opaque sample (T10) to 55°C for a few minutes until it turned transparent and then its H-bonding was calculated. The opaque and transparent forms of T10 gave bonding values of 60 and 62 respectively. Thus a preliminary conclusion may be that the transparency in polyurethanes cannot be explained by H-bonding and it seems likely to be morphological in character. The effects of H-bonding will be discussed in greater depth in a later chapter.

TABLE 2.2.2

Percent Hydrogen Bonding in Selected Crosslinked Polyurethanes

Sample No.* (chain extender(s))	Hydrogen Bonding (%)
C-1 (1,4-BD + TMP)	60.0
C-2 (1,3-BD + TMP)	60.0
C-3 (1,6-HD + TMP)	60.7
C-4 (1,4-CHDM + TMP)	60.7
C-5 (1,3-CHD + TMP)	60.0
C-15 (1,4-CHDM + CAPA 305)	58.0
C-16 (1,4-BD + CAPA 305)	59.0
C-17 (1,6-HD + CAPA 305)	59.0
C-18 (1,3-BD + CAPA 305)	57.0
C-19 (1,3-CHD + CAPA 305)	58.0
C-20 (TMP + CAPA 305)	57.0
C-21 (CAPA 305)	58.0
C-22 (TMP)	58.0

* All the samples are based on CAPA 220/H_{12}MDI prepolymer system

TABLE 2.2.3

Percent Hydrogen Bonding in Selected Thermoplastic Polyurethanes

Sample No* (Chain extender (s))	Hydrogen bonding (%)
T-1 (1,4-BD + 1,4-CHDM)	64
T-2 (1,4-BD + 1,6-HD)	60
T-3 (1,4-BD + 1,3-BD)	62
T-4 (1,4-BD + 1,3-CHD)	63
T-5 (1,4-CHDM + 1,4-BD + TMP)	60
T-6 (1,4-CHD + 1,4-BD)	63
T-7 (1,4-BD + 1,4-CHD)	65
T-8 (1,4-CHD + 1,4-BD + TMP)	61
T-9 (1,4-CHDM + 1,3-CHD)	62
T-10 (1,4-CHDM + 1,6-HD)	59
T-12 (1,4-CHDM + 1,3-BD)	60

* All the samples are based on CAPA 220/H_{12}MDI prepolymer system

Fig. 2.2.3: A typical infrared spectra of a prepared polyurethane sample C1(crosslinked).

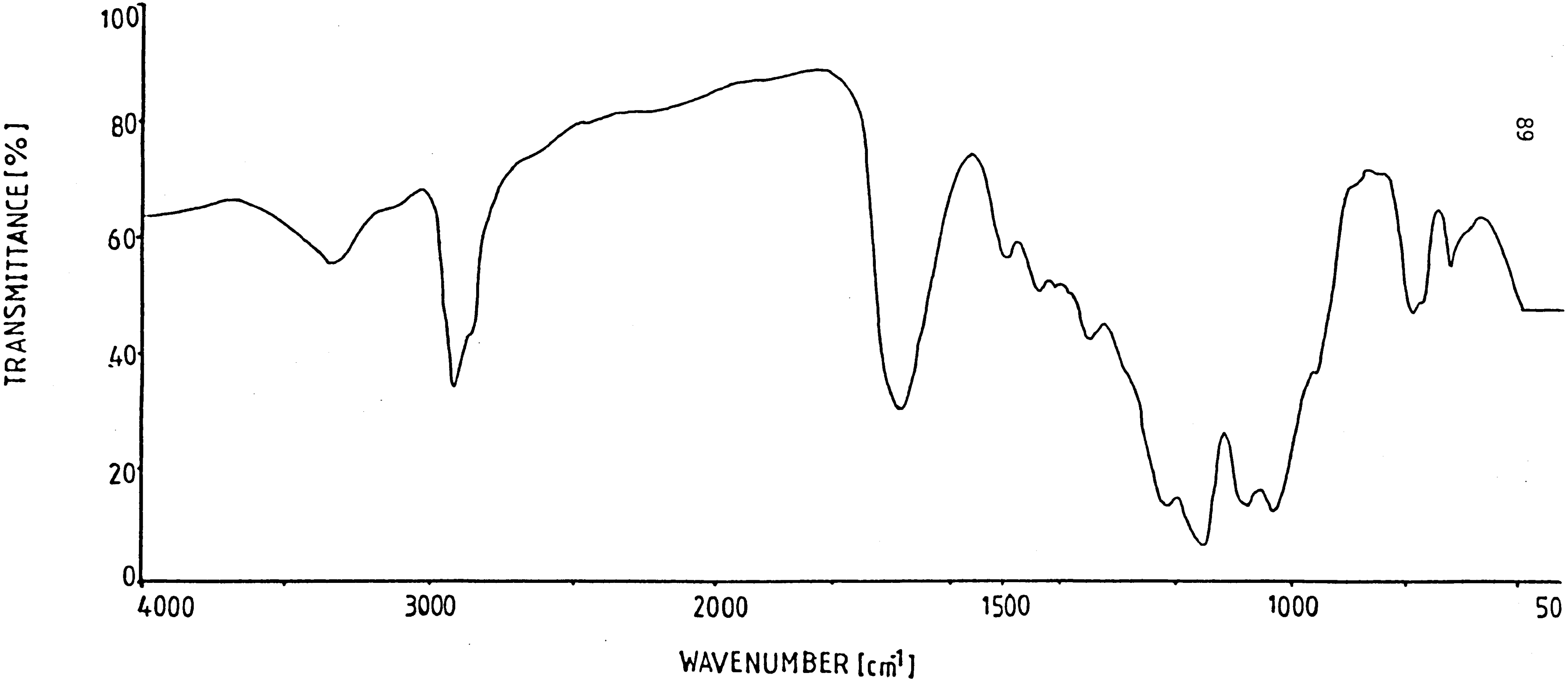


Fig. 2.2.4: A typical infrared spectra of a prepared polyurethane sample T1 (thermoplastic).

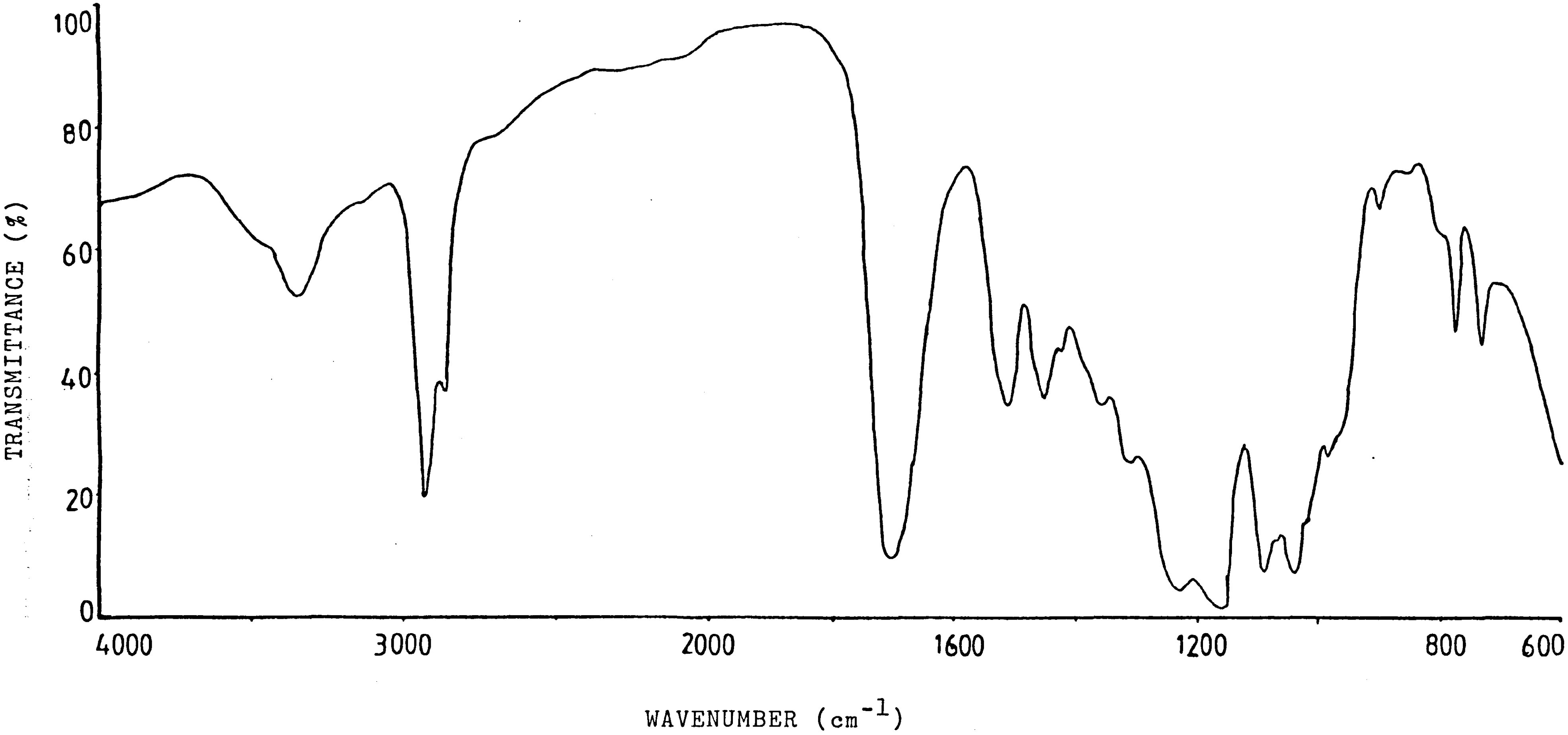


Fig. 2.2.5: A typical characteristic NH absorption band in a polyurethane elastomer.

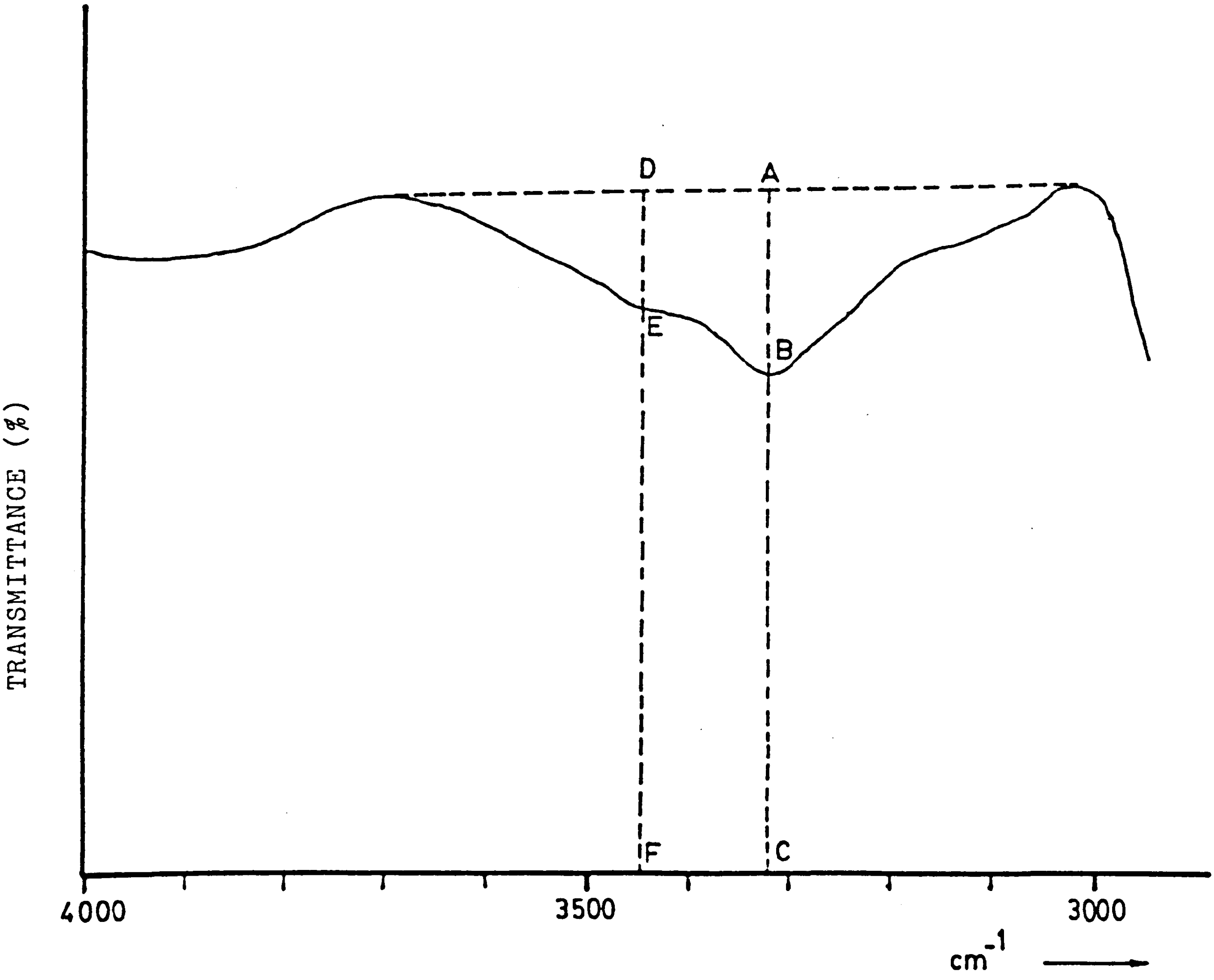


FIGURE 2.2.6: Characteristic NH Absorption Bands in Various Cross-linked Urethanes

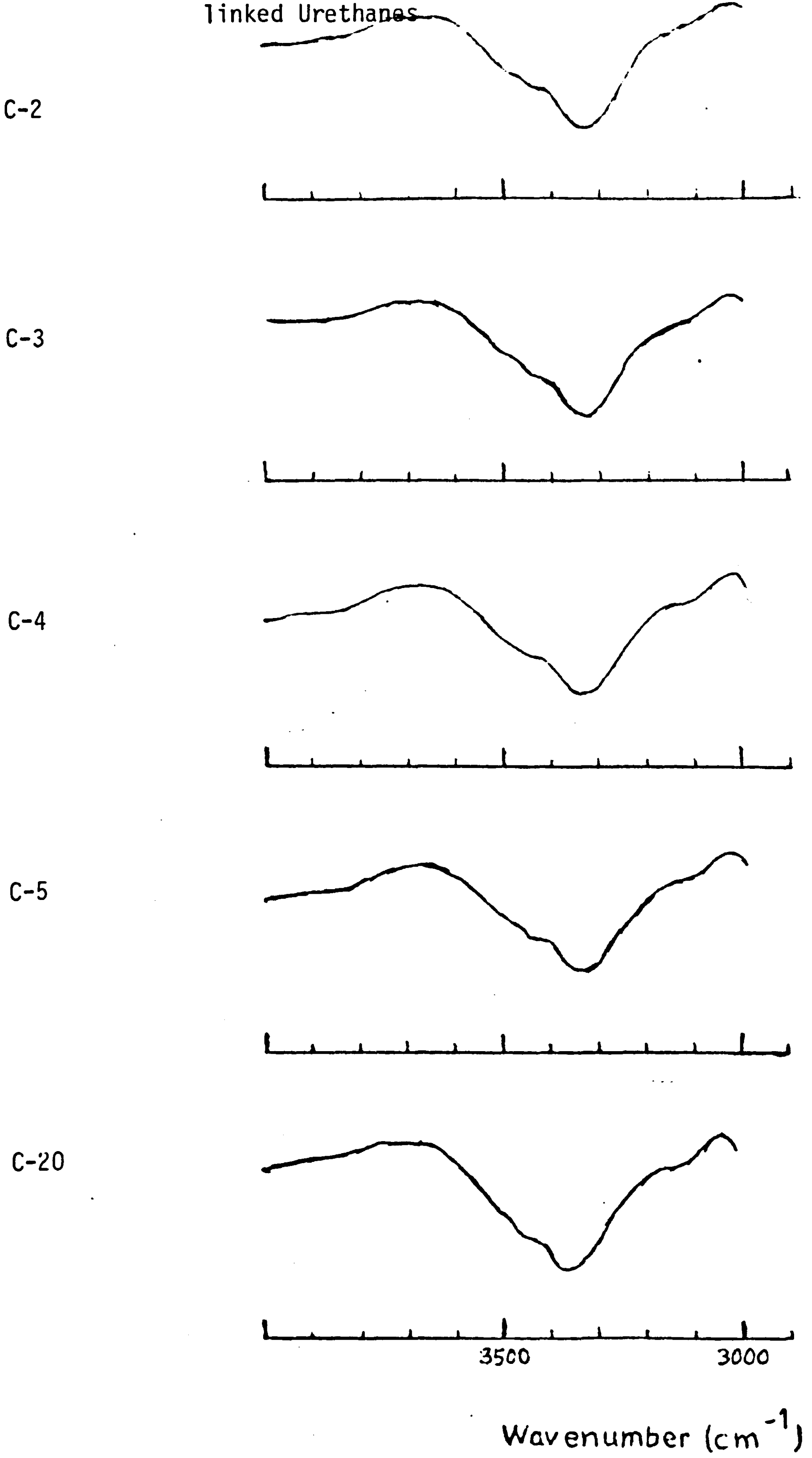
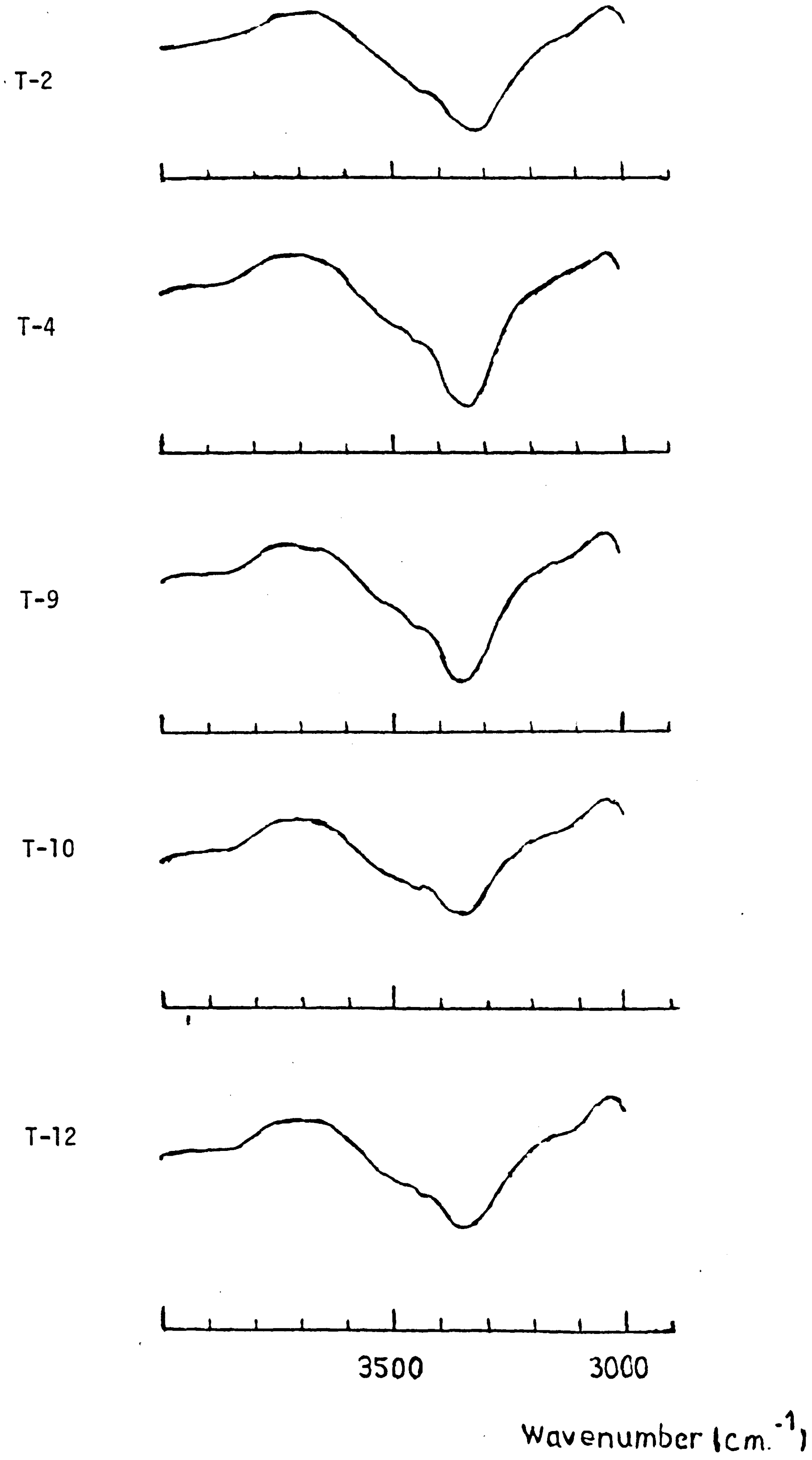


FIGURE 2.2.7:CharacteristicNH Absorption Bands in Various TPU's



2.2.2 Thermal Analysis

Differential Scanning Calorimetry (DSC) is one of the thermal analytical techniques widely used for the characterization of polymers. This is an excellent tool for investigating the property-determining morphological state of polyurethanes and provides a wide range of information on the two phase structure and the extent of phase segregation which is now acknowledged as a major contributory factor for outstanding urethane performance.

The DSC instrument heats or cools a small (usually 10-15 mg) sample under very carefully controlled and reproducible conditions. The instrument has a differential thermocouple arrangement consisting of two thermocouples wired in opposition. One thermocouple is placed in a sample of the material to be analysed, whereas the second one is placed in an inert reference material, which has been selected so that it will undergo no thermal transformations over the temperature range being studied. When the temperature of the sample equals the temperature of the reference material, the two thermocouples produce identical voltages, and the net voltage output is zero. At this point there is no change in heat capacity of the sample. As the controlled heating proceeds, the sample thermocouple continuously monitors changes in the heat capacity of the sample, which are recorded as a thermogram. This is usually a plot of temperature differential, ΔT as a function of either time or temperature. ΔT is proportional to the heat flow (m.cal/sec/in) into or out of the sample with respect to reference. Sample heat capacity changes whenever the temperature reaches a point where it causes a change in the organization of the molecules in the sample.

Such detectable changes are called thermal responses or thermal transitions.

As mentioned earlier, for polyurethanes three endotherm regions are normally seen above room temperature by DSC and were attributed by several earlier workers to the break-up of intersegmental hydrogen bonds. For the sake of discussion these three regions will be termed as the T_1, T_2 and T_3 in the progressively increasing temperature order. Recent DSC studies [38,64,65] of urethane block polymers that have no capability of hydrogen bonding confirm that the DSC endotherm do not result from disruption of specific secondary bond interaction. These multiple endotherms are believed to reflect the segmental melting/disruption of hard segment domains having different degrees of organization which were developed during prior polymer thermal and processing history. T_1 is attributed to the melting temperature of the shortest average hard segment. Sometimes this transition reflects the melting of soft segments crystallites. Likewise, the T_2 transition represents hard segment melting but of a relatively long range order. The highest temperature peak, T_3 may be assigned to relatively well-ordered microcrystalline aromatic polyurethane segments, the number and perfection of which are determined by segment length and thermal history. Hard segments display some but not all the classical characteristics of the crystalline state and for this reason have been called paracrystalline. This is due to the strong mutual attraction of the hard segments which restrict their mobility and thus this ability to organise themselves into a true crystalline lattice. It is notable that the T_3 peak which is due to microcrystalline regions cannot be seen in polyurethanes with short hard segment length. Seymour et al

[65] confirmed that the appearance of the DSC endotherm is a function of hard segment length. Polyurethanes having shortest average hard segments, exhibited only the T_1 peak, moderate hard segments showed T_1 and T_2 whereas the highest hard segment content gives all the three endotherms.

In addition to the transitions at higher temperatures, a peak appears well below the room temperature, in the minus region, and is attributed to the glass transition temperature (Tg) of the soft segment. Tg has practical significance in thermoplastic polyurethanes since it indicates the temperature at which the polymer will lose appreciable flexibility as it cools. Low temperature flexibility can be significantly regulated by the choice of polyol molecular weight and thus soft segment length (mol. wt). The variation of Tg of the soft matrix in segmented polyurethanes as a function of composition or segmented chemical structure has been monitored and used as an indicator of the degree of microphase separation.

Thus in segmented polyurethanes strength is enhanced by long, rigid hard segments with high cohesive energy. Although hydrogen bonding can contribute to domain cohesiveness, hydrogen bonding itself is not directly responsible for high strength. The presence of hydrogen bonds serves to increase the overall cohesion of the material, as these bonds are stronger and more directional than other intermolecular forces.

In the present work DSC thermograms of prepared polyurethanes were measured on a Du Pont 990 Thermal Analyzer in conjunction with a standard Du Pont heating cell. Thermograms were recorded using urethane samples of approximately 17 mg, which were encapsulated in a small aluminium pan. An empty pan (air) was used as a reference and the sample pan placed in the sample component; the cell was cooled to approximately -120°C by pouring liquid nitrogen into the surrounding steel jacket provided. Precautions were taken to avoid liquid nitrogen entering into the cell as the resulting ice formation would lead to undesired transitions associated with thermal behaviour of water. When the temperature was brought down to -120°C the cooling jacket was quickly replaced by a steel cover and a glass surround. The cell was heated at a constant rate of 20°C/minute with a steady purge of dry nitrogen passing through. All the thermograms were recorded between -100°C and +250°C on a two pen recorder each being set at different sensitivity of 5 and 10 mV/cm.

In Figures 2.2.8 to 2.2.14 are shown the thermograms of various prepared polyurethanes and their constituents. The analysis of these thermograms provide useful information on overall polymer morphology explaining the manner in which the various chemical constituents of urethane elastomers and elastoplastics control light transmission characteristics and mechanical properties. It is useful to study the thermal behaviour of the individual hard and soft segments as this information helps in determining the hard/soft segment phase mixing in the copolymer and hence their mutual effect on transparency. Figure 2.2.8 shows the thermal transition of Capa 220 polyol alone and the soft segment obtained by reacting Capa 220 and H_{12}MDI based on 1/1 equivalent ratio. It can be seen that the melting endotherm peak of the soft segment (45°C) is 15° below its pure polyol melting peak (60°C). This is due to the reaction of the relatively high melting polyol (60°C) with low melting H_{12}MDI (below 16°C) resulting in reaction product where the soft segment has an intermediate melting temperature. Since all the materials prepared in this research are based on Capa 220 and H_{12}MDI they showed a constant soft segment Tg at -42^{o}C and melting point of crystallites at 45^{o}C (T_s). The Tg was measured at the point of base line shift and the melting point of the soft segment crystallites were considered to be located at the peak point of the endotherm transition temperature. It is to be noted that the endotherm at 45^{o}C which is due to the soft segment crystallization was observed only in the phase segregated materials e.g. T9-T12 (Figure 2.2.11). These samples have good physical properties but show poor transparency due to the incompatibility of hard and soft segments (heterogenous phase formation).

The transparent urethanes did not show any T_s transitions which indicates that the translucency in the polymers is mainly due to soft segment crystallization. Similar to the pure soft segments, the 100% hard segments were also prepared using different blends of diols at a ratio of NCO/OH = 1 and their thermal transitions measured. These are shown in Figure 2.2.9. It is interesting to note that the melting temperature of T10 and T12 hard segments (curves 2 and 3) which is similar to the melting point of pure soft segments shown earlier in Figure 2.2.8. Since the copolymer based on these soft and hard segments are opaque, it is suspected that the hard/soft segment cocrystallization may have occurred causing light scattering (translucency) due to the formation of large crystals. This effect is not observed in transparent copolymers whose soft and hard segments constituents melting temperatures differ considerably (Figure 2.2.10b).

Figures 2.2.10 and 2.2.11 shows the thermogram of both transparency and opaque thermoplastics materials. The existence of two transitions in opaque materials (T21 and T26) clearly indicate the existence of two incompatible phases in these polymers. On the other hand transparent polyurethanes exhibited only a single transition and the absence of any peak at 45^{o}C due to soft segments crystallization indicates the compatibility and existence of only a one phase system in these polymers. This phenomena can be better understood by observing Figure 2.2.10(b) where the melting point of T1 copolymer lies in between the melting points of its respective constituents soft and hard segments. However it has been observed that the opaque crystallized materials when heated to their melting temperature become transparent: however such transparency obtained by the melting of crystallized phases on ageing reverts to translucency due to soft segment crystallization. Figure 2.2.12 shows the development of soft segment crystallization with time of a typical crystallized sample (T10).

In contrast to the thermoplastic materials the chemically crosslinked polyurethanes retain their permanent transparency due to their ability to maintain an irregular structure in which crstyallization is prevented due to polymer chain immobility. These effects can be seen in Figures 2.2.13 and 2.2.14.

FIGURE 2.2.8: DSC Thermogram of Pure Soft Segment and Capa 220 Polyol

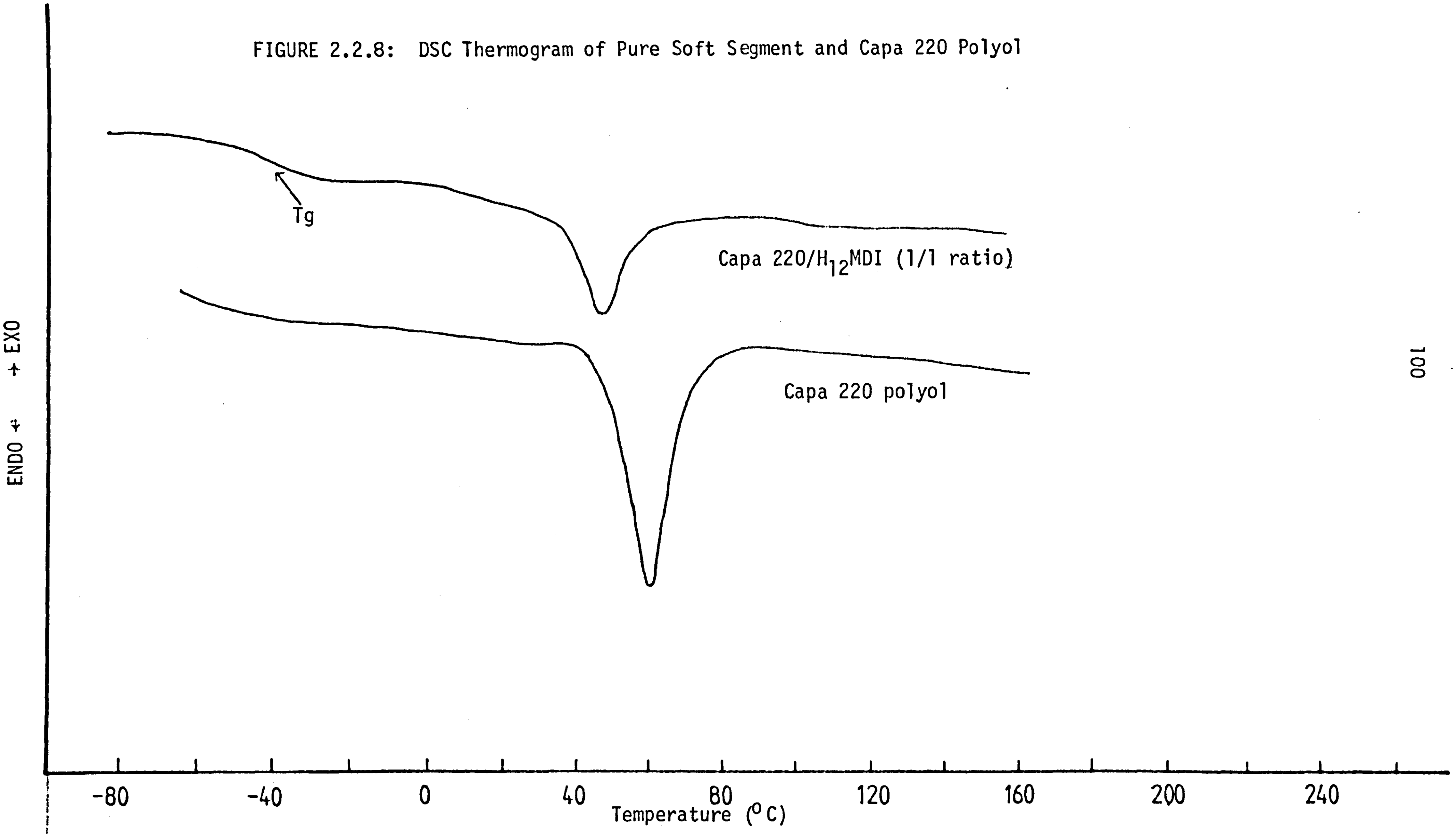


FIGURE 2.2.9: DSC Thermogram of the Pure Hard Segments Based on H_{12} MDI/chain Extenders at 1/1 Equivalent Ratio

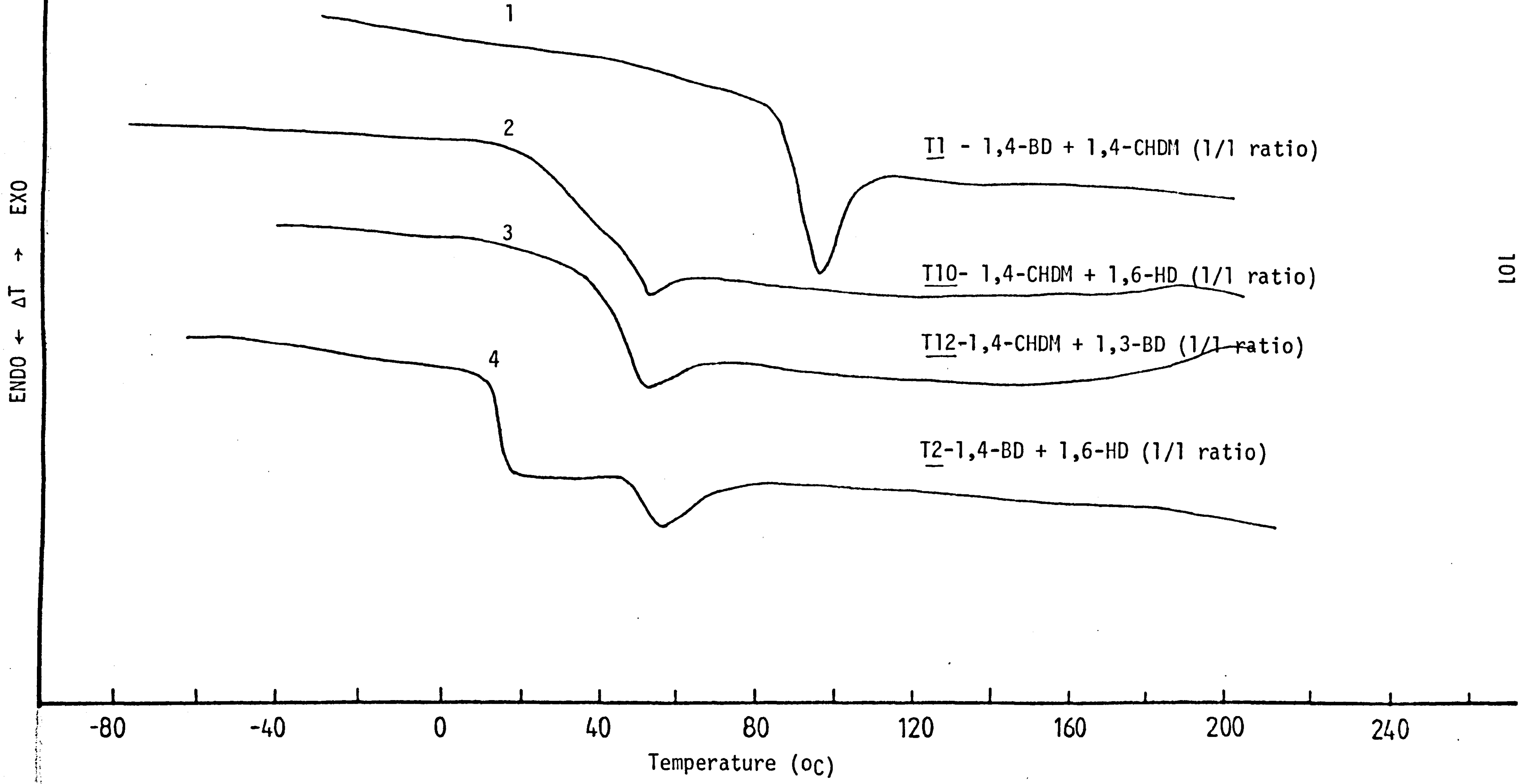


FIGURE 2.2.10(a): DSC Thermogram of Various Thermoplastic Polyurethanes

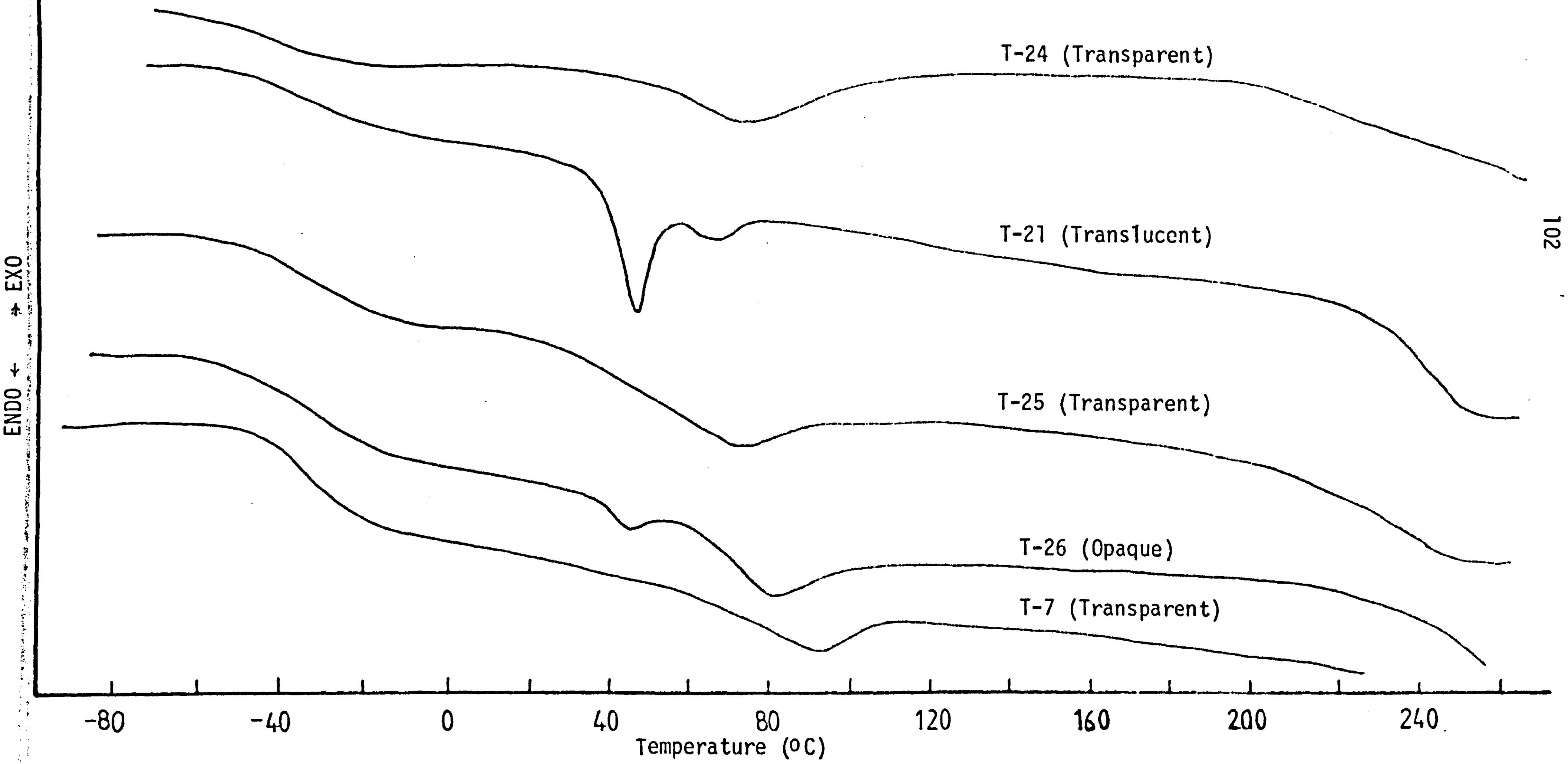


FIGURE 2.2.10(b): DSC Thermograms of Transparent Thermoplastic T-1 Polyurethane and its Pure Soft and Hard Segments

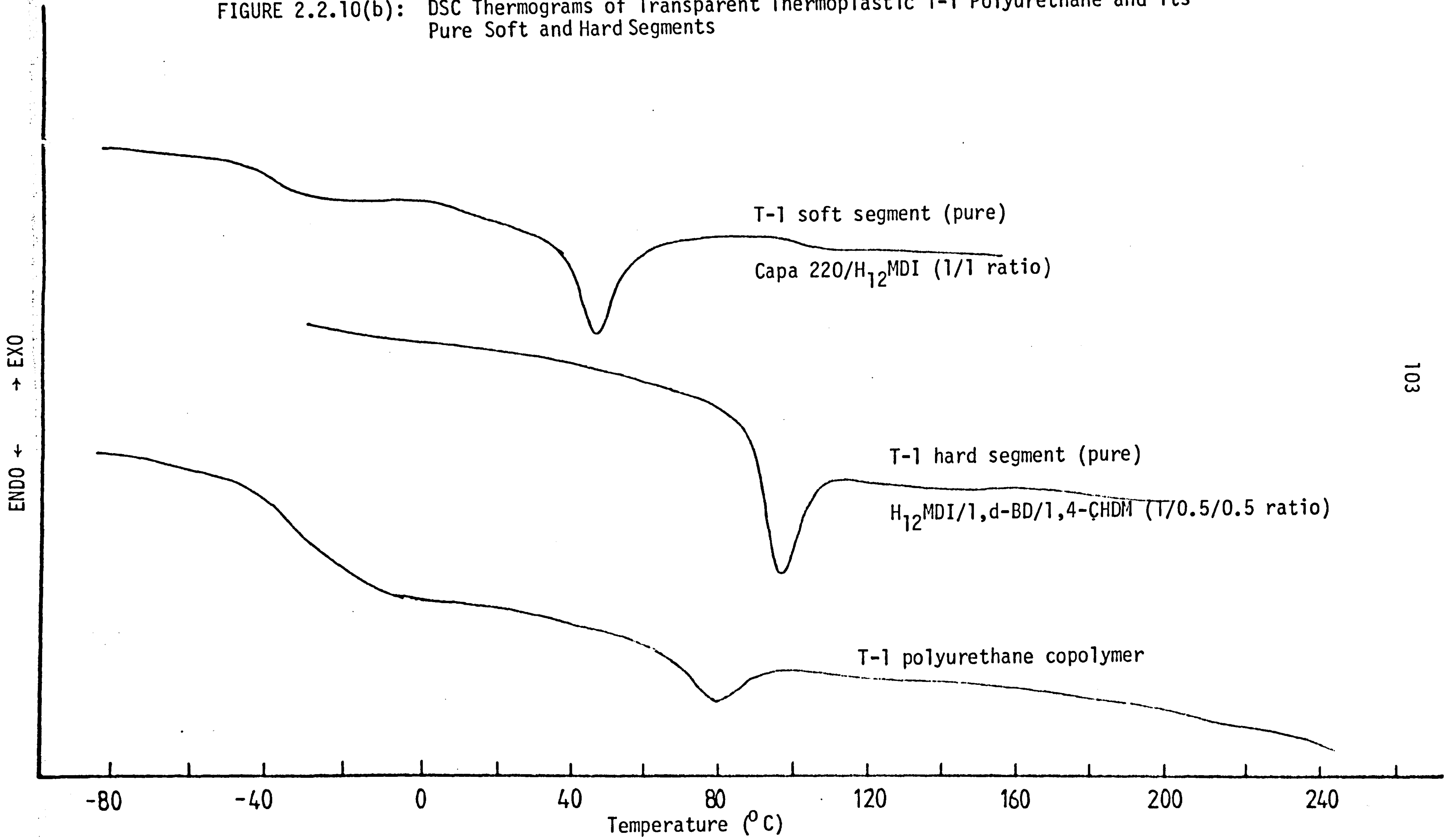


FIGURE 2.2.11: DSC Thermograms of Thermoplastic Polyurethanes that turned translucent on Ageing

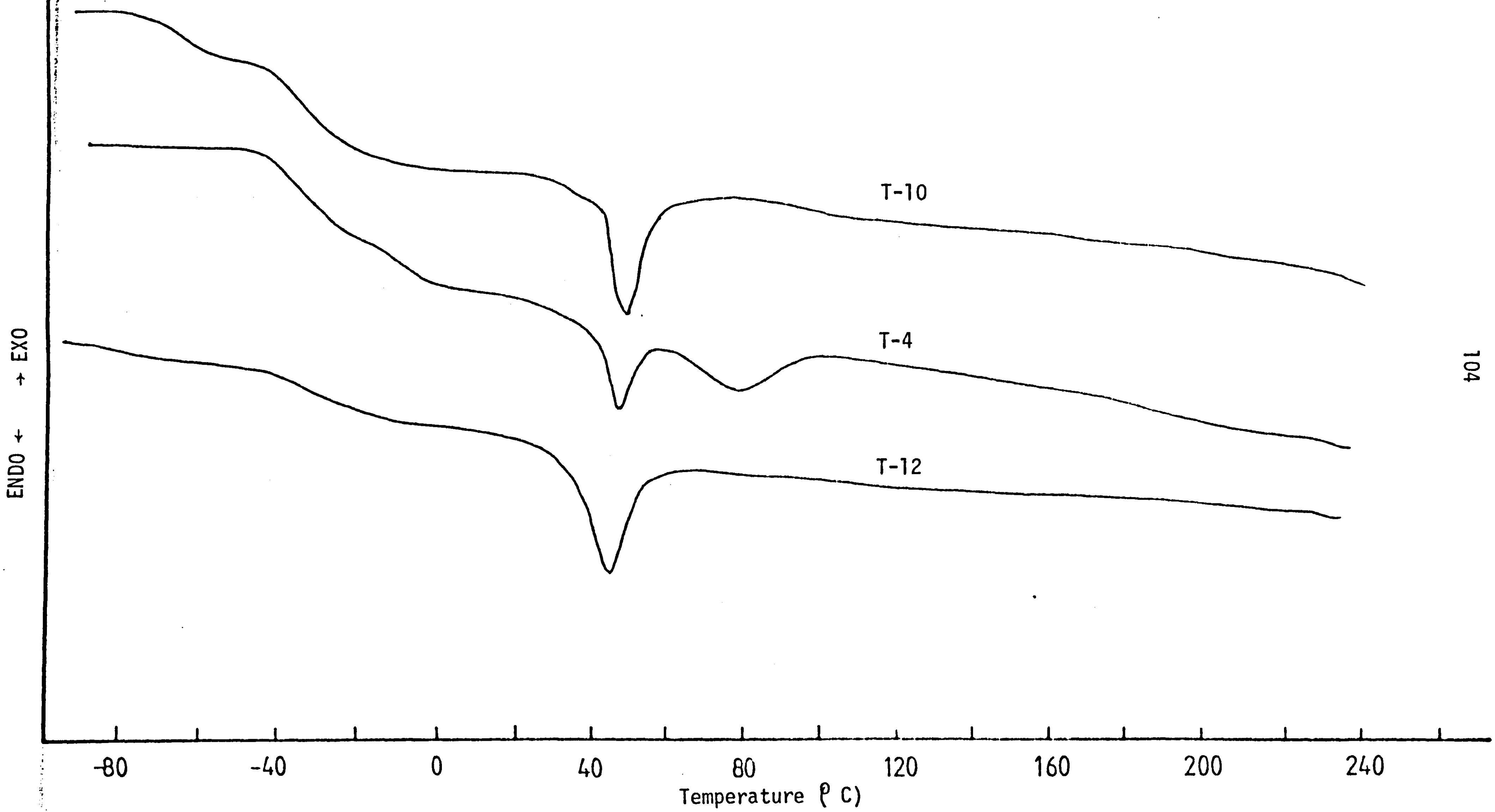


FIGURE 2.2.12: Development of Soft Segment Crystallization (Phase Separation) with time of T-10 Sample after Annealing at 60°C for 1 hour

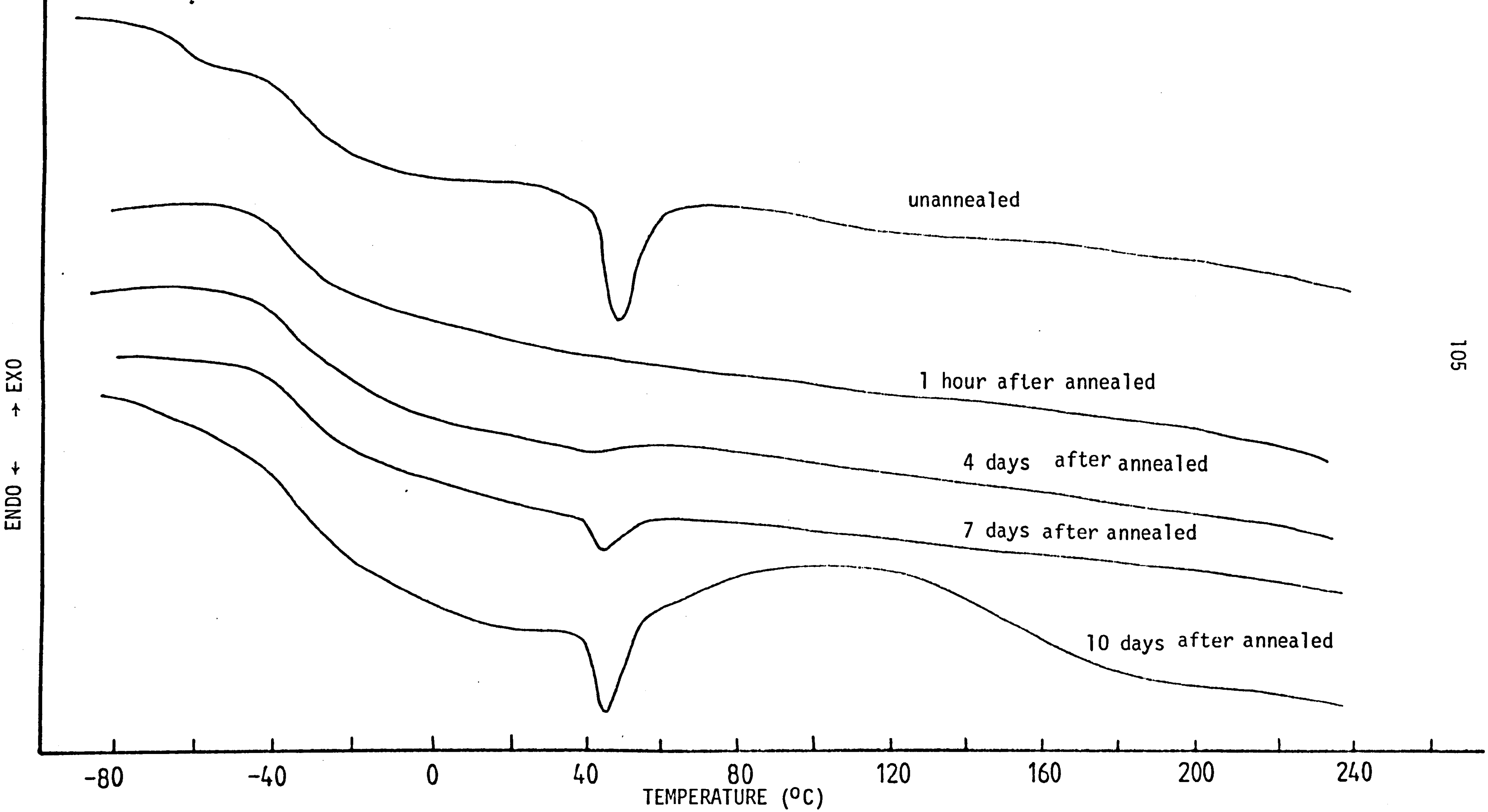


FIGURE 2.2.13: Some Crosslinked Polyurethanes Chain Extended with TMP Triol

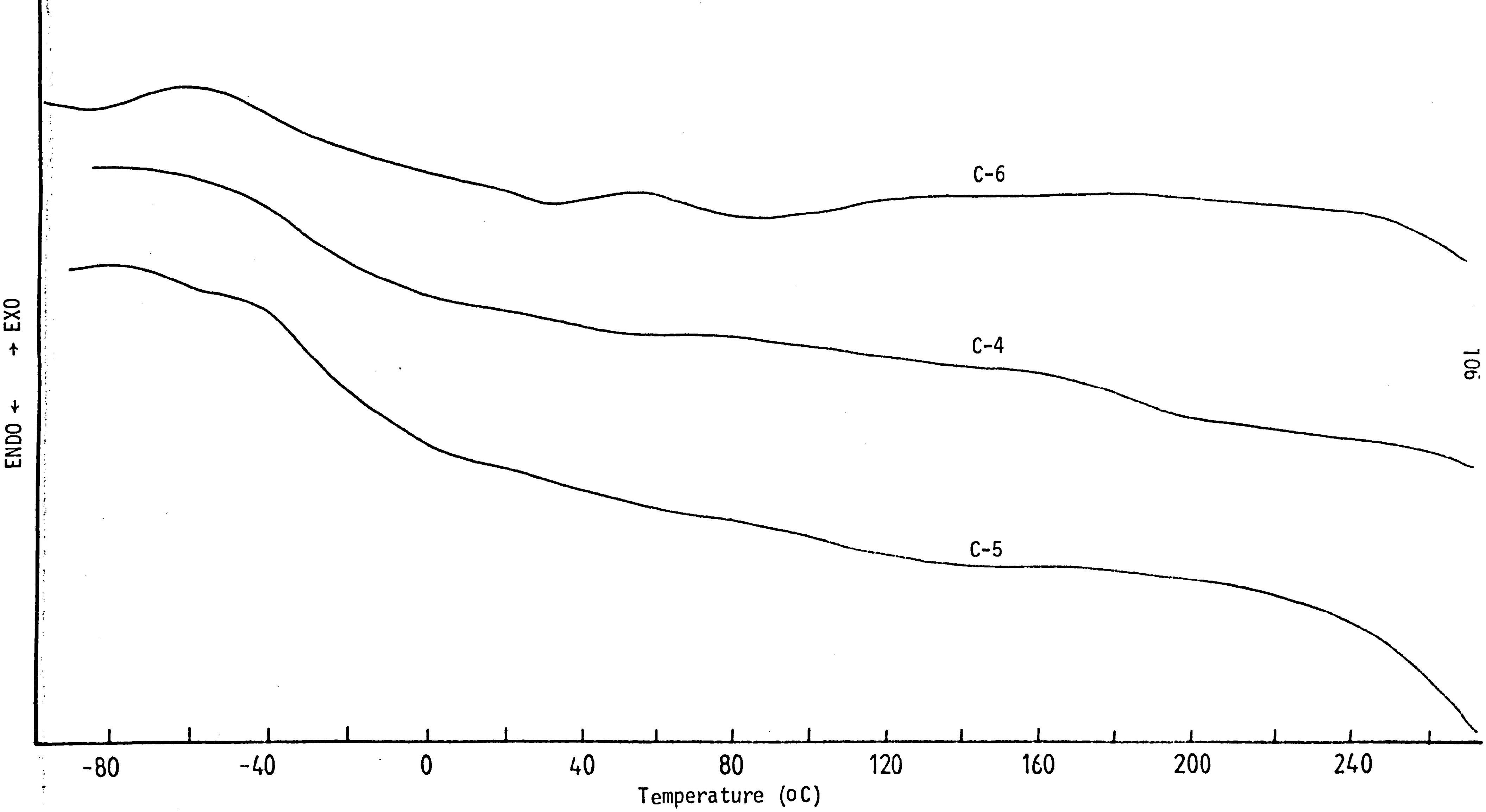
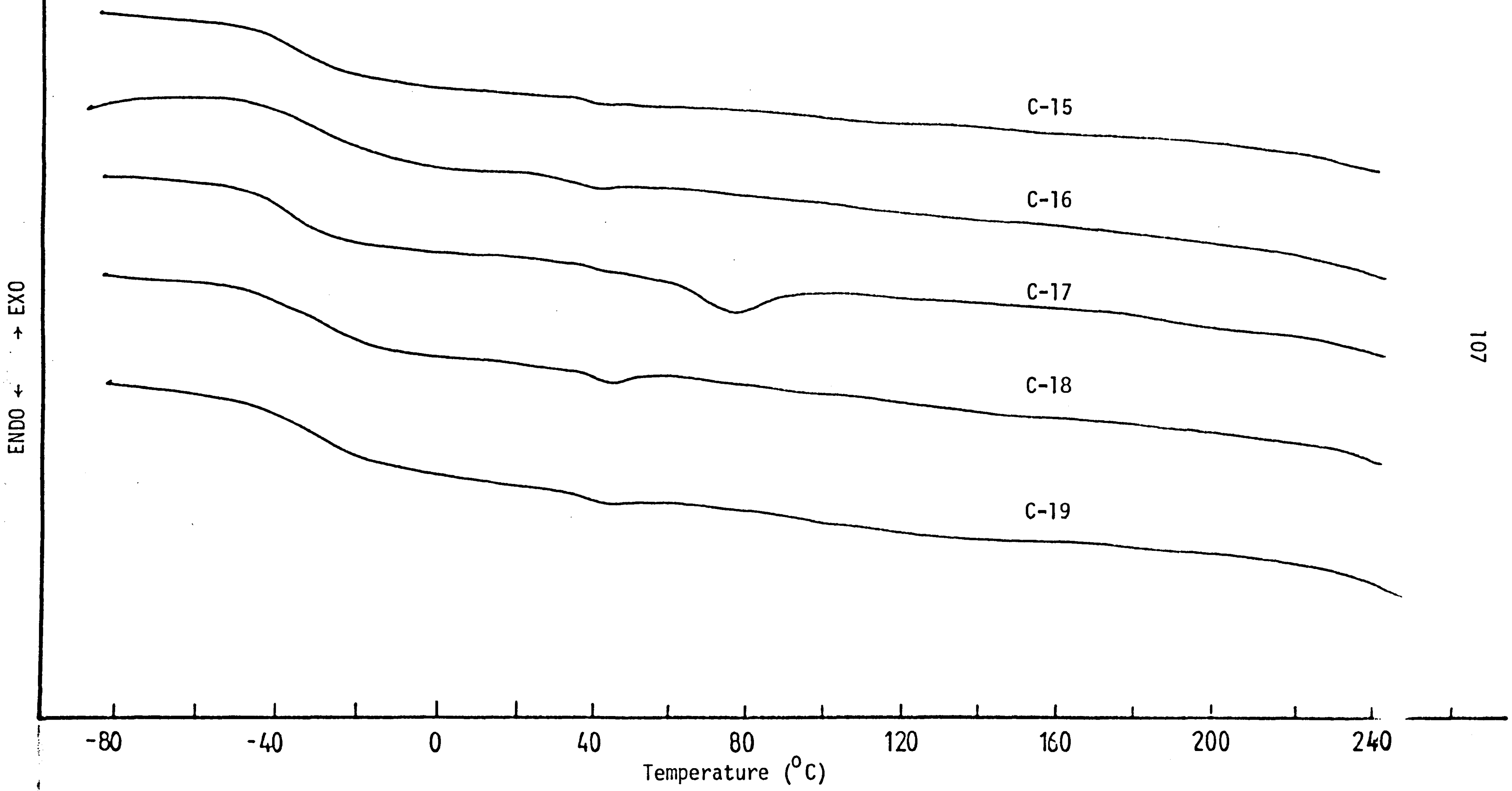


FIGURE 2.2.14: Some Crosslinked Polyurethanes Chain Extended with Capa 305 Triol



2.2.3 Dynamic Mechanical Thermal Analysis (DMTA)

Polymers are termed viscoelastic because some fraction of the energy required to cause recoverable deformation is dissipated within the material. The viscoelastic nature of polymers is well known and is unique in the field of material properties. The term is used to describe the time dependent (reversible) mechanical properties of polymers, which in limiting cases can behave either as elastic solids or as viscous liquids (fluids). A knowledge of the viscoelastic behaviour of polymers, and its relation to molecular structure is essential to an understanding of both processing and other related properties.

The time dependent changes in polymers, subjected to constant stress (creep) or constant strain (stress relaxation) - static studies - give insight into viscoelastic behaviour, but more information can be obtained, often on a more convenient time scale by the study of dynamic mechanical properties.

In dynamic mechanical tests the polymer is subjected to cyclic deformation and the stress and strain are monitored. Generally, the applied force and the resulting deformation are varied sinusoidally with time. From such a test it is possible to obtain simultaneously an elastic modulus and a mechanical damping. There are three modulii which are used to describe the viscoelastic behaviour of rubber.

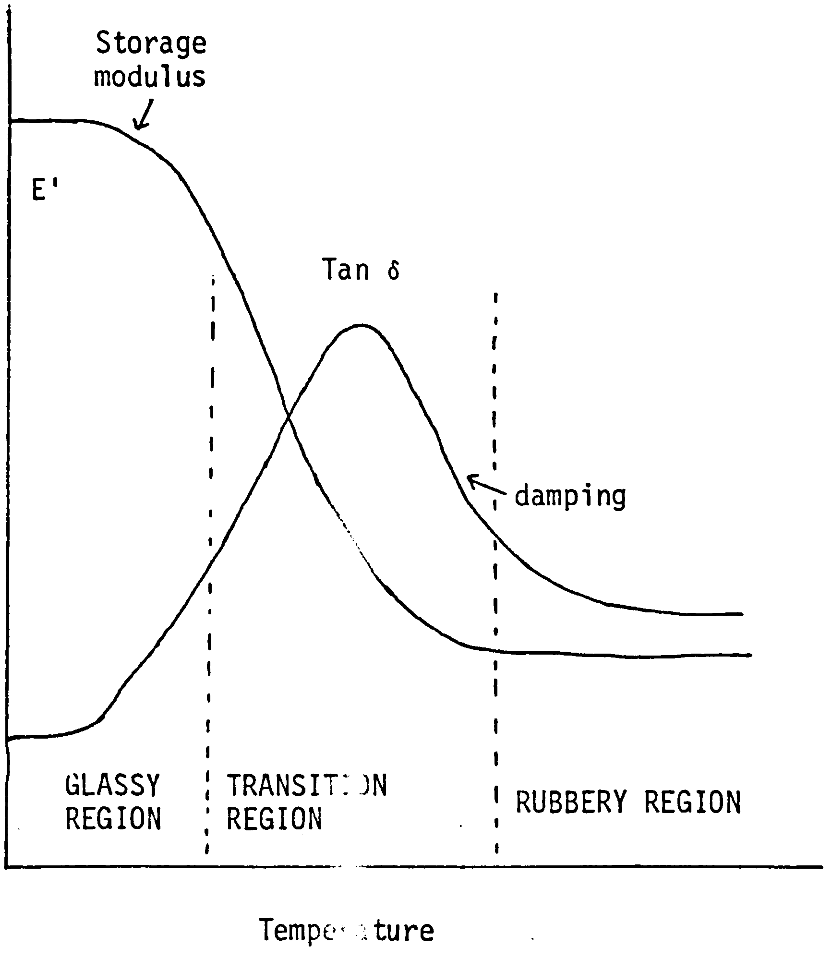
Storage modulus (E'). A single prime is used for the elastic modulus and defined as the stress in phase with the strain in a sinusoidal deformation (in tension or compression) divided by the strain. It is also a measure of the energy stored and recovered per cycle when different systems are compared at the same strain amplitude. It is usually plotted against frequency or temperature with logarithmic scale.

Loss modulus (E"). A double prime is used for the friction moduli which are also known as viscous moduli. It is defined as the stress 90^o out of phase with the strain divided by the strain and also it is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation when different systems are compared at the same strain amplitude.

Loss tangent (tan δ). A useful parameter which is dimensionless and conveys no physical magnitude but is a measure of the ratio of energy lost to energy stored in a cyclic deformation is the lost tangent, $\tan \delta = E'/E''$.

Dynamic properties are dependent on both frequency and temperature and it is possible to approximately relate the two effects quantitatively. The general form of the effect of temperature on storage modulus (E') and tan δ is shown in the figure on the next page.

The effect of increasing or decreasing frequency is to shift the curves to the right or left respectively along the temperature axis. At room temperature the order of magnitude of the effect of temperature on modulus for a typical rubber is 1% per ^oC and the effect of frequency



of the order of 10% per decade.

The dynamic mechanical analysis have been extensively used and are in fact considered as one of the most effective tools in the investigation of polyblend and block copolymer systems. The relative compatibility of polymers can be readily examined by comparing their transition shift (Tg and/or Tm) in polyblends where a true blend shows a single transition peak.

Ideally, for block copolymers e.g. polyurethane, these transitions are located at the Tm or Tg of the corresponding component homopolymers (soft and hard segments). However, sample composition, segmental length, inherent intersegmental solubility, thermal history and sample preparation method have been found to influence the degree of phase separation and thereby the shape and temperature location of the dynamic-mechanical transition points. Phase mixing between domains has been indicated by a decreased slope in storage modulus transitions and by a broadened loss peak.

In the present work the dynamic mechanical thermal analysis was used to study the morphology and the hard/soft segment mixing in the prepared polyurethanes. In addition the viscoelastic behaviour and mechanical integrity of these materials over a broad temperature range was also exploited. These properties were measured on both crosslinked and thermoplastic polyurethanes using the Polymer Laboratory's DMT analyser. The test specimen of dimensions 40 mm x 4 mm having approximately 2 mm thickness were used on the DMT analyser which is capable of generating automatic temperature scans of storage modulus (log E') and mechanical damping (tan δ) simultaneously from -120^{o}C to +250^{o}C. All the tests were carried out at 1 Hertz frequency and at a heating rate of 4^{o}C per minute. The temperature at which the log E' reached a value of 6.0 MPa was taken as an arbitrary indication of the loss of mechanical integrity and melting of hard segment, and the tests were stopped.

Figure 2.2.15 shows a typical DMTA thermogram of a representative crosslinked material, C-4 which exhibits a constant log E' value of 9.25 MPa in its glassy region (below Tg). A rapid decrease in modulus is followed as the temperature is increased through the glass transition region up to approximately 80^{o}C where both the segments are melted.

This corresponds to the broad damping (tan δ) peak reaching a maximum value of 0.4. At this stage the strength of material is only due to its chemical crosslinkages which reflect the stabilized modulus in rubbery regions where no further decrease in modulus is observed with temperature rise. All the crosslinked polymers showed similar trend of relaxation.

In contrast with the thermoset materials, the segmented polyurethanes showed continuous drop in storage modulus above its hard segment melting point. This drop is expected as above their melting point, the TPU's become soft and lose their mechanical integrity.

Figures 2.2.16 to 2.2.20 compare the dynamic mechanical behaviour and hence the morphology of transparent (T1, T2) translucent (T4) and opaque (T9, T10 and T12) TPU polyurethanes. The storage moduli of these polymers at room temperature and their loss tangent (peak tan δ) values with corresponding temperatures are given in Table 2.2.4. It is seen that the transparent polyurethanes (T1 and T2) demonstrated relatively high tan δ values which are located in the minus temperature region. This indicates the flexibility of the material and the absence of any soft segment crystallinity is evidenced by their lower modulii at room temperature. In contrast, all the opaque samples (T9, T10 and T12) exhibited higher modulus at room temperature due to their rigidity attributed to the soft segment crystallization. These samples also showed lower tan δ peak values with their corresponding temperatures close to the soft segment crystallites melting point (T_s). However the opaque crystallized urethanes when annealed at 50°C (above T_s) for 1 hour became transparent indicating phase mixing. The DMTA thermograms of these annealed samples showed the characteristics of original transparent urethanes (T1 and T2) discussed above. It is to be noted that the translucent material T4 demonstrated intermediate values of storage modulus and damping i.e. it lies between that of transparent and opaque materials.

TABLE 2.2.4:

Dynamic Mechanical Properties of Synthesiszed Thermoplastic Polyurethanes as Measured on Dynamic Mechanical Thermal Analyser

Sample No.*	Storage modulus at 20°C (log E') MPa	Loss angle at damping peak Tan δ (corresponding temp. °C)
T1 (transparent)	6.8	0.46 (-2°C)
T2 (transparent)	6.55	0.44 (-15°C)
T4 (translucent)	7.1	0.35 (10°C)
T9 (opaque)	8.1	0.27 (38°C)
T9 (annealed) (transparent)	6.8	0.47 (7°C)
T10 (opaque)	7.9	0.31 (33°C)
T10 (annealed) (transparent)	6.8	0.5 (10°C)
T12 (opaque)	8.3	0.27 (38°C)
T12 (annealed) (transparent)	6.7	0.5 (5°C)

* See page 68 for sample compositions

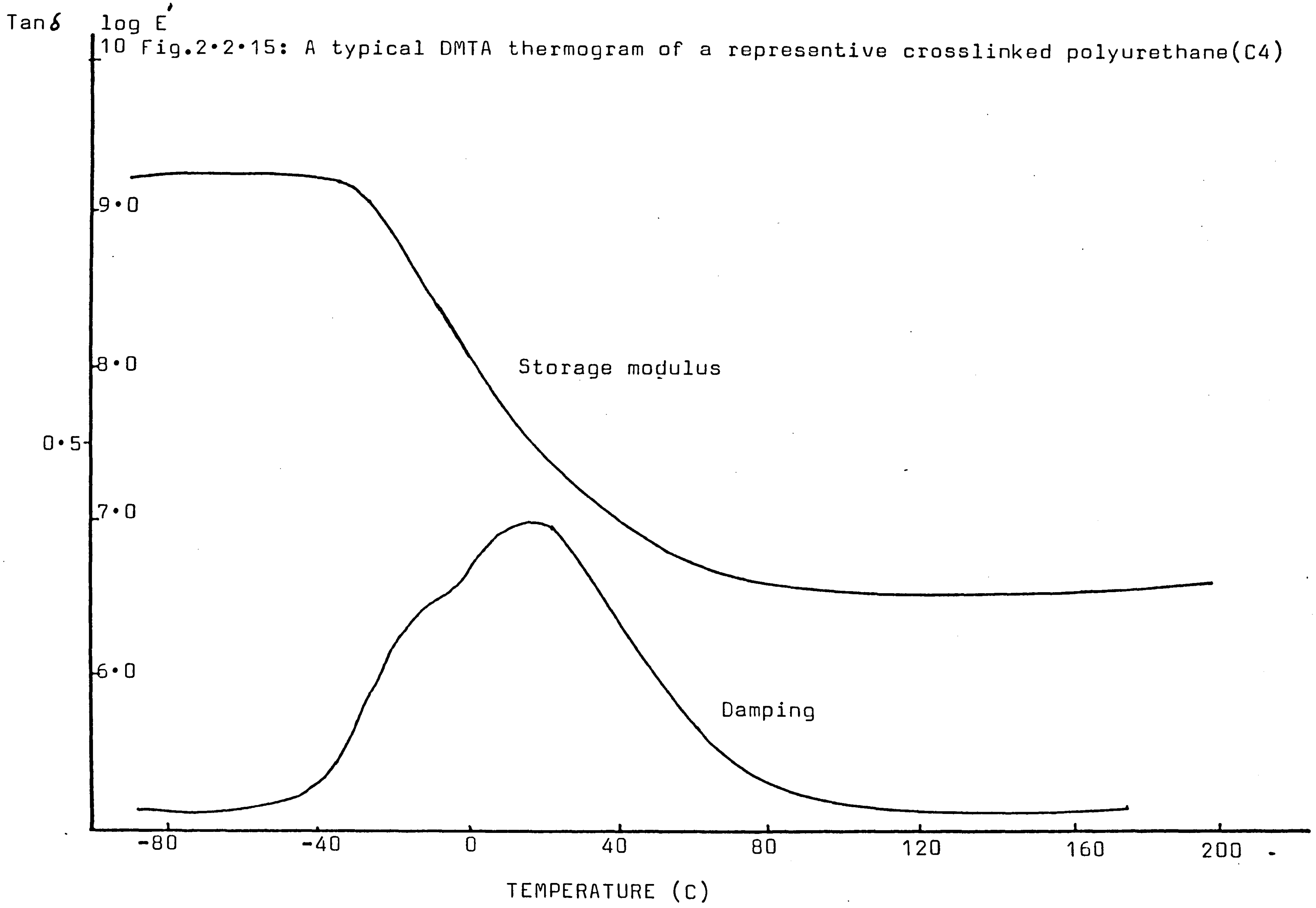


Fig.2·2·15: A typical DMTA thermogram of a represention crosslinked polyurethane(C4)

Fig.2•2•16: A typical DMTA thermograme of transparent thermoplastic polyurethane samples T1 T2

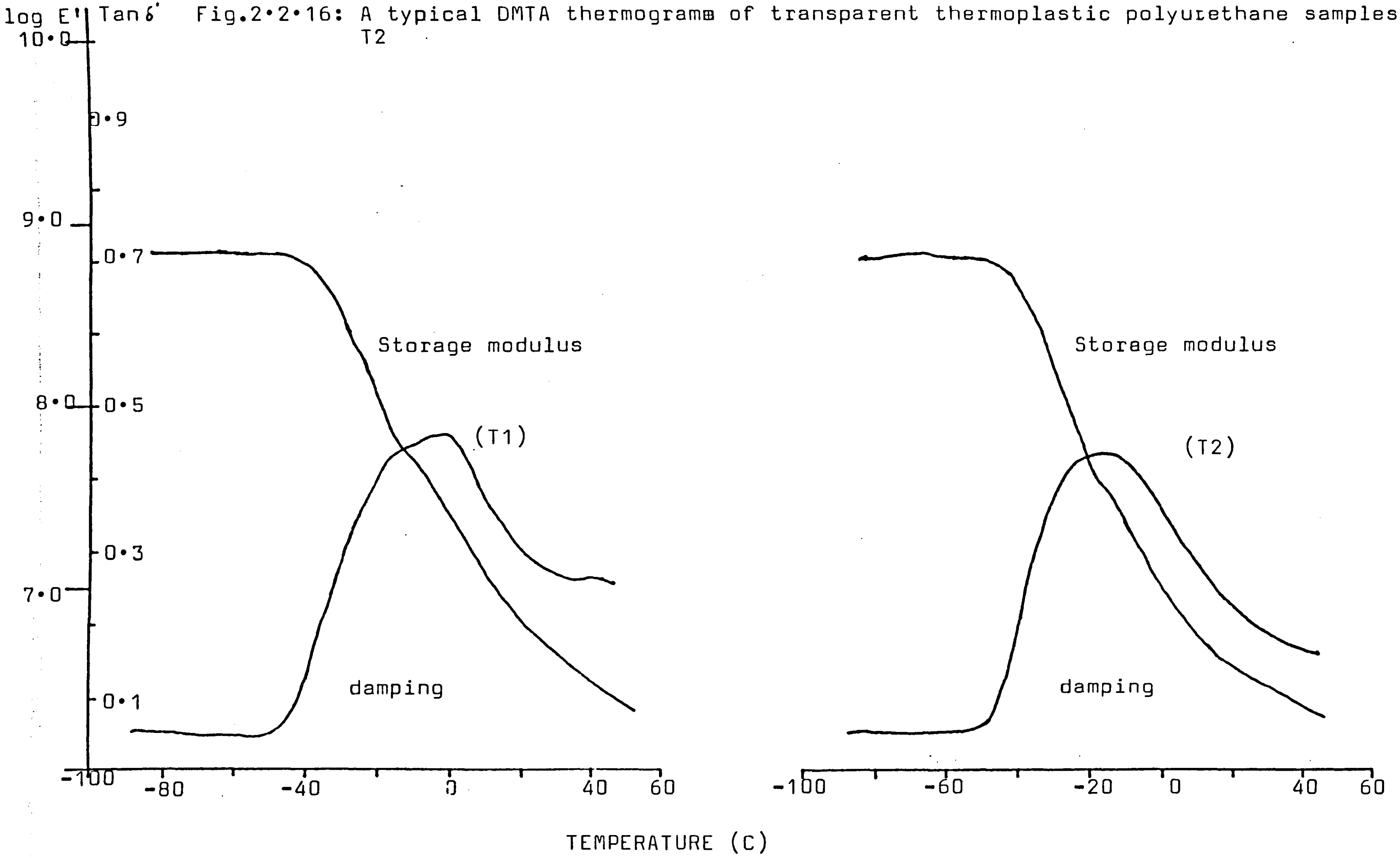


FIG.2·2·17:A typical DMTA thermogram of a transparent PU sample T4.

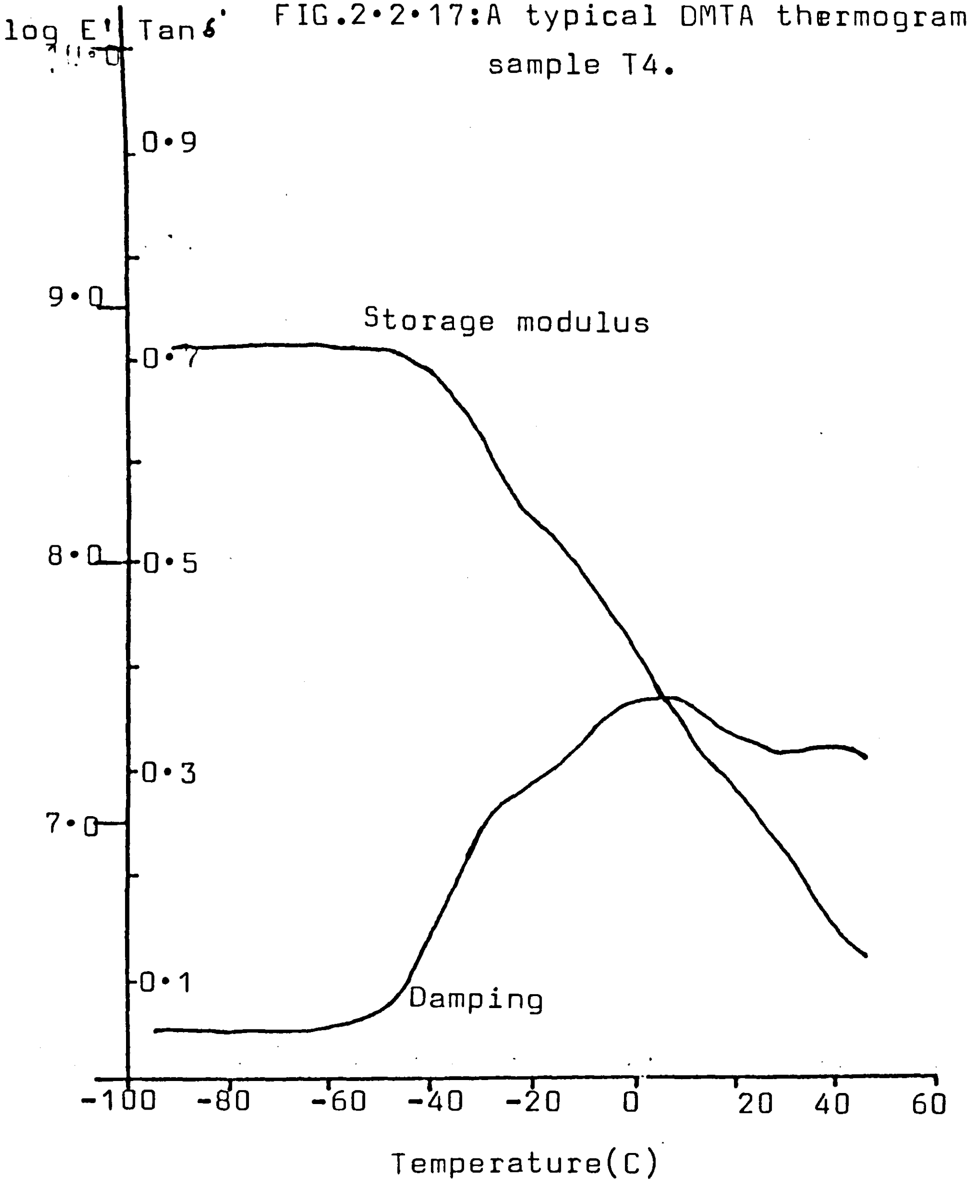


FIG.2•2•18:A typical DMTA thermogram of an annealed and unannealed TPU sample T9.

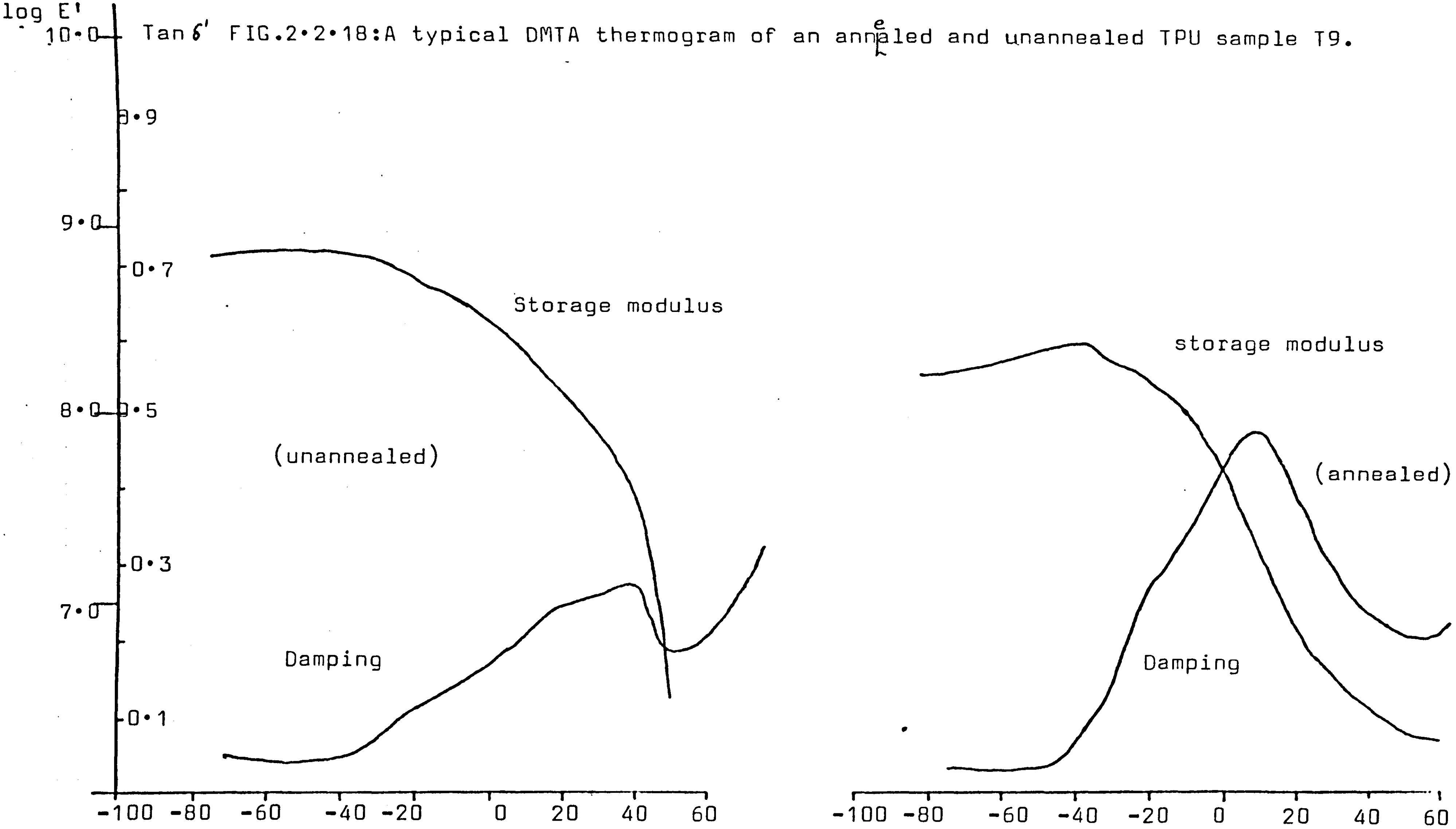


FIG.2•2•19: A typical thermogram of an annealed and unannealed sample of TPU; T10.

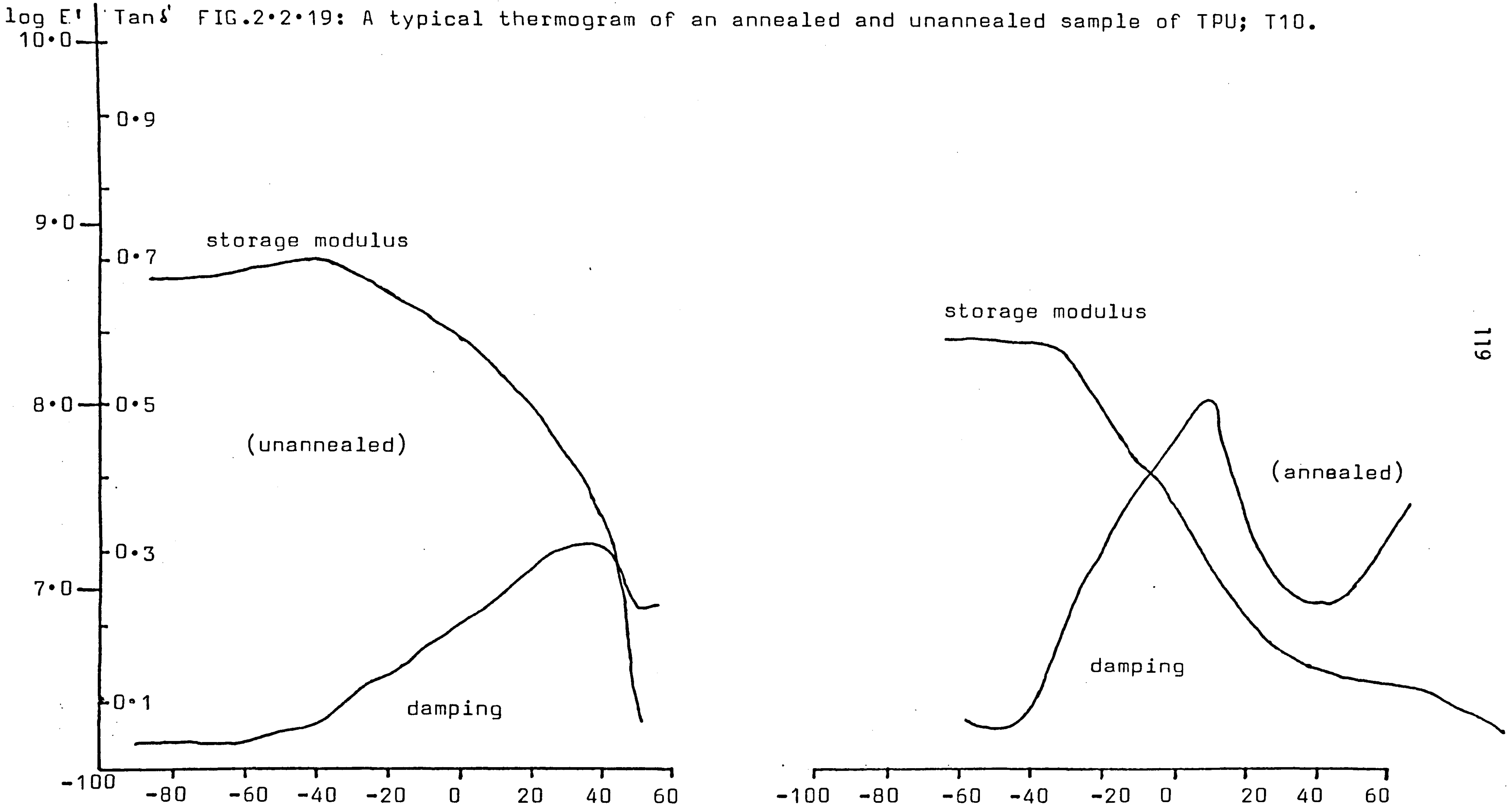
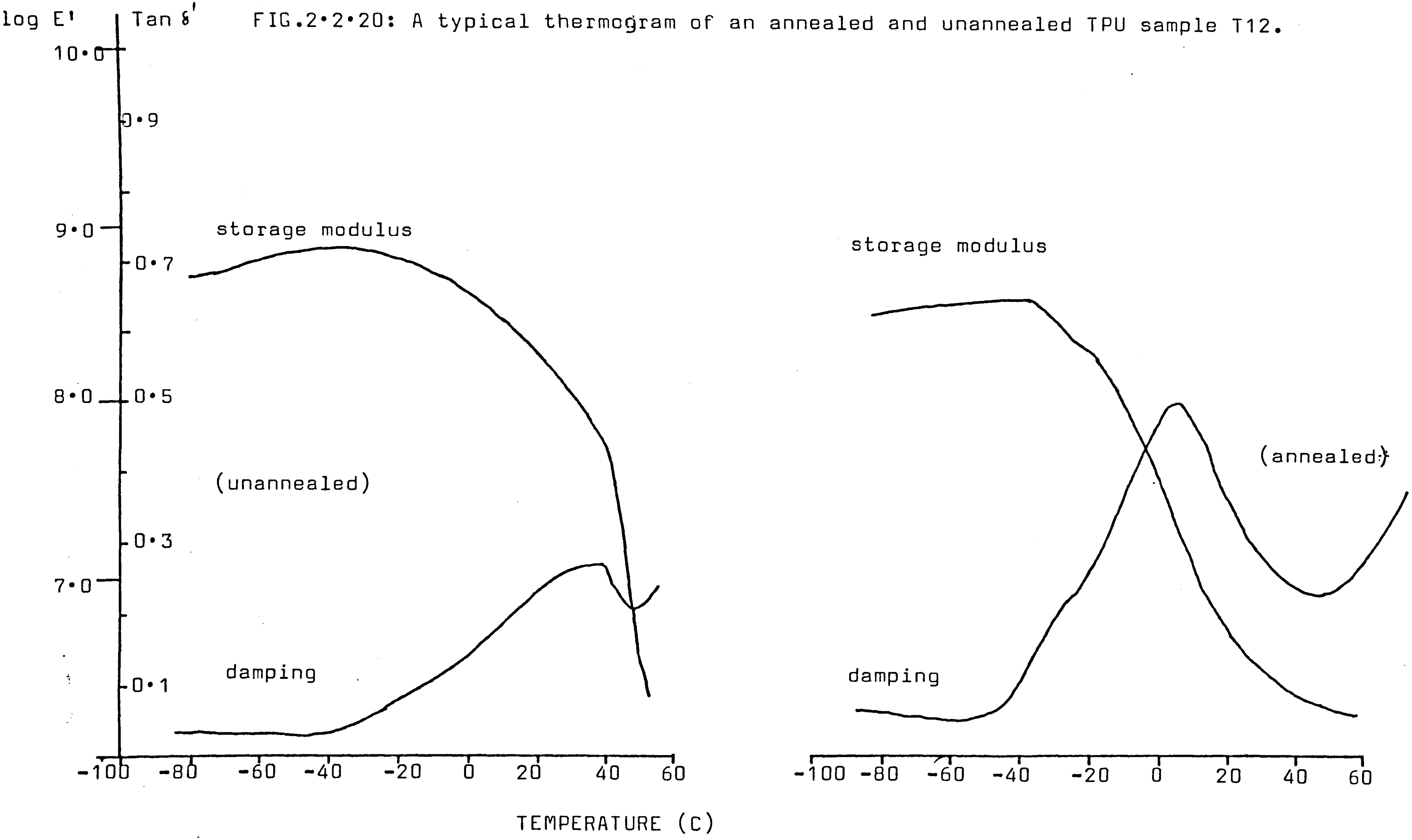


FIG.2·2·20: A typical thermogram of an annealed and unannealed TPU sample T12.



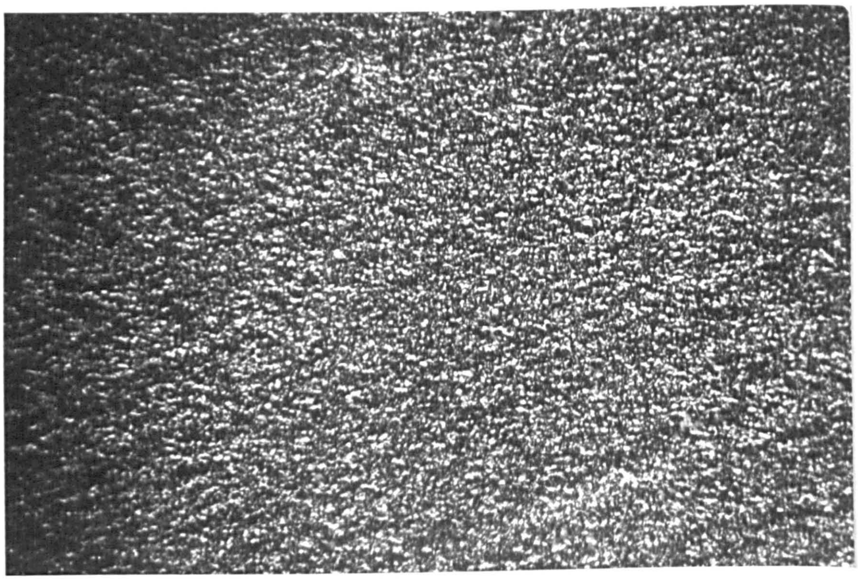


PLATE 1: Photomicrograph of Soft Segment Crystals (sample T9)

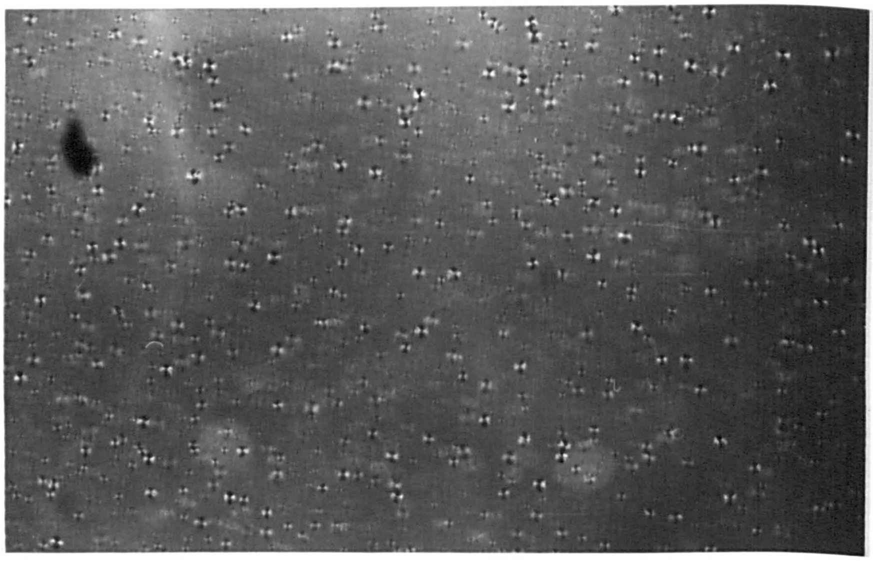


PLATE 2: Photomicrograph of Hard Segment Crystals (sample T2)

2.4.2 Optical Microscopy

The use of an optical microscope was made to detect any crystals of hard and soft segments present in the prepared polyurethanes.

The specimen was placed on a standard sledge microtome, then cooled to -80°C using solid carbon dioxide and a thin section was cut. Cooling specimens well below their Tg is necessary to obtain thin sections. These specimens were then observed under Reichert Biovar optical microscope of 25 magnification with cross-polar adjustment.

All the opaque samples due to soft segment crystallization gave micrographs similar to plate 1. The transparent materials, however, either did not show any crystals or indicate very fine hard segment crystals given in plate 2. These crystals are believed to have very small size and unable to scatter the incident light which results in good transparency.

2.3 PHYSICAL AND MECHANICAL PROPERTIES

The following section deals with the measurement of physical and mechanical properties of the prepared polyurethanes. These include the strength properties, elongation at break, hardness, tear, compression set, tension set and stress relaxation. In addition the values of transparency and melt flow index (MFI) are also cited in the tables for appropriate polymers.

2.3.1 Strength properties

The tensile strength properties were determined on a J J Tensile testing machine* according to the British Standard (BS 903 Part A2). A load cell having a maximum load of 500 Newtons was used. The crosshead speed was maintained 100 mm/minute and the stress-strain curves were recorded on a J J chart recorder. Test specimens were BS dumbell type 2 cut from 1-2 mm thick cast sheets using a die punch cutter. Five specimens were used for each determination and marked with 20 mm bench marks using a very fine ink pen in order to measure the elongation at break. Where an obvious failure occurred either due to the voids present in the specimen or a jaw break, the results for that specimen were disregarded. All the specimens were conditioned for at least 2 weeks at 23°C (50% relative humidity) prior to test.

The following properties were measured and the results cited in appropriate tables:

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* J J Lloyd Instruments Ltd., Warsash, Southampton, England.

Ultimate tensile strength, UTS in MN/m^2 (MPa)

Modulus at 100% and 300% strain in MPa

Ultimate elongation in percentage

Hardness in IRHD (BS 903 Part A26)

The hardness of all polyurethane samples was measured on a Wallace microhardness tester*. This instrument is designed to make it possible to determine the hardness values of small moulded specimens or thin sheets without moulding a special test piece. Die cut specimens of 2 mm thickness were used in the form of discs having 23 mm diameter.

Compression Set

Compression set is the proportionate residual contraction in the rubber test piece after it has been released from compression under specified conditions. The compression set for all the prepared polyurethanes was measured according to the BS 903 Part A6 method using a constant compression strain of 25%. A non-standard specimen thickness of 5 mm was compressed at 70^{o}C for 24 hours before the set was calculated according to the following formula:

$$\begin{array}{l}\text{Compression set (25\%)}\\ \text{(in percentage)}\end{array} = \frac{t_o - t_r}{t_o - t_s} \times 100$$

t_o = original thickness of test piece

t_r = thickness of test piece after recovery

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* H W Wallace and Co. Ltd., Croydon, England.

t_s = thickness of the spacer

Transparency

The percent light transmission through 2 mm thick specimens were recorded on an Unicam-Pye visible spectrophotometer over 350-700 nm range. All the transmittance values shown in the appropriate tables are derived at 575 nm as this is close to the wavelength at which the human eye is sensitive.

Melt flow index (MFI)

The MFI of a thermoplastic is the gravimetric flow rate of the sample melt extruded from a die of specified length and diameter under prescribed conditions of temperature and pressure.

The MFI values of the prepared thermoplastic polyurethanes were determined on a Davenport melt indexer which is designed to the specifications given in BS 2782 part 1. The apparatus may be regarded as a simple capillary rheometer operating at conditions of low shear. Although the applied shear stresses and resultant shear rates are much lower than those used in most fabricating processes the results obtained do provide a useful indication of the relative ease with which different samples will flow when they are fabricated. Hence, higher MFI values indicate easier melt flow.

Basically the Davenport melt indexer is a dead weight extrusion plastimeter consisting of a thermostatically controlled heated steel cylinder with a die situated at the lower end and a piston, operating within the cylinder, which can be loaded with suitable weights.

In the present work a tungsten carbide die having 0.2096 cm diameter bore was used with a load of 2.16 kg at two different temperatures viz 150°C and 190°C.

Five extrudates, for 1 minute each of extrusion, were collected, weighed and averaged to give the value of MFI from the following expression:

$$\mathrm{MFI} = \frac{10w}{T} \quad \text{(gms/10 min)}$$

where 'w' is the average weight of extrudates in gms and 'T' is the time in minutes.

RESULTS

The general trend of mechanical properties observed in the prepared thermoplastic and thermoset urethanes is shown graphically in Figures 2.3.1 and 2.3.2. Figure 2.3.1(a) represents the properties of polymers which are based on the Capa 220/H_{12}MDI prepolymer systemand chain extended with 1/1 blend of 1,4-BD and TMP. The block ratio varied from 1/3/2 to 1/7/6 i.e. increasing hard segment content. As expected, when the hard segment content increases the hardness increases and the tensile strength decreases, the latter is considered due to the excessive crosslink density. Also, it can be seen from Figure 2.3.1(a) that when the proportion of TMP triol increases then this has a negative effect on overall tensile performance. As it will be seen later (samples C6 and C7 in the Table 2.3.1), the use of chain extenders in the form of blends (diol + TMP) was made in the present research programme in order to obtain a good combination of both tensile properties and transparency. The diol (e.g. 1,4-BD, 1,4-CHDM etc) gives strength to the polymers whereas the TMP or other triol merely serves to improve the transparency by introducing irregularity in the chain and also reducing the ability of the diol derived urethane groups to aggregate. However at higher block ratios of 1/6/5 and above, the light transmittance starts dropping gradually due to the increased concentration of diol which when present in high proportions tends to crystallise causing haziness.

A similar effect in the same base polymer is demonstrated in Figure 2.3.1(b) where the increase in TMP/diol ratio from 0/1 to 1/0 (i.e. 0% to 100% crosslinking) improved light transmittance due to the reduced chain mobility. However, as expected the tensile strength, hardness and compression set decreased.

The behaviour of thermoplastic materials of varying block ratios from 1/3/2 and 1/8/7 and based on only the diol, 1,6-HD is demonstrated in Figure 2.3.2(a). The hardness and tensile strength were found to increase sharply with increased hard segment content. Reduced light transmittance and poor optical clarity was observed up to a block ratio of 1/5/4 and this is attributed to soft segment crystallization. There is seen in Figure 2.3.2(a) to be an optimal block ratio range between 1/5/4 and 1/6/5 at which the materials are highly transparent. It is thought that at this level of block ratio, the hard/soft segment solubility is at its maximum and that neither segments tend to crystallise. However, as the hard segment concentration (block ratio) further increases, the transparency reduces apparently due to the crystallization as a result of hard segment aggregation.

In contrast, where a mixed diols system is employed, no crystallization at low block ratio due to soft segments was observed, or at least found to be minimal, to cause any light scattering and hence haziness. This is demonstrated in Figure 2.3.2(b) where translucency/opacity occurs only at high block ratios (i.e. 1/6/5 onwards) which is considered due to hard segment crystallization.

Since in the present work, low block ratios were used to obtain soft materials, the use of mixed diols was made which yielded polyurethanes with good transparency and excellent tensile properties.

The physical properties of both crosslinked and thermoplastic polyurethanes are given in Tables 2.3.1 to 2.3.7. All the crosslinked materials shown in Table 2.3.1 generally exhibited good mechanical properties, low compression set and high degree of transparency (greater than 80% not shown in the table). The ultimate tensile strength of sample C6 and C7 (25% and 75% crosslinking respectively) suggest that TMP does not enhance strength in the urethane but tends to reduce significantly haziness and improve transparency when compared with most of the samples that do not contain TMP (Tables 2.3.4 and 2.3.5). Samples C10 and C11 show that as the UTS, compression set and elongation at break decreases and the modulus and hardness increases as the block ratio or free isocyanate content in prepolymer increases. Lower block ratio (e.g. C8 at 1/2.5/1.5) yielded a low hardness material with acceptable mechanical properties but exhibited high compression set. Moreover these materials turn appreciably hazy on ageing due to soft segment crystallization. The cycloaliphatic diols were also found to give urethanes with good physical properties and a high degree of transparency.

Table 2.3.2 compares the properties of TMP based materials with urethanes derived from Capa 305 which is a trifunctional caprolactone of relatively high molecular weight (540). The Capa 305 owing to its relatively high molecular weight was observed to give low hardness and more flexible material. Although the TMP extended materials showed relatively better strength due to their rigidity, Capa 305 based urethanes have advantages of low hardness, better flexibility and optical clarity as judged by visual comparison. This is considered to be due to their more effective mixing (compatibility) of hard/soft segments and to the incorporation of a crosslinker which has a refractive index similar to the base material. Table 2.3.3 indicates the effect of diisocyanate structure on the hardness of polyurethanes by comparing IPDI with H_{12}MDI. It can be seen that the IPDI consisting of one benzene ring in its structure can be compared to H_{12}MDI which contains two aromatic rings. IPDI gives considerably lower hardness and a more flexible product. Samples C24 to C26 based on IPDI showed lower hardness values compared to their counterpart the H_{12}MDI derived urethanes which have approximately the same amount of free isocyanate content in their prepolymer.

The thermoplastic polyurethanes showed excellent mechanical properties and are given in Table 2.3.4. It appears from the table that those urethanes which are based on unsymmetrical diols e.g. 1,3-BD and 1,3-CHD, accelerate phase segregation and soft segment crystallization. As a consequence the materials become rigid exhibiting high hardness values and opacity. Such opaque polymers, however, when heated up to 100°C for 1 hour become transparent due to phase mixing and also their hardness is considerably reduced. This change in values is given in Table 2.3.7.

In Table 2.3.6.is shown the melt flow index (MFI) values of those polyurethanes which were successfully injection moulded. These materials exhibited a wide range of MFI depending on the structure of diol chain extenders. For example the sample T9 which contained a blend of two cycloaliphatic diols showed very low MFI value of 0.3 at 190°C due to the rigid diol structure. In contrast the aliphatic diols based polymer (T11) exhibited an MFI of 11 at the same temperature.

2.3.2 Tear strength

The tear strength of both crosslinked and thermoplastic urethanes were measured according to the British Standard BS 903 Part A3 using crescent test pieces. The tests consist of cutting a nick of accurate depth in a specified test piece and measuring the force required to tear across the width of the uncut portion. A J J Tensile testing machine was employed at a constant crosshead speed of 100 mm/minute, where the forces acted in a direction substantially normal to the plane of the cut. The following formula was used to calculate the tear strength in Newtons per standard test piece of 2 mm thickness.

$$\text{Tear strength} = \frac{t_s F}{t} = \frac{2F}{t}$$

where F = maximum force in Newtons

t = thickness in mm of test piece

t_s = standard thickness of test piece = 2 mm

Table 2.3.8 shows the tear strength in Newtons calculated per standard test piece of 2 mm thickness. The thermoplastic polyurethanes are observed to possess much higher strength values compared with the crosslinked samples indicating their strong resistance toward crack growth. The relatively better tear property of a thermoplastic material can be explained on the basis of their two phase structure. Dispersed phases tend to interfere with the crack propagation step, redistributing energy that would otherwise cause the cracks to reach catastrophic size. The presence of hard segment domains increases energy dissipation by hysteresis and other viscoelastic mechanism. Growing cracks can be deflected and bifurcated at phase boundaries.

Moreover TPU's are relatively more resistant to tear propagation due to strong intermolecular attraction forces as compared to thermoset urethanes where crosslinks are the main tie points for tear prevention.

2.3.3 Tension set

The tension set of the prepared polyurethanes was measured according to British Standard BS 903 Part A5 at room temperature. Specimens used were of dumbell type 2 and marked with 20 mm bench marks using a very fine ink pen. The specimens were elongated to 300% strain on a J J tensile testing machine at a speed of 100 mm/minute. After the specimens were held for 10 minutes, they were relaxed at the same speed and left to recover for another 10 minutes before the tension set was calculated. The following formula was used:

$$\text{Tension set } (\%) = 100 \times \frac{\ell_1 - \ell_o}{\ell_s - \ell_o}$$

where ℓ_o = original unstrained reference length

ℓ_s = strained reference length

ℓ_1 = reference length after recovery

Tables2.3.9 and 2.3.10 show the tension set of the respective crosslinked and thermoplastic polyurethanes which were measured after 10 minutes and 1 hour recovery time.

As expected the crosslinked polyurethanes showed lower set due to their high elasticity. In contrast phase segregated urethane samples (opaque) exhibited considerably higher set values presumably because of their rigid structure which causes them to act more like a plastic.

TABLE 2.3.1: General Mechanical Properties of Crosslinked Polyurethanes based on CAPA 220/H_{12}MDI Prepolymer System

Sample No	Chain Extenders Used	100% Modulus MPa	300% Modulus MPa	UTS MPa	Elongation at break %	Hardness (IRHD)	Compression set (%)
C1	1,4-BD + TMP at 1/1	2.9	6.6	26	390	60-61	18.5
C2	1,3-BD + TMP at 1/1	1.9	4.5	18	400	59	7.5
C3	1,6-HD + TMP at 1/1	2.0	4.7	15	400	59	10.5
C4	1,4-CHDM + TMP at 1/1	3.1	8.1	24	350	61	14
C5	1,3-CHD + TMP at 1/1	2.6	5.0	16	400	62	9.5
C6	1,4-BD + TMP at 1.5/0.5	2.3	10.8	23.5	390	64	29
C7	1,4-BD + TMP AT 0.5/1.5	2.2	-	11	210	62	16
C8	1,4-BD + TMP at 1/0.5	1.7	4.57	16.5	441	59-60	37
C9	1,4-BD + TMP at 1.5/1.0	1.9	11.0	13	313	63-64	11
C10	1,4-BD + TMP at 1.5/1.5	2.9	-	11.2	224	69-70	6
C11	1,4-BD + TMP at 2/1	2.9	-	17.5	293	68-69	15.5
C13	1,4-BD + 1,4-CHD + TMP at 1/0.9/0.1	1.0	5.68	28.3	441	63-64	41

Note: All these materials exhibited good transparency i.e. greater than 80%

TABLE 2.3.2: Comparison of Polyurethane Mechanical Properties based on TMP and CAPA 305 Triols

Sample No Experiment No.	Chain Extenders Used	100% Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Hardness (IRHD)
C1	1,4-BD + TMP at 1/1	2.9	26	390	60-61
C16	1,4-BD + CAPA 30£ at 1/1	2.5	13	550	60-61
C2	1,3-BD + TMP at 1/1	1.9	18	400	59
C18	1,3-BD + CAPA 305 at 1/1	2.1	18	410	55-56
C3	1,6-HD + TMP at 1/1	2.0	15	400	59
C17	1,6-HD + CAPA 305 at 1/1	1.72	12	500	55-56
C4	1,4-CHDM + TMP at 1/1	3.10	24.0	350	61
C15	1,4-CHDM + CAPA 305 at 1/1	2.0	19	425	57
C5	1,3-CHD + TMP at 1/1	2.6	16.0	400	62
C19	1,3-CHD + CAPA 305 at 1/1	2.0	19.0	400	57
C20	TMP + CAPA 305 at 1/1	2.4	10.0	325	58
C21	CAPA 305	1.9	6.0	290	59-60
C22	TMP	3.0	11.0	275	62-63

TABLE 2.3.3: Hardness Comparison of IPDI and H_{12}MDI Based Polyurethanes

Sample No		Free NCO in Prepolymer (%)	Hardness (IRHD)
	Capa 220:IPDI (1,4-Cyclohexane dimethanol + TMP)		
C24	1:3:2 : (1.1 + 1.1)	6.6	31-32
C25	1:4 : (1.5 + 1.5)	8.71	56
C26	1:5 : (2 + 2)	10.79	75-77
C4	Capa 220:H_{12}MDI:(1,4-Cyclohexane dimethanol + TMP)		
	1:3 : (1 + 1)	6.0	58-59
C10	Capa 220:H_{12}MDI:(1,4-BD + TMP)		
	1:4 : (1.5 + 1.5)	8.36	69-71

TABLE 2.3.4: General Mechanical Properties of Thermoplastic Polyurethanes

Sample No	Chain Extenders Used	100% Modulus (MPa)	300% Modulus (MPa)	UTS (MPa)	Elongation at break %	Hardness (IRHD)	Light Transmittance (%)
T1	1,4-CHDM + 1,4-BD at 1/1	2.0	6.6	30	500	65-66	>80
T2	1,4-BD + 1,6-HD at 1/1	2.8	6.9	32	575	65-66	>80
T3		2.0	5.7	31	505	65-66	>80
T4	1,4-BD + 1,3-CHD at 1/1	2.8	6.9	28	575	72	50
T6		1.9	4.6	21	505	62	68
T7		2.2	5.8	23	480	65	70
T8		3.2	6.7	18	505	62	78
T9	1,4-CHDM + 1,3-CHD at 1/1	3.6	9.5	38	550	76	0
T10	1,4-CHDM + 1,6-HD at 1/1	5.45	11.26	26	650	>98	0
T12	1,4-CHDM + 1,3-BD at 1/1	6.5	10	23	650	>98	0
T16		1.14	1.7	6.8	487	50	0
T17		1.6	3.2	9.5	658	52	30

TABLE 2.3.5: General Mechanical Properties of Hard Thermoplastic Polyurethanes (Hardness value = above 90 IHRD)

Sample No*	100% Modulus (MPa)	300% Modulus (MPa)	UTS (MPa)	Elongation at break %	Light Transmittance (%)
T20	4.0	10.0	21.7	510	30
T21	10.4	26.7	39.0	372	30
T22	8.3	16.6	28.0	395	75
T23	3.2	6.5	13.0	475	60
T24	6.0	15	27	441	60
T25	8.8	27	42.0	460	75
T26	4.32	9.25	9.25	300	0
T27	3.57	6.8	15.0	482	70
T28	4.75	12.0	25.0	408	72

* See page 68 for sample compositions

TABLE 2.3.6: MFI Values of Injection Moulded Thermoplastic Polyurethanes Based on CAPA 220: Desmodur W: Chain Extenders at 1/3/2 Ratio

Sample No. (Expt. No)	Chain Extenders Used	MFI gms/10 mins at 150°C	MFI gms/10 mins at 190°C
T1	1,4-CHDM + 1,4-BD at 1/1	0.4	2.0 to 2.75
T4	1,4-BD + 1,3-CHD at 1/1	2.8	10.58 to 11.4
T2	1,4-BD + 1,6-HD at 1/1	0.43	1.85 to 2.27
T10	1,4-CHDM + 1,6-HD at 1/1	0.55	2.6 to 3.0
T11	1,3-BD + 1,6-HD at 1/1	3.3	11.0 to 11.68
T9	1,4-CHDM + 1,3-CHD at 1/1	0.04	0.3 to 0.46
T12	1,4-CHDM + 1,3-BD at 1/1	0.061	1 to 2

TABLE 2.3.7 Transparency and Hardness Property Changes of Some Opaque Thermoplastic Polyurethane Before and After Heat Treatment at 100°C for 3 Hours

Sample No. (Expt. NO)	Chain Extenders Used	Untreated		Treated	
		Hardness (IRHD)	Light transmission (%)	Hardness (IRHD)	Light transmission (%)
T10	1,4-CHDM + 1,6-HD	>98	0	52	>65
T9	1,4-CHDM + 1,3-CHD	76	30-40	56	>70
T12	1,4-CHDM + 1,3-BD	>98	0	50	>70

TABLE 2.3.8: Tear Strength of Crosslinked and Thermoplastic Polyurethanes

** Sample No	Tear Strength of Crosslinked Materials. Newtons (N) per 2 mm standard specimen*	** Sample No	Tear Strength of Thermoplastic Materials. Newtons (N) per 2 mm standard specimen*
C1	70	T1	160
C2	68	T2	148
C3	63	T3	152
C4	62	T4	128
C5	60	T6	106
C6	92	T7	131
C7	54	T8	86
C8	83	T9	129
C9	85	T10	138
C10	78	T12	142
C11	95	T16	30
C13	93	T17	42

* 1 Newton tear strength per standard specimen = 0.5 kN/m

** See page 66 for sample compositions

TABLE 2.3.9: Tension Set of Crosslinked Polyurethanes

Sample No.*	Tension set (%) after 10 minutes recovery	Tension set (%) after 1 hour recovery
C1	5	2.0
C2	5	2.0
C3	6	2.5
C4	6.25	2.0
C5	6.25	2.0
C6	10.0	6.25
C7	5	2.0
C8	-	-
C9	8	4.5
C10	-	-
C11	-	-
C13	12.5	6.25
C15	12.5	10.0
C16	12.5	10.0
C17	13.75	10.0
C18	12.5	10.0
C19	13.75	8.75
C20	2.5	0
C21	-	-
C22	-	-

* See page 66 for sample compositions

TABLE 2.3.10: Tension Set of Thermoplastic Polyurethanes

Sample No*	Tension set (%) after 10 minutes recovery	Tension set (%) after 1 hour recovery
T1	12.5	5
T2	15	5
T3	15	5
T4	17.5	8.75
T6	16.25	6.25
T7	16.25	6.25
T8	12.5	5
T9	30	10.5
T10	43	22
T12	52	30
T16	-	-
T17	-	-

* See page 68 for sample compositions

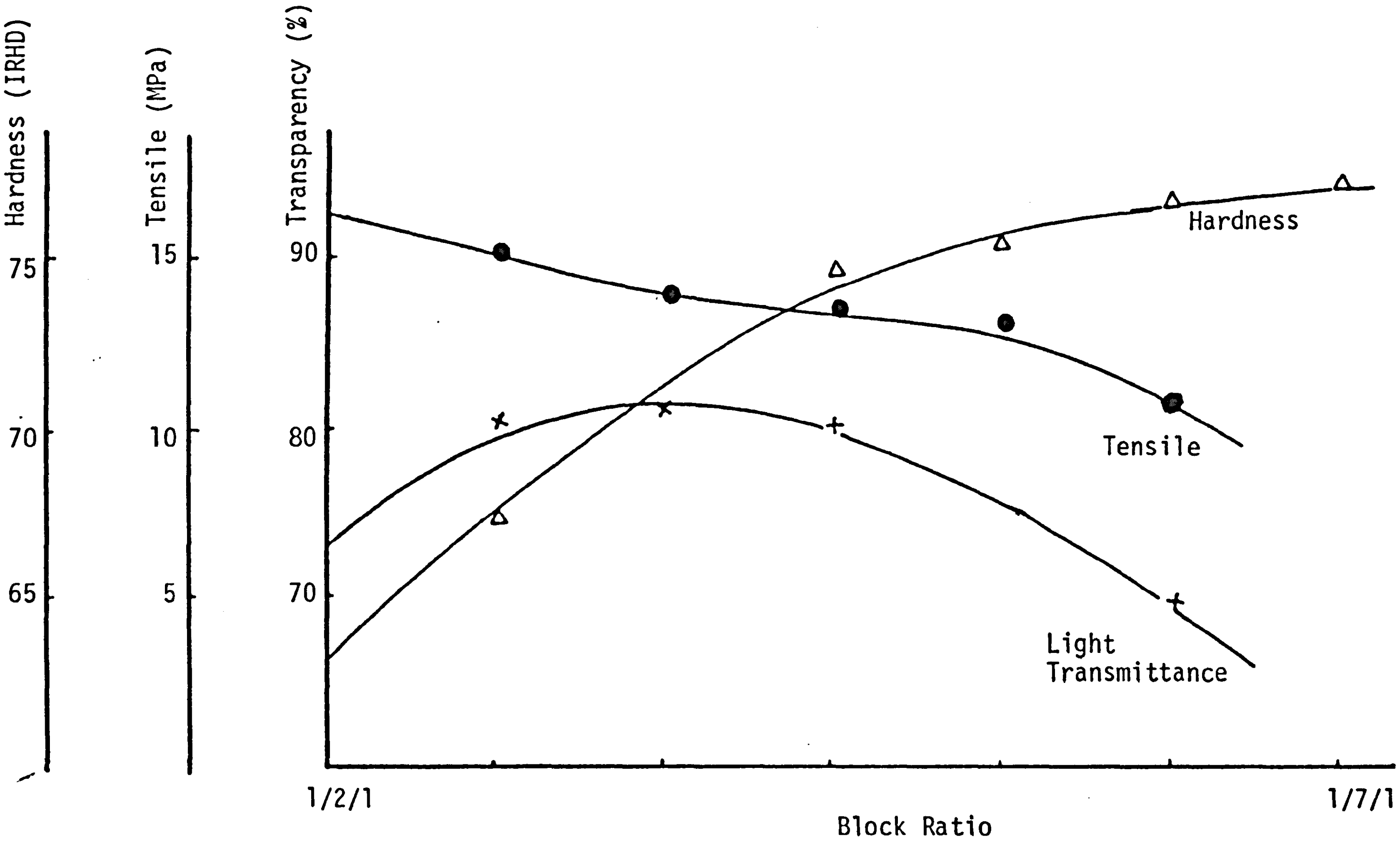

FIGURE 2.3.1(a): Effect of Block Ratios on the Properties of Typical Thermoset Polyurethanes Based on Capa 220/H_{12}MDI Chain Extenders - 1,4-BD + TMP at 1/1 Ratio

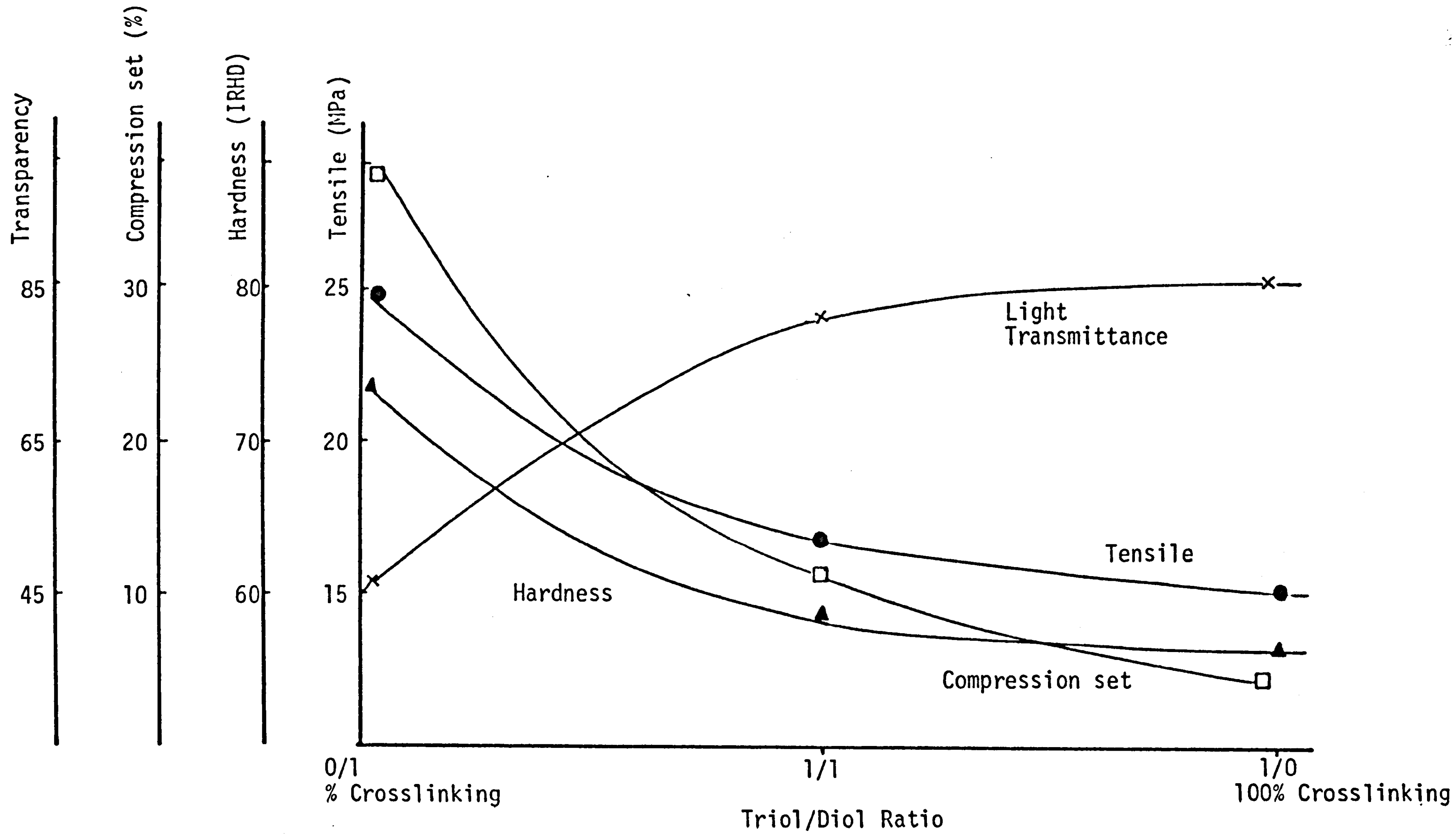

FIGURE 2.3.1(b): Effect of Crosslinking on the Properties of a Typical Thermoset Polyurethane

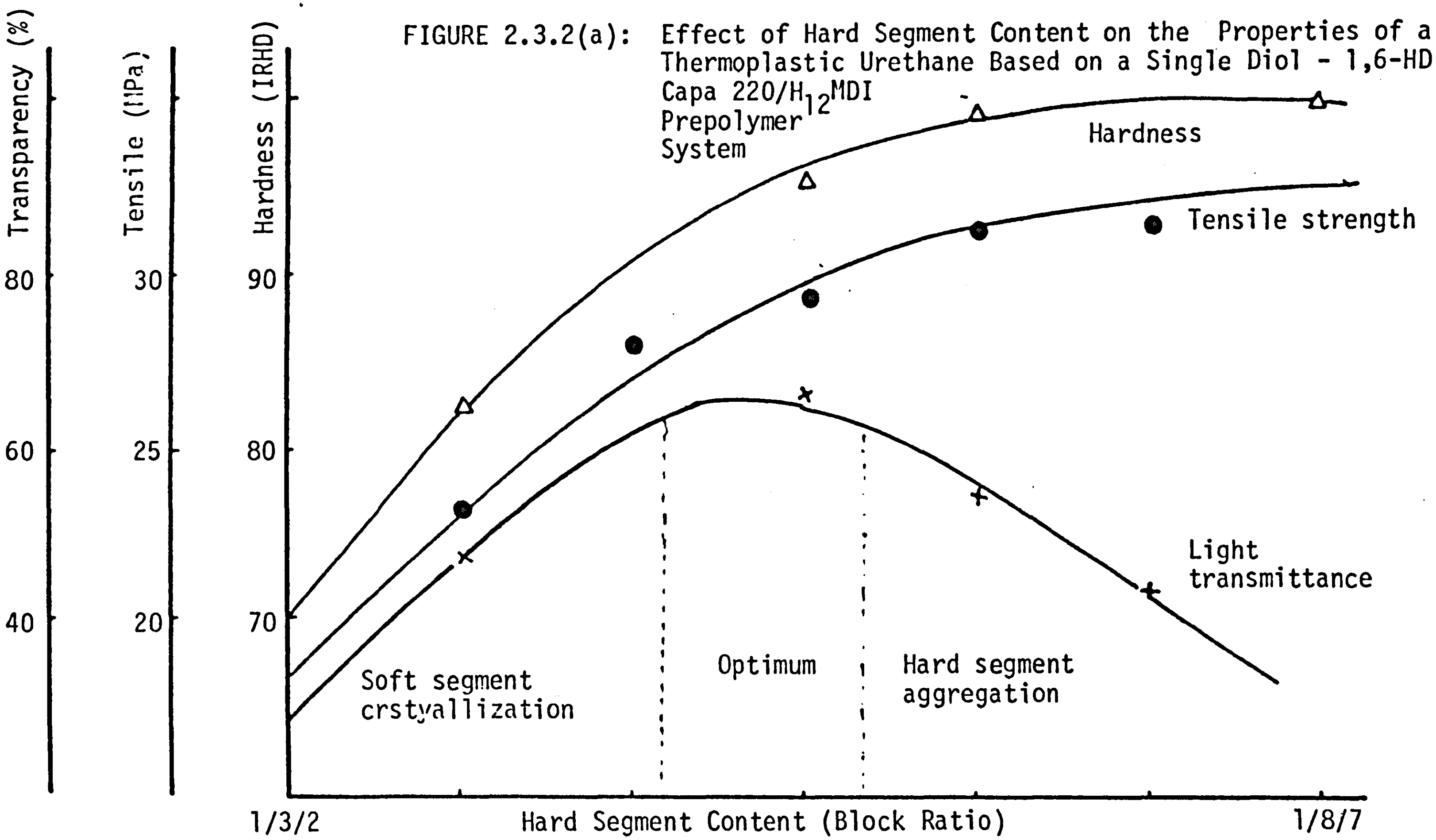

FIGURE 2.3.2(a): Effect of Hard Segment Content on the Properties of a Thermoplastic Urethane Based on a Single Diol - 1,6-HD and Capa 220/H_{12}MDI Prepolymer System

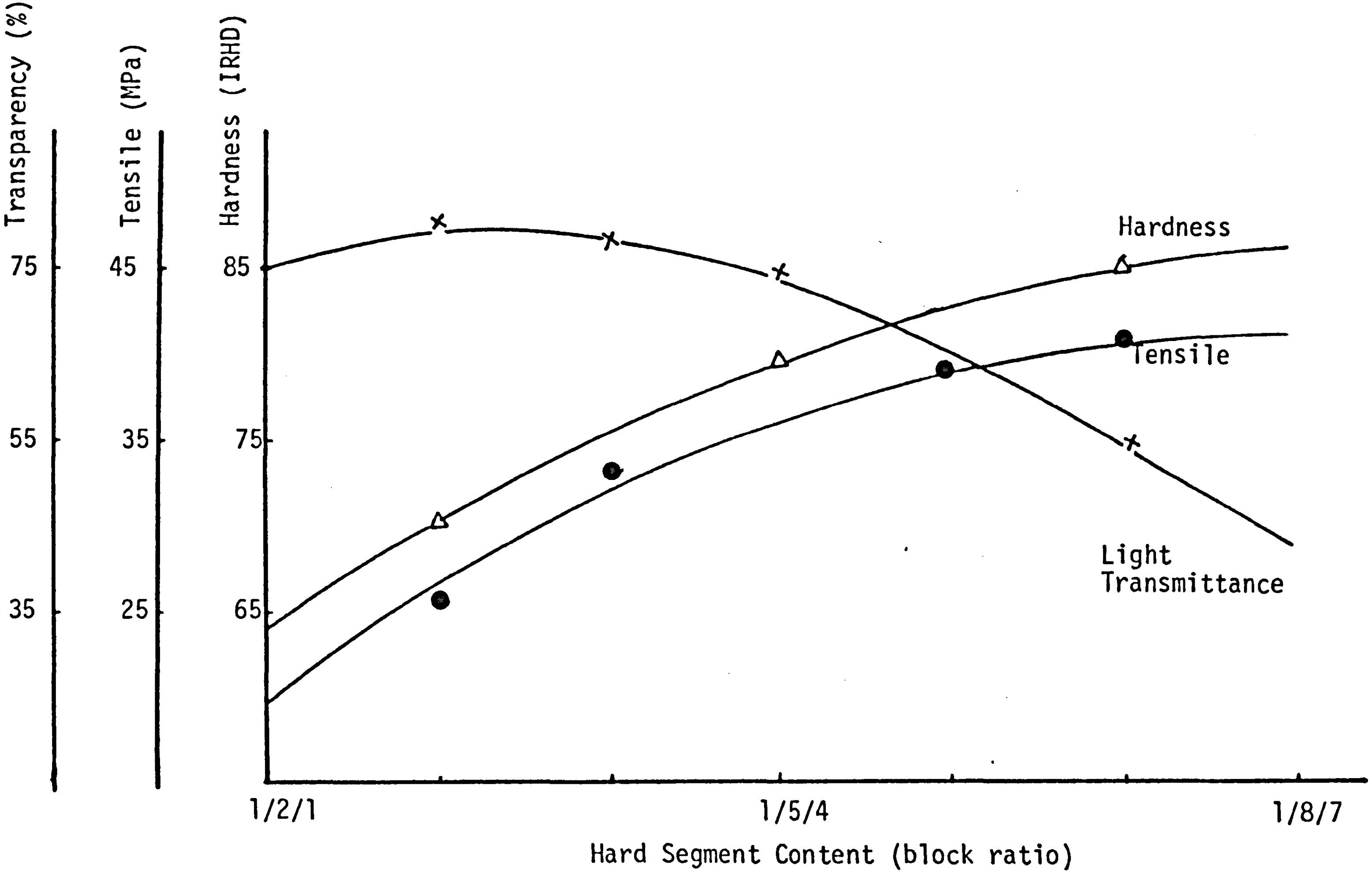

FIGURE 2.3.2(b): Effect of Hard Segments on the Properties of a Thermoplastic Urethane Based on Mixed Diols - (1,4-BD + 1,4- CHDM)

2.4 AGEING PROPERTIES

The following section deals with different types of ageing studies carried out on the prepared polyurethanes and their measurement of their subsequent degradation rates.

Polyurethanes are subject to degradation under various environmental conditions. Among the different types of degradation thermal (non-oxidative), thermo-oxidative, hydrolysis and radiation degradation (especially UV light) are the most important. The degradation of polyurethanes is quite complex due to the fact that they may contain in addition to urethane and urea groups other functional groups such as ether, ester, amide, allophanate, biuret etc. In the present research programme the following ageing properties were studied.

2.4.1 Storage properties of thermoset polyurethanes

Some selected crosslinked polyurethane samples (Table 2.4.1) were aged at -25°C for not less than 16 weeks to accelerate any possible crystallization and to test transparency retention. Apparent density of each polymer was measured before and after ageing to observe any change in density due to crystallization. Then density was measured using Archimedes principle by taking the weight of each specimen in air and water at 25°C. The formula $D = A/A-B$ was used where 'A' is the weight of specimen in air and 'B' is its weight in water. Table 2.4.1 shows the values of density measured. Aged samples were also tested for transparency by visual spectrometer.

No appreciable difference in transmittance values of aged and unaged specimens was noticed.

Similarly some selected crosslinked samples were also aged in the Wallace Agetester at 72^{o}C for 4 weeks in dry air and the mechanical properties measured. Table 2.4.2 shows the property retention of the aged samples. It should be pointed out that the specimen did not turn yellow (which hydrolysed PU shows) and remained colourless and transparent after the test period.

2.4.2 Thermo-oxidative degradation (stress relaxation technique) of crosslinked PU

It has been found that in thermooxidative degradation the urethane linkages are resistant to oxygen attack and degradation starts in polyol segments (66). It is notable that in non-oxidative thermal degradation cleavage of the urethane linkage takes place yielding either the starting components or forming amines (urea), olefins and carbon dioxide depending upon the nature of substituents on the urethane linkage. Factors influencing thermo-oxidative degradation include the effects of the structure of polyols and isocyanates, the effects of urethane and urea groups, crosslink density, and the urethane catalysts.

Polyether polyols are more susceptible to degradation than polyesters and this reaction proceeds by a free-radical chain process, forming hydroperoxides at the carbon atoms adjacent to the ether linkage (67,68).

The effect of isocyanate structure is less significant in the case of polyether urethanes compared to polyester urethanes as polyether segments oxidize prior to the urethane groups. In the case of the polyester urethanes, the rate of thermooxidation as a function of the diisocyanate decreases in the following order (68,69):

hexamethylene diisocyanate > 4,4'-diphenylmethane diisocyanate > tolylene diisocyanate > 4,4'diphenylether diisocyanate > 1,5-Napthalene diisocyanate.

The higher aromaticity of these isocyanates results in increased resistance to thermooxidation. Reegan and Frisch (70) observed an increase in resistance to thermooxidation for polyether films as the crosslink density increased. In polyester urethanes (71) the resistance to thermal as well as thermooxidative degradation increased with higher polyester ratios.

Tarakanov observed that the addition of urethane or urea compounds to polyether glycols retarded thermooxidation (72). This was thought to be due to the hydroperoxides, forming a hydrogen bond with these compounds thus reducing the amount of free radicals being formed.

The observation that no marked property degradation is caused by oxidation of aromatic urethanes is perhaps due to the about equal probability of chain scission and radical recombination processes (73). Moreover, the increase in modulus may be explained by an increase in crosslinking due to addition of structural units containing active hydrogen to form a quinoid system.

Contrary to the general belief that aliphatic urethanes are stable to oxidation, these materials are quite readily attacked by oxygen. The pronounced sensitivity of aliphatic urethanes to oxidative attack is very aptly demonstrated by stress relaxation measurements on a 3-dimensional urethane network prepared from polyester and HMDI. Both continuous and intermittent relaxation data at $130^{\circ}C$ in air show a fast decrease of modulus with time while stress in nitrogen stays nearly constant. This behaviour provides strong evidence for oxidative, irreversible network cleavage (74).

Brokenbrow and co-workers observed (75) that polymers made with the aliphatic ω - ω'-xylylene diisocyanate (XDI) or HMDI lost 60-70% of their original tensile strength upon ageing for 23 days at $80^{\circ}C$ in air while urethanes derived from aromatic diisocyanates (TDI and MDI) gained 30-40% tensile strength under the same conditions.

In the present work thermooxidation of the prepared crosslinked polyurethane samples was studied using a tension stress relaxation technique. A Wallace extension stress relaxometer was employed which consists of a thermostatically controlled cast aluminium block heating unit having a series of circular chambers. Each chamber may be used in conjunction with a single stress relaxation unit. Samples, in the form of strips 4 mm wide, were die cut from cast sheets between 1-2 mm thick.

A sample held at an elongation giving 100% stress on the chart was connected to one end of a metal beam and located in a heating chamber. The beam is pivoted at the other extreme, and the downward movement applied by the sample under stress is balanced by a spring arranged centrally above the beam. Any change in stress of the sample is automatically compensated by a change in the extension of the spring. A marker pencil attached directly to the spring is placed in contact with a drum chart rotating at a constant rate of one revolution every 12 hours. The stress relaxometer operated in the continuous mode at a constant temperature between 70-125^{o}C with air flowing through the chamber at a rate of 3 cu.ft/hour. Stress relaxation was recorded graphically on the Wallace stress relaxometer as a percentage decrease in force with time. Figures 2.4.1 to 2.4.7 show a comparison of stress relaxation due to thermooxidation of different chain extension agents and urethane concentration at fixed temperatures over the range 70^{o}C-125^{o}C. Figures 2.4.1 and 2.4.3 show the relaxation behaviour of C1-C5 polyurethanes in air which were found to be fairly resistant to thermooxidation and chain scission up to 100^{o}C. The 1,4-BD based urethanes were relatively more affected than 1,3-BD and 1,6-HD derived materials and lost their original stress by 15-18% in 20 hours after which no further relaxation occurred. 1,6-hexane diol extended materials remained unaffected and did not show any relaxation at all. Most interestingly the unsymmetric diol contained urethanes exhibited negative stress relaxation and in fact gained modulus presumably due to additional crosslinking which could not take place initially due to steric hindrance effect. This phenomena can perhaps be attributed to the tendency of these diols to realign their structure during heating under stress. A similar negative stress relaxation effect was observed by Lou (76) in diamine extended polyurethanes. He attributed this to volume shrinkage which resulted from the contraction of the hard segments brought about at the relatively high test temperature by conversion of branching biuret linkages to linear urea linkages in the presence of free amine. However at higher test temperature of 125°C all the urethanes showed considerable initial relaxation before their stresses were stabilised.

Figure 2.4.5 clearly indicates that at 100°C the sample C7 owing to its high crosslink density when compared to sample C6, is relatively more stable at high temperatures and resists thermo-oxidative degradation.

Similarly Figures 2.4.6 and 2.4.7 suggest that the stability of polyurethanes at 100°C toward thermooxidation can be increased by increasing hard segment content and/or chemical crosslinking.

2.4.3 Hydrolytic stability

The hydrolysis of polyester PUs is considered to be the chemical decomposition of polymer by water as shown below:

$$\sim\!\sim \underline{\underline{\mathrm{OCO}}}(\mathrm{CH_2})_4\ \underline{\underline{\mathrm{CO}}} \,\vdots\, \mathrm{O{-}(CH_2)_2O{-}\ CO\ {-}NH{-}R{-}NH{-}\ CO\ {-}O} \sim\!\sim$$

$$+\ \mathrm{H_2O}$$

$$\mathrm{OCO(CH_2)_4COOH + HO{-}\ (CH_2)_2{-}}\underline{\mathrm{O{-}CO{-}\ NH}}\mathrm{{-}R{-}NH{-}CO{-}\ O}$$

In this reaction the water reacts with a carboxylic ester link (doubly underlined) in a poly(ester-urethane) chain. The reaction breaks the polymer chain at the point of attack producing two shorter chains. One of these chains ends in a hydroxyl group (-OH) and the other in a carboxyl group ($-CO_2H$) which is acidic. This acidic carboxyl group speeds up the further hydrolysis of the polyester segments in the poly(ester-urethane) and the degradation becomes autocatalytic (77). The urethane linkage (or carbamate linkage) single underlined in the above equation, is an ester of (a substituted) carbamic acid. This urethane linkage can also be hydrolysed, but less readily than the carboxylic ester linkages. Hydrolysis of this urethane linkage in polyurethane chains produces two shorter new chains, one ending in a hydroxyl group (-OH) and the other in an amino group ($-NH_2$). But unless a poly (ester-urethane) elastomer contains special sterically hindered carboxylic ester linkages in its chain the dominant reaction in its hydrolysis in normal service is cleavage of the carboxylic ester groups as shown above (78).

In the present work the hydrolytic stability of prepared transparent polyurethanes were studied to investigate the extent of deterioration caused by hydrolysis in different chain extended materials. Although the major factor that promotes hydrolytic degradation is generally cited as being due to polyols* the aim of the present work is to determine the effect of various chain extender and crosslinking on hydrolytic resistance holding all other reactant variables forming soft segments, constant. As there is

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* Most polyols contain free acid, except polycaprolactones.

no standard procedure available to determine the hydrolytic stability of urethanes, a non-standard method, used by Schollenberger (78), was adopted to test the prepared polyurethanes.

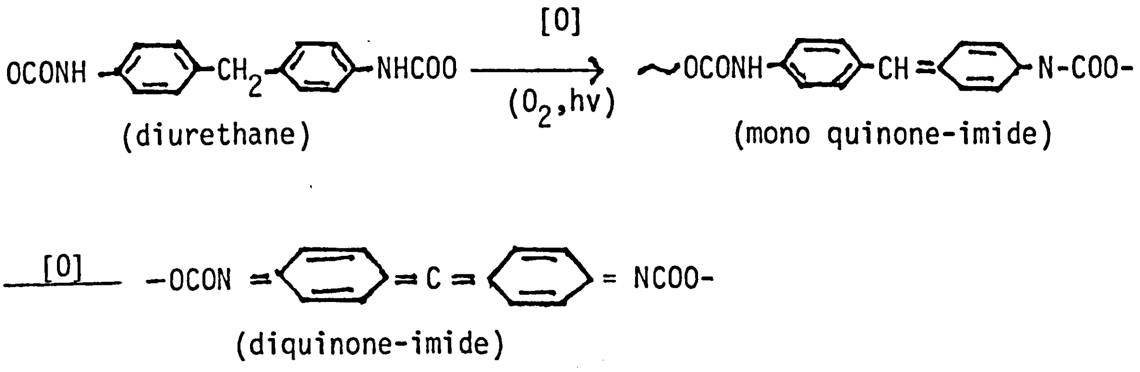
The test samples (Tables 2.4.3 and 2.4.4) were immersed in water for two separate periods of time at constant temperature of 70°C for respectively 8 days and 14 days before they were removed and dried in a drying cabinet at 50°C overnight (15 hours). All the samples at the end of the test period turned from water-like transparent to yellow transparent. Table 2.4.3 shows the percentage retention of the original properties. Samples T1 and T3 which are thermoplastic linear polymers exhibited poor resistance toward hydrolytic attack. On the contrary crosslinked materials showed much better performance and specifically samples C4 and C5 which were derived from cycloaliphatic diols remains unaffected.

Another series of crosslinked polyurethanes extended with Capa 305 triol was also tested for hydrolytic stability and compared with their counterpart TMP based materials. Results are shown in Table 2.4.4 in the form of percent property retention. These specimens were aged for a period of 2 weeks in water at 70°C. The hydrolysed sample turned yellow after one week though retained its transparency.

2.4.4 UV stability

Polymers are usually susceptible to degradation due to the ultraviolet portion of sunlight from 290 to 400 nm which reaches the surface of the earth and constitutes about 5% of the total radiation from the sun (79). In ultraviolet degradation (80) the initiation reaction is due to the absorption of incident radiation of wavelength around 290 nm. Shorter wavelength radiation has higher energy available for degradation of polymers. The photolytic and chemical processes after initiation lead to colouration and loss in mechanical properties of the polymers. UV initiated degradation proceeds at all temperatures and is a function of the amount of radiation.

The effect of ultraviolet radiation (UV) on polyurethane has been studied by several workers. Schollenberger (81) et al reported substantial differences in UV stability related to the diurethane bridge structures of different diisocyanate based polyurethanes. They showed that those polyurethanes having antiquinoid (e.g. m-phenyldiisocyanate based) or non-quinoid (e.g. H_{12}MDI based) diurethane bridge structure considerably out-performed the polyurethanes having proquinoid diurethane bridge structure e.g. the one derived from MDI. Schollenberger and co-workers interpreted this result to support their view that the UV activated degradation of polyurethanes involves the tendency of the polymer chain diurethane linkages to autoxidize to the quinone imide linkages as shown below:



Additional supporting evidence for the formation of quinoid structure as a result of UV initiated degradation of aromatic isocyanate base urethanes can also be found in the studies by Adams and Anderson (82). In contrast to the aromatic isocyanates, aliphatic and cycloaliphatic isocyanates impart greater stability toward UV radiation as compared to aromatic isocyanates (66,70)

Nine thermoset transparent polyurethane samples (see Table 2.4.5) were tested for their resistance towards UV attack. These samples were aged in Climatest Exposure equipment at PERME, Waltham Abbey for a period of 500 hours at 40°C and in the presence of 40-50% humidity. The UV source used was a combination fluorescent sunlamp and black lamp. All the specimens were tested before and after UV exposure for their 100% modulus, tensile strength, hardness and light transmission properties. Table 2.4.5 shows percentage property retention on UV exposure where transparency, measured by visible spectroscopy of the specimens, which were previously treated with the oil of the same refractive index to eliminate any surface dirt or contamination. The structure changes in these polyurethanes as a result of UV radiation attack was studied by Du Pont 900 differential thermal analyser and polymer laboratory dynamic mechanical thermal analyser. Figures 2.4.8 to 2.4.11 show variation in thermal transitions of UV treated and untreated polyurethanes.

In the present work all the specimens which were subjected to UV exposure based on saturated MDI (Desmodur W) therefore had a non-quinoid oxidation tendency and hence according to the above mentioned theory no significant degradation should occur. However the purpose of the present programme was to study the effect of different hard segment structures and crosslinking on UV resistance and discolouration while keeping the backbone soft segment constant. As indicated in Table 2.4.5 the hardness and 100% modulus of polyurethane samples increases and tensile strength decreases on UV exposure. It was obvious from these results that the hard segment structure is responsible for the changes in morphology and light transmission property of UV treated urethanes. To further investigate these effects, differential thermal analysis (DTA) and dynamic mechanical thermal analysis (DMTA) were carried out. Figure 2.4.8 shows the thermogram of untreated and UV treated thermoset urethanes based on cycloaliphate diols where 1,3-cyclohexane diol (1,3-CHD) being unsymmetrical exhibited better resistance than symmetrical 1,4-cyclohexane dimethanol (1,4-CHDM) derived polymer. The poor tensile strength retention of 1,4-CHDM extended urethane is considered to be due to the methanol groups attached to the diol which has low cohesive energy and is readily affected by UV energy vibrations resulting in urethane cleavage (disintegration). A sharp endotherm around 40°C in Figure 2.4.8 for the UV treated 1,4-CHDM sample resembles soft segment transition (Figure 2.2.8) indicating a reversion process. The isolated hard segment in such a case tends to crystallise and aggregate with other intact hard segments of the polymer chain giving rise to phase separation and consequently 100% modulus and translucency (or opacity) increases. Similar effects can be observed in Figures 2.4.9 and 2.4.10 for the same UV treated and untreated sample C4 where two distinct damping peaks indicate phase separation. Figure 2.4.11 shows the visible spectra of these untreated and UV treated polyurethanes. The reversion or hard/soft segment disintegration was also observed with the long chain diol based sample e.g. 1,6-hexane diol. It has also been noticed that UV radiation enhances phase separation in soft segment materials with low block ratio and urethane concentration (Figures 2.4.12 and 2.4.13). Thus it is concluded that the structure of diol and stoichiometry markedly influence phase separation and crystallization and consequently optical clarity when they are subjected to vibrational UV energy.

2.4.5 Gamma radiation effects

It has been found that radiation damage to solids is the result of displacement of atoms caused by energy absorption from incident particles and electromagnetic radiations. These particles and rays can cause several phenomena, one of which, ionization, is the predominant mechanism which changes the properties of elastomers and other organic solids. This is due to the type of internal bond and structure of these materials.

Ionization is known to bring about changes which are chemical ones: ions or free radicals are formed within the polymer and the materials may be embrittled, polymerized, crosslinked, discoloured, dehydrogenated, decomposed and/or cracked. As a consequence organic materials are more severely changed or degraded than other solids. Upgrading changes can also sometimes occur in organic polymers in instances where the radiation dose is controlled, but more often than not, especially on long exposures, these materials are degraded. The degree of change depends upon a number of factors, such as incident rate of radiation, length of irradiation time, energy of the radiation, chemical composition of the materials, environment (stress, temperature, pressure, atmosphere, fluid, etc), initial state (often associated with the history of the material), and type of radiation.

In the present work gamma radiation from a cobalt-60 isotope source was used at the rate of 1 mega-Roentgen (M-rad) per hour. The Roentgen unit is equal to the gamma ray ionization producing one electrostatic unit of charge in one cubic centimetre of air and is equivalent to the absorption of 83.8 joules of energy absorbed per gram of air. Dose rate, the amount of energy absorbed in a material per unit time, is expressed as Roentgens per hour (rad/hr).

In the present work three urethanes viz T18, C5 and C6, which varied in their crosslink densities, were subjected to gamma radiation for 5, 10, 15 and 20 M-rad doses. The effect of crosslinking in these samples on the structure changes due to irradiation was studied by the continuous stress relaxation technique and compared with the untreated specimen. This test technique was found appropriate for the measurement of any polymer structure modification (such as extra crosslinking formation) or degradation (due to chain scission) as a result of the urethane-gamma radiation interaction. The crosslinking in the urethanes studied was introduced by the use of a TMP triol which was blended with 1,4-BD at different proportions to control the extent of crosslinking in a fixed block ratio polymer. For example all the specimens tested were based on a 1/3/2 block ratio with varying TMP/1,4-BD ratio of 0/1 (no crosslinking), 0.33/1 (intermediate crosslinking) and 1/1 (high crosslinking) for the representative samples T18, C6 and C5. The results of stress relaxation are shown in Figures 2.4.16 to 2.4.18 where the thermoplastic material (T18) demonstrated an improved stress relaxation property i.e. increased residual stress with increasing gamma radiation doses. In contrast, the sample C5 having the highest crosslinking in this series was adversely affected by radiation and chain scission progressed with increased doses. However sample C6 having the crosslink density between that of T18 and C5 samples initially showed increased relaxation (decreased residual stress) with radiation doses up to 15 M-rad, after which increase in stress was observed presumably due to the reformation of broken polymer chains.

TABLE 2.4.1: Densities of Selected Thermoset Polyurethanes Before and After Ageing at -25°C for 4 Months

Sample No.	Capa 220:H_{12}MDI:Chain Extender	Density Before Ageing (gm/cc)	Density After Ageing at -25°C for 4 Months (gm/cc)
C1	1:3:2(1,4-BD+TMP at 1/1 ratio)	1.1211	1.1236
C2	1:3:2)1,3-BD+TMP at 1/1 ratio)	1.1155	1.1124
C3	1:3:2(1,6-HD+TMP at 1/1 ratio)	1.1142	1.1135
C6	1:3:2(1,4-BD+TMP at 1.5/0.5 ratio)	1.1190	1.1183
C7	1:3:2(1,4-BD+TMP at 0.5/1.5 ratio)	1.1180	1.1178
C8	1:2.5:1.5(1,d-BD+TMP at 1/0.5 ratio)	1.1157	1.1139
T3	1:3:2(1,4-BD+1,3-BD at 1/1 ratio)	1.1173	1.1130
C9	1:3.5:2.5(1,4-BD+TMP at 1.5/1.0 ratio)	1.1221	1.227
C10	1:4:3(1,4-BD+TMP at 1.5/1.5 ratio)	1.1237	1.1214
C11	1:4:3(1,4-BD+TMP at 2/1 ratio)	1.1256	1.1234

TABLE 2.4.2: Property Retention of Polyurethanes on Ageing in Dry Air at 72°C for 4 Weeks

CAPA 220: H_{12}MDI: Chain Extenders at 1/3/2 block ratio

Sample No	Chain Extenders Used	Property Retention (%)			
		100% Modulus	Tensile Strength	Elongation	Hardness
C1	1,4-BD+TMP at 1/1	86	57	92	101
C16	1,4-BD+CAPA 305 at 1/1	72	119	84	91
C2	1,3-BD+TMP at 1/1	142	111	100	100
C18	1,3-BD+CAPA305 at 1/1	95	100	97	101
C3	1,6-HD+TMP at 1/1	115	153	93	100
C17	1,6-HD+CAPA305 at 1/1	127	79	85	100
C4	1,4-CHDM+TMP at 1/1	93	129	104	100
C15	1,4-CHDM+CAPA305 at 1/1	112	100	91	100
C5	1,3-CHD+TMP at 1/1	130	106	87	104
C19	1,3-CHD+CAPA305 at 1/1	115	97	87	105
C20	TMP + CAPA305 at 1/1	95	110	92	101
C21	CAPA 305	136	133	98	101
C22	TMP	123	136	109	101

TABLE 2.4.3: Property Retention of Polyurethanes on Ageing in Water at 70°C for 8 Days

Sample No *	Property retained on Hydrolysis (%)				
	100% Modulus	300% Modulus	UTS	Elongation at break %	Hardness
C1	95	-	90	108	100
C2	95	-	80	100	90
C3	100	60	83	128	93
C4	122	-	91	100	104
C5	120	-	100	100	100
C6	68	60	75	100	85
C7	60	46	75	101	83
C8	50	29	57	111	78
C9	70	57	67	101	87
C10	90	-	98	100	97
T1	44	28	42	101	78
T3	58	54	28	**	82

* See page 66 for sample compositions

** Sample failed

TABLE 2.4.4: Property Retention of Polyurethanes (Thermoset) on Ageing in Water at 70°C for 2 Weeks

CAPA 220: H_{12}MDI: Chain Extenders at 1/3/2 block ratio

Sample No (Expt. No)	Chain Extenders Used	Property Retention (%)			
		100% Modulus	Tensile Strength	Elongation	Hardness
C1	1,4-BD + TMP at 1/1	86	70	96	103
C16	1,4-BD + CAPA305 at 1/1	104	130	100	95
C2	1,3-BD + TMP at 1/1	136	105	100	100
C18	1,3-BD + CAPA305 at 1/1	95	102	97	100
C3	1,6-HD + TMP at 1/1	125	126	97	100
C17	1,6-HD + CAPA305 at 1/1	88	87	85	98
C4	1,4-CHDM + TMP at 1/1	83	95	107	100
C15	1,4-CHDM+CAPA 305 at 1/1	100	102	94	100
C5	1,3-CHD + TMP at 1/1	134	125	88	101
C19	1,3-CHD+CAPA 305 at 1/1	125	105	87	101
C20	TMP + CAPA305 at 1/1	108	100	96	103
C21	CAPA 305	90	100	91	100
C22	TMP	113	136	109	101

TABLE 2.4.5: UV Effect on Transparent Polyurethanes (Thermoset) of Climatest Exposure 500 Hours (21 days) at 40°C, 40-50% RH

Source: Combination fluorescent sunlamp and black lamp

Sample No. (Expt. No)	CAPA 220/H_{12}MDI/ Chain Extenders	Property retained on exposure %			Light* Transmission of UV Treated Samples
		100% Modulus	Tensile Strength	Hardness	
C1	1:3:2 (1,4-BD+TMP at 1/1)	96	84	98	>80
C3	1:3:2 (1,6-HD+TMP at 1/1)	155	91	114	4
C5	1:3:2 (1,3-CHD+TMP at 1/1)	117	85	104	>80
C4	1:3:2 (1,4-CHDM+TMP at 1/1)	228	76	134	0
C7	1:3:2 (1,4-BD+TMP at 0.5/1.5)	94	-	107	61
C8	1:2.5:1.5 (1,4-BD+TMP at 1/0.5)	149	81	126	0
C9	1:3.5:2.5 (1,4-BD+TMP at 1.5/1.0)	139	94	109	40
C10	1:4:3 (1,4-BD+TMP at 1.5/1.5)	103	88	108	>80
C11	1:4:3 (1,4-BD+TMP at 2/1)	160	80	108	76

* Specimens were treated with the oil of same refractive index beforehand to eliminate any surface dirt or contamination

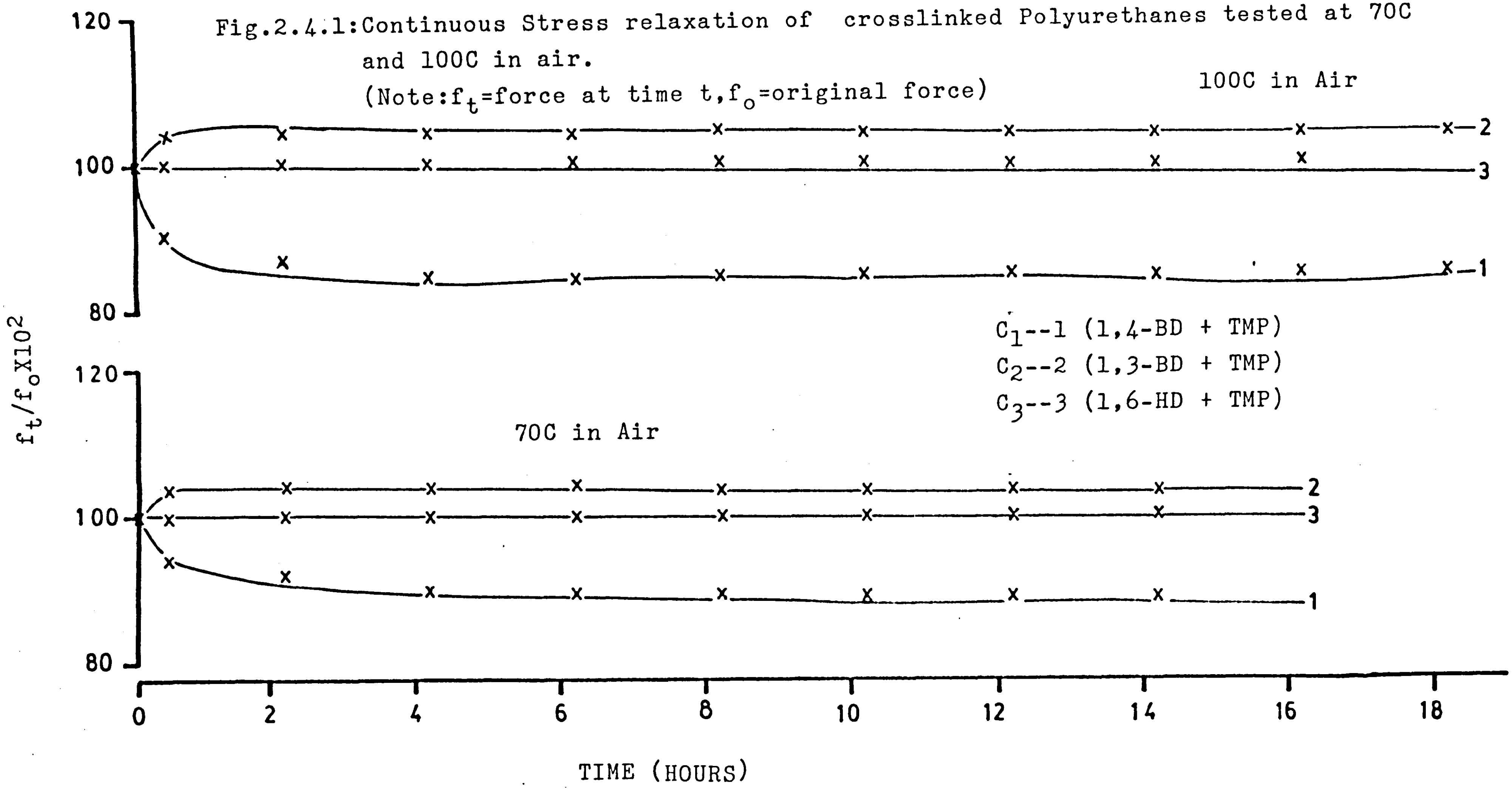


Fig.2.4.1:Continuous Stress relaxation of crosslinked Polyurethanes tested at 70C and 100C in air.
(Note:f_t=force at time t,f_o=original force)

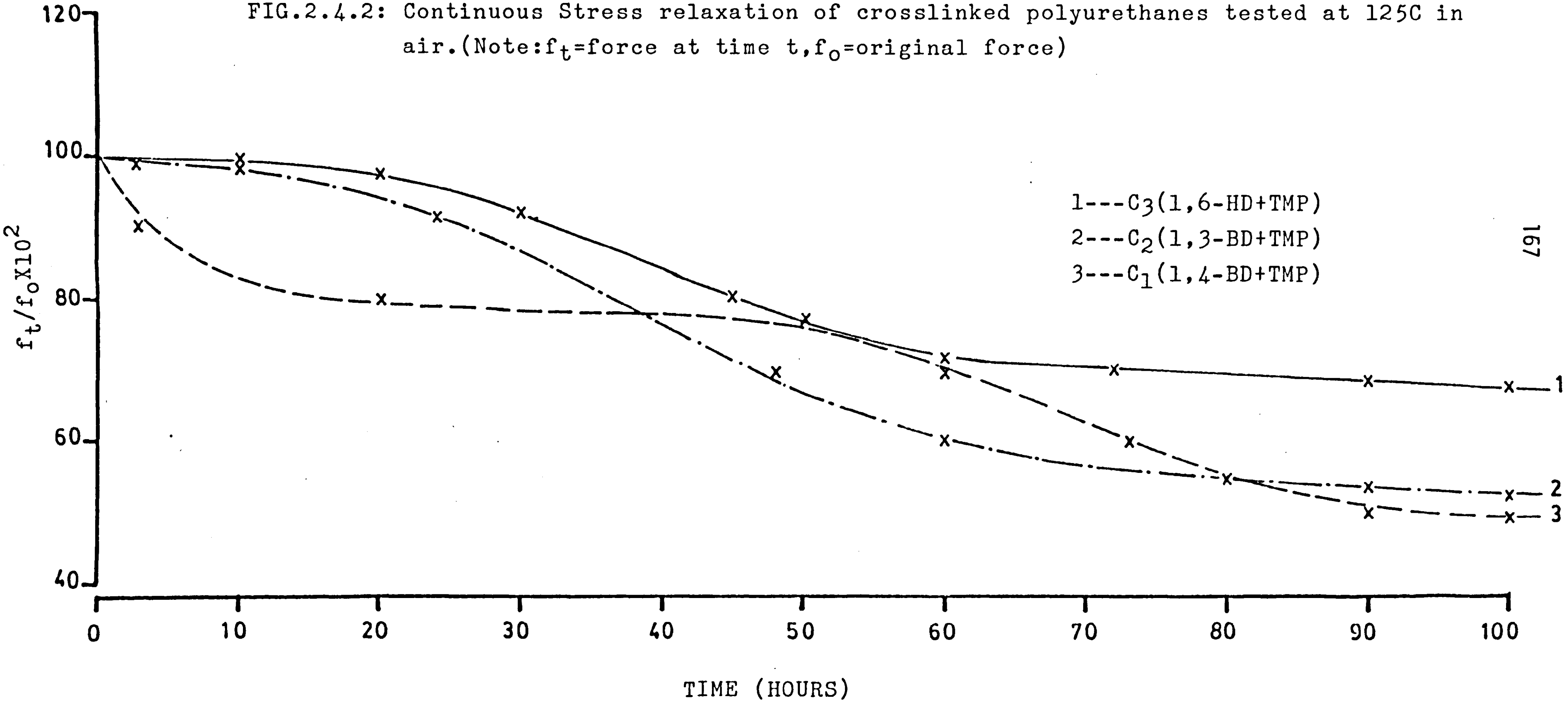
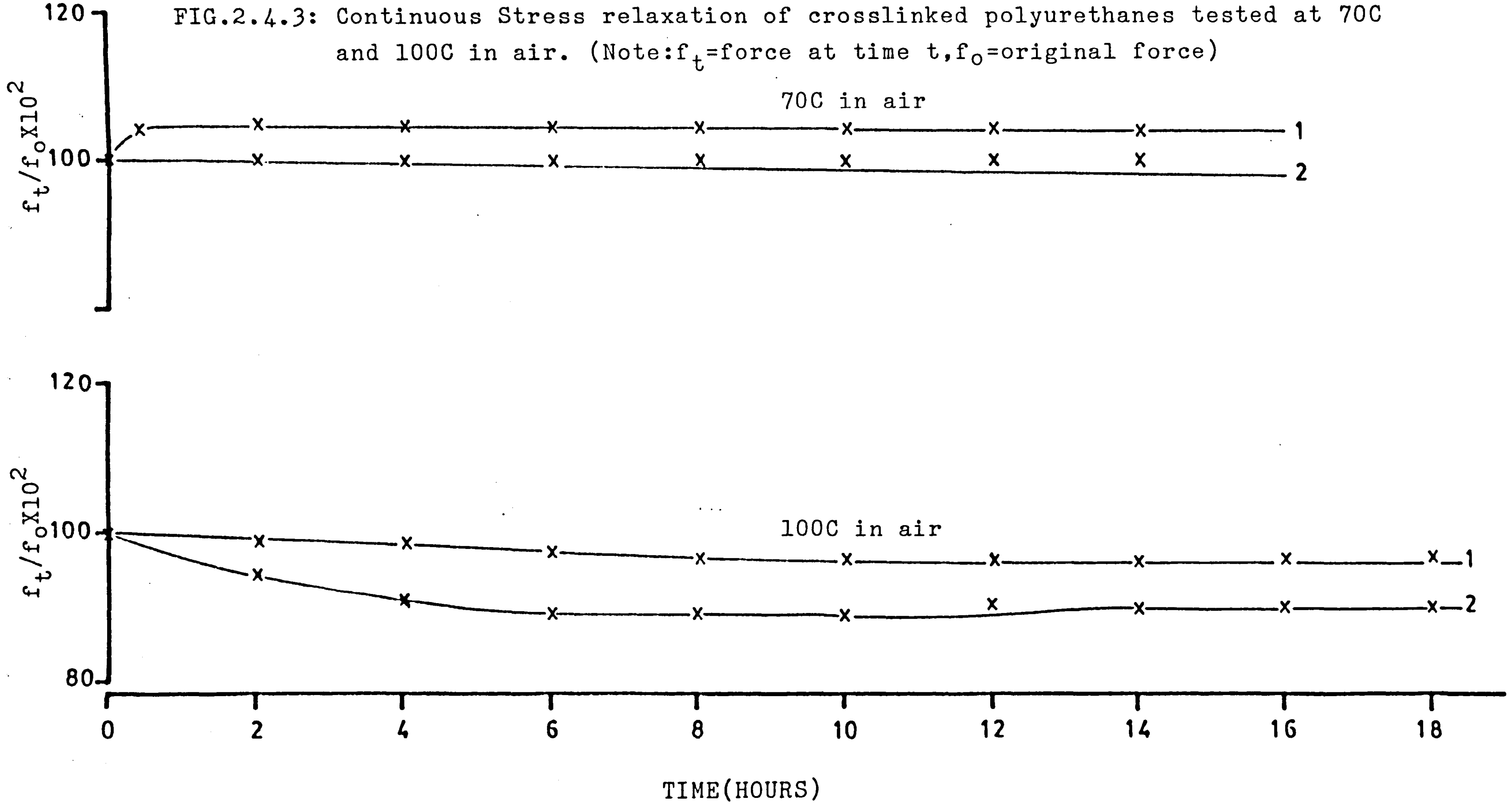


FIG.2.4.2: Continuous Stress relaxation of crosslinked polyurethanes tested at 125C in air.(Note:f_t=force at time t,f_o=original force)

FIG.2.4.3: Continuous Stress relaxation of crosslinked polyurethanes tested at 70C and 100C in air. (Note: f_t=force at time t, f_o=original force)



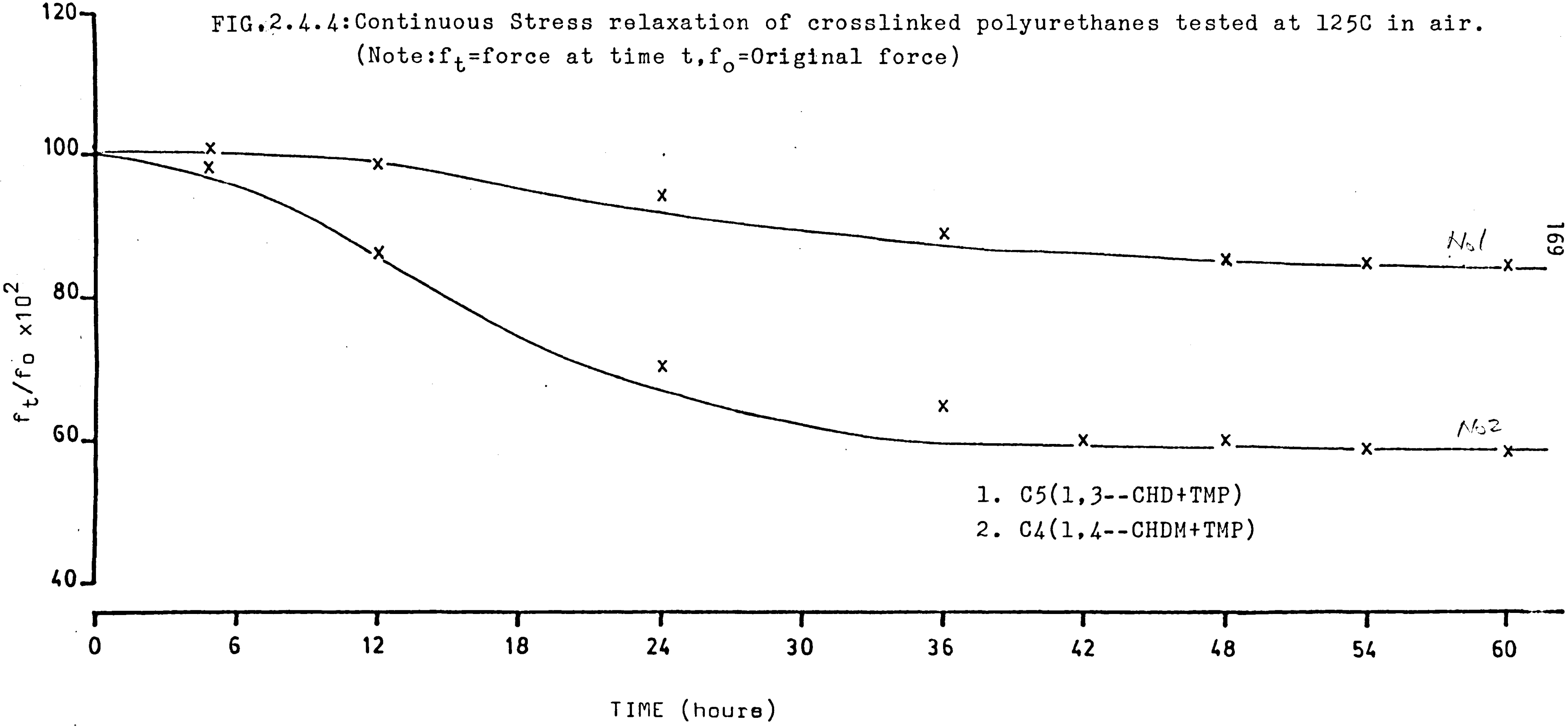
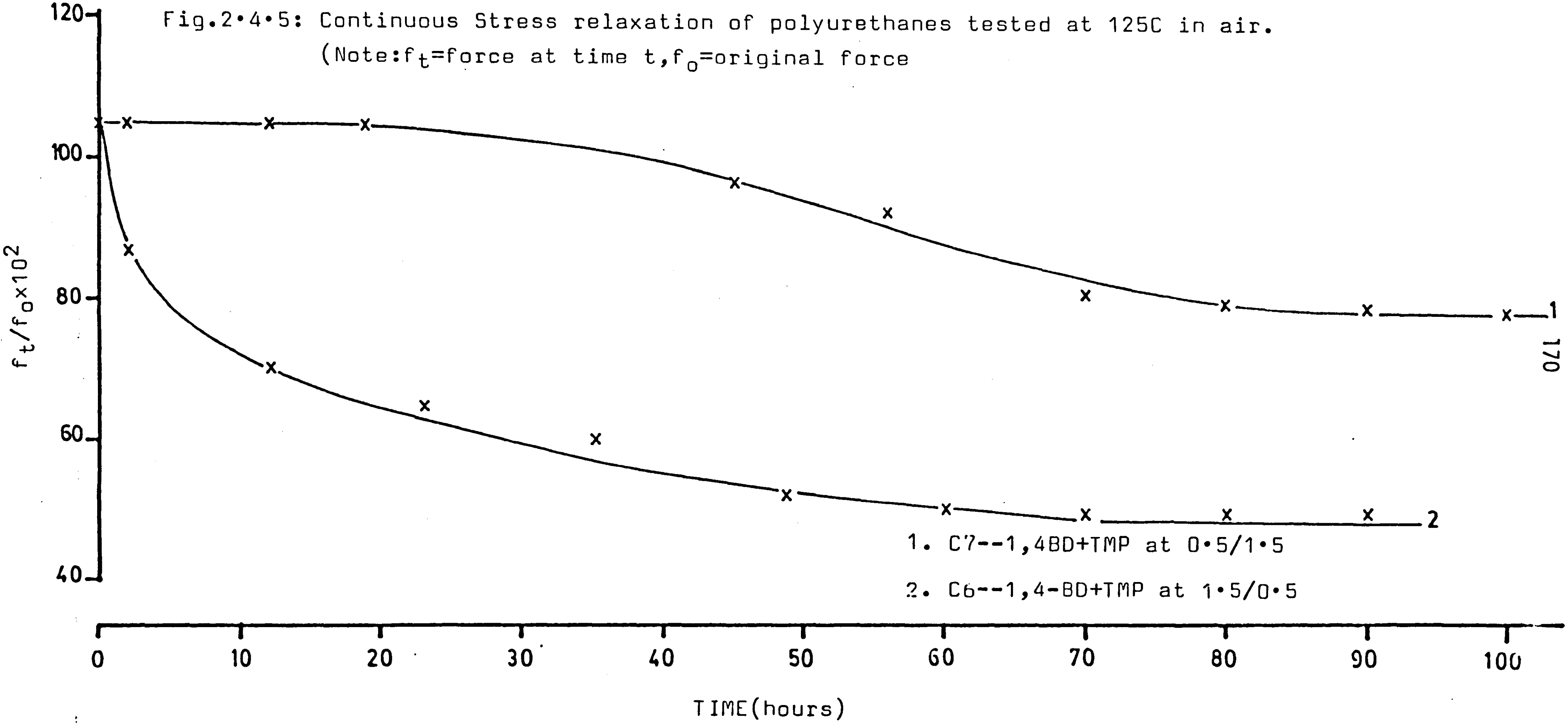


FIG.2.4.4:Continuous Stress relaxation of crosslinked polyurethanes tested at 125C in air. (Note:f_t=force at time t,f_o=Original force)

Fig.2·4·5: Continuous Stress relaxation of polyurethanes tested at 125C in air.
(Note: f_t=force at time t, f_o=original force



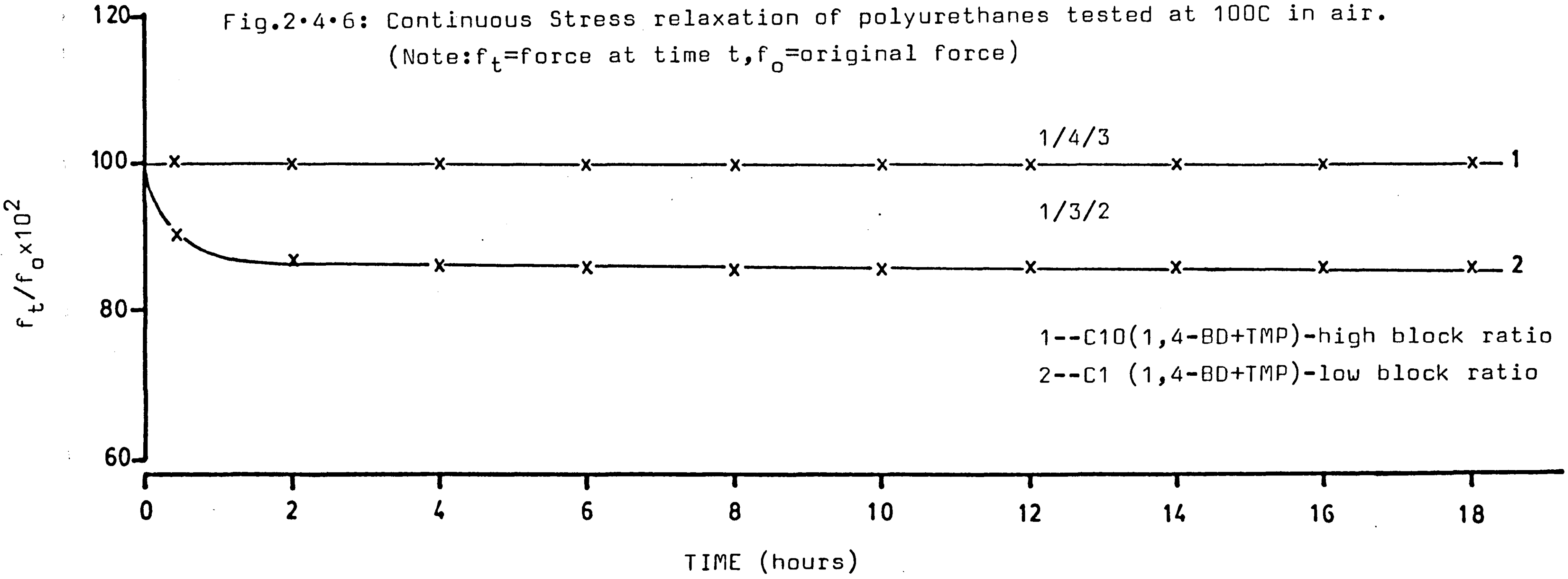


Fig.2·4·6: Continuous Stress relaxation of polyurethanes tested at 100C in air. (Note: f_t=force at time t, f_o=original force)

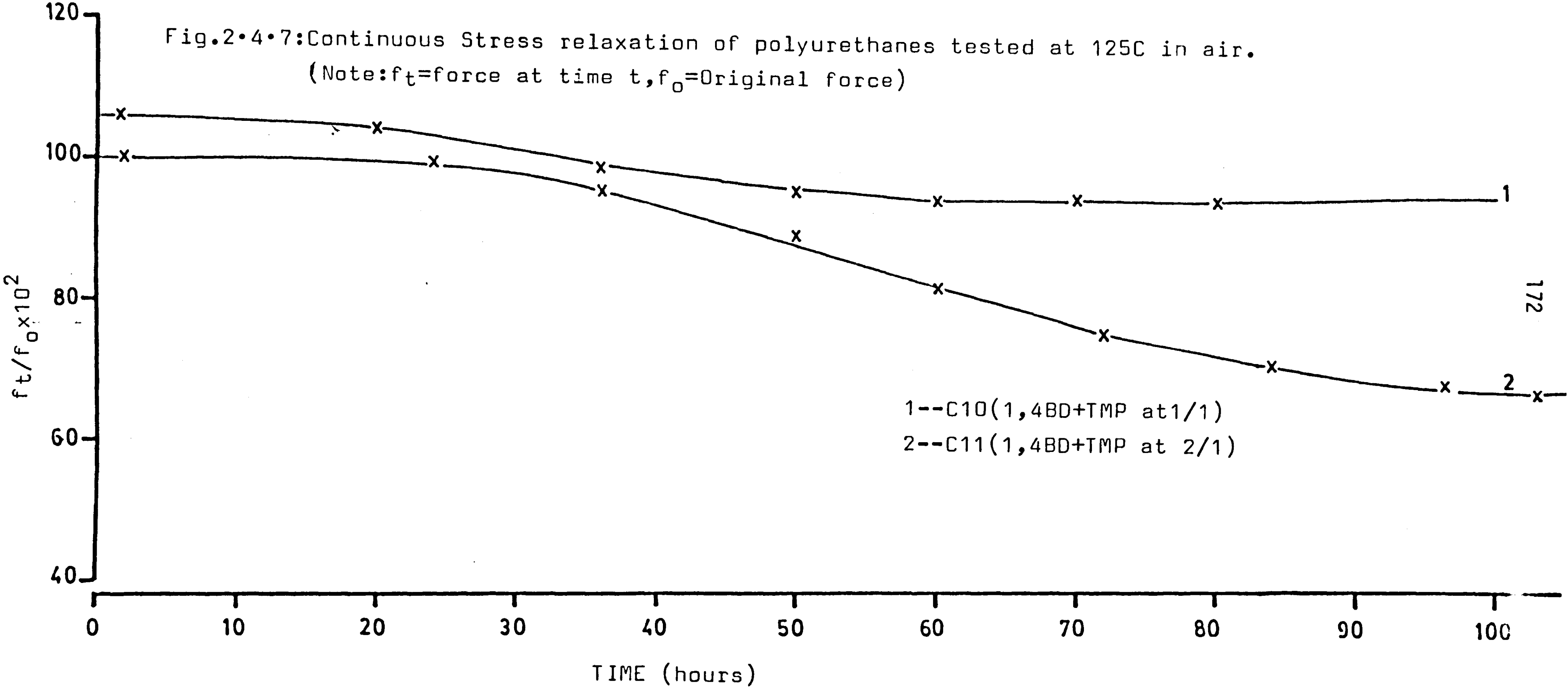
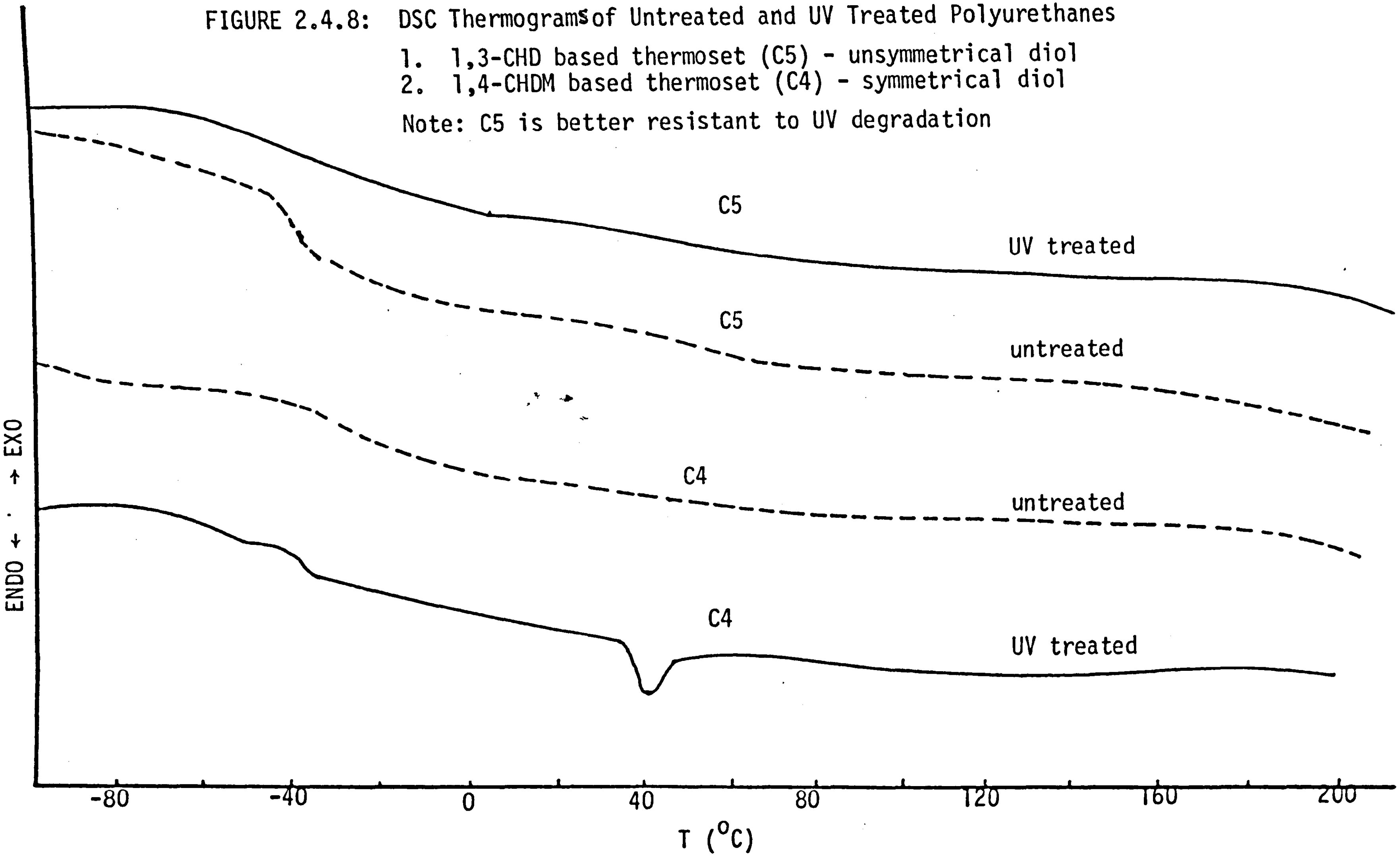


Fig.2·4·7:Continuous Stress relaxation of polyurethanes tested at 125C in air. (Note: f_t=force at time t, f_o=Original force)

FIGURE 2.4.8: DSC Thermograms of Untreated and UV Treated Polyurethanes

1. 1,3-CHD based thermoset (C5) - unsymmetrical diol
2. 1,4-CHDM based thermoset (C4) - symmetrical diol

Note: C5 is better resistant to UV degradation



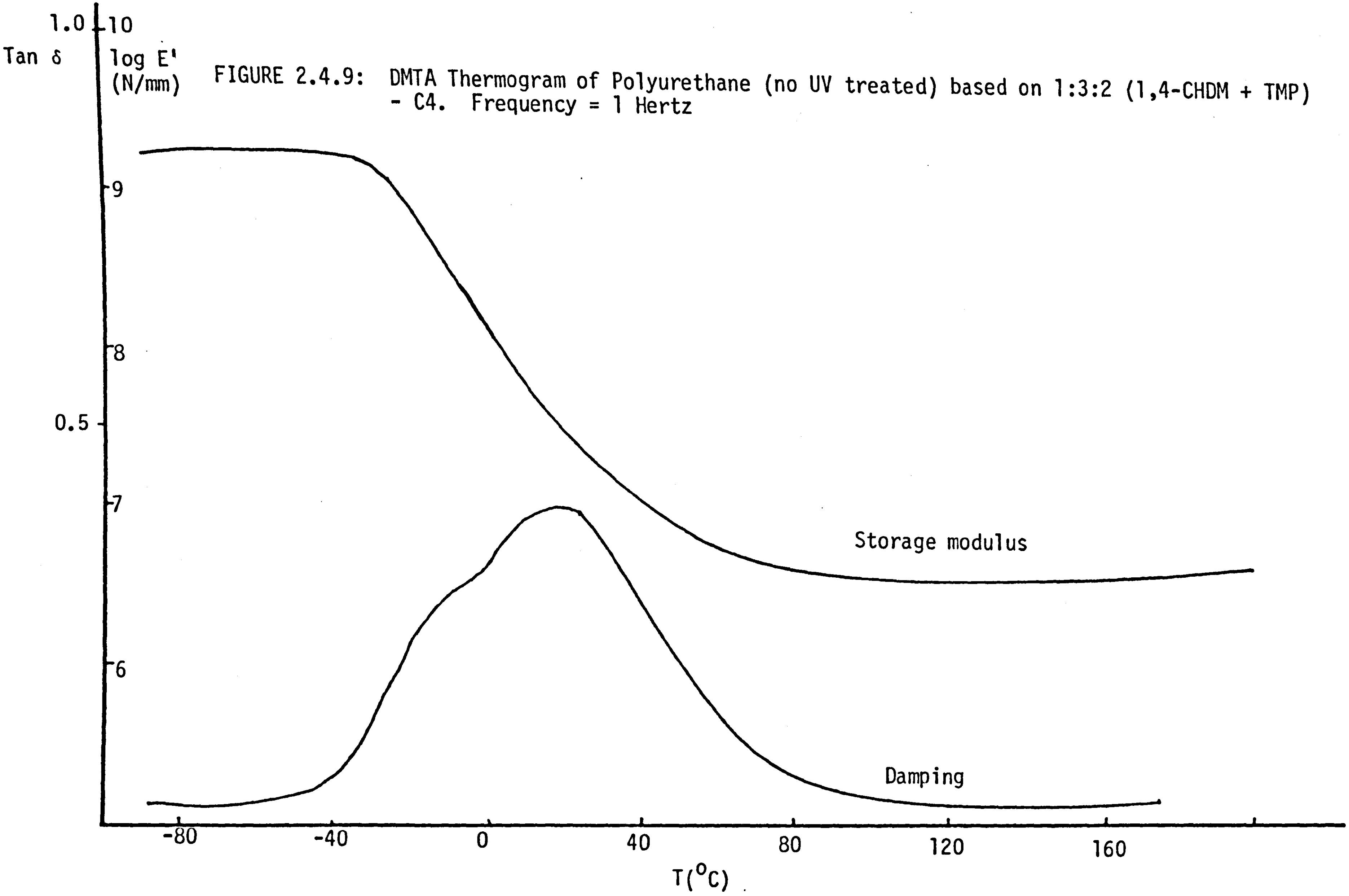


FIGURE 2.4.9: DMTA Thermogram of Polyurethane (no UV treated) based on 1:3:2 (1,4-CHDM + TMP) - C4. Frequency = 1 Hertz

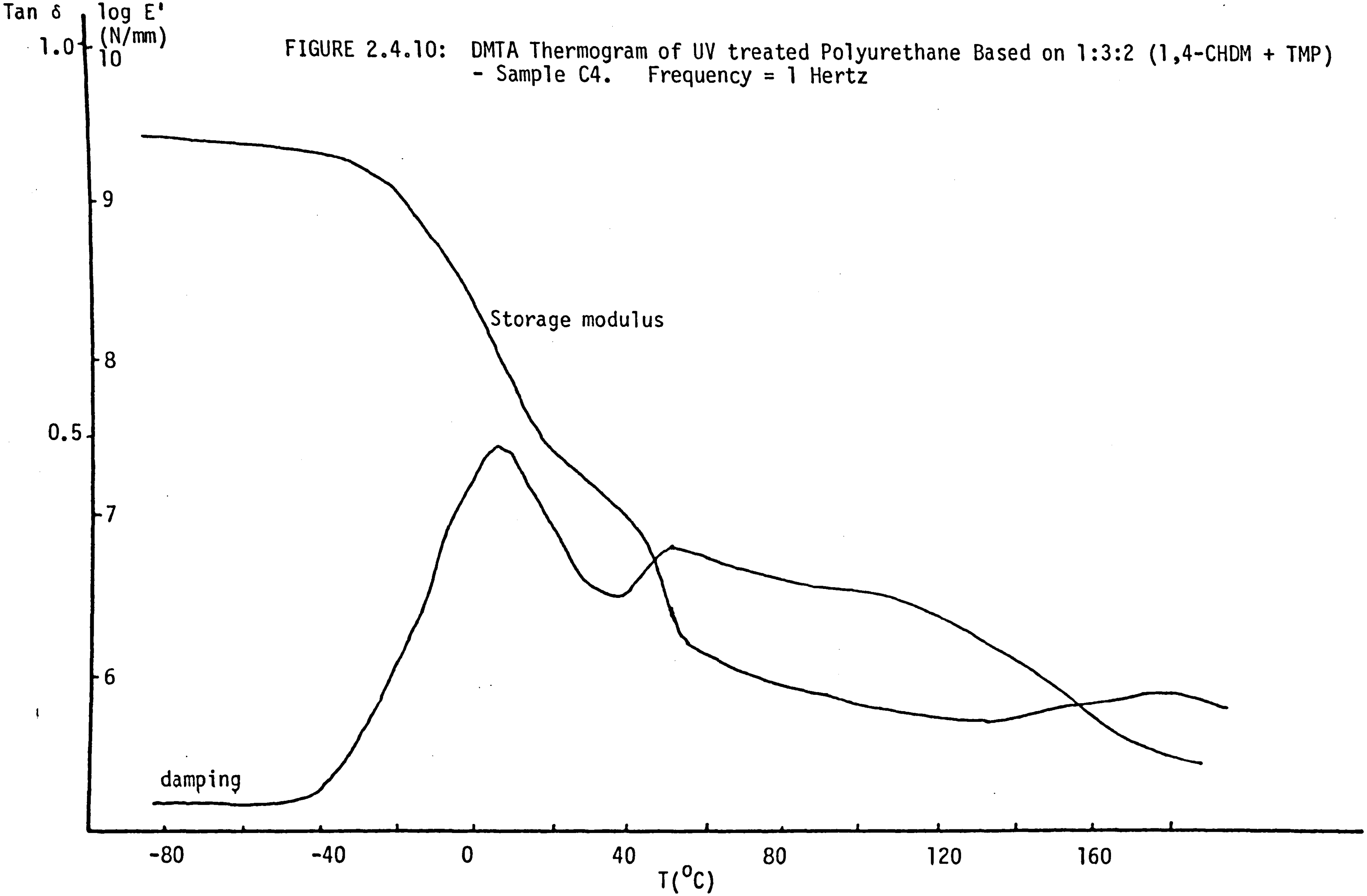


FIGURE 2.4.10: DMTA Thermogram of UV treated Polyurethane Based on 1:3:2 (1,4-CHDM + TMP) - Sample C4. Frequency = 1 Hertz

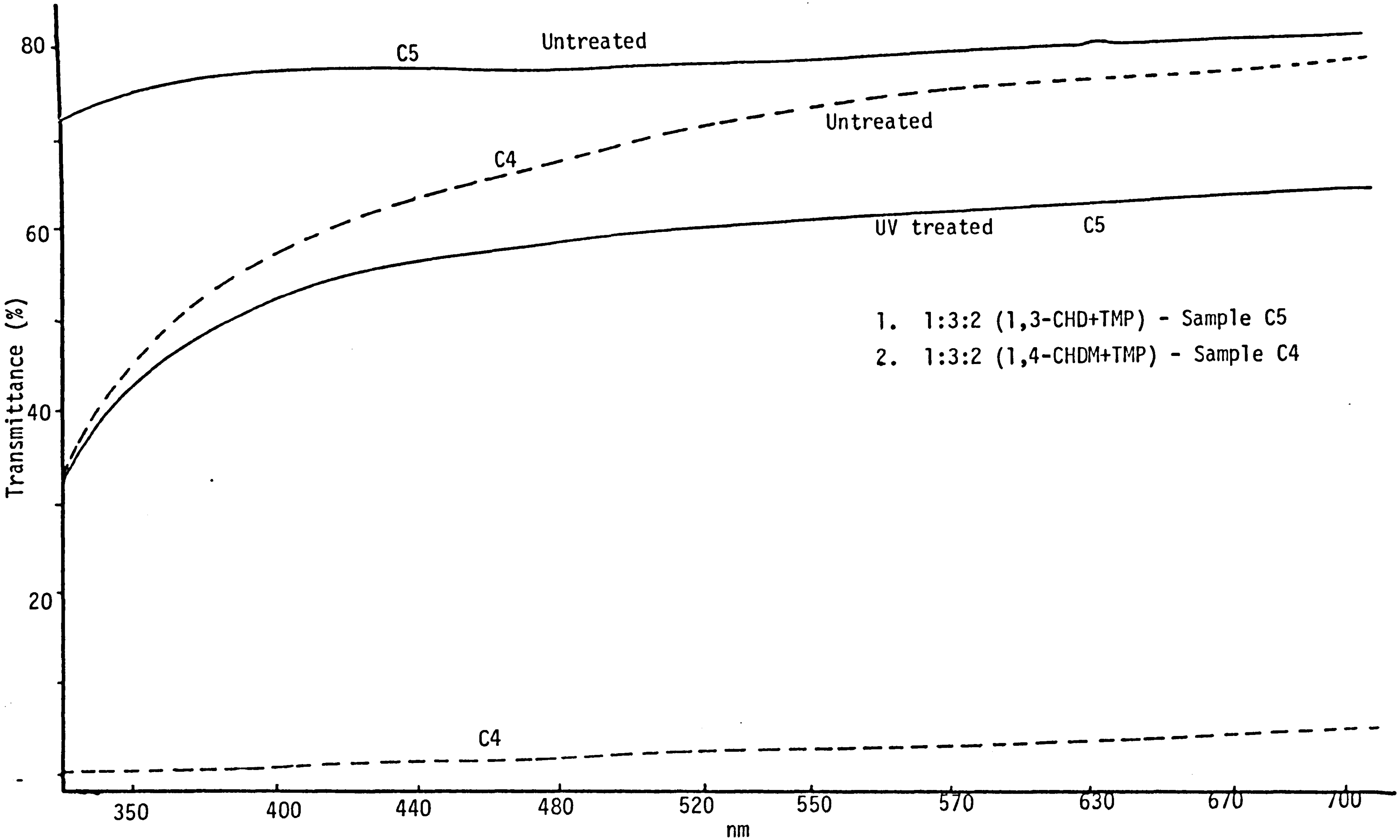


FIGURE 2.4.11: Visible Spectra of Untreated and UV Treated Polyurethanes

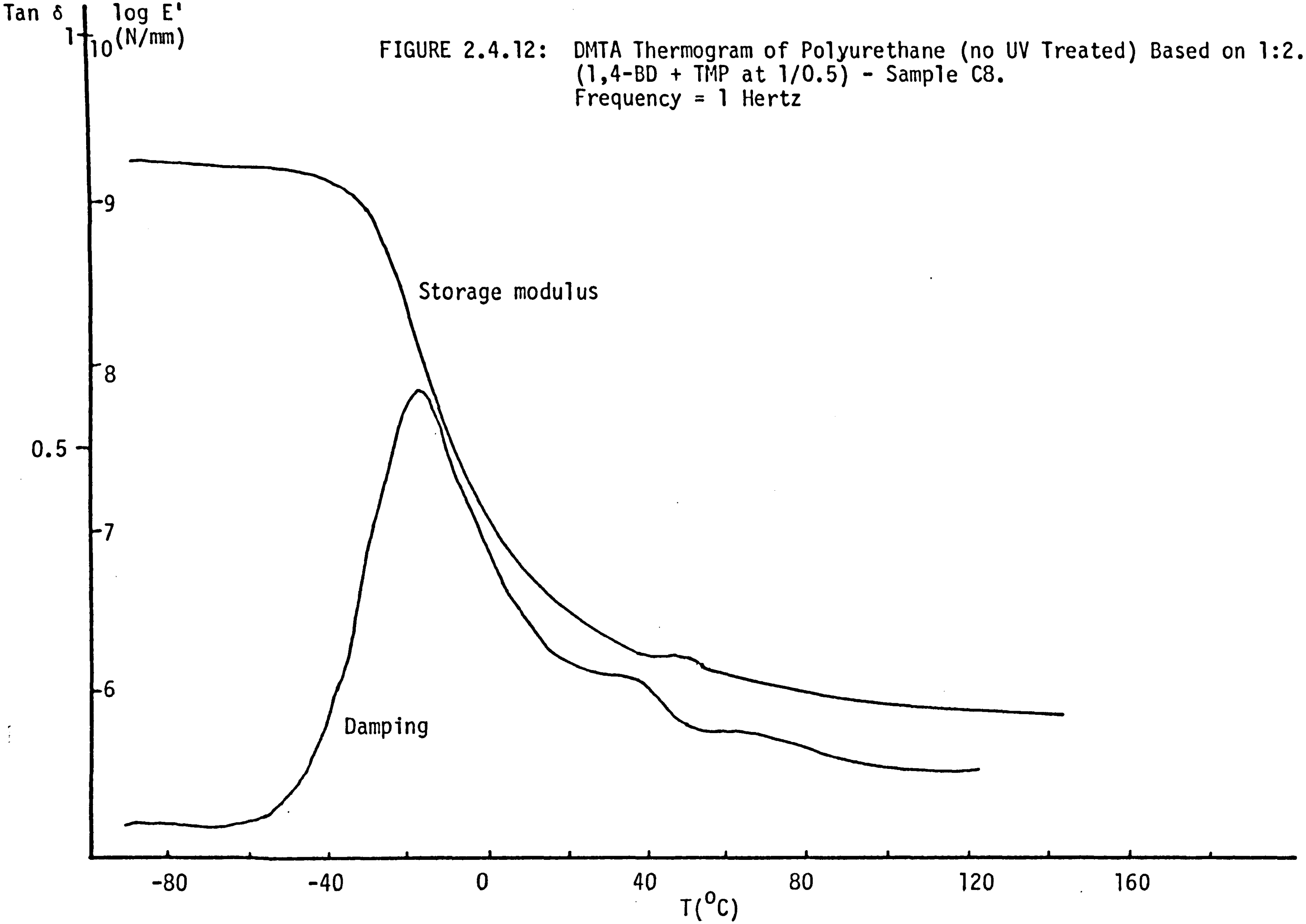


FIGURE 2.4.12: DMTA Thermogram of Polyurethane (no UV Treated) Based on 1:2.5:1.5 (1,4-BD + TMP at 1/0.5) - Sample C8.
Frequency = 1 Hertz

FIGURE 2.4.13: DMTA Thermogram of a UV Treated Polyurethane Based on 1:2.5:1.5 (1,4-BD + TMP at 1/0.5) - Sample C8

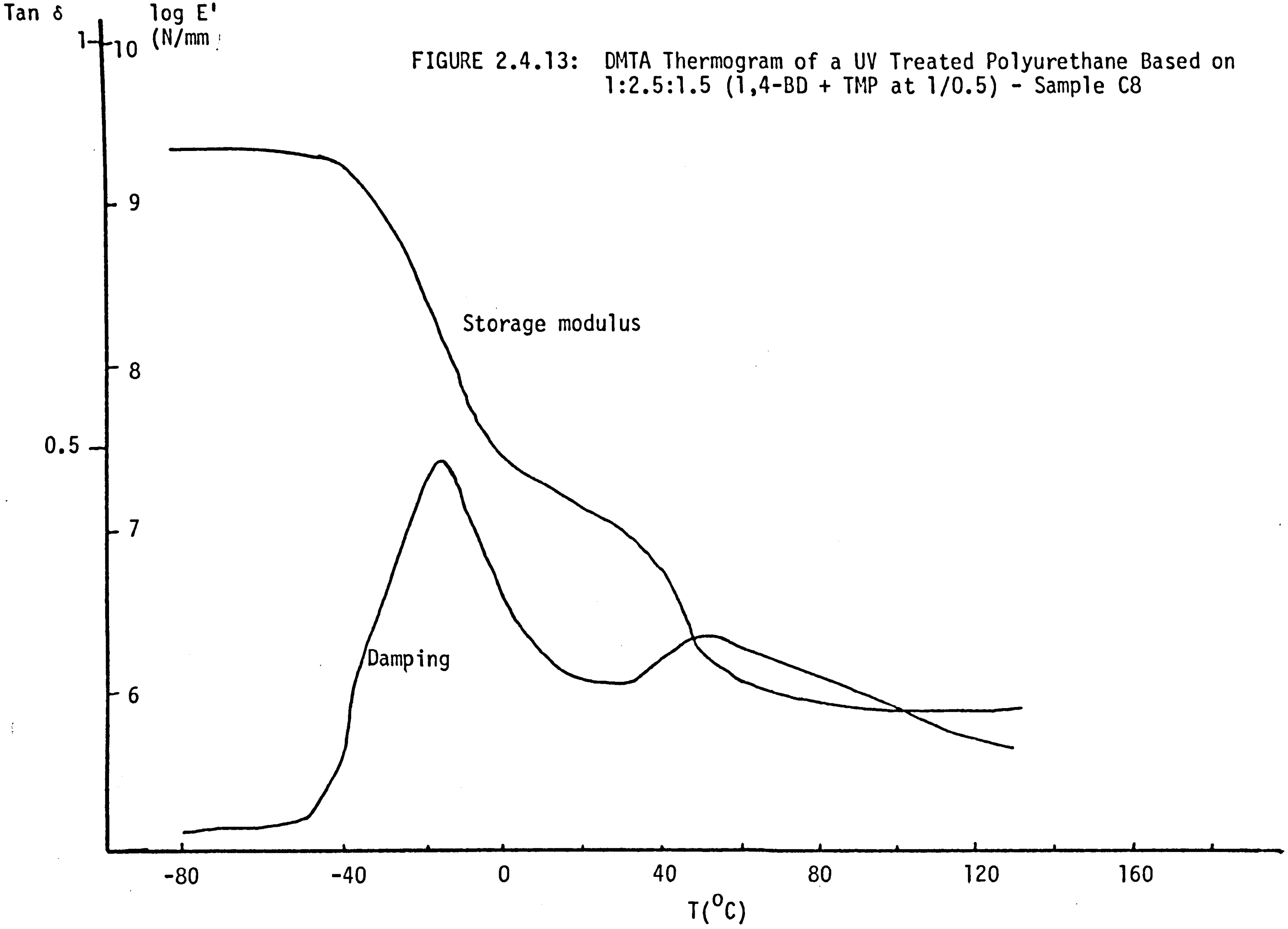
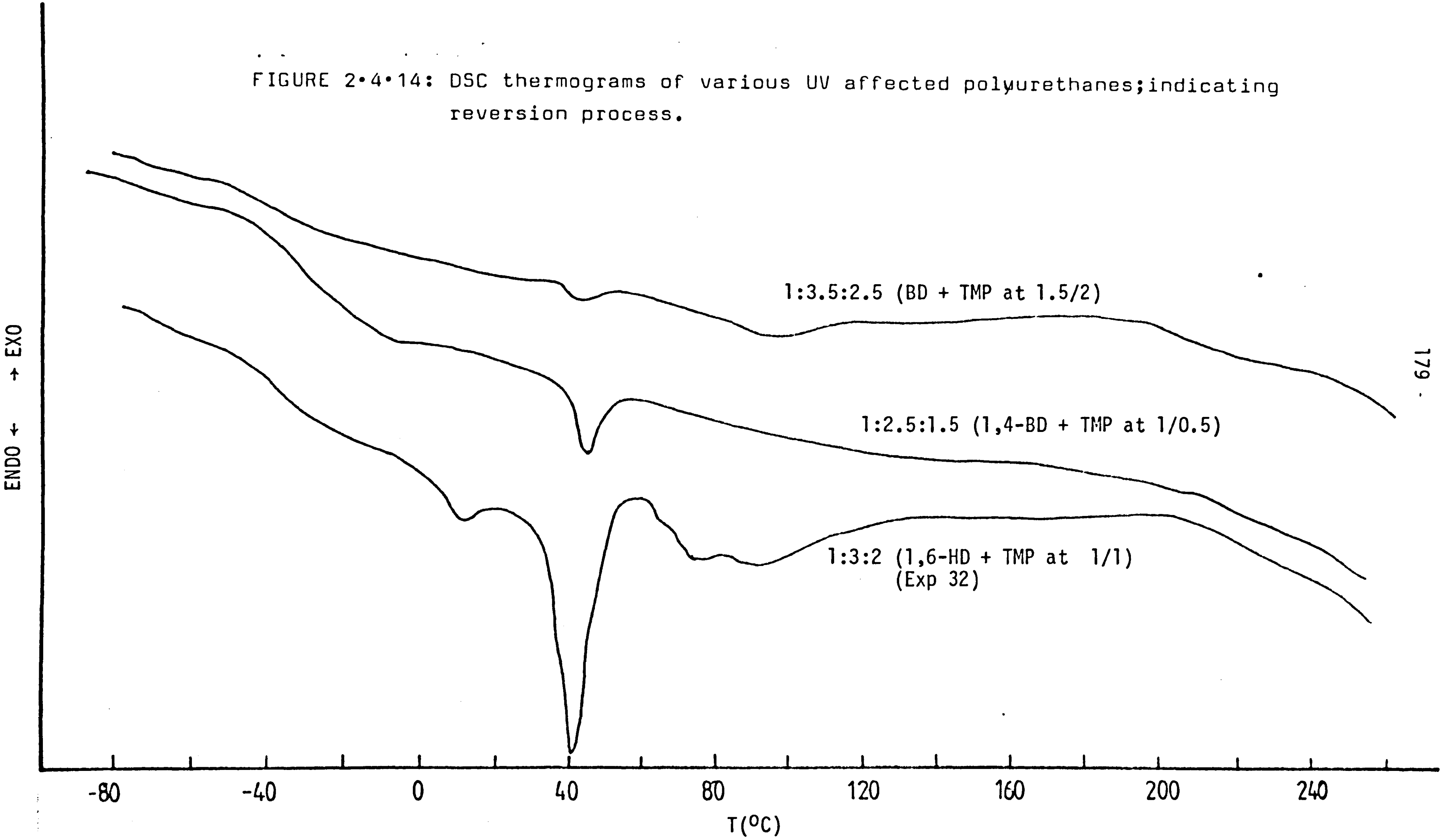


FIGURE 2·4·14: DSC thermograms of various UV affected polyurethanes; indicating reversion process.



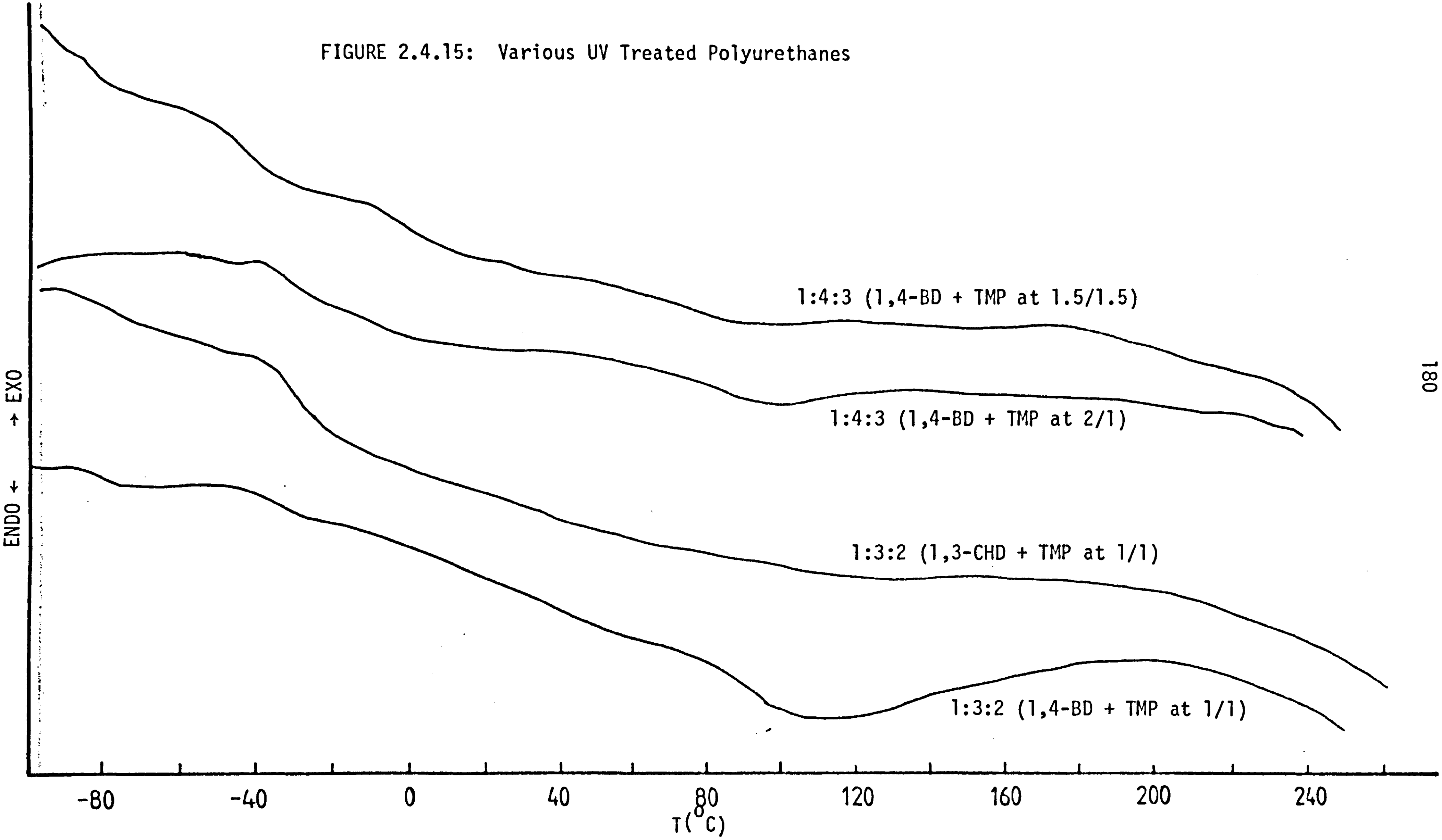


FIGURE 2.4.15: Various UV Treated Polyurethanes

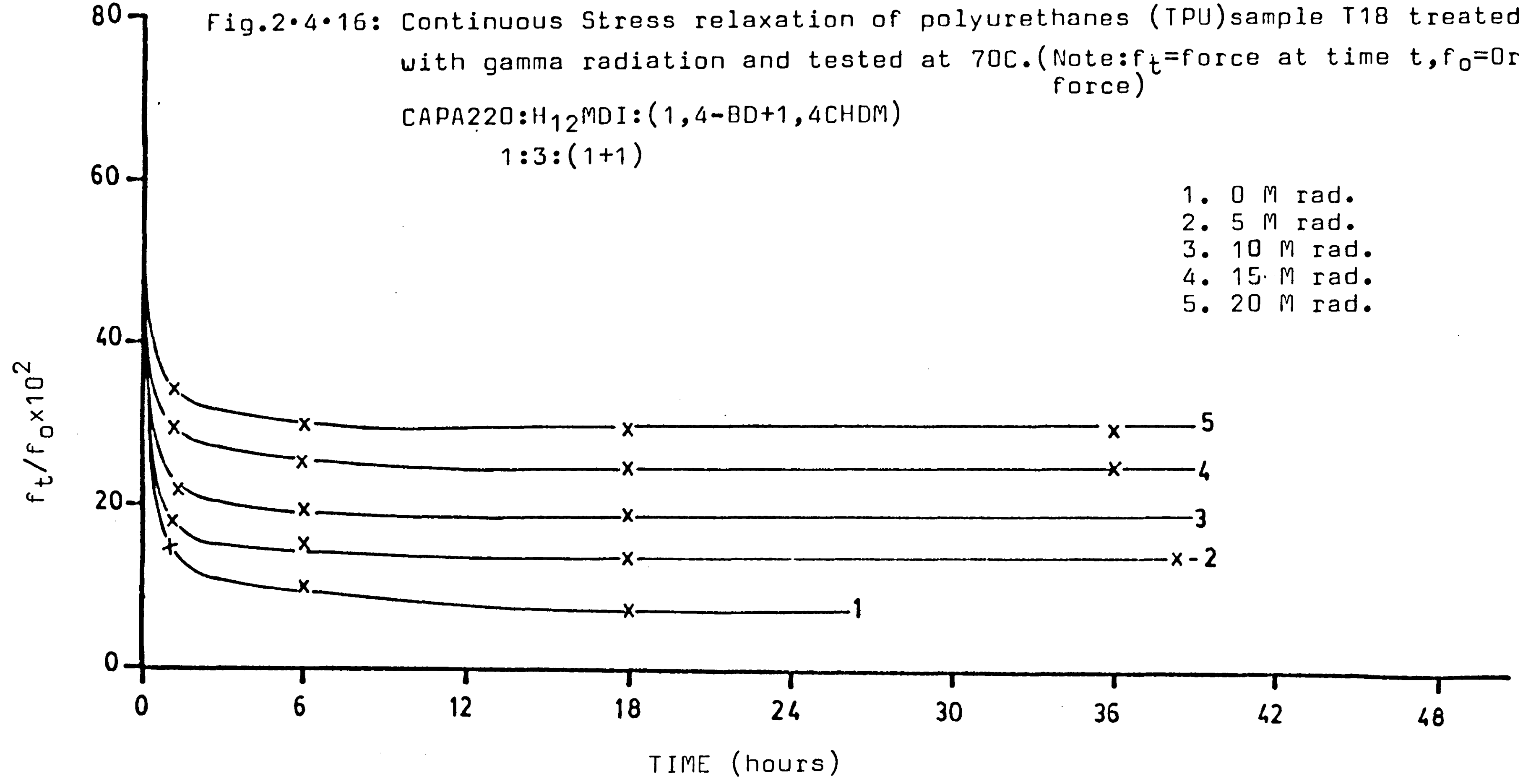


Fig.2·4·16: Continuous Stress relaxation of polyurethanes (TPU)sample T18 treated with gamma radiation and tested at 70C.(Note:f_t=force at time t,f_o=Original force)

CAPA220:H_{12}MDI:(1,4-BD+1,4CHDM)
1:3:(1+1)

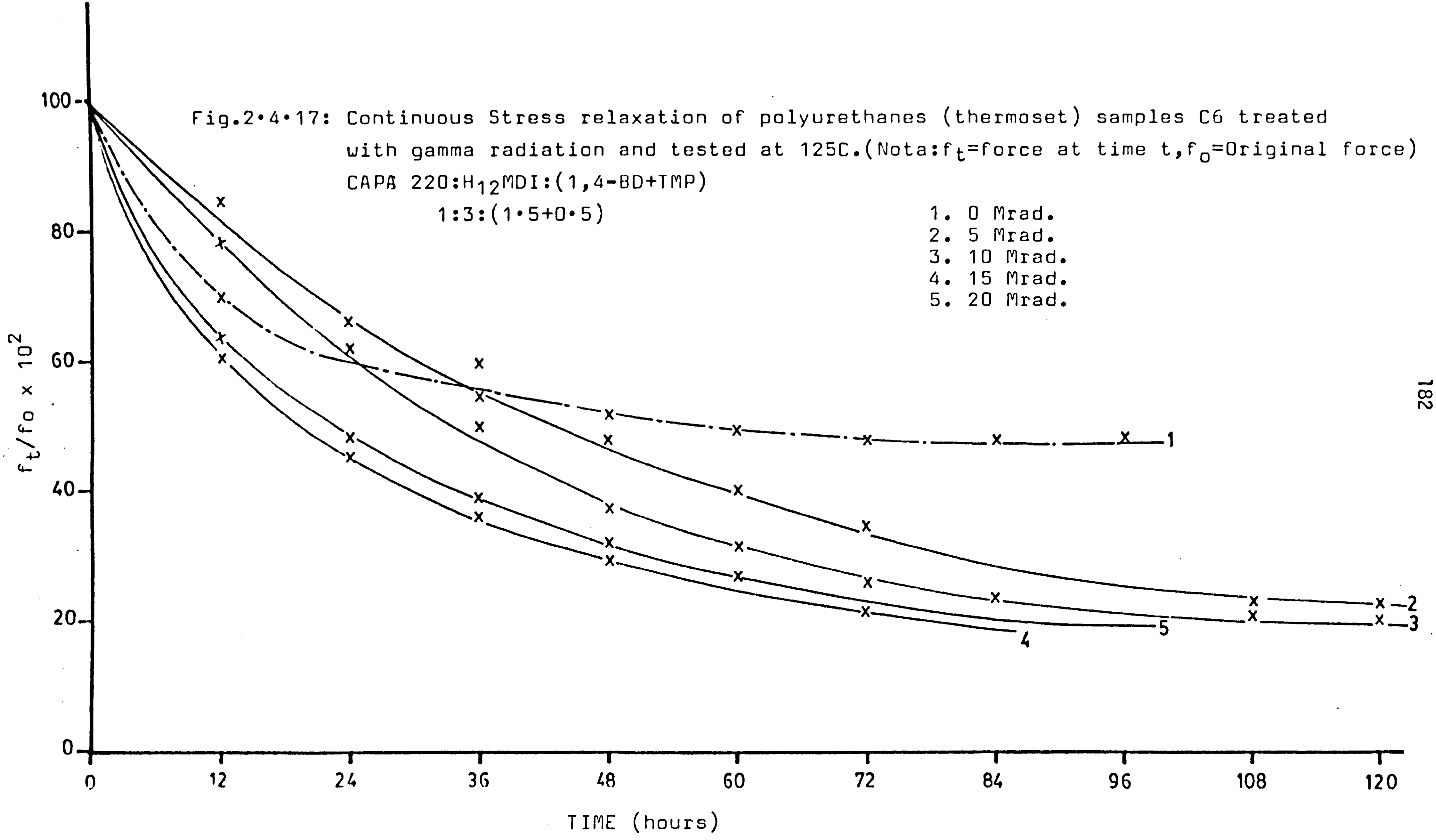


Fig.2•4•17: Continuous Stress relaxation of polyurethanes (thermoset) samples C6 treated with gamma radiation and tested at 125C.(Nota:f_t=force at time t,f_o=Original force)

CAPA 220:H_{12}MDI:(1,4-BD+TMP)
1:3:(1•5+0•5)

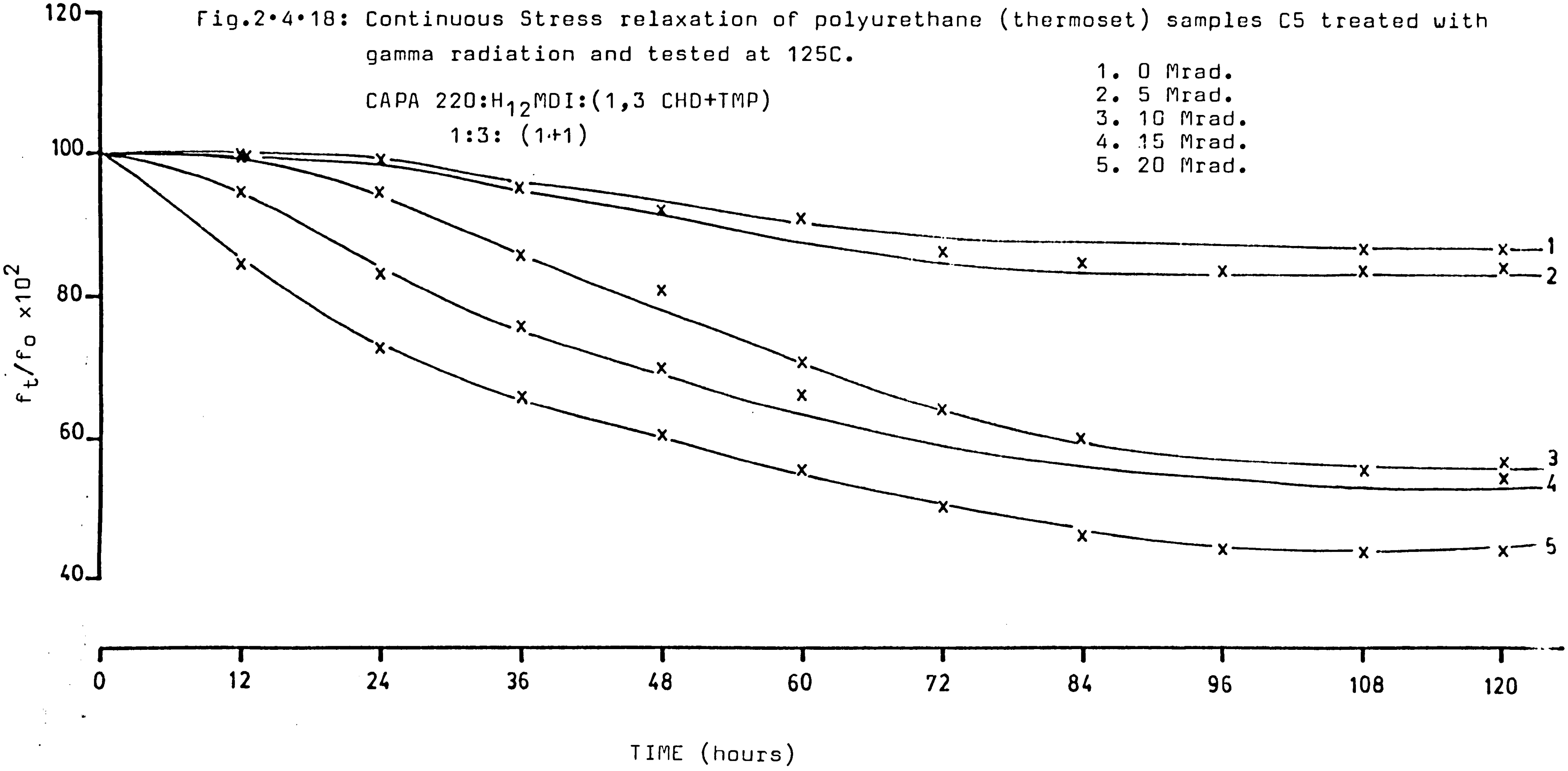


Fig.2·4·18: Continuous Stress relaxation of polyurethane (thermoset) samples C5 treated with gamma radiation and tested at 125C.

CAPA 220:H_{12}MDI:(1,3 CHD+TMP)
1:3: (1+1)

CHAPTER 3

GENERAL DISCUSSION AND CONCLUSIONS

The present research programme was initiated with the aim of establishing a synthesis technique for the preparation of flexible, transparent polyurethane elastomers to be used as moulded face pieces or visor inserts for respirators. It was also intended to study the manner in which the various chemical constituents of urethane elastomers and elastoplastics control light transmission characteristics. The required materials were successfully made and the programme was taken to completion by studying the prepared polyurethanes for their structure-property relationship and ageing characteristics.

Similarly, in a preliminary investigation different polyurethane reactants were examined but the one chosen for detailed study was based on a 2000 MW polycaprolactone diol (CAPA 220) and H_{12}MDI prepolymer system. Since CAPA 220 contains a single repeating unit and this factor allied to the complete absence of water as a reaction by-product during polymerization, results in polymers of exceptional purity, a prerequisite for void-free transparent polyurethanes. CAPA polyols, in general were found appropriate for use in transparent urethanes due to their ability to blend with a wide range of chemical constituents yielding mixed and compatible polymer systems. Also the high polarity in CAPA (Tables 2.2.2 and 2.2.3) increases the intermolecular attraction in urethanes and hence improves mechanical properties.

Polyether polyols (polyoxy propylene glycol and polytetra methylene ether glycol), although exhibiting outstanding optical clarity in the final urethane product necessitated the use of catalyst due to their considerably low reactivity toward diisocyanates which then resulted in reducing the mechanical properties drastically. The use of catalysts was also considered to promote hydrolytic instability and discolouration (yellowness) and hence avoided in order to obtain products of high purity.

Isophorone diisocyanate (IPDI) was found to give very soft urethane elastomers (Table 2.3.3) and therefore a high diisocyanate content was required to obtain the specified hardness value of 60 IRHD. The use of high block ratios (i.e. high IPDI content) made for difficulties in controlling the reaction rate due to the big difference in reactivity between the two NCO groups present in IPDI. The resulting urethanes therefore had imperfect surfaces (wavy pattern).

H_{12}MDI, a liquid aliphatic diisocyanate on the other hand yielded high quality non-discolouring urethanes with good surfaces (when cast on to highly polished moulds). It is very important to note that the Desmodur W (H_{12}MDI) is a mixture of cis and trans-isomers and that this product consequently tended to separate or stratify when frozen (83). Since the isomers do not react with hydroxy compounds at the same rate, it is eesential that material which is frozen, or suspected of having been frozen, be completely thawed and well mixed before use. In the earlier experiments when this precaution was not taken, inconsistent results were obtained.

CAPA 220 and H_{12}MDI were found to provide a good combination for a prepolymer system with respect to their acceptable (moderate) reactivity in an uncatalysed system, compatibility, stability and optical clarity when used according to the synthesis method described in Section 2.1.4. The reaction temperature (especially chain extension and curing) was observed to have a profound influence on the transparency and tensile property of final urethane products. Figure 3.1 demonstrates these effects on the two polyurethanes, T1 and C1, each chosen from their respective thermoplastic and thermoset series and each of which was synthesised at the respective temperatures 85°, 90°, 100°, 110°, 120° and 130°C. The extent of reaction was monitored using the IR technique and measuring the disappearance of NCO peak at 4.4 microns. As indicated in Figure 4.1, at lower synthesis reaction temperatures, up to 95°C, the tensile strength of thermoplastic polyurethane continuously increases and thereafter equilibrated with respect to reaction temperatures. The reaction time, however, sharply decreased with increase of reaction temperature and only became relatively constant above 115°C. Similarly the material was found to be translucent/hazy when prepared at reaction temperatures below about 100°C but above this temperature all the urethanes had good transparency. This observation can be explained by considering the melting point of the hard segment which appears at about 95°C in the DSC thermogram of Figure 2.2.10(b). This suggests that the urethane reaction should be carried out at temperatures above its hard segment melting point (95°C in the present case) in order to cause soft/hard segment mixing in the molten state which is a requirement for good transparency. At high reaction temperatures, due to higher chain mobility, the hard segments are uniformly dispersed in the soft segments which upon cooling establish a permanent structure and hence prevent any hard segment aggregation forming which may cause crystallization or haziness. This does not hold good for urethanes derived from non-symmetrical diols where the hard phase separates out with time causing soft segment crystallization (see later part of this section). If the reaction is carried out below its hard segment melting point the resulting product will have two distinct phases and segregated structures. This may lead to a relatively better tensile property but poor transparency (Figure 4.1).

The transparency of crosslinked polyurethanes seems to be less affected by the reaction temperatures presumably due to chain branching which prevents crystallization and phase segregation.

Regarding the tendency of polyurethanes to turn yellow on prolonged curing and at high temperature curing; it is observed that the main cause of this discolouration is associated with the repeated reheating and evacuation during the degassing process used with the polyol which is carried at an elevated temperature. In the past it was the practice to melt and degas the polyol content in a single master container at 100^{0}C under vacuum and then to use the required quantity from it. The unrequired polyol was stored under nitrogen for the next synthesis and hence repeated degassing and reheating of polyol caused discolouration. When this reheating (and oxidation) was eliminated the resulting materials were found to be non-yellow and transparent. Additionally it is observed that it is only at above 120^{0}C curing temperature for say 18 hours where cured elastomers show a slight discolouration or yellowness presumed due to surface oxidation.

The chain extenders are found to play the most dominant role in the preparation of flexible, transparent, segmented polyurethanes. As mentioned early the use of a low block ratio (i.e. low hard segment content) is necessary to obtain the specified soft materials and this then promotes soft segment crystallization due to insufficient hard segment content required to disrupt polyol chain regularity. Samples T20, T21 and T23 (Table 2.1.3) are examples where the soft segment crystallization occurred in the only diol based materials which showed opacity and high hardness values. However, certain diol blends were observed to inhibit such crystallization at low block ratio say 1/3/2 and yield polyurethanes which have low hardness and good transparency. Such a blend should be based on symmetrical diols and among them, the most preferred one was found to consist of an aliphatic/cycloaliphatic diol system. T1 (Table 2.3.4) is an exmaple of a soft thermoplastic polyurethane where the chain extenders used are 1,4-BD (aliphatic) and 1,4-CHDM (cycloaliphatic) and which exhibited outstanding transparency and mechanical properties. The inclusion of an unsymmetrical diol was observed to have an adverse effect on light transmittance characteristics because such diols due to their poor structural-fit separate out from the soft segment matrix allowing the latter to crystallise. This tendency of unsymmetrical diols to segregate is much reduced in chemically cross-linked polyurethanes due to restricted chain mobility and as a consequence outstanding transparency results. It should be noted that the 1,4-BD blends well with almost all the diols investigated and gave good transparency when used in CAPA 220/H_{12}MDI prepolymer system. This indicates the tendency of 1,4-BD derived urethane group to dissolve in the soft segment matrix.

Mould surfaces were also found to have profound effects on the optical clarity of polyurethanes. The polished aluminium and steel moulds yielded urethanes with the desired transparency and release property when a thin layer of Cilase 1818 release agent was used. The advantages associated with aluminium trays are their low cost, light weight and good optical and mould release property. However, the polish diminishes on repeated use and it is impractical to repolish due to the relative softness of the aluminium. Likewise, the steel moulds with highly polished surfaces (mirror-like) yielded clear materials while a slight roughening on such mould surfaces caused translucency in the final product. This was further confirmed when surface defects of polymers were eliminated by immersing or coating a specimen in a clear liquid of the same refractive index (1.412) where the opaque or cloudy PU became transparent.

The polymer structure and their morphology were studied using infrared spectroscopy, differential thermal analysis and dynamic mechanical thermal analysis techniques.

The hydrogen bonding in the crosslinked and thermoplastic urethanes (Tables 2.2.2 and 2.2.3), as measured by IR technique was observed to lie between 57-65%. The thermoset materials showed relatively lower values of H-bonding which can be explained by considering reduction in intermolecular attractive forces that result from a spatial separation of chains due to increased crosslinking. The fact that both the transparent (T1-T7) and opaque (T9-T12) thermoplastic samples showed the same level of H-bonding indicates that the transparency is not directly influenced by such bonding. This was further confirmed by warming up an opaque sample (T10) to 55°C for a few minutes until it turned transparent and then its H-bonding was calculated. Both the opaque and transparent forms of T10 gave bonding values of 60% and 62% respectively. Thus a conclusion may be that the transparency in the polyurethane systems investigated cannot be explained by H-bonding.

The DSC technique was found to be the most effective tool for characterizing the transparent and opaque polyurethanes. A detailed discussion on the DSC studies (Figures 2.2.8 to 2.2.14) has been made in Section 2.2.2. Briefly, the opaque thermoplastic urethanes exhibited two distinct transitions in the DSC thermogram, one of them corresponding to the soft segment crystallites melting point (T_s). This indicates that the translucency in these materials is due to soft segment crystallization and consequently to phase separation. On the other hand transparent polyurethanes demonstrated only a single transition, and, the absence of any peak (T_s) due to the soft segment crystallization indicates compatibility and the existence of only one phase in these polymers.

The physical and mechanical properties of the prepared polyurethanes were generally found good. In particular the translucent thermoplastic urethanes, considering their low hardnesses, demonstrated very high tensile cut tear strengths. It was found that the diols (e.g. 1,4-BD, 1,4-CHDM etc) give physical strength to the polymers whereas the TMP or other triol merely serves to improve the transparency by introducing irregularity in the chain and also reducing the ability of the diol derived urethane groups to aggregate.

Therefore, in the present work the use of chain extenders in the form of blends (diol + TMP) was made in the crosslinked polymers in order to obtain a good combination of both tensile properties and transparency.

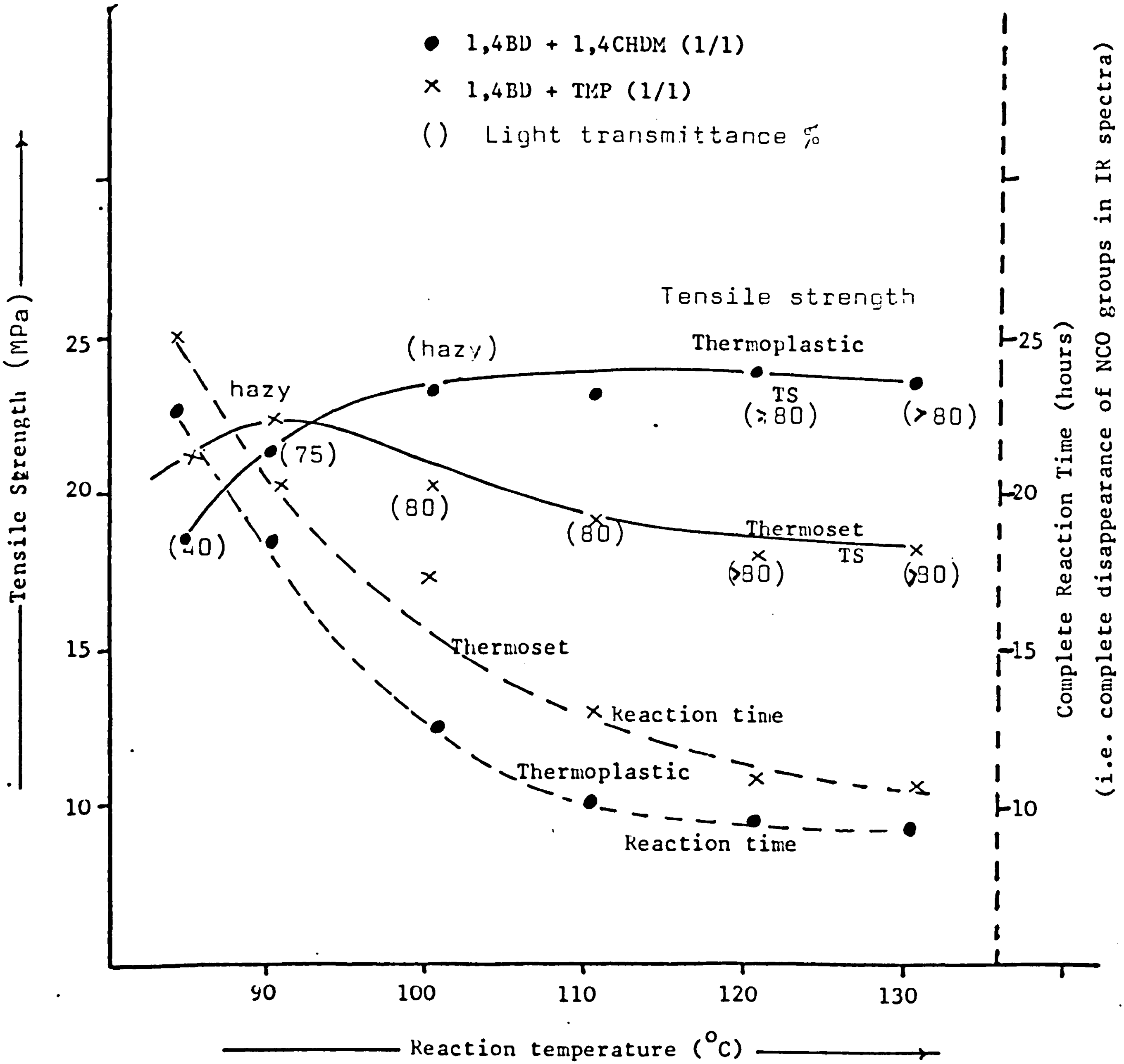
The prepared crosslinked polymers were aged at -25^{o}C and 72^{o}C in dry air to study the transparency retention on storage. After a test period of 4 months the urethanes did not show any appreciable change in their light transmittance values or discolour (yellowness).

The thermooxidative study by continuous stress relaxation technique revealed that all the crosslinked samples are fairly resistant to thermooxidative degradation up to 100^{o}C. However, at above 100^{o}C there is seen a slight degradation and after 24 hours the residual stress (reduced stress) was noticed to be in between 60 and 80%.

Likewise, the hydrolytic stability test showed the thermoset materials to be fairly resistant toward hydrolysis when tested at 70^{o}C for 2 weeks. However, at the end of the test, the materials discoloured badly and turned yellow though retained their transparency. The thermoplastic urethanes (Table 2.4.3) on the other hand showed poor resistance toward hydrolysis and their tensile strength retention was measured to be between 30 and 40% when aged at 70^{o}C in water for 8 days. This can be explained on the basis of the TPU's melting temperature (T_m). DSC data show T_m to normally exist between 50^{o} and 70^{o}C. Thus at the hydrolytic test temperature of 70^{o}C the specimens are very soft and weak which allows water to penetrate into them causing hydrolysis.

The UV stability of the thermoset polyurethanes was also studied and the result, in the form of mechanical property retention is given in Table 2.4.5. Generally the modulus was increased with time of UV exposure (presumably due to phase separation) and the tensile strength decreased.

Figure 3·1 Effect of reaction temperature on tensile strength and reaction time of polyurethane based on 1 : 3 : 2 block ratio.



CONCLUSION

1. The thermoset (cast) and thermoplastic polyurethanes which are flexible and transparent can be reproducibly prepared by using an uncatalysed CAPA 220/H_{12}MDI prepolymer system which is chain extended and cured with mixed chain extenders. This is achieved when the prepolymer is prepared under a nitrogen atmosphere at 130°C for 1½ hours then cooled to 100°C before being mixed with chain extenders. After degassing under vacuum the mixture was cast and left to cure at 120°C for 18 hours.

2. All the thermoset polyurethanes based on the diol/triol blend systems exhibit excellent light transmittance characteristics. Also it was found that the aliphatic and cycloaliphatic diols can be used with TMP or CAPA 305 triols in the form of a 1/1 blend to chain extend the prepolymer and to obtain optimum transparency. Thus this thermoset type of urethane system provides a very good combination of mechanical properties, transparency and colour stability of ageing. Specifically the following are the preferred formulations based on 1/3/2 block ratios with the CAPA 220/H_{12}MDI prepolymer system.
   a) 1,4-BD + TMP at 1/1 equivalent ratio
   b) 1,4-CHDM + TMP at 1/1 equivalent ratio
   c) 1,3-CHD + TMP at 1/1 equivalent ratio (for UV stability).
   These polymers were found to remain transparent and colour

stable for not less than 3 years when stored at ambient temperatures, pressures and humidities.
For rapid production of thermoset materials it is worthwhile and recommended to explore the use of reaction injection moulding (RIM) *technology which* is so far only being extensively used for fibre reinforced polyurethane products.

3. A similar type of prepolymer system as that mentioned in (2) above is found satisfactory for the production of soft transparent TPU's. These specific formulations are as follows:

   d) CAPA 220/H_{12}MDI/1,4-BD+1,4-CHDM) at 1/3/(1+1)
   e) CAPA 220/H_{12}MDI/(1,4-BD+1,6-HD) at 1/3/(1+1)
   f) CAPA 220/H_{12}MDI/(1,4-BD+1,3-BD) at 1/3/(1+1)
   g) CAPA 220/H_{12}MDI/(1,4-BD+1,4-CHD) at 1/3.5/(1.5+1)

   Formulations (d) and (e) were processed by injection moulding and found to be colour stable i.e. remained water like in transparency for a minimum of 1½ years to date. Tests are still in progress. Samples (f) and (g) which are also TPU's are observed to remain transparent and flexible for at least 3 years to date.

4. The TPU's mentioned in (3) above can be readily injection moulded at a temperature of 190°C without causing any discolouration or polymer deterioration. The fact that these TPU's having hardnesses of about 65 IRHD were colour (i.e. water white) stable at normal injection moulding temperature and pressure was consi-

dered surprising, but important, as no anti-oxidant was present in the TPU or any of its base chemical building blocks.

It is generally agreed and reportedly claimed by several workers (e.g. Ref 37) that the TPU's of low hardnesses are not suitable for the injection moulding process. But these specially prepared transparent urethanes both process as TPU's and are transparent and simultaneously possess good mechanical properties.

APPENDIX 1

PROVISIONAL SPECIFICATION FOR A TRANSPARENT FACEPIECE MATERIAL

a) Mechanical Properties

Hardness	∿60 IRHD	(BS 903 Part A26)
Rebound Resilience	∿50	(BS 903 Part A8 Method B)
Compression Set	>25%	(BS 903 Part A6 Method A24 hr @ 70°C)
Tension Set	>20%	(BS 903 Part A5 10' @ 300% strain/10' recovery)
Tear Strength	<50N	(BS 903 Part A3)

(Note: Tensile properties and elongation are not considered critical, but could be used as quality control checks).

The following to be included later after correlation between test results and service requirements.

Scratch Resistance	(BS 3900 Part E2)	
Flexibility @ -34°C	(EAQ 37)	Details of these test methods to be obtained from the USA
Flexibility @ 71°C	(EAQ 37)	
Puncture resistance	(EAQ 38)	

b) Optical Properties

Light transmission	<80%	(ASTM D1003)

The following to be included later after correlation between test results and service requirements.

Haze	(ASTM D1003)	Details of these test methods to be obtained from the USA
Colouration	(MIL 197-51-350)	
Optical Uniformity	(ASTM D637)	

c) Storage Properties

The material shall satisfy the conditions listed under (a) and (b) above after nine weeks storage at:

i) 71°C 10% RH
ii) -34°C

d) Processing Behaviour

Moulding	Injection or transfer moulding possibly with mould release incorporated.
Moulding Time	> 18 hours, desirably ½ hr
Moulds	Desirably metal.

e) Toxic Properties

Effect on the skin	Acceptable to CDE (CDE TN 19)

f) Permeability to Liquid Mustard Gas

Penetration time	50 minutes	(CDE TN 160)
Blot off after	60 minutes 70%	(CDE TN 160)

APPENDIX 2

LIST OF RAW MATERIALS USED WITH THEIR STRUCTURE AND RELEVANT TECHNICAL INFORMATION

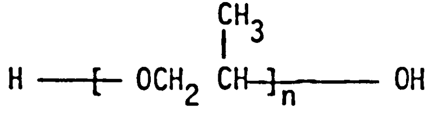
1. CAPA 220 (hydroxyl terminated polycaprolactone)

$$HO - [- (CH_2)_5 - COO - R - COO - (CH_2)_5 -] - OH$$

R = polymerisation initiator

Mol. wt. = 2000, Eq. wt. = 1000, m.p. = ∿ 60^{o}C
Hydroxyl value mg KOH/g = 56.
Supplier: Laporte Industries, Interox Chemicals Ltd., Luton Bedfordshire.

2. D2002 (Polyoxypropylene diol)

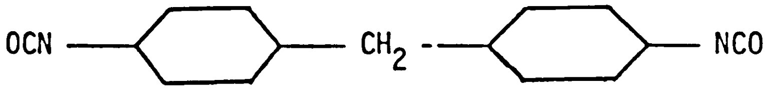


$$H - [- OCH_2\overset{\overset{CH_3}{|}}{CH} -]_n - OH$$

Mol. wt. = 2000, Eq. wt. = 1000, physical state = clear liquid,
Hydroxyl value (mg KOH/g) = 53-59, Acid Value (mg KOH/g) = 0.1 max.

Supplier: Diamond Shamrock, Industrial Chemicals Ltd, Manchester.

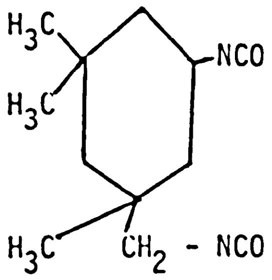
3. Desmodur W (4,4'-methylene bis cyclohexyl diisocyanate, H_{12}MDI)



Mol. wt. 262, Eq. wt. = 131, physical state = clear liquid.
NCO content, % = 31.8 min.

Supplier: Bayer Ltd.
(Formerly supplied by Du Pont Ltd. under the trade name of Hylene W).

4. IPDI (Isophorone diisocyanate)
(3-Isocyanatomethyl - 3,5,5-trimethyl cyclohexyl-isocyanate)



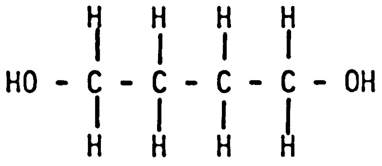
Mol. wt. = 222.3, Eq. wt. = 111.15, Physical state = clear liquid.
NCO content = 37.8 wt %.

Supplier:- Veba-Chemie AG, Belgium.

5. 1,4-butane diol (Tetramethylene glycol)

$C_4H_{10}O_2$ M.W. = 90.12, Eq. wt. = 45.06

Fl.p 134°C, Freezing points → Not below 18.5°C, Boiling range 227-230°C.
m.p. = 16°C



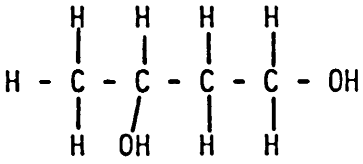
$$HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$$

Supplier: Gh Chemie (GAF) UK.

6. 1,3-butane diol (1,3-Butylene glycol)

$C_4 H_{10} O_2$. M.W. = 90.12. Eq. wt = 45.06.

Fl.p 110°C. b.p. = 203-204°C



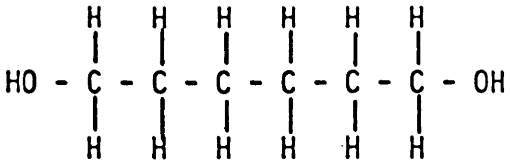
$$\mathrm{H-CH_2-CH(OH)-CH_2-CH_2-OH}$$

Supplier: Koch-Light Laboratories Ltd.

7. 1,6-Hexane diol (Hexamethylene glycol)

$C_6 H_{14} O_2$. M.W. = 118 .18 Eq. wt. = 59.09

m.p. = 40-42°C. B.P. = 250°C. Fl.p = 98-100°C.



$$\mathrm{HO-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-OH}$$

Supplier: Koch-Light Laboratories Ltd.

8. Cis, trans-1,2-Cyclohexanediol (Hexahydrocatechol)
Mixture of Cis and trans
$C_6 H_{12} O_2$. M.W. = 116.16. Eq. wt = 58.08
m.p. 72-75°C. b.p. 118-120°C/10 mm
Supplier: Aldrich Chemical Co. Ltd.

9. Cis,trans-1,4-Cyclohexane diol (Quinitol)

$C_6H_{12}O_2$ M.W. = 116.16. Eq. wt = 58.08

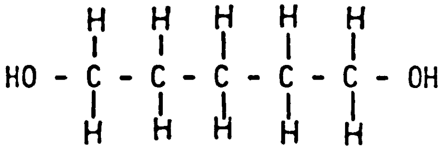
m.p. 98-100°C. b.p. 150°C/20 mm. Fl. p 65°C

Supplier: Aldrich Chemical Co. Ltd.

10. 1,5-Pentane diol (Pentamethylene glycol)

$C_5H_{12}O_2$. M.W. = 104.15. Eq. wt = 52.07.

b.p. = 240°C. Fl.p = 129°C



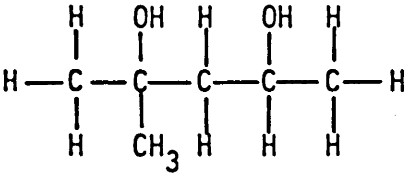
$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ HO & - & C & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

Supplier: Hoch Light Laboratories Ltd.

11. Hexylene glycol (2-methyl-2,4-pentane diol)

$C_6H_{14}O_2$. M.W. = 118.18. Eq. wt. = 59.09.

b.p. = 196-197°C Fl.p = 100°C



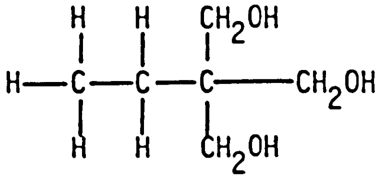
$$\begin{array}{ccccccccccccc} & & H & & OH & & H & & OH & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & CH_3 & & H & & H & & H & & \end{array}$$

Supplier: BP Chemicals.

12. Trimethylol propane (2-Ethyl-2 hydroxymethyl propanediol)

$C_6 H_{14} O_3$. M.W. = 134.18. Eq. wt = 44.73.

m.p. = 56-58°C

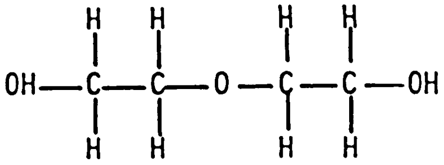


Supplier: BDH Chemicals Ltd.

13. Diethylene glycol (2-hydroxyethyl ether <u>or</u> 2,2'-oxydiethanol)

$C_4 H_{10} O_3$ M.W. = 106.12 Eq. wt. = 53.06

b.p. 245°C Fl.p = 124°C



14. 1,3-Cyclohexanediol (Hexahydroresorcionol) mixture of Cis and trans

$C_6 H_{12} O_2$. M.W. = 116.16. Eq. wt. = 58.08.

m.p. = 30°C. b.p. = 246-247°C

Supplier: Aldrich Chemical Co. Ltd.

15. 1,4-Cyclohexanedimethanol (cis,trans-1,4-Bis-(hydroxymethyl)-cyclohexane)

$C_6H_{10}(CH_2OH)_2$ M.W. = 144.21. Eq. wt = 72.10

b.p. = 283°C.

Supplier: Aldrich Chemical Co. Ltd.

16. CAPA 305 (Polycaprolactone triol)

Mol. wt. = 540. Eq. wt = 180 Physical state = clear viscous liquid

OH value mg KOH/g = 310.

Supplier: Laporte Industries, Interox Chemicals Ltd. Luton, Bedfordshire.

17. Phenyl mercury oleate (catalyst).
Nuodex PMO of Durham Chemicals.

18. Contour 1711)
DI Cilase 1818) Mould release agents

Supplier: Compounding Ingredients, Manchester, UK.

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