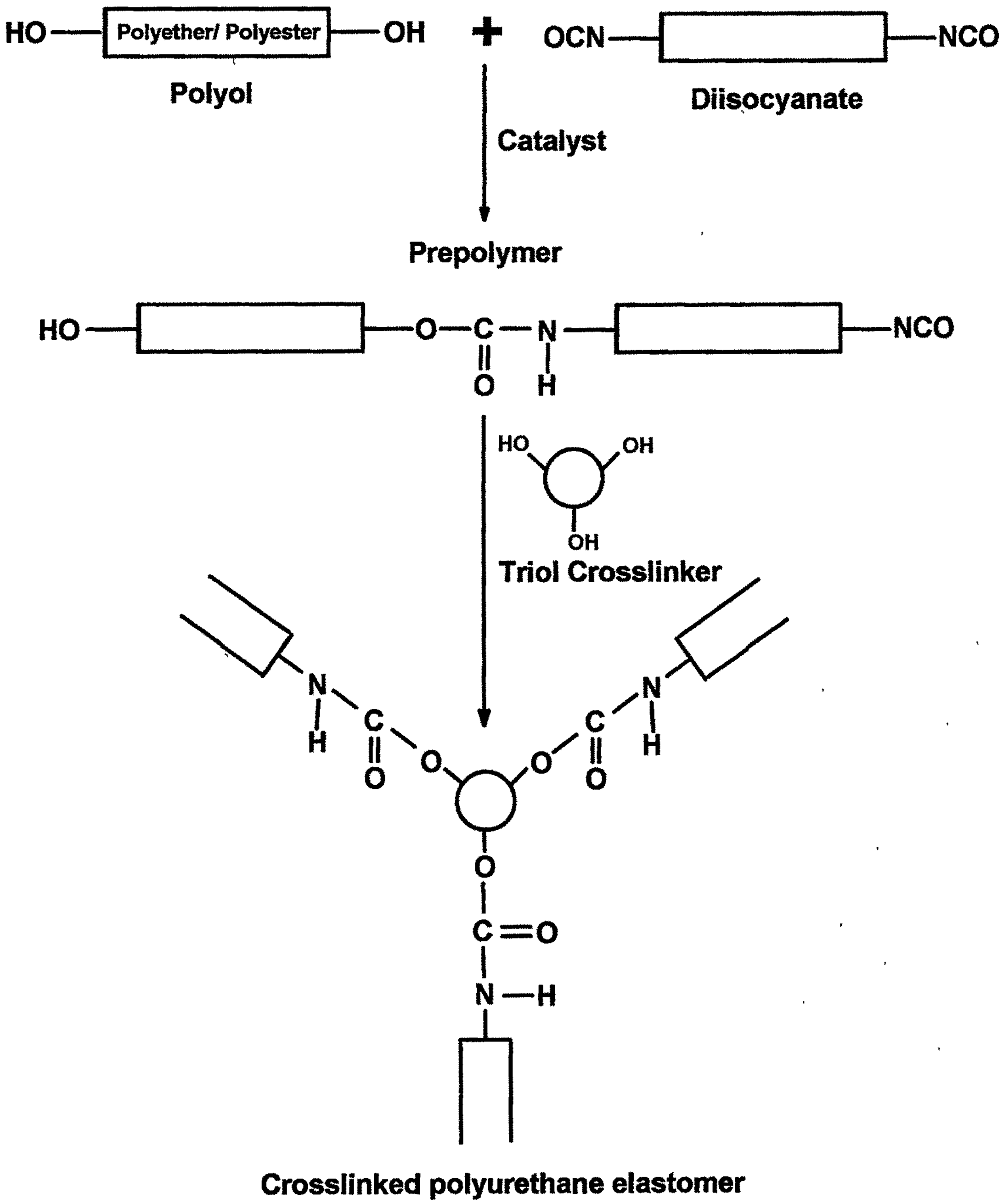
The basic patents for polyurethanes obtained as early as 1848 quoted that "These highly porous, lightweight materials can be used as structural materials in aircraft construction and shipbuilding as thermal or acoustical insulation materials. It can also be used in residential construction, for making toys, furniture, wheels, artificial limbs, shoe soles and orthopedic casts"[1-4]. Inventors had realized potential of polyurethanes even during those days. The first commercial polyurethanes were Igamid U and Perlon U.

After the success of flexible foam in the furniture industry, rigid foams made their way as unmatched insulation materials. During sixties, considerable progress in chemical research, technology and processing applications led to a broad spectrum of commercial uses of polyurethanes in many significant areas. Besides considerable growth was noticed in the applications of flexible and rigid foams and novel semi-rigid foams in automobiles. Development of novel PU coatings led to high quality products for the textile and surface coating industries and new vapor permeable PU substrates called Poromerics for leather industry.

Most of these PUs are composed of at least three basic components:

1. long chain polyether or polyester polyols,
2. diisocyanate and
3. glycol, water or diamine as chain extender or a triol as crosslinker

which are characterized as segmented structures (primary chain). The secondary and tertiary structure and consequently, the morphology of these PUs are dependent on the chemical composition and the length of segments (blocks). The reason for the better properties of these products is attributed to the two or



Formation of Crosslinked polyurethane

polyphase structure. Typical segmented thermoplastic PU elastomers (TPU) as well as fibers and coatings based on PU polyureas, are predominantly linear whereas flexible and semi - flexible foams, cast elastomers and most reactive systems are crosslinked PUs where triol crosslinker is used instead of diol chain extender.

- ***Hard and soft segments***

The ideal structure of PU prepared from one mole of long chain diol, one mole of short chain diol and two moles of diisocyanate consist of highly flexible soft segments, which are quite mobile and are normally present in coiled conformation along with the alternately placed hard segments of stiff oligourethane units.

- ***Segregation and domain morphology***

The two phase nature of the original reaction mixture is related to the fact that low molecular weight glycol has a relatively high polarity and therefore, it has only limited compatibility with a long chain glycol (polyol) and diisocyanate. In the first step the oligomeric glycol reacts with the diisocyanate, forming polar urethane groups, responsible for improved compatibility. As the reaction proceeds, macromolecules are formed which exhibit the outlined segmented structure. The nonpolar low melting soft segments are incompatible with polar high melting hard segments. Hard segments, which are prepared separately are usually insoluble in oligomeric glycols at temperatures below 120 °C. As a result, phase separation occurs and simultaneously covalently linked microphases are formed.

The resulting morphology of polyurethane can be explained in the following manner. The coherent matrix which consists of flexible soft segments results in the high deformability of the resulting material. In contrast, within the hard segment domains, the molecules are fixed by physical interaction. Because of the covalent coupling with the soft segments, they inhibit plastic flow of the chains, thus creating elastomeric resiliency. Hard segment domains can be looked at as multifunctional crosslinked areas.

The degree of segregation between hard and soft segments depends on the interaction between the hard segments or between the hard and the soft segments respectively. Therefore the segregation is less pronounced in polyester urethanes compared to polyether urethanes and is most pronounced in polybutadiene urethanes.

• *Effect of hard segment domains on mechanical and thermal properties*

The thermo-mechanical properties of linear segmented polyurethanes are substantially different from those of chemically crosslinked products. When mechanical forces are applied, changes in the orientation and mobility of structures within the hard segment domains, which depend on temperature, can occur (eg. plastic deformation, strain-induced softening). The single bonds are less overstressed as the tension is more evenly distributed. As a result, the resistance of the material against further stress increases. Furthermore, this effect contributes to the high tensile strength, elongation and tear strength. The melting range of the hard segment domains determines the dimensional thermal stability of linear segmented PU. Above the melting range the material behaves as thermoplastic.

• *Effect of the soft segment matrix on thermal and mechanical properties*

The mobility of the molecular chains causes the reversible elastomeric properties of these elastomers, specifically the cold flexibility and ultimate stress values. The mobility depends to a large extent on the chemical nature and chain length of the soft segment. In order to obtain good elastomeric properties, especially impact resistance, the soft segment should be amorphous and should possess a low enough glass transition temperature.

Apart from the soft and the hard segments, the properties of PUs depend on the NCO : OH equivalent ratio (R value), diol : triol ratio and conditions of synthesis. Due to many factors affecting the thermo-mechanical properties of PUs, it is of interest to examine the structure - property relations in a series of polyurethanes. Polyurethanes are finding increasing applications in the field of fibers, foams, elastomers and coatings. They are best known for their high tensile strength, load bearing capacity and resistance to abrasion. With a wide range of structural variations, end products with diverse characters and properties have been manufactured. Further, polyurethanes have been blended with many other polymers to obtain high performance materials with desirable properties. One such form of PU blends is Interpenetrating Polymer Network.

• *Interpenetrating Polymer Networks*

Properties of polymer mixtures resulted from chemical and physical combinations of polymers have been of commercial and academic interest, since they provide a convenient route for the modification of the properties to meet specific needs. Among these methods interpenetrating networks (IPNs) represent a new approach to the problem of mutual incompatibility of polymers. IPNs possess excellent engineering properties because of the synergistic effect of individual polymers.

Interpenetrating Polymer Networks were first synthesized by Miller in 1960s[6]. Since that time the term has been used to describe the combination of two or more different polymer networks,. which consist of purely physical entanglements of the polymer chains synthesized either simultaneously or sequentially with respect to each other. At present in spite of various definitions of IPN systems proposed by Sperling, Lipatov and Klempner et al, and in view of the incompatibility of the polymers forming IPN system, they are classified as polymer blends. Interpenetrating polymerisation is a mode of blending two polymers to produce a mixture in which phase separation is not as extensive as it would otherwise be. However, in this case the extent of phase separation is restricted due to their interlocking phase configuration. These specialty blends have attracted a lot of attention in recent years because of many diverse aspects.

A critical variable that controls the IPN character is the presence of crosslinks. The crosslinking controls the properties such as toughness, fatigue, sound and vibration damping capabilities and swelling in solvents. Crosslinking of the first formed polymer is thought to limit phase separation of the second polymer.

The exhaustive literature survey carried out by us showed that, IPNs synthesized so far exhibit varying degrees of phase separation depending mainly on the miscibility of the polymers. Hence, our goal is to understand the important factors governing the final properties of the resulting IPNs so that materials with properties tuned to the required application may be produced.

• Proposed Work

We have tried to develop compatiblised IPNs and blends of polyurethanes with poly (methyl methacrylate) and nitrile rubber. The blends / IPNs of PU and nitrile rubber have been studied only to a limited extent whereas those of polyurethane / poly (methyl methacrylate) (PU / PMMA) have been reported by many researchers. However, they are based on some other polyurethanes and in many cases, structure - property relationships have not been established. Hence, we have developed polyurethanes derived from various polyols and diisocyanates and made a thorough investigation of various factors affecting their thermo-mechanical properties.

The work was executed in the following steps :

1. Synthesis of polyurethanes based on various polyols and diisocyanate.
2. Study of the effect of polyols, diisocyanate, NCO / OH equivalent ratio and crosslink density on the mechanical, thermal, dynamic mechanical, morphological and transport properties.
3. Development of full and semi IPNs of polyol and polymethyl methacrylate and study the effect of PU composition and crosslink density on their properties.
4. Development of compatibilized IPNs containing Glycidyl Methacrylate (GMA) and 2 – Hydroxyethyl Methacrylate (2 - HEMA) to improve the compatibility between the two networks.
5. Preparation and characterization of PU / NBR blends.
6. Synthesis and characterization of PUs containing starch as crosslinker and their comparison with PUs containing conventional crosslinker.

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Chapter 1

Synthesis & Characterisation of Polyurethanes

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Study of structure property relationship in segmented polyurethanes has acquired importance due to the broad range of applications of polyurethanes. Their properties can be tailored simply by varying the components such as rigid diols, flexible polyols and polyisocyanates. At room temperature the macroglycol segments are above their glass transition temperature (Tg) and act as soft segments and the aromatic diisocyanates, which are below their Tg act as hard segments. The hard domains act as filler particles and as crosslinks to restrain the motion of soft segment chains. The soft segment provides elastomeric character for the polymer, while hard segment provides dimensional stability.

1.1 Applications of Polyurethanes

Thermoplastic polyurethanes were introduced in the early 1960s. Since then a variety of polyurethanes, based on various polyesters / polyethers, various diisocyanates, chain extenders and crosslinkers, exhibiting a wide range of applications are synthesized. Some of the significant and extensively studied applications are discussed here in brief.

1.1.a Polyurethane as Foam :

One of the most widely used common form of PU is the foam. Innumerable references and patents are available on a variety of polyurethane foams and their modifications. The preparation of foams involves the use of blowing agents such as chlorofluorocarbon compounds, which bring about ozone depletion. Hence in the recent years, Kanetani et al[1] have developed foams with uniform cell structure by predispersing the heat decomposable blowing agent.

Attempts were also made to obtain foams without using blowing agents[23] or by using blowing agents that do not cause ozone depletion[4].

Quinn et al[5] have reviewed the developments and applications of PU foams. Amayoshi et al[6] have patented the method of preparing heat insulating polyether based PU foams. Mechanical properties of closed cell PU encapsulant foam were measured as a function of foam density by Goods et al[7].

1.1.b PU in Coatings :

Another important application of PU is in coatings. Number of reviews are available on speciality PU coatings and on the trends in their development[8-10]. Low temperature curable liquid PU compositions for thick film coatings have been prepared by Hanabusa et al[11]. Takayanagi et al[12] have synthesised acrylic based aqueous PU coatings while Chihara et al[13] have developed EPDM based PU coating materials useful in automobiles.

1.1.c PU as Adhesive :

PUs also find applications in the field of adhesives. Adhesive compositions having good flexibility, alkali resistance and storage stability have been prepared by Yanagusawa et al[14] and Muenzmay et al[15]. Nagai et al[16] developed a method for the synthesis of one component moisture curable PU adhesive compositions. Several reviews are available on urethane adhesives[17-21]. Ratnam et al[22] have developed solvent based polyurethane adhesives for shoe soles by polymerizing toluene diisocyanate (TDI), polypropylene glycol (PPG) and propylene glycol (PG). The polymerisation was carried out in methyl ethyl ketone at 75 °C using NCO / OH ratio 1:1.1. The product with 30 % solid content was tested as adhesive for bonding leather with rubber, PU, and polyvinyl chloride soles and the bonding characteristics were studied.

1.1d PU as Vibration Damper:

This is one of the very interesting and well-known application of polyurethane elastomers. A large number of PU compositions, which can serve as vibration dampers have been developed. Thermoplastic elastomer compositions have been developed by Yamaguchi et al[23], as vibration dampers whereas viscoelastic compositions as vibration dampers have been reported by Masuhara et al,[24] Higashiyama et al[25] and Endo et al[26].

Vibration damping property of PU resins based on polyester polyols has been studied by Ryou et al[27] and Guo et al[28]. Dynamic mechanical properties of polyether based PUs derived from polyoxypropylene glycerine ether and TDI have been studied by Sasagi et al[29] and those of PPG and xylene diisocyanate based PUs by Yamamoto et al[30]. Use of polyurethane foams for sound and vibration damping is also reported[31,32].

1.2 Review of work done on Polyurethanes

The properties of elastomeric polyurethanes depend very much on their chemical structure and morphology. The polyol, which constitutes the soft segment, and the isocyanate and chain extender/crosslinker, which constitute the hard segment, affect the properties of polyurethanes in various ways. Hence a variety of polyols, diisocyanates, chain extenders and crosslinkers have been used in the synthesis of PUs[33-38].

Effect of type and reactivity of diisocyanate on thermal and mechanical properties, is also extensively studied[39-41]. Effect of various diisocyanates such as TDI, 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) on the properties of poly (ester based urethane) is studied by Pandya et al[41]. Wang et al[42] studied structure property relationship by preparing a series of segmented polyurethanes containing a novel diisocyanate 4,4'-diphenylethane diisocyanate, (P_2PDI) and three types of polyether polyols [polyethylene glycol (PEG), PPG, and polyoxytetramethylene glycol (PTMG)]. They observed that tensile properties of polyurethanes prepared from P_2PDI were inferior to the conventional polyurethanes prepared from MDI. This was also exhibited in the lower Tg values obtained for the hard-segments in the P_2PDI containing polyurethanes.

Many times the soft segment forms a major portion of the PU elastomer and its nature dominates the PU properties. Petrovic etal[43] have studied the effect of soft segment length and concentration on phase separation in the PUs synthesised from PPG of different molecular weights and different chain extenders such as BD, pentane diol and hexane diol. The utility of 1,3-propanediol (1,3-PDO) was evaluated through a comparison of the physical, mechanical, and thermal properties of thermoplastic polyurethanes (TPUs) containing chain-extenders 1,3-PDO and 1,4-butanediol (1,4-BD)[44]. These MDI-based TPUs were prepared with PTMG, PPG, poly(1,4-butanediol adipate) and polycaprolactone (PCL) soft segments. In general, at room temperature the physico-mechanical properties were similar for both 1,3-PDO-and 1,4-BD-chain extended TPUs. However, 1,3-PDO-chain extended TPUs tend to have higher softening temperature. Further 1,3-PDO-chain extended TPUs derived from PPG-1000, were observed to have significantly higher tensile strength compared to the 1,4-BD chain-extended TPUs. The morphology of PUs was studied by DSC, SEM and DMA. The prepolymers synthesized from TDI, MDI and polyether polyols such as PTMG and PPG with various compositions were used by Lee et al[45] as a single-component moisture curing prepolymer, which reacts with surface humidity of substrate. Reactivity, structural changes, and properties of these prepolymers were studied as a preliminary step for the manufacture of PU-based adhesives and sealants. The compositions with NCO :OH molar ratio 1.78 were reported to show highest reactivity. It was observed that the prepolymer reactivities were dependent more on polyol nature than on isocyanate nature. Tensile properties of TDI-based PUs were reported to be better than those of MDI-based PUs. Similarly PTMG based PUs exhibited superior tensile properties than PPG-based PUs.

Petrovic et al[46] studied the mechanical and dielectric properties of two series of PU elastomers having soft segment concentration of 50 – 70 % and varying degrees of crosslinking. It was observed that tensile strength and elongation decrease but elastic recovery increases with increasing crosslinking. Effect of average length of soft segment on morphology and properties of PU elastomers was studied by Martin et al[47] using PTMG of varying molecular weights (433 to 1180). Vibration damping of polyether based PUs with $R<1$ was studied through viscoelastometry by Huang et al[48]. Whereas Kim et al[49] carried out a comparative study of thermoplastic polyurethane elastomers containing different soft segments. Two series of thermoplastic polyurethane elastomers based on PPG and PTMG ($\overline{Mn}$ 2000) were synthesized using IPDI and 1,4-butanediol (BD). The hard segment content of polyurethanes varied from 40 – 73 weight percentage. The viscoelastic and dielectric properties of (PPG)-tris-(4-isocyanatophenyl) thiophosphate (commercial Desmodur RFE) networks were studied by Sleeman and Nusselder[60] with special focus on the relaxation behavior near the glass transition. Two relaxation mechanisms respectively due to PPG chain segments and less mobile crosslink moieties were observed in the glass transition range;. A study on the synthesis and electrical conductivity of polyurethane ionomers based on PPG, MDI was carried out by Maeng et al[61]. The electric conductivity of copper sulphate-doped ionomer was reported to be 100 times higher than undoped one. The morphology of doped and undoped polymer surfaces ~~was studied through~~ SEM.

Hydroxy terminated polybutadiene (HTPB) based polyurethane binders were reported to have many advantages[62-64]. They differ from those synthesised from polyethers in many respects. When polyether /polyester soft segment in polyurethane was replaced by oligobutadiene, increased resistance to acid, base hydrolysis, good adhesion and retention of elastomeric properties were reported by Zawadski and Ackeruld[65]. Moreover, the complete hydrocarbon structure of polybutadiene prevents intersegment hydrogen bonding, which is usually present in polyether or polyester based polyurethanes, causing phase segregation[66,67].

The effect of aliphatic diols on the structure and mechanical properties of PU elastomers containing HTPB and three different diisocyanates was studied by Siegmann et al[68]. Huang and Lai[69] synthesized a series of HTPB based PUs with various diisocyanates, hard segment contents, NCO:OH ratios and polymerisation techniques. The same authors[60] have modified HTPB-based polyurethanes by crosslinking soft segments or complexing the hard segments or developing interpenetrating networks (IPNs) with 4-vinylpyridine (4-VP). The PUs were characterised by DSC, TGA and tensile properties. The effect of hard-segment content, DVB content, and 4-VP content on the tensile properties was also investigated. Increase in stress was observed for the modified PUs, no variation in strain was reported.

Hao et al[61] examined the effect of free isocyanate content, the chain-extender level, and the molecular weight of HTPB, on the mechanical properties of polyurethane elastomer synthesised from HTPB of different molecular weights, 2,4 TDI and N,N-bis (2-hydroxypropyl) aniline chain extender. The authors[62] also studied synthesis and properties of polyurethane elastomers derived from HTPB / polytetrahydrofuran (PTHF) and TDI. The effect of free NCO content and the HTPB / PTHF ratio on the physical properties of the elastomers was discussed. Good comprehensive properties of elastomers were obtained when the free NCO content was 8.5%. With decreasing HTPB/PTHF ratio improved tensile strength and tear resistance was reported.

Singh et al[63] examined the effect of allophanate on the properties of polyurethanes prepared from TDI and HTPB prepolymers with different functionality distribution, at NCO:OH stoichiometric ratios 0.8 to 1.5. The resulting networks were characterized in terms of crosslink density (ν_e), sol content and elongation at break. The effective chain length and the ratio of urethane to allophanate, were calculated. Spectroscopic and stress-strain studies were carried out to elucidate the structure-property relationship existing in these polymers. Thermal and mechanical properties of HTPB based PUs have been investigated by a number of authors using DSC and DMA[64,65]. Two phase morphology was reported by Brunette et al[66] for HTPB based PUs through thermal and dynamic mechanical studies. A polyurethane elastomer having desirable mechanical and adhesive properties for liners in solid rocket propellants was developed using HTPB based prepolymer and IPDI as the curing agent[66]. The effect of NCO/OH ratio (R value) and the triol / diol ratio on the mechanical properties of the polyurethane matrix was investigated. At R value 1 the elastomer showed maximum tensile strength and 200% elongation at break.

In the comparative study of HTPB-based polyurethanes containing aliphatic (1,3-propanediol, 1,4-butanediol and 1,6-hexanediol) and aromatic [bis (2-hydroxy isopropyl)aniline] chain-extenders, Zawadski and Akceruld[65] observed a different trend in mechanical properties than those reported earlier for the similar systems. The difference in properties was interpreted on the basis of reactivities, experimental procedures and morphology examined through swelling studies, DSC and SEM.

The morphology and properties of polybutadiene based elastomeric polyurethanes consisting of HTPB soft segment and TDI, 1,4-butanediol hard segments were reported to exhibit microphase separated structure through FT-IR, WAXD (wide-angle x-ray diffraction), SAXA (small angle x-ray scattering) and DSC studies[67]. Glass transition temperature was reported to increase with increasing hard segment content. Relation between morphology and various properties of polybutadiene-based polyurethane elastomers was examined thoroughly.

The mechanical properties of the PU elastomers prepared from HTPB, aromatic, alicyclic, and aliphatic diisocyanates and chain extenders containing OH and NH_2 groups, were interpreted in terms of hard and soft segment structures by Villar and Akceruld[68].

The kinetics of formation of copolyurethane network based on HTPB, a copolyester polyol derived from 12-hydroxystearic acid and 1,1,1 - trimethylolpropane (TMP) and different isocyanates was studied by Sekkar et al[69] through viscosity built up during the cure reaction. They also carried out a systematic study on a composite solid propellant formulation containing HTPB based prepolymers of varying molecular weights and hydroxyl values[70]. In this set of experiments, varying levels of diol and triol contents were used at two different NCO / OH ratios to arrive at the optimum level needed for different grades of HTPB resins in the above mentioned formulations. The authors have also established correlation between network parameters such as crosslink density and sol content and mechanical properties of the above mentioned copolyurethane systems[illegible]. Further, they have developed models for the prediction of network properties of these copolyurethane systems of varying compositions[72]. The mechanical properties of the solid propellants were correlated to binder properties and the volume fraction of filler loading. Fairly good agreement observed between the calculated and experimental values confirms the utility of the proposed model. Copolyurethanes of HTPB and a castor oil-based polyol (ISRO-Polyol), were also prepared by them using TDI and HMDI to develop solid propellant binders. The mechanical and swelling properties of these copolyurethanes cured with TMP and triethanolamine were studied. By varying the ratios of the pre-polymers, chain extenders, and crosslinkers, copolyurethanes having a wide range of tensile strength and elongation were obtained.

Synthesis, characterisation and propellant binder studies of polyurethanes based on polyethers and polyesters was carried out by Kothandaraman et al[72]. Structure-property relationships of polyurethane elastomers based on new saturated hydrocarbon diols consisting of ethylene-butylene copolymers of narrow mol. wt. distribution with terminal, primary hydroxyl groups have been discussed by Frisch et al[73]. Both thermoplastic and casted polyurethane elastomers (TPUs) were prepared from these diols and diisocyanates employing various chain extenders and curatives. These TPUs exhibited a very broad operational temperature, good oxidative and hydrolytic stability and resistance to corrosive media when compared to PTMO and PPG-based elastomers.

Number of reviews have appeared pertaining to segmented PU block copolymer morphology[74], recent developments in PUs[75-78], their preparation, properties and uses[79-83] and structure property relations[84,85]. Effect of method of preparation such as prepolymer method or one shot method on mechanical properties of PU networks has been studied by Furukawa et al[86]. Foks et al[87] have also studied morphology and thermal properties of PUs prepared under different conditions. Ethylene glycol was also used here in addition to 1,4 BD. The temperature of synthesis and curing temperatures were varied and different PUs were thus synthesized and characterized. The same authors[88] have studied the structure of segmented PUs with different hard segment derived from poly (ethylene adipate), MDI and 1,4 BD through microscopy. Estes et al[89] proposed a morphological model of PUs having interlocked hard domains. Chau and Geil[90] further studied the domain morphology of polyester polyurethanes by dark field electron microscopy. Morphology of segmented PUs based on HTPB, MDI and 1,4 BD, prepared by varying the hard segment, has been studied through SEM, SAXS and HVEM[91].

Number of attempts were made to establish a correlation between morphology, hard segment content, synthetic conditions, thermal treatment and physical properties[92,93] of polyurethanes. It has been observed by many authors[94,95] that better properties are achieved when the microphase segregation between soft and hard segment increases. Influence of NCO:OH ratio and chain extender on primary and secondary crosslinks has been studied by Rutkowska et al[96] for the PUs based on PEA MDI and chain extenders, 4,4'-methylene bis chloroaniline (MOCA) and 1,4 BD. Apukhtina et al[97] have studied the properties of segmented polyurethane based on poly (diethylene glycol adipate), TDI and a mixture of 1,4 BD and TMP.

Sorption and diffusion of number of solvents through commercial PU membranes is studied by Aminabhavi et al[98-100]. They have investigated the sorption of a series of alkanes in the temperature range of 25 – 60 °C. Schneider et al[101,102] studied the effect of structural variation on transport of solvents in polyurethanes. Solvent induced changes in thermal stability of PU have been observed by Nair et al[103]. Sorption of PPG of various molecular weight by a PPG, triisocyanate based PU has been studied by Petrovic et al[104].

The properties of a polymer depend upon several factors such as molecular weight, chemical nature of the units composing the polymer, mode of synthesis and the morphology. In case of polyurethanes, due to thermodynamic differences the two segments usually segregate to form a pseudo - two - phase structure[105]. From the literature survey it can be summarized that The desirable thermo-mechanical properties of these Polyurethanes are directly related to the two phase micro structure where the hard domains act as multifunctional crosslinks and reinforcing fillers for the flexible soft segments giving rise to materials with high modulus and elastomeric properties[106]. Hence among many other factors, NCO:OH equivalent ratio and diol : triol ratio also affect PU properties.

As discussed earlier, polybutadiene soft segment imparts much different properties to polyurethanes, compared to a polyether or polyester soft segment. Similarly among diisocyanates, the most commonly used diisocyanate, TDI, is generally 80 / 20 % mixture of 2,4 and 2,6 isomers. The asymmetry of the 2,4 TDI creates a disruptive influence within the hard segment structure. On the other hand MDI has no such isomeric asymmetry.

Hence a systematic study of understanding the effect of type of polyol and diisocyanate, NCO:OH ratio and degree of crosslinking on the thermal, mechanical and morphological properties of PUs synthesised from two polyols (HTPB and PPG) and diisocyanates (TDI and MDI) is undertaken.

1.3 Experimental

1.3.1 Materials

Details of the chemicals used for the synthesis of polyurethanes are given in Table-1.1.

Table 1.1 : Chemicals used for the synthesis of polyurethanes

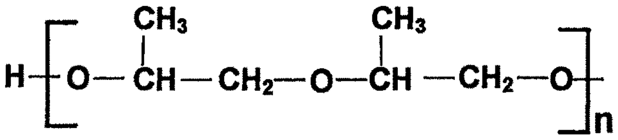
Materials	Description	Source
1. Polypropylene glycol (PPG 2000)	colourless viscous liquid Hydroxyl value : 56.1 mg KOH /g Molecular weight : 2000	Fluka AG, Switzerland
2. Hydroxy terminated Polybutadiene (HTPB)	yellowish viscous liquid Hydroxyl value :45.8 mg KOH/g Molecular weight : 2600	Vikram Sarabhai Space Centre, Thiruvananthapuram, India
3. Toluene diisocyanate (TDI)	80 / 20 mixture of 2,4 and 2,6 isomers	Fluka AG, Switzerland
4. Methylene diphenyl diisocyanate (MDI)	Mixture of di- and tri- isocyanates	Vikram Sarabhai Space Centre, Thiruvananthapuram, India
5. 1,1,1 - trimethylolpropane (TMP)	-	Fluka AG, Switzerland
6. Dibutyl tin dilaurate (DBTDL)	-	Fluka AG, Switzerland

Components of Polyurethanes

1. Polyols

$$HO-\left[CH_2-CH=CH-CH_2\right]_n-OH$$

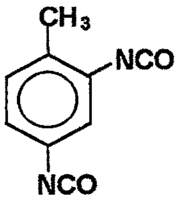
Hydroxy terminated Polybutadiene (HTPB)



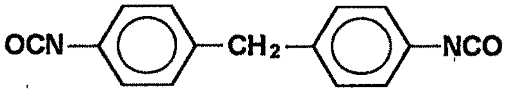
$$H-\left[O-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-O\right]_n$$

Polypropylene Glycol (PPG)

2. Diisocyanates

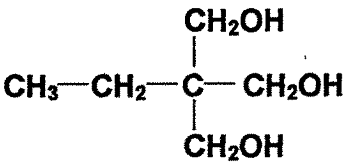


2,4 - Toluene Diisocyanate (TDI)



Methylene Diphenyl Diisocyanate (MDI)

3. Crosslinker



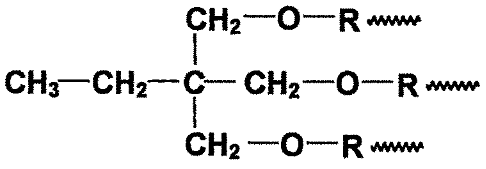
$$CH_3-CH_2-\underset{CH_2OH}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CH_2OH$$

1,1,1 - Trimethylol Propane (TMP

The hydroxyl number of the polyols and the isocyanate number of the diisocyanates were measured from time to time. The polyols and the diisocyanates were used without further treatment. TMP was dried in a vacuum oven at 40 °C till moisture content was reduced to less than 0.1%. Tetrahydrofuran (THF) (A. R. grade) was distilled and dried over sodium sulphate before use.

1.3.2 Synthesis of polyurethanes

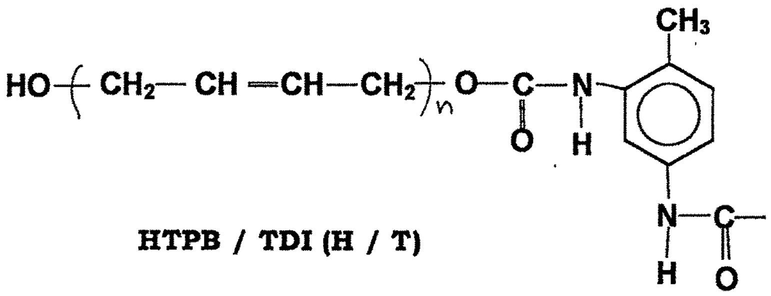
The polyol, PPG/HTPB was dried under vacuum at 80 °C, for one hour. It was allowed to react with a calculated quantity of diisocyanate, TDI or MDI at room temperature in five-neck reaction kettle fitted with a mechanical stirrer and nitrogen inlet. The diisocyanate was added dropwise from the dropping funnel over a period of 15 minutes. The mixture was stirred continuously for about 45 minutes to obtain NCO terminated prepolymer. It was allowed to react further with the required amount of the crosslinker for about 5 minutes until the reaction mixture became viscous. The mixture after degassing was poured into preheated glass moulds. The curing was carried out initially at room temperature for 15 hours and later at 80 °C for 3 hours. On cooling the crosslinked polyurethanes were obtained in the form of films. In the TDI based polyurethanes the catalyst DBTDL was added to the polyol in the beginning, whereas in the MDI based polyurethanes the catalyst was added along with the crosslinker in order to avoid gelation in the early stages of the reaction. The compositions of the polyurethanes synthesised are given in Table 1.2.



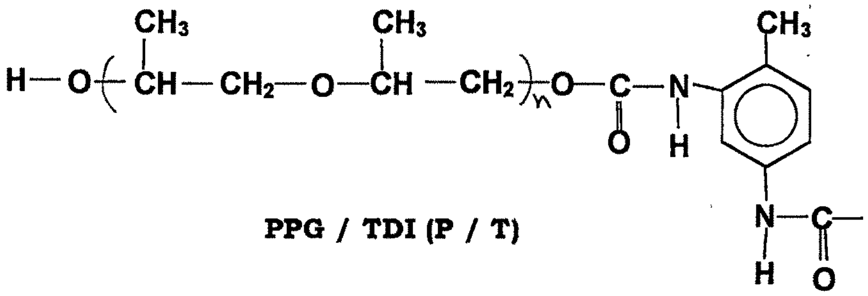
$$\begin{array}{c} \qquad\qquad CH_2-O-R\sim \\ CH_3-CH_2-\overset{|}{\underset{|}{C}}-CH_2-O-R\sim \\ \qquad\qquad CH_2-O-R\sim \end{array}$$

Crosslinked Polyurethane

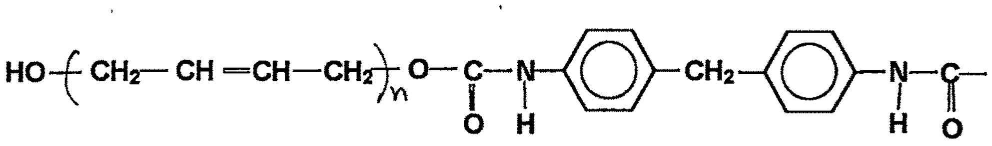
where R =



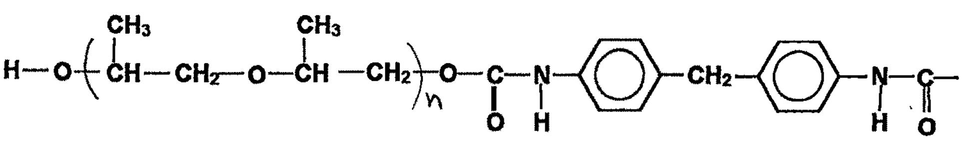
HTPB / TDI (H / T)



PPG / TDI (P / T)



HTPB / MDI (H / M)



PPG / MDI (P / M)

Table 1.2 : Molar composition of polyurethanes

Code	Polyol/Diisocynate/Crosslinker	NCO:OH ratio	% Hard segment
H/T	HTPB/TDI/TMP		
H/T A1	1.0 / 3.0 / 1.5	1.2	21.6
H/T A2	1.1 / 3.0 / 1.4	1.2	23.4
H/T A3	1.2 / 3.0 / 1.3	1.2	25.5
H/T B1	1.0 / 3.25 / 1.5	1.3	26.6
H/T B2	1.1 / 3.25/ 1.4	1.3	26.9
H/T B3	1.2 / 3.25 / 1.3	1.3	28.3
H/M	HTPB/MDI/TMP		
H/M A1	1.0 / 3.0 / 1.5	1.2	21.0
H/M A2	1.1 / 3.0 / 1.4	1.2	22.6
H/M A3	1.2 / 3.0 / 1.3	1.2	24.7
H/M B1	1.0 / 3.25 / 1.5	1.3	25.3
H/M B2	1.1 / 3.25/ 1.4	1.3	26.1
H/M B3	1.2 / 3.25 / 1.3	1.3	27.7
P/T	PPG/TDI/TMP		
P/T A1	1.0 / 3.0 / 1.5	1.2	21.8
P/T A2	1.1 / 3.0 / 1.4	1.2	22.5
P/T A3	1.2 / 3.0 / 1.3	1.2	23.2
P/T B1	1.0 / 3.25 / 1.5	1.3	23.9
P/T B2	1.1 / 3.25/ 1.4	1.3	24.5
P/T B3	1.2 / 3.25 / 1.3	1.3	25.6
P/M	PPG/MDI/TMP		
P/M A1	1.0 / 3.0 / 1.5	1.2	20.9
P/M A2	1.1 / 3.0 / 1.4	1.2	21.6
P/M A3	1.2 / 3.0 / 1.3	1.2	22.2
P/M B1	1.0 / 3.25 / 1.5	1.3	23.0
P/M B2	1.1 / 3.25/ 1.4	1.3	23.8
P/M B3	1.2 / 3.25 / 1.3	1.3	24.6

1.3.3 Characterisation

a. Specimen preparation

As per ASTM standards dumbbell shaped specimens of dimensions 110 x 6 x 2 mm were cut from the PU films using sharp edged steel dye. The dimensions were accurately determined using digital Vernier calliperse and used for the calculation of tensile properties.

b. Tensile Tests

Stress / strain properties of all the polyurethanes were measured on a standard Instron testing machine (No. 4204) according to ASTM-D 638 procedure. The crosshead speed used was 10 mm / min at 25 °C and 50 % humidity. At least 8-10 specimens were tested for each sample. The specimens, which do not break between predetermined gauge (50.0 mm) marks or those breaking at some obvious fortuitous flaw, were discarded.

c. Shore A hardness

Shore hardness was measured on Frank hardness tester with shore A durometer at several points on the surface of the specimen. An average of 8 measurements was taken as the result.

d. Electrical properties

The volume resistivity and tan δ were measured on Hewllett Packard 4329A, high resistance meter and dielectric constant was measured on shearing bridge.

e. Thermal Analysis

Prior to the measurements all the samples were kept in a vacuum dessicator and in the presence of silica gel for about seven days in order to avoid any effect of moisture.

Differential Scanning Calorimetry

The thermal transitions of selected polyurethanes were examined by modulated DSC (DSC 2910 T. A. Instruments, USA) following standard procedure. The samples (~9-10 mg) were quench cooled using liquid nitrogen to the required temperature and heated with a uniform heating rate of 10 °C /min under nitrogen atmosphere (45 ml / min). The glass transition temperature (T_g) was defined as the temperature at the point of intersection between tangents drawn at point of inflection of transition and at the flat part of the curve before transition.

Thermo-gravimetric Analysis

This technique involves measurements of the extent and rate of change of the mass of the sample continuously either as a function of increasing temperature (dynamic study) or at a constant heat flux over a period of time (isothermal study) in a controlled atmosphere. The thermo-gravimetric analysis was carried out on Shimadzu TG 30 thermal analyzer. Accurately weighed sample (~ 5 mg) was heated at a heating rate of 10 °C / min in air from 25 °C to 650 °C. The initial decomposition temperature (IDT) and temperature at which sample undergoes 50 % decomposition (T_{50}) were calculated from the thermograms.

f. Transport properties

The diffusion of some organic solvents through the polyurethane films was investigated using conventional sorption method[107]. For sorption studies circular samples, cut from the polyurethane films using a sharp edged steel die of 1.5 cm diameter were used. Thickness of each sample was measured at various places using a screw gauge and average of the values were considered for the analysis. About 15 - 20 ml of the solvents of varying solubility parameters were taken in the sorption bottles and preweighed samples were immersed into them. At regular time intervals, the samples were taken out of the bottles and the wet surfaces were gently pressed to remove surface adsorbed solvents. They were weighed quickly and reimmersed in the respective bottles. The process was repeated till equilibrium was attained. The possibility of an error introduced due to the evaporation of solvent while weighing was minimised by weighing as quickly as possible within 30 seconds and taking the mean of five observations. The sorption was carried out at 27° C. Various parameters such as swelling coefficient, molecular weight between crosslinks, degree of crosslinking and crosslink density were calculated.

g. Dynamic Mechanical Analysis

DMA measurements of the selected samples were carried out on a Seiko DMS 200 SDM 5600 analyser. The samples were of 30 mm length with a cross section area of ca. 1.8 mm^2. The rate of scanning was 2 °C/min. The range of temperature in which the analysis was carried out was -100 °C to 100 °C at the frequencies of 1, 2, 5 and 10 Hz. The nitrogen atmosphere was maintained using 200 ml / min flow rate.

h. Microscopic Studies

The Surface morphology and fracture topography of polyurethanes was examined by using Leica Cambridge, U. K. (stereoscan 440) Scanning electron microscope (SEM). In order to avoid surface charging under the electron beam, the polymer specimens were coated with gold (50 µm thick) in an automatic sputter coater (Polaron equipment Ltd., USA). An accelerating potential of 10 kV was used for the analysis of sample. The photographs of representative areas of the samples were taken at different magnifications.

Post-swollen PUs were also examined for surface morphology in order to study the change in morphology after swelling. For this the PUs were allowed to undergo complete swelling in 1,4-dioxane and then dried for 15 hours at room temperature and 6 hours at 50 °C under vacuum.

i. Gel content

The insoluble fraction was determined by carrying out the extraction of 2 mm cube of the polyurethane with various solvents in a Soxhlet extractor for 10 hours. After extraction the specimen was dried for 15 hours at room temperature and 6 hours at 60 °C in a vacuum oven. The initial and final weights of the specimen were compared to obtain gel fraction.

1.4 Results And Discussion

The polyurethanes were synthesized using 1.2 (set A) and 1.3 (set B) NCO : OH equivalent ratios. In order to study the effect of crosslinking extent each set was synthesized with three diol / triol ratios (1:1.5, 1.1:1.4, 1.2:1.3). The elastomers were obtained in the form of films of about 2 mm thickness. The HTPB based PUs were yellowish and translucent indicating phase separation while PPG based PUs were colourless and transparent indicating a certain degree of phase mixing. Based on the type of polyol and diisocyanate. HTPB - TDI PUs were designated as H/T, PPG -TDI PUs as P/T, HTPB - MDI PUs as H/M and PPG - MDI PUs as P/M.

1.4.1 Mechanical Properties

Effect of molar concentration of TMP on the tensile strength and elongation at break of polyurethane systems is illustrated in Fig. 1.1 - 1.5. A comparative account of the set B of all PU systems (R value 1.3) is given in Fig. 1.1 while the data for individual PU systems is illustrated in Fig. 1.2 – 1.5.

Effect of diisocyanate

It was observed that TDI based polyurethanes showed higher tensile strength and lower elongation compared to MDI based PUs irrespective of the type of polyol (Fig. 1.1). Both TDI and MDI being aromatic the stiffness imparted by the aromatic ring cannot explain this observation. However, the difference in the structure of the diisocyanates can account for the difference in the mechanical properties. MDI has a linear symmetric structure consisting of two aromatic rings, imparting lower tensile strength due to the lack of rigidity in the backbone. But in the case of TDI a higher rigidity is imparted due to the direct association of the two isocyanate groups with the same phenyl ring. In addition higher reactivity of TDI resulting from the greater extent of delocalisation of negative charge on -NCO by aromatic structure[40], also is responsible for greater tensile strength.

Effect of polyol

HTPB systems could be considered to contain non-, di- and tri-functional species[108]. Reaction of difunctional components with TDI results in chain extension while that with a trifunctional component leads to network formation. Network formation reduces flexibility of the polymer whereas chain extension affects the flexibility to a much smaller extent. PPG on the other hand reacts with the diisocyanate to

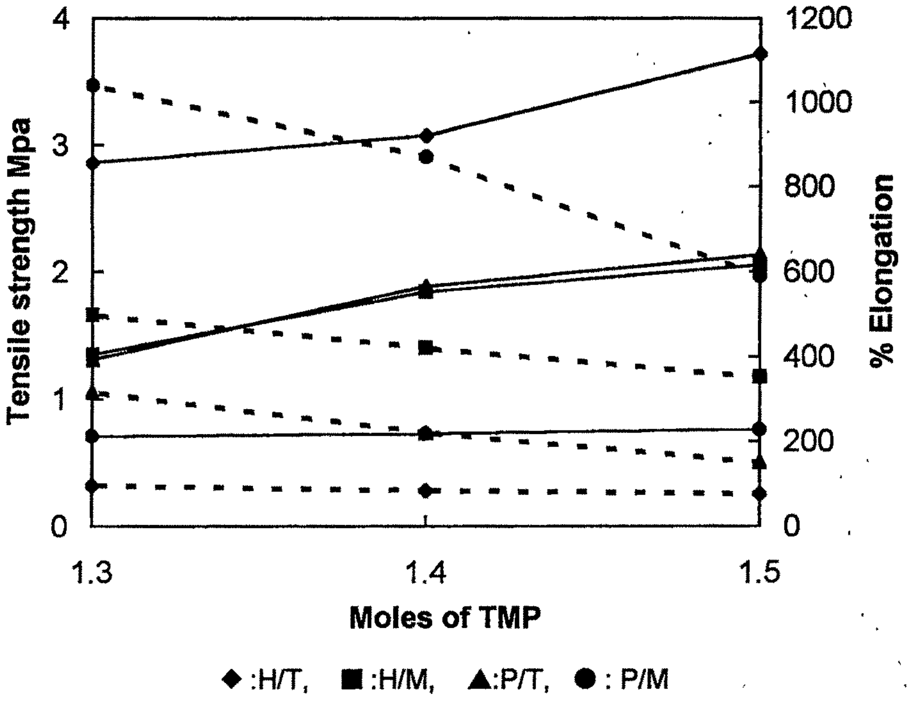


Fig. 1.1: Effect of TMP concentration on tensile strength (____) and elongation (----) of PUs (NCO:OH =1.3)

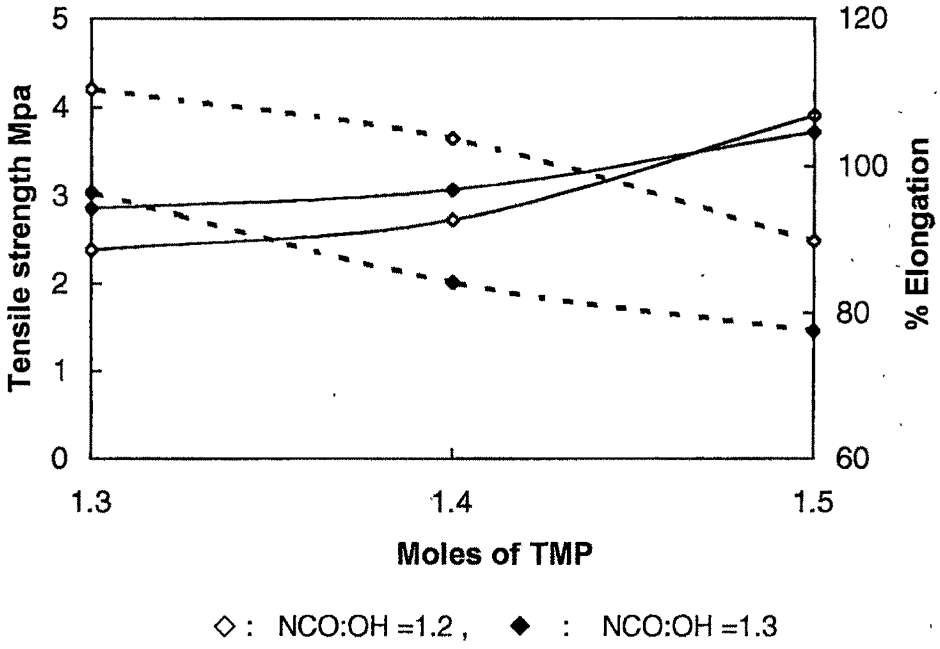


Fig. 1.2: Effect of TMP concentration on tensile strength (_____) and elongation (----) of HTPB-TDI (H/T) system.

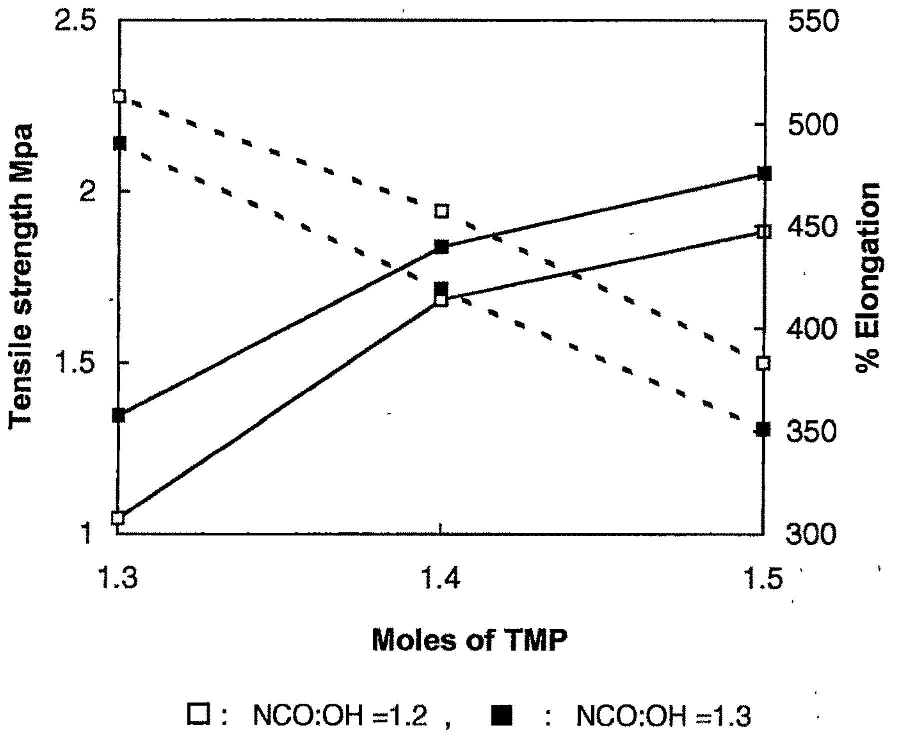


Fig. 1.3 : Effect of TMP concentration on tensile strength (____) and elongation (------) of HTPB-MDI (H/M) system.

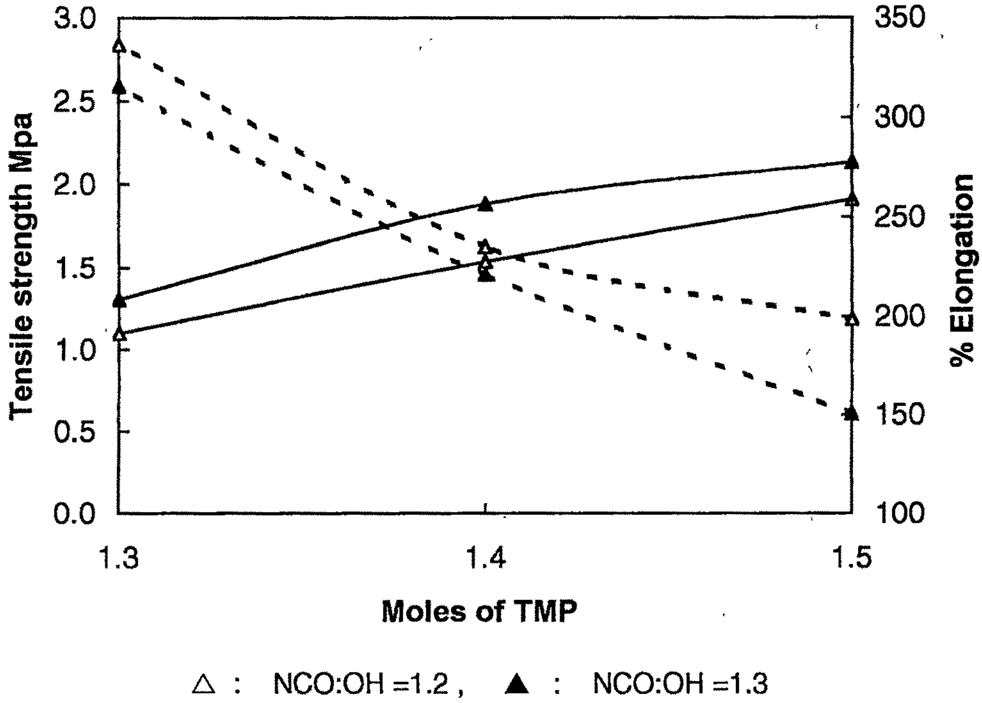


Fig. 1.4 : Effect of TMP concentration on tensile strength (___) and elongation (-----)of PPG-TDI (P/T) system.

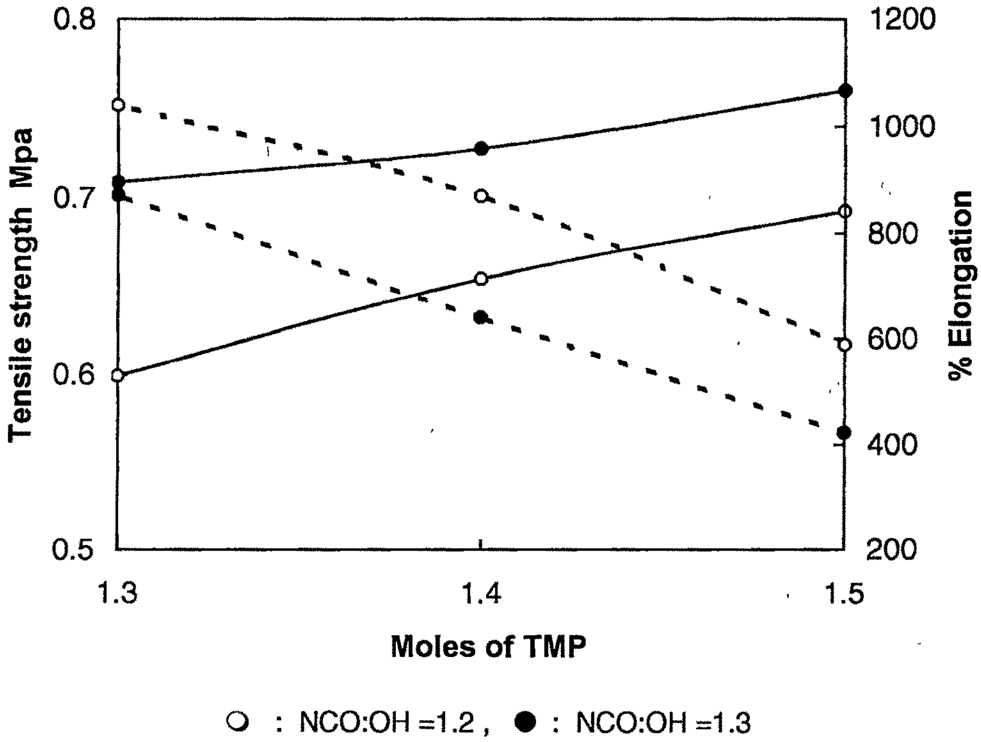


Fig. 1.5: Effect of TMP concentration on tensile strength (____) and elongation (----) of PPG-MDI (P/M) system.

give rise to completely chain extended species. Thus, HTPB based PUs showed higher tensile strength and lower elongation compared to PPG based PUs, due to additional crosslinking from trifunctional species. In addition to that the pendant methyl groups in PPG[73] hinder the close packing of mutually attracting functional groups like urethane/ester group and also act as internal plasticiser thus reducing the intermolecular forces and causing irregularity in the chain. Another reason for the poor mechanical properties is the lower reactivity of the secondary hydroxyl groups[109,110] in PPG. It has been observed that the reactivity of the aliphatic secondary hydroxyl groups towards isocyanate group is approximately one third of the primary hydroxyl group. Due to the difference in relative reactivities defective network formation may take place because of incomplete cure reaction[69] leading to poor mechanical properties.

Effect of hard segment content

The Figs. 1.1 - 1.5 show that irrespective of the type of polyol and diisocyanate, the stress at break increases and strain at break decreases with an increase in hard segment content. As the percentage of hard segment increases the intermolecular attraction between hard segments increases due to hydrogen bonding between -NH and –C =O of hard segment, resulting into increase in stress and decrease in strain properties[69].

Effect of NCO/OH ratio

Two different NCO:OH ratios were selected to obtain two different sets of PUs viz A (NCO:OH = 1.2) and B (NCO:OH = 1.3). Since the NCO:OH ratio is greater than 1 the polyurethanes formed will be NCO terminated. The free NCO groups react further with the urethane linkage increasing the chemical crosslinking leading to a change in morphology and affecting the mechanical properties and hardness (Fig. 1.5 and 1.6). The increase in NCO:OH ratio increases the intermolecular attraction between hard segments, which in turn increases the tensile strength, and decreases the elongation.

Effect of ratio of polymeric to monomeric hydroxyls

Results in Fig. 1.1 – 1.5 clearly indicate that as the concentration of the polyol increases and that of the crosslinker decreases, decrease in the tensile strength and increase in the elongation is observed and the polymer becomes increasingly soft.

1.4.2 Shore hardness

Shore hardness showed a trend similar to the tensile strength. The plots of shore hardness vs. molar concentration of TMP (Fig 1.6) show increase in hardness with increase in crosslinker concentration and NCO:OH ratio. The magnitude of hardness follows the sequence H/T > P/T ≥ H/M > P/M.

1.4.3 Electrical properties

The results of measurement of volume resistivity, tan δ and dielectric constant for the PUs with NCO:OH ratio 1.3 and diol / triol ratio 1:1.5 are given in Table 1.3.

In a condenser system, which is a device for storing charge, a massive quantity of a species of atoms or molecules forming a dielectric mass is placed between two plates. The influence of a particular dielectric mass on the capacitance of a condensor is expressed by the dielectric constant, also known as the relative permitivity or sometimes specific inductive capacity[111]. A low dielectric constant is a character of Insulators.

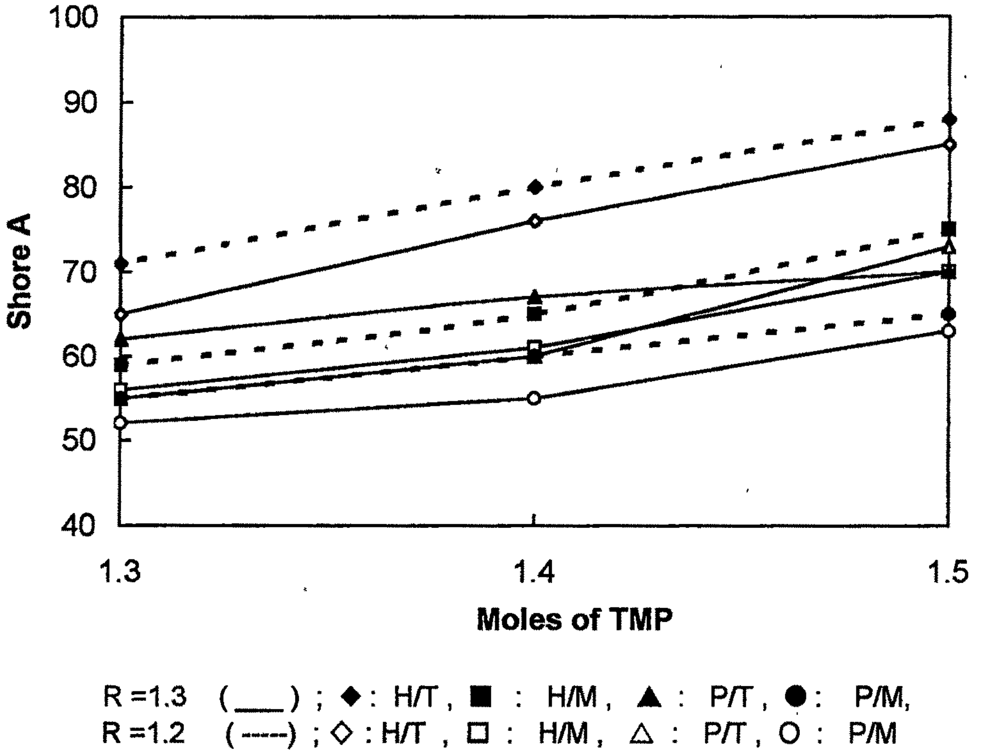


Fig. 1.6 : Effect of TMP concentration on shore hardness of PUs

Table 1.3 : Electrical properties of PUs with R value : 1.3 and diol / triol ratio 1:1.5

Polyurethanes	**Volume Resistivity Ω cm**	**tan δ**	**Dielectric constant**
H/T	1.0×10^{14}	0.01	2.68
H/M	2.0×10^{13}	0.02	3.12
P/T	0.6×10^{10}	0.09	8.30
P/M	0.5×10^{10}	0.12	8.60

The dissipation factor denoted by tan δ is one of the measures of the fraction of energy absorbed per cycle by the dielectric mass from the field[111]. For the determination of δ, change in the voltage in terms of change in current of the condensor due to the presence of dielectric mass is measured as θ. The value of $90 - \theta$ is known as loss angle and is given as δ. The dissipation factor is tan δ. It is observed that dielectric constant which has direct relationship with conductance is considerably high in P/T system than in H/T system. This can be explained on the basis of the fact that PPG 2000 has a number of ether linkages. The lone pair of electrons on oxygen promotes conduction. Replacement of TDI by MDI increases the conductance to some extent due to greater delocalisation of electrons in the latter. The observed increase was found to be smaller in case of PPG based polyurethanes when compared to HTPB based polyurethanes. This may be attributed to the extension in conjugation that may have resulted due to delocalised electrons coming from the two phenyl rings in MDI. No significant change was observed with change in hard segment content, as major portion of the elastomer is soft segment, which contributes to a greater extent.

1.4.4 Thermal Analysis

Differential Scanning Calorimetry

The differential scanning calorimetric plots of representative samples are given in Fig. 1.7. It was observed that PPG based PUs show higher T_g compared to HTPB based PUs. This is because the linear structure of HTPB provides greater flexibility and mobility to the chain, resulting into lowering of T_g whereas the pendant methyl groups in PPG restrict the movement of the chain. Among the isocynates MDI based PUs showed slightly lower values of T_g due to the linear nature of MDI, which imparts flexibility to the network. The glass transition temperature was found to increase with increase in NCO/OH ratio because of the formation of three-dimensional allophanate or biuret structures, which restrict the mobility of the molecular chain. Similarly as the concentration of the crosslinker increases the formation of additional crosslinks imparts rigidity to the network resulting into increase in Tg.

Another important feature is the existence of a single glass transition temperature in the thermograms. Siegmann et al[56] observed several transitions which are generally characteristic of multiphased elastomers. The lower and higher transitions were assigned to T_gs of the soft and hard segments respectively. On the other hand Zawadski et al[55] observed T_g only for soft segment. This may be because of the very small increase in calorific capacity due to glass transition in the hard domains, which is beyond the detection limit especially when the hard segment content is relatively low. The

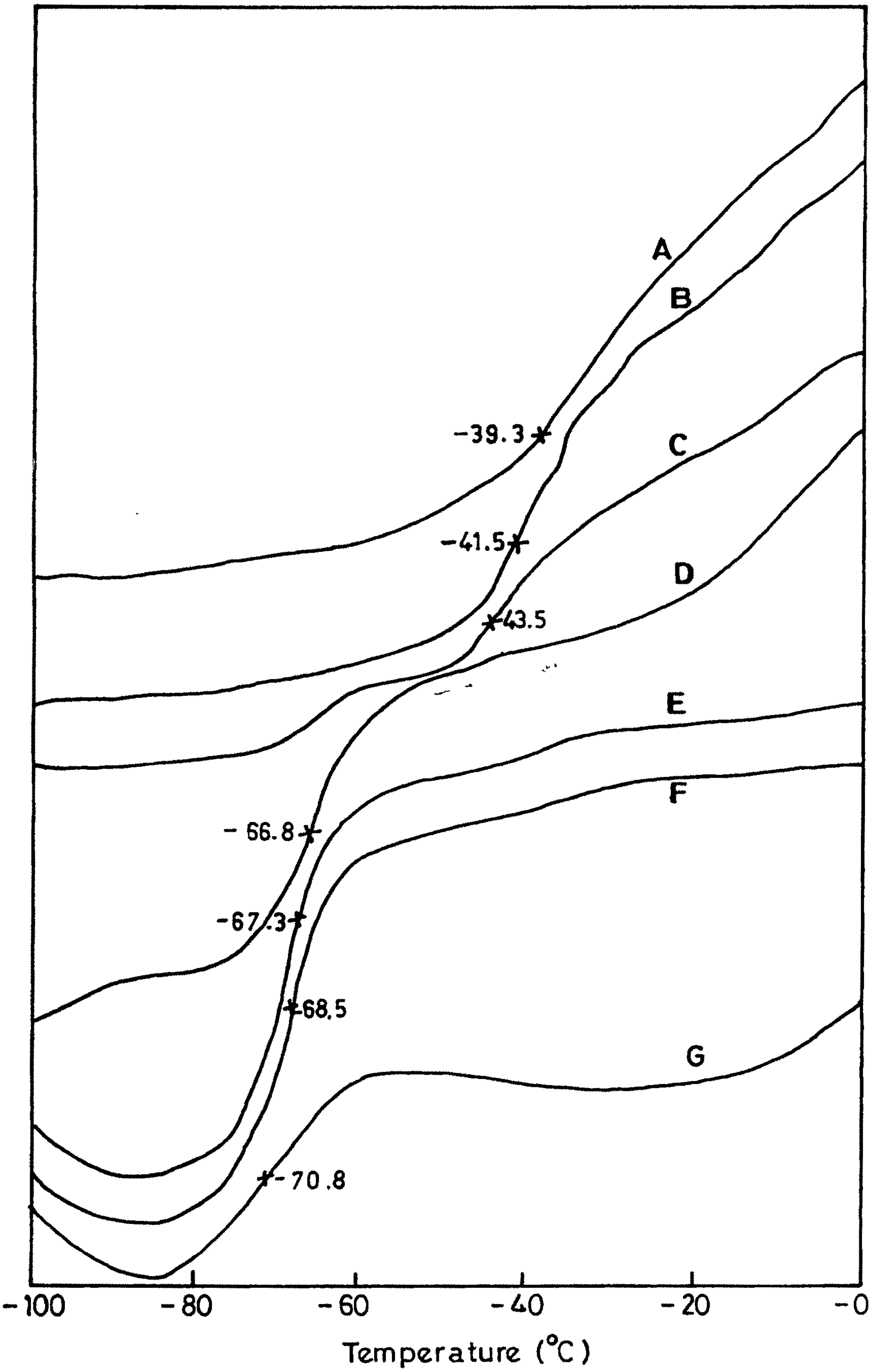


Fig. 1.7 DSC thermograms of PUs (A) P/T B_1 (B) P/T A_1
(C) P/M B_1 (D) H/T B_1 (E) H/T A_1 (F) H/T B_3
(G) H/M B_1

T_g of the soft segment shifts to some extent with change in molar concentrations of various components of the polyurethanes. This is an indication of a certain degree of phase mixing. In the case of a perfect phase separation between hard and soft segments, the T_g of the soft segment should be relatively insensitive to variations in the ratio of soft/hard segment[112-116]. The existence of chemical crosslinks in the PUs under investigation decreases the chain mobility and thus significantly reduces the aggregation of the hard segment into domains.

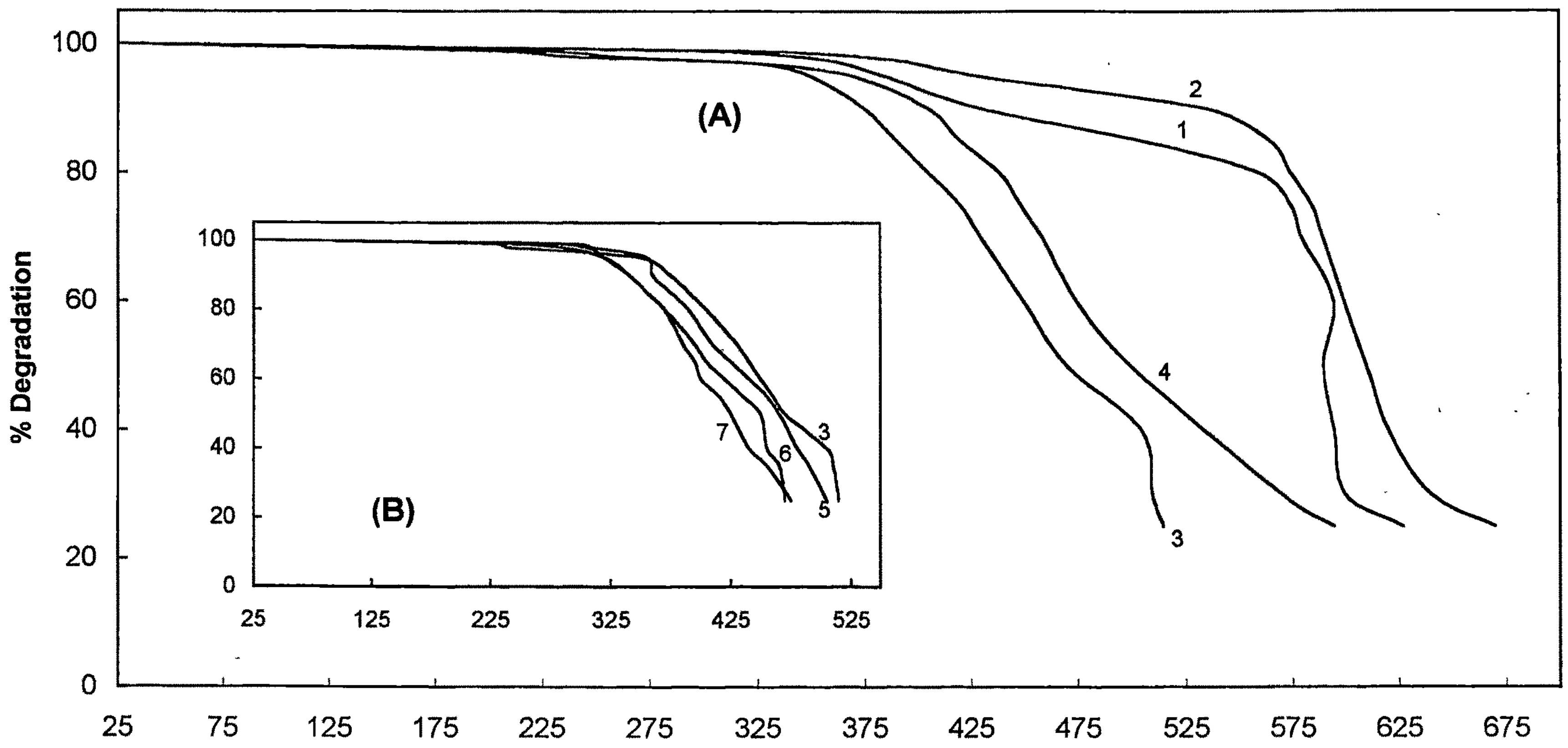
Thermogravimetric Analysis

The TGA of some selected samples was carried out in air in order to investigate their thermal stability. The results obtained are given in Fig. 8 and Table 1.4. The comparison of thermal stability of various PU systems with NCO:OH ratio 1.3 (Fig. 1.8A) shows that HTPB based PUs show higher thermal stability than PPG based PUs, and PUs containing MDI show higher thermal stability than those containing TDI. Increased thermal stability with increased degree of crosslinking is also seen in Fig. 1.8B.

From the decomposition temperatures given in Table 1.4 it was observed that the PUs under study show good thermal stability up to 300 °C.

1.4.5 Transport properties

The sorption and diffusion of a number of solvents in the polyurethanes was studied at room temperature. Swelling behavior of the PUs containing PPG and TDI, in benzene, toluene and xylene is discussed here in detail. The solvents selected for the study belong to a homologous series of aromatic hydrocarbons and are industrially



(A) ; 1 : H/T B1 , 2: H/M B1, 3 : P/T B1 , 4 : P/M B1, (B) ; 5 : P/T A1 , 6 : P/T A2 , 7 : P/T A3.

Fig. 1.8: Thermogravimetric curves for PUs.

Table 1.4 : Decomposition temperatures of polyurethanes with R value : 1.3 and diol / triol ratio 1:1.5

% Degradation	Temperature °C			
	H/T	H/M	P/T	P/M
1	295	315	200	220
5	385	430	350	370
25	575	585	425	449
50	590	610	470	500
75	605	670	515	595

important. The results are expressed as moles of solvent sorbed by 100 g of the polymeric material (Q_t) at time t as per the practice followed in the literature. This was calculated by using equation[116],

$$Q_t = (M_S / M_{r(S)} / M_P) \times 100 \qquad (1)$$

where M_S is the mass of solvent absorbed at equilibrium, $M_{r(S)}$ is the relative molecular mass of the solvent and M_P is the initial mass of the polymer sample. At equilibrium Q_t is taken as Q_∞ i.e. the mole percent uptake at infinite time.

From the results in figures 1.9 to 1.14, for P/T polyurethanes with variable extent of crosslinking and isocynate content it is observed that extent of sorption goes on increasing from xylene to toluene to benzene in all cases. The degree of swelling was found to be inversely proportional to the crosslink density of the polymers. The samples with NCO:OH ratio 1.3 (B series) have higher content of isocyanate and thus higher crosslinking due to formation of

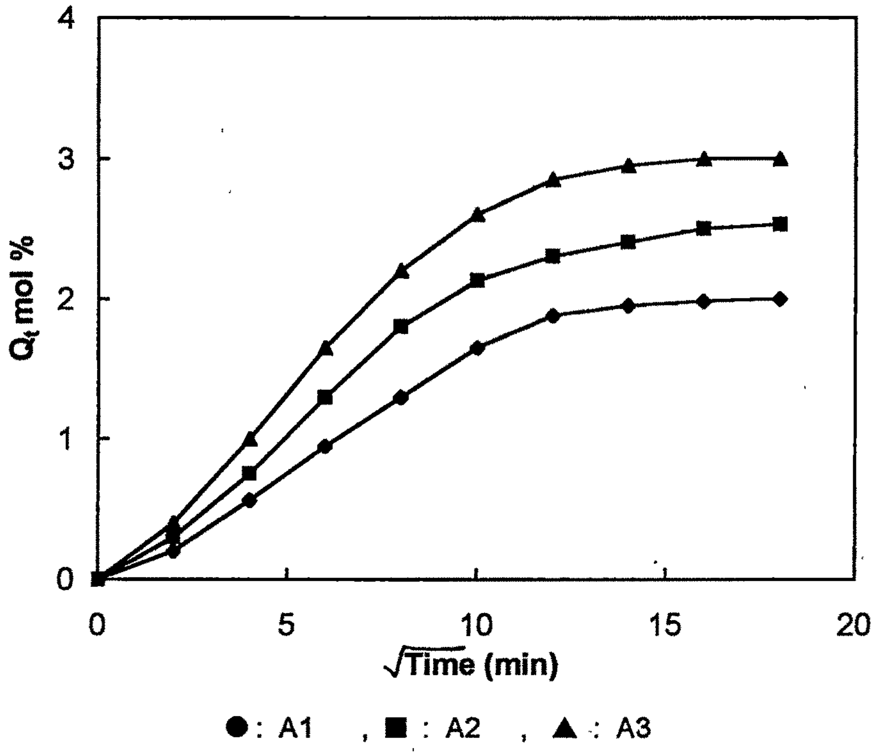


Fig. 1.9 : Benzene sorption plots for PPG-TDI polyurethane (NCO:OH=1.2).

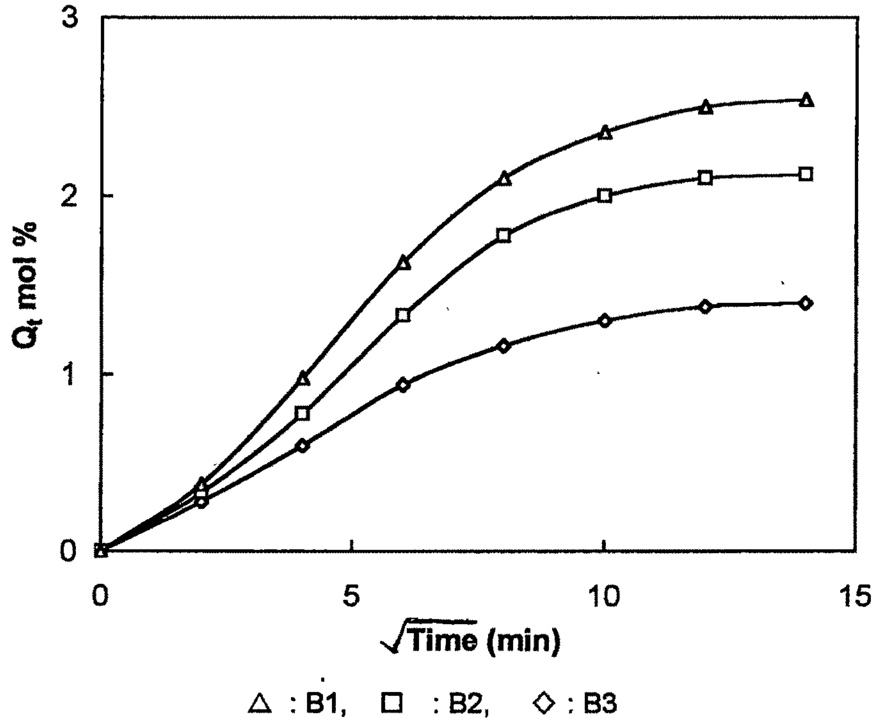


Fig. 1.10 : Benzene sorption plots for PPG-TDI polyurethanes (NCO:OH=1.3).

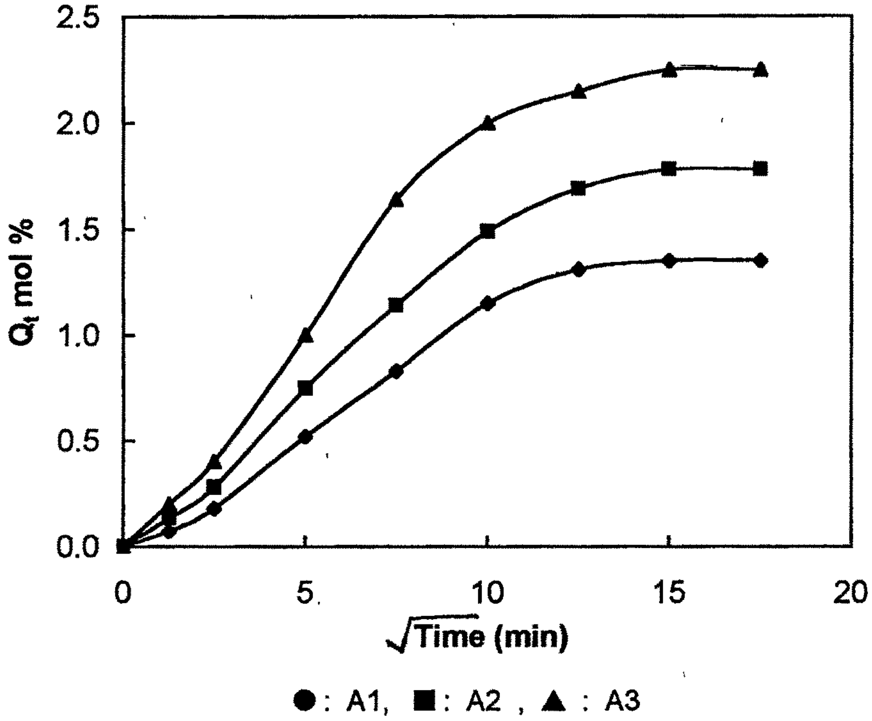


Fig. 1.11 : Toluene sorption plots for PPG-TDI polyurethanes (NCO:OH=1.2) .

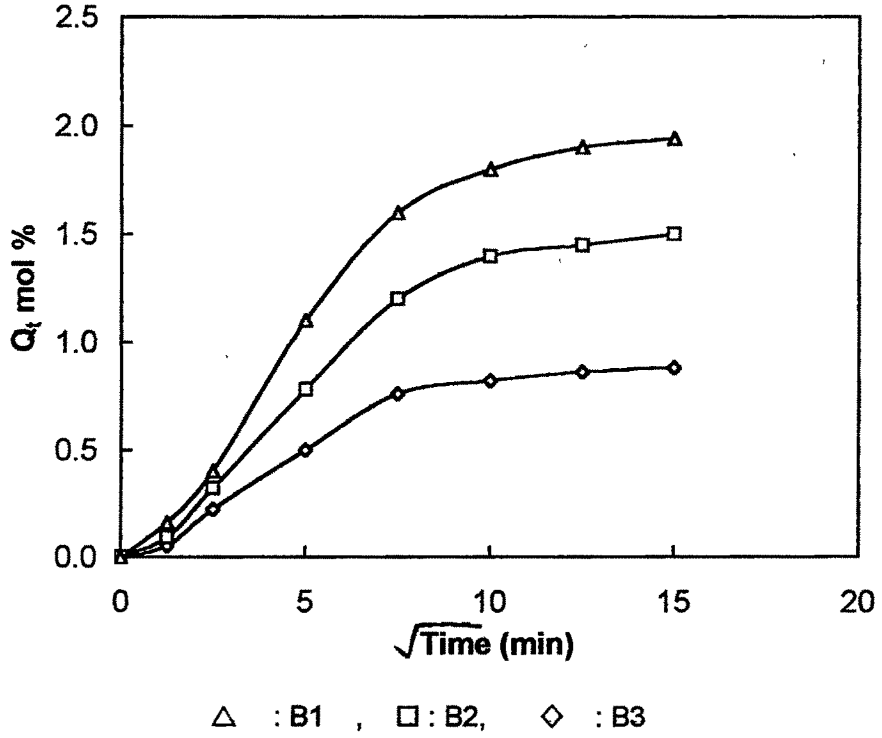


Fig. 1.12 : Toluene sorption plots for PPG-TDI polyurethanes (NCO:OH=1.3).

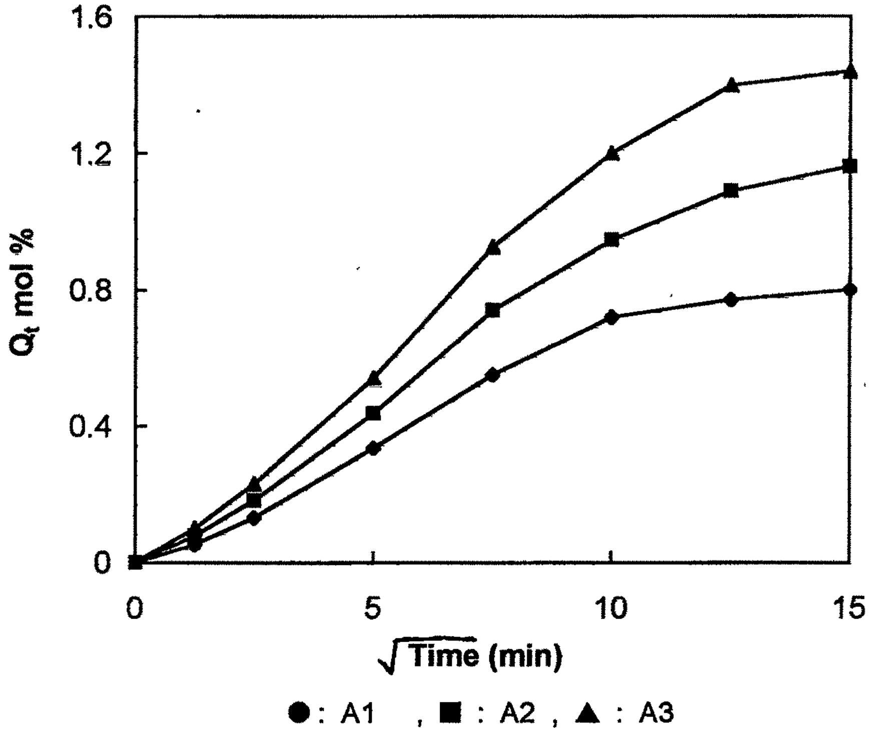


Fig. 1.13 : Xylene sorption plots for PPG-TDI polyurethanes (NCO:OH=1.2)

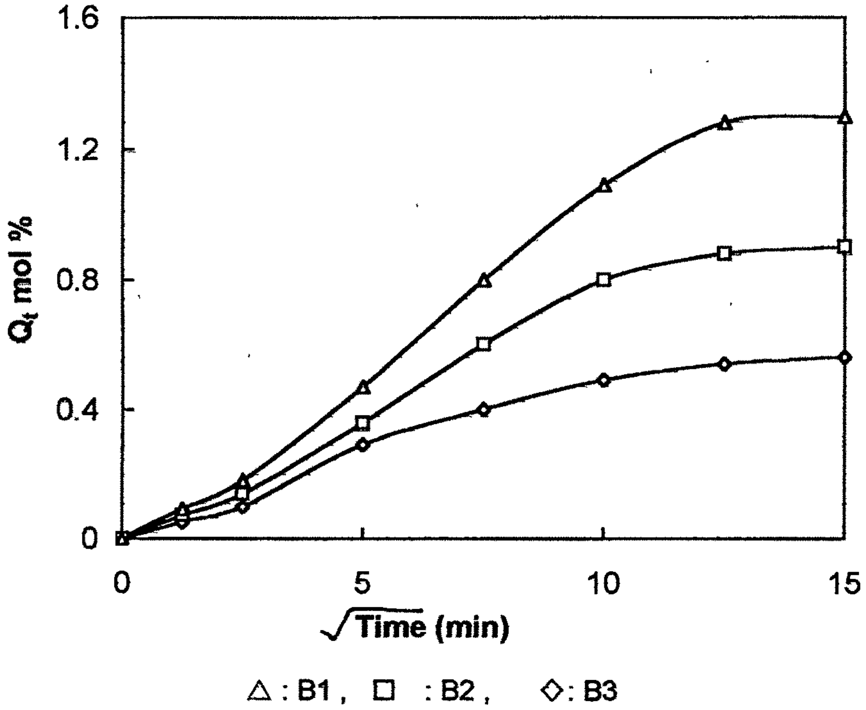


Fig. 1.14: Xylene sorption plots for PPG-TDI polyurethanes (NCO : OH = 1.3)

allophanates. As a result they show lower swelling compared to the samples with lower NCO:OH ratio, which comprises series A. This was observed in all the solvents. Thus the polymers with higher NCO:OH ratio are efficiently crosslinked, less flexible and hence show lower solvent uptake. The plot of molar volume of solvent versus Q_∞ is given in Fig. 1.15 for all samples. The moler volumers of benzene, toluene and xylene are 89.4, 106.8 and 121.9 respectively. It can be seen that the change in Q_∞ values is large from toluene to benzene compared to that from xylene to toluene. This is because of the large difference in solubility parameter of benzene and toluene.

Diffusion Process

One-dimensional diffusion of a liquid in a polymer matrix is described by the Fick's laws[117]. According to Fick's first law,

$$F = - Dz \ (dc/dz) \qquad (2)$$

where F is the rate of mass transfer of a penetrant through an unit area of polymer; (dc/dz) is concentration gradient and Dz is the diffusion coefficient. Fick's second law is obtained on differentiating equation (1) with time

$$dc/dt = - (dF/dt) = - d/dt \{ Dz \ (dc/dz)\} \qquad (3)$$

The diffusion of liquid in a polymer is said to be of the Fickian type if both the laws are obeyed. In a Fickian diffusion the rate of diffusion is much lower than that of relaxation due to mechanical and structural modes of the polymer solvent interaction. Deviation from Fickian diffusion can occur when sorption equilibrium is not achieved at a film surface due to appreciable surface evaporation rate or when diffusion and relaxation rates are comparable. As a result non-Fickian or anomalous sorption curves exhibit sigmoidal shapes. The sorption curves shown in Figs. 1.9 to 1.14 indicate that the transport is very rapid in the beginning and then gradually levels off as the equilibrium is approached. In order to study the diffusion mechanism the results obtained were fitted in the equation[118] derived from the empirical equation

$$(Q_t / Q_\infty) \; \alpha \; t^n \tag{4}$$

$$(Q_t / Q_\infty) = k t^n \tag{5}$$

$$\log (Q_t / Q_\infty) = \log k + n \log t \tag{6}$$

where k is a constant which indicates the extent of polymer solvent interaction and is a characteristic property of the polymer. The value of n indicates the type of sorption phenomenon. For Fickian diffusion n=0.5 whereas for n values between 0.5 to 1, the diffusion is said to be anomalous. The values of n and k were determined by linear regression analysis and are given in Table 1.5. It may be noted that the equation (1) can be used to analyze the sorption data before attainment of 50 % equilibrium saturation. The sorption curves shown in Figs. 1.9 to 1.14 show that the extent of sorption increases rapidly upto about 50 % of equilibrium sorption. In the beginning the curves seem to be showing a slight sigmoidal shape, which indicates the non-Fickian trend. This deviation from the Fickian diffusion is also further supported by the values of n, which are varying between 0.58 to 0.69. Thus the diffusion mechanism observed in the present study is of the non-Fickian type. The solvents used in the study cause significant amount of swelling (~ 4 times by volume or weight) of the polymers which may result in greater surface evaporation resulting into non-Fickian type of diffusion.

Table 1.5 : Slope n and intercept k (g / g.min²) for diffusional behavior

Code No.	Benzene		Toluene		Xylene	
	n	k x 10^2	n	k x 10^2	n	k x 10^2
P / T A1	0.60	6.86	0.58	7.24	0.67	4.75
P / T A2	0.69	5.26	0.69	4.21	0.62	4.73
P / T A3	0.58	6.78	0.60	6.53	0.65	4.69
P / T B1	0.59	8.16	0.59	8.09	0.64	5.37
P / T B2	0.59	8.13	0.62	7.89	0.69	5.29
P / T B3	0.69	6.12	0.69	5.08	0.63	4.91

The observed order of sorption of solvents under study can be explained on the basis of solubility parameters. It is well known that maximum swelling of a crosslinked polymer can take place in the solvent whose solubility parameter is close to that of the polymer. The solubility parameters of the polymers were calculated by allowing them to swell in a series of solvents of varying solubility parameters. The extent of sorption at equilibrium was measured in each solvent. The swelling coefficient α was calculated by using the equation[119].

$$\alpha = \{M_S / M_P\} \times \{1 / \rho_S\} \tag{7}$$

where ρ_s is density of the solvent. α is indicative of the volume of solvent per unit mass of the polymer. The results obtained are given in Table 1.6. Solubility parameter of the polymer was calculated by plotting solubility parameters of the solvents against α. Some representative plots are given in Fig 1.16. It is observed that maximum swelling takes place in dichloromethane. Hence solubility parameter of this set of polyurethanes was considered to be 9.7. For the homologues series of the solvents under study it is observed that benzene has the closest solubility parameter to the polymers under study and hence shows highest swelling coefficient.

Table 1.6 Swelling coefficient α for P / T PUs

Code No.	Dichloromethane ($\delta = 9.7$)	Chlorobenzene ($\delta = 9.5$)	Dioxane ($\delta = 10$)	Benzene ($\delta = 9.2$)	Toluene ($\delta = 8.9$)	Xylene ($\delta = 8.8$)
P/T A1	3.213	2.585	2.470	2.055	1.826	1.674
P/T A2	3.712	3.121	3.007	2.580	2.352	2.181
P/T A3	4.201	3.535	3.492	3.065	2.799	2.430
P/T B1	3.052	2.318	2.215	1.965	1.772	1.539
P/T B2	3.578	2.907	2.819	2.565	2.317	1.966
P/T B3	4.091	3.395	3.221	2.895	2.650	2.314

δ = Solubility parameter in $(\text{cal} / \text{cm}^3)^{1/2}$

The volume fraction of a polymer Φ in the swollen sample was calculated by using the equation[120]

$$\Phi = M_P / \rho_P / M_S / \rho_S + M_P / \rho_P \qquad (8)$$

where ρ_P is the density of the polymer sample . The values of Φ have been listed in Table 1.7.

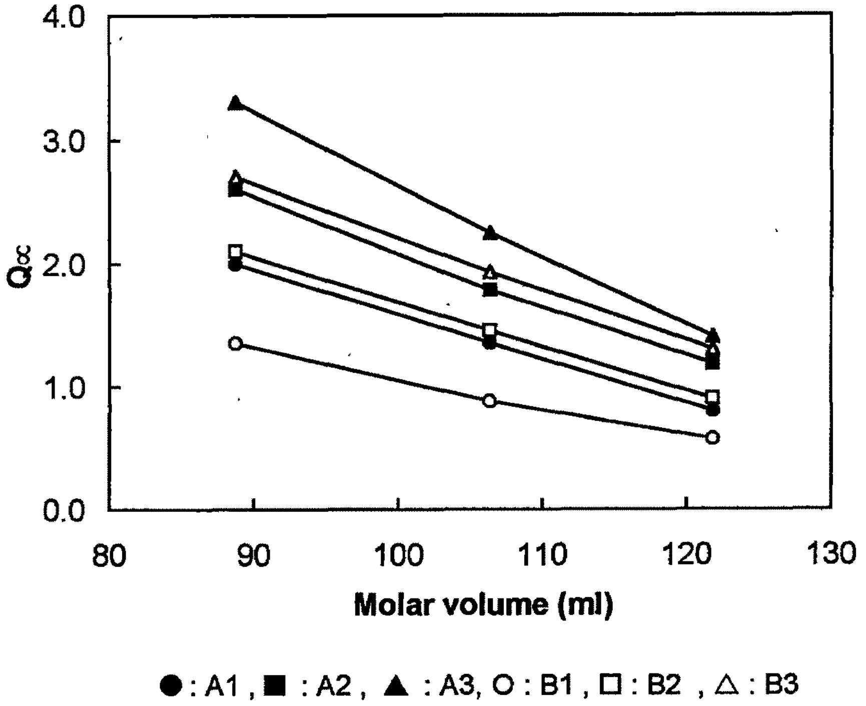


Fig. 1.15 : Variation of equilibrium mole percent uptake with molar volume of solvents.

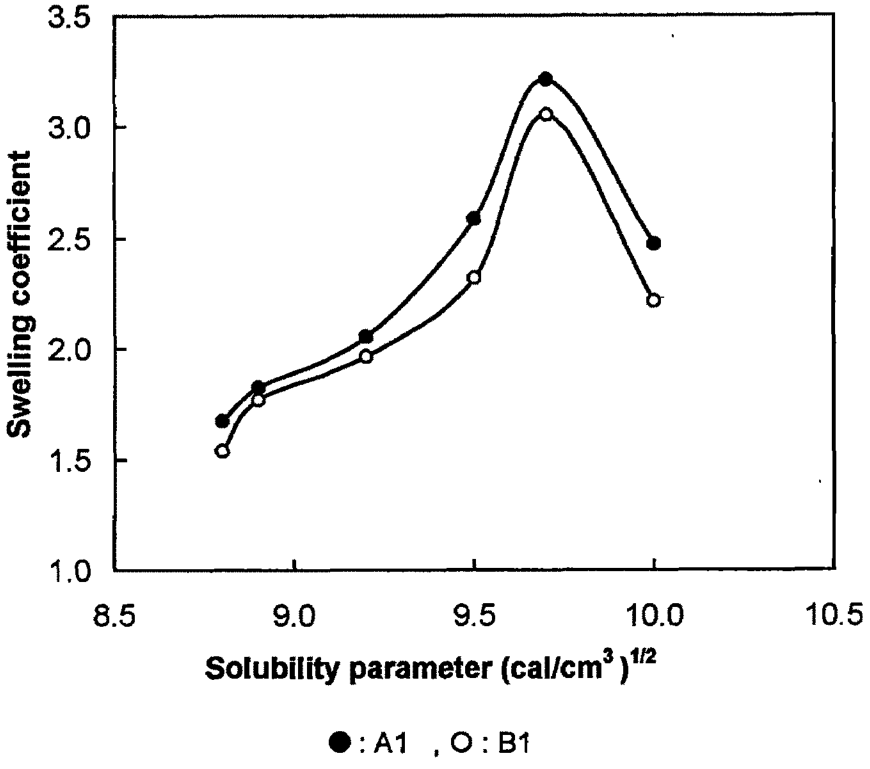


Fig. 1.16 : Swelling coefficient vs. solubility parameters of solvents.

Table 1.7 : Volume fraction of polymer, Φ for P / T PUs

Code No.	Benzene	Toluene	Xylene
P / T A1	0.309	0.335	0.358
P / T A2	0.267	0.285	0.301
P / T A3	0.239	0.256	0.284
P / T B1	0.317	0.340	0.372
P / T B2	0.267	0.287	0.322
P / T B3	0.248	0.266	0.292

From the results it is observed that the volume fraction of the polymer (Φ) is directly proportional to the crosslinked density of the polymer and inversely proportional to the sorption extent of the solvents. Hence the volume equilibrium degree of swelling q was calculated as the reciprocal of the volume fraction of the polymer. The results are given in Table 1.8.

Table 1.8 : Volume equilibrium degree of swelling q in different solvents

Code No.	Benzene	Toluene	Xylene
P / T A1	2.234	2.987	2.726
P / T A2	3.744	3.503	3.320
P / T A3	4.186	3.911	3.527
P / T B1	3.151	2.941	2.686
P / T B2	3.748	3.480	3.106
P / T B3	4.039	3.755	3.429

In order to calculate the degree of crosslinking and molecular weights between crosslinks the polymer solvent interaction parameter (χ) was calculated using the solubility parameter obtained from swelling studies and equation[121]

$$\chi = \beta + V_S \ \{(\delta_P - \delta_S)^2 / RT\} \qquad (9)$$

where β is the lattice constant whose value is about 0.34[121], V_S is the molar volume of the solvent and δ_P and δ_S are the solubility parameters of the polymer and the solvent respectively. The polymer solvent interaction parameter (χ) for benzene, toluene and xylene were found to be 0.38, 0.45 and 0.51 respectively. The results obtained show that lower χ indicates higher interaction of the polymer with benzene resulting into greater sorption as observed in the sorption studies.

When the polymer sample is immersed in a solvent, the solvent molecules diffuse into the polymer until the elastic retraction of network balances the osmotic pressure, driving the solvent into the swollen polymer[121]. As the retraction of the network depends upon the molecular weight between crosslinks (M_c) it was calculated from the Flory-Rhener equation[122],

$$M_c = \rho_P V_S \ \phi^{1/3} / \ln(1 - \phi) + \phi + \chi\,\phi^2 \qquad (10)$$

ρ_P is the density of the polymer, which was determined using the method reported for resins[123].

The degree of crosslinking (υ) is inversely proportional to the molecular weight between crosslinks and is given by the equation[124]

$$\upsilon = 1 / 2 M_c \qquad (11)$$

M_c is related to the no. of polymer chains per unit volume (crosslink density, υ_e) and the polymer density (ρ) as follows[68]

$$\upsilon_e = \rho / M_c \qquad (12)$$

The values for M_C, υ and υ_e are given in Table 1.9 and 1.10 respectively.

Table 1.9 : Molecular weight between crosslinks Mc

Code No.	Benzene	Toluene	Xylene	Theoretical
P / T A1	2674	3656	4631	391
P / T A2	4090	5450	7638	441
P / T A3	4601	7072	8960	499
P / T B1	2508	3529	4109	372
P / T B2	3666	5399	6291	416
P / T B3	4251	6438	8333	468

Table 1.10 Degree of crosslinking υ

Code No.	υ X 10^4			
	Benzene	Toluene	Xylene	Theoretical
P / T A1	1.87	1.37	1.08	12.79
P / T A2	1.22	0.92	0.67	11.34
P / T A3	1.09	0.71	0.56	10.02
P / T B1	1.99	1.42	1.22	13.44
P / T B2	1.36	0.93	0.79	12.02
P / T B3	1.18	0.78	0.60	10.68

Molecular weight between crosslinks (M_C) were theoretically calculated using the knowledge of the mole fractions of the various components of the polyurethanes and equation[126] (13) and are given in Table 1.9.

$$M_c = M_r / 2X1 \qquad (13)$$

where $M_r = X_1 MW_1 + X_2 MW_2 + X_3 MW_3$

X_1 is the mole fraction of crosslinker, X_2 and X_3 are the mole fractions of components. Considerable variation was observed between theoretically calculated and experimentally obtained values and the extent of deviation was observed to be more for the solvents with which the polymer has lesser interaction. The deviations were also observed within the different solvents. Similar results are reported earlier[117]. The variation may be due to the limitations of the Flory-Rhener theory for a heterogeneous system. The observed deviation may also be due to the complexity of polymer-solvent interaction affecting the micro domain structure of polyurethane to different extent. However, the trend observed in the experimentally calculated M_C is in agreement with the trend observed in theoretically obtained values.

The diffusion coefficient D characterises ability of the solvent molecules to move along the polymer segments. It was calculated from the initial thickness (h) of the sample and mole percent uptake at infinite time ($Q\infty$), by using the following equation[126]

$$D = \pi h\theta / 4Q\infty \qquad (14)$$

where θ is the slope of the initial linear portion of the sorption curves. The values of diffusion coefficient show dependency on the degree of crosslinking. The samples A1 and B1 with highest crosslinking, show, lowest value of Q_∞ and hence higher D. A3 has lowest D value, as it contains minimum crosslinker and isocyanate.

Thus the diffusivity data from Table 1.11 indicates that for the aromatic hydrocarbons used in the study, the sample A3 with lowest diol : triol (1.2 : 1.3) ratio and R value (1.2) could serve as a better barrier material than the other compositions[117].

Table 1.11 : Diffusion coefficient D in different solvents

Code No.	**D X 10^7 ($cm^2\ sec^{-1}$)**		
	Benzene	**Toluene**	**Xylene**
P / T A1	38.58	39.66	40.60
P / T A2	23.80	25.21	31.79
P / T A3	23.02	29.96	34.97
P / T B1	44.09	49.05	58.89
P / T B2	29.31	33.39	37.75
P / T B3	28.17	34.08	36.98

The sorption coefficient (S) which is related to the maximum sorption of the penetrant can be obtained from the ratio of weight of the solvent taken up at equilibrium (M_s) to the initial weight of the polymer (M_P)[116].

$$S = M_s / M_P \qquad (15)$$

The sorption coefficient was observed to be higher for the PUs having lower crosslinking and vice versa (samples with lower R value showing higher values than samples with greater R values) (Table 1.12).

Table 1.12 : Sorption coefficient S in different solvents

Code No.	S (g/g)		
	Benzene	Toluene	Xylene
P / T A1	1.81	1.58	1.46
P / T A2	2.27	2.03	1.90
P / T A3	2.69	2.42	2.11
P / T B1	1.73	1.53	1.34
P / T B2	2.25	2.00	1.71
P / T B3	2.54	2.27	2.01

The permeabilities of polyurethanes are expressed by the permeability coefficient (P), which is calculated from the following equation[116].

$$P = D \times S \qquad (16)$$

The permeability coefficient, the product of the diffusion and the sorption coefficient, implies the net effect of sorption and diffusion. Its values are given in the Table 1.13.

The swelling behaviour of all the PUs with NCO:OH ratio 1.3 and diol/triol ratio 1:1.5 was investigated in a number of solvents of varying solubility parameters and the swelling coefficient α was calculated. Fig.1.17 shows the plot of solubility parameters of the solvents vs. swelling coefficient of the PUs in the respective solvents. It was observed that P/T and P/M systems showed highest swelling coefficient in dichloromethane. Hence, the solubility parameter of

Table 1.13 : Permeation coefficient P in different solvents

Code No.	$P \times 10^7 (cm^2 sec^{-1})$		
	Benzene	**Toluene**	**Xylene**
P / T A1	56.08	89.42	37.80
P / T A2	50.53	60.46	24.63
P / T A3	49.30	40.36	20.51
P / T B1	35.52	34.38	19.20
P / T B2	41.33	35.68	19.07
P / T B3	43.09	36.16	19.98

these systems was considered to be 9.7 $(cal / cm^3)^{1/2}$. In case of H/T and H/M systems an interesting phenomenon was observed. These systems showed greater swelling (solvent uptake) in carbon tetra chloride (solubility parameter 8.6 $(cal/cm^3)^{1/2}$, but swelling coefficient was found to be highest in chlorobenzene (solubility parameter 9.5 $(cal/cm^3)^{1/2}$. Hence the solubility parameter of these systems was considered to be 9.5 $(cal / cm^3)^{1/2}$. The observed difference in solubility parameters of the two systems was because of the difference in polarity of polyol. The soft segment which constitutes the major portion of the polyurethane elastomer largely determines the solubility parameter of the systems. Hence solubility parameter of the system remained same irrespective of the type and concentration of diisocynates and concentration of crosslinker, although the extent of swelling was found to change in each case. The MDI based PUs showed greater extent of swelling in the respective solvents with closest solubility parameter. Once again this can be explained by the greater flexibility offered by the linear nature of the MDI which promotes the diffusion of solvents. Among polyols PPG based PUs showed greater swelling than the HTPB based PUs for the same reasons which give them poor mechanical properties.

During sorption studies it was observed that P/T samples got disintegrated. Such a disintegration was also observed by Petrovic and Fajnik[40] for PUs based on polyethylene glycol and TDI. They proposed[40] that the existence of an inhomogeneous structure in crosslinked polymer is the consequence of the mechanism of the crosslinking. According to them, due to dominating intramolecular structure 'gel balls' are formed which at the end of the reaction get the form of globules (nodules) embedded in a matrix of the same polymer of lower crosslink density[127]. They assumed that microcracks were formed at the boundaries of the gel balls, which led to the disintegration of the sample.

Fig. 1.18 shows the variation of M_c values for each system in different solvents. Once again a large deviation in the M_c values was obtained in different solvents, which may be due to the limitations of the Flory - Rehner theory for a heterogeneous system. The other results of the swelling studies in dichloromethane and chlorobenzene are given in Table 1.14. The degree of crosslinking and crosslink density were found to be highest in H / T system which exhibited highest tensile strength and elongation compared to the other PU systems. Thus, the order observed in the degree of crosslinking and crosslink density also explains the trend observed in mechanical properties.

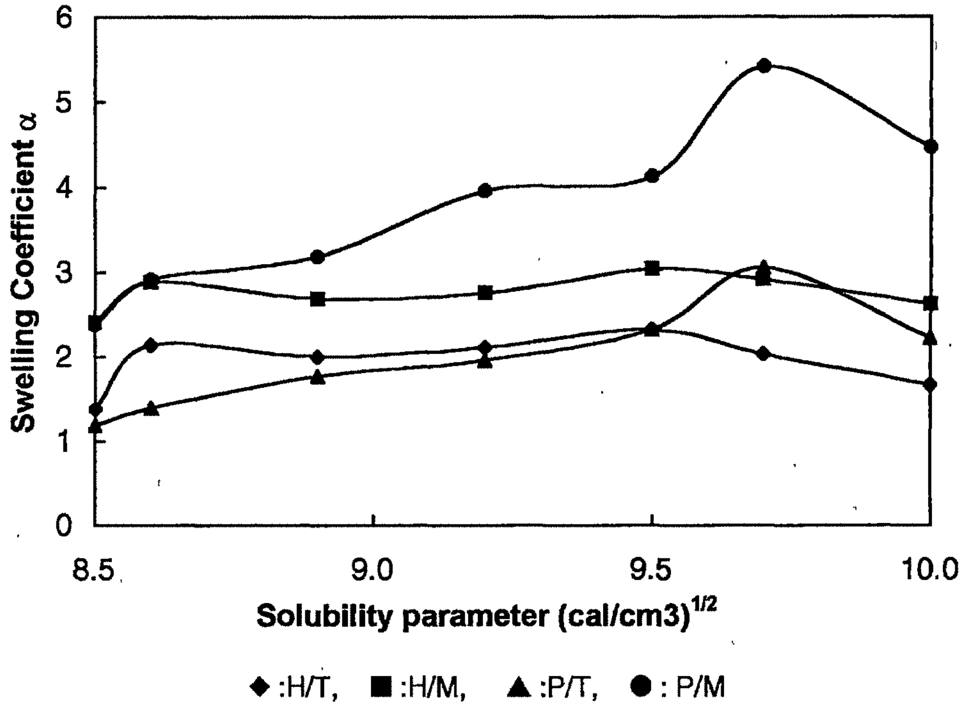


Fig. 1.17 : Swelling of PUs with NCO:OH ratio1.3 and diol / triol ratio 1:1.5 in various solvents

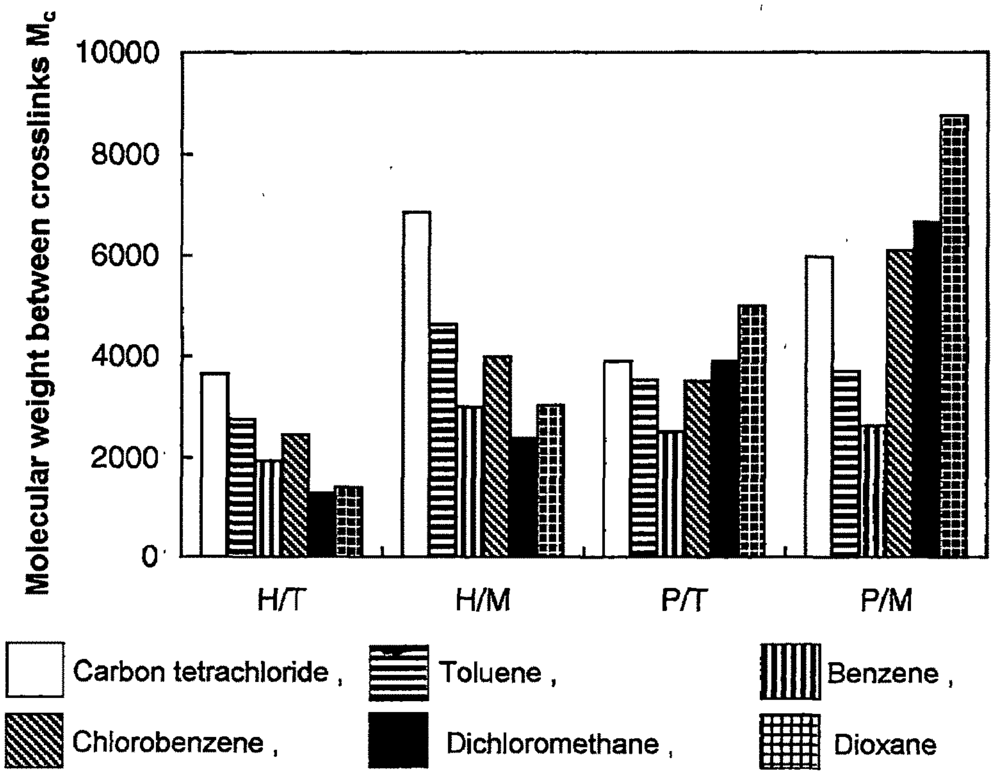


Fig. 1.18 : Molecular weights between crosslinks of PUs in various solvents

Table 1.14 : Swelling data for PUs with R value : 1.3 and diol / triol ratio 1:1.5

Code	Φ	χ	V X10^4	ρ	Ve X10^4
H/T				0.98	
a	0.306	0.340	2.04		3.99
b	0.334	0.344	3.90		7.64
H/M				1.00	
a	0.248	0.340	1.03		2.51
b	0.256	0.344	2.35		4.18
P/T				1.11	
a	0.179	0.347	1.43		3.17
b	0.140	0.340	0.93		2.07
P/M				1.12	
a	0.280	0.347	0.56		1.25
b	0.228	0.340	0.57		1.28

a : Chlorobenzene , b : Dichloromethane

1.4.6 Dynamic mechanical analysis

The dynamic mechanical analysis of the PUs with NCO:OH ratio 1.3 and diol / triol ratio 1:1.5 was carried out at 1 Hz. The plots of E', E" and tan δ vs. temperature have been shown in Fig. 1.19 - 1.22. The activation energy for glass transition can be calculated from the relation between frequency and tan δ peak temperatures[126] using equation.

$$\ln \omega_1 / \omega_2 = E_A / R\,(1/T_2 - 1/T_1) \qquad \textbf{(17)}$$

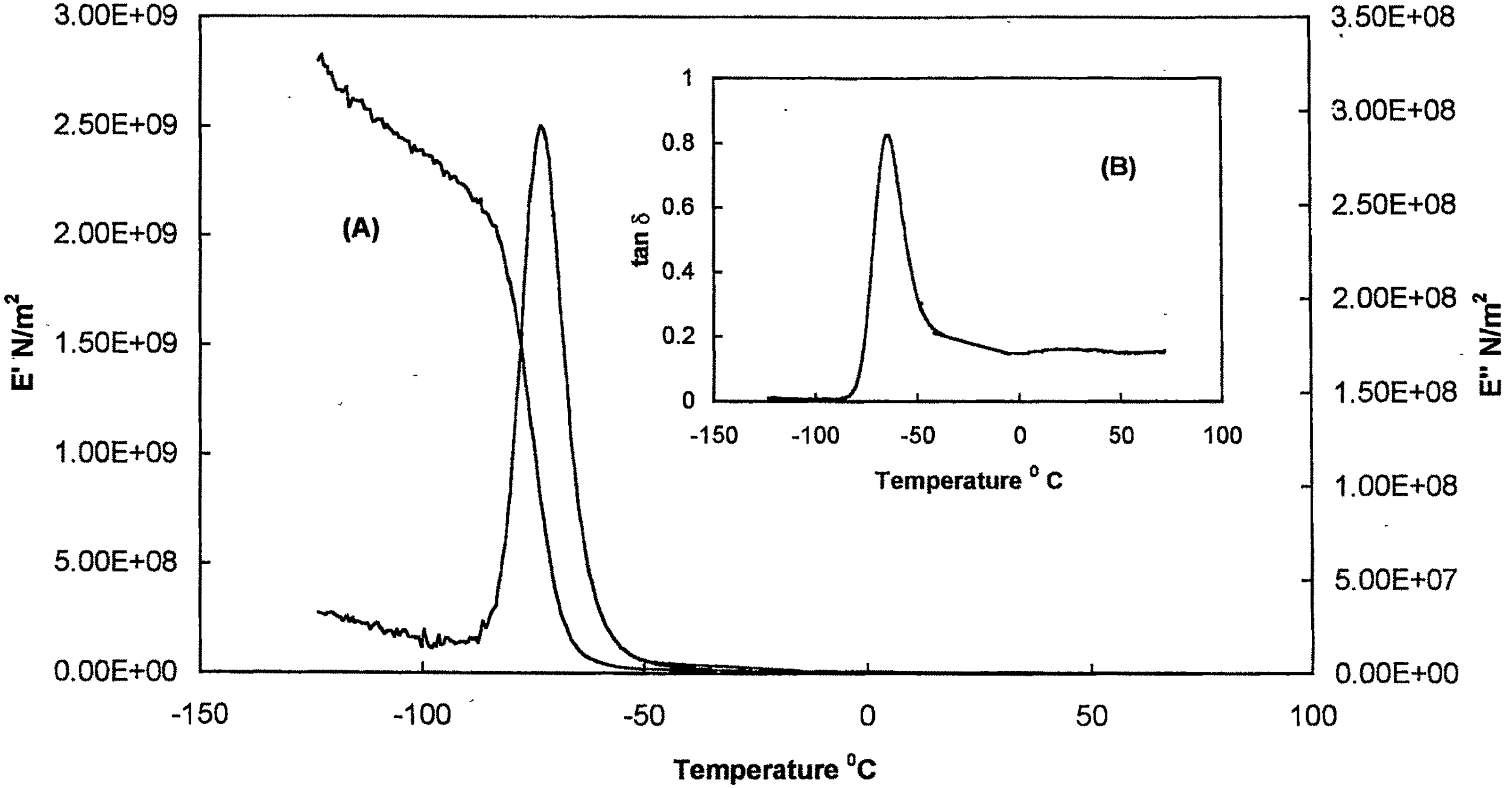


Fig. 1.19: Variation of E' and E"(A) and tan δ (B) with temperature for H / M B1 at 1 Hz .

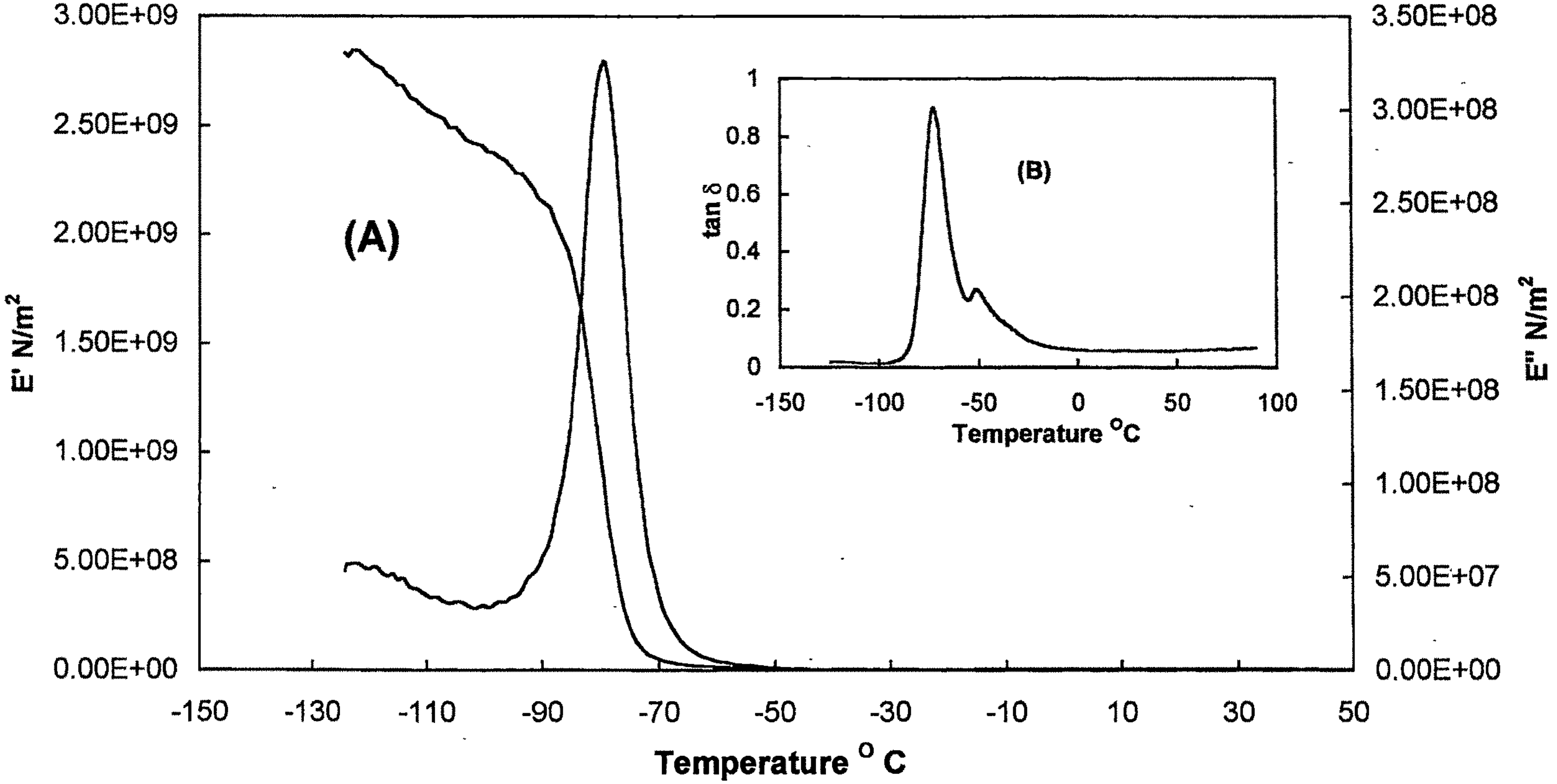


Fig. 1.20 : Variation of E'and E" (A) and tan δ (B) with temperature for H / T B1 at 1 Hz .

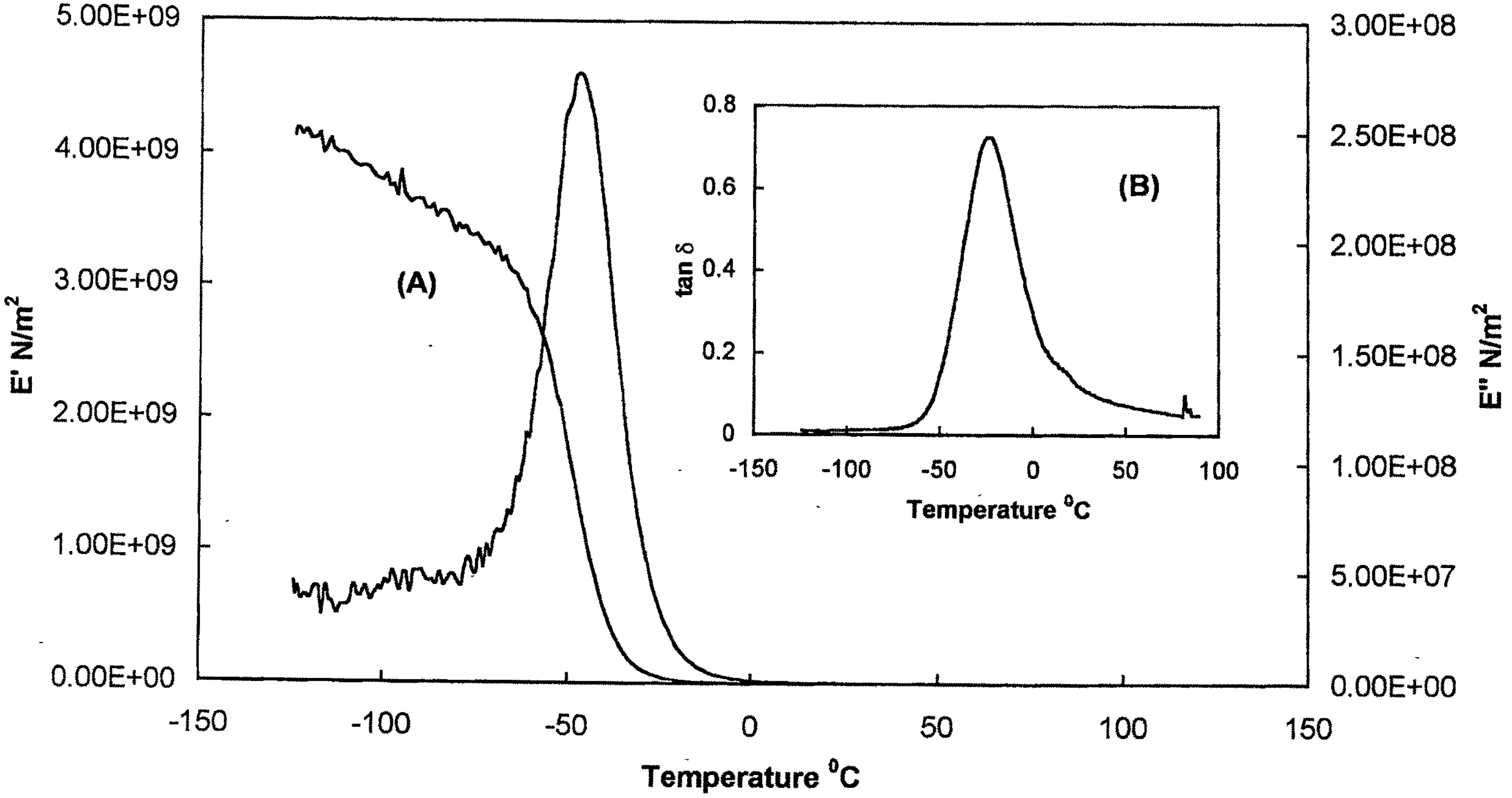


Fig. 1.21: Variation of E' and E"(A) and tan δ (B) with temperature for P / T B1 at 1 Hz .

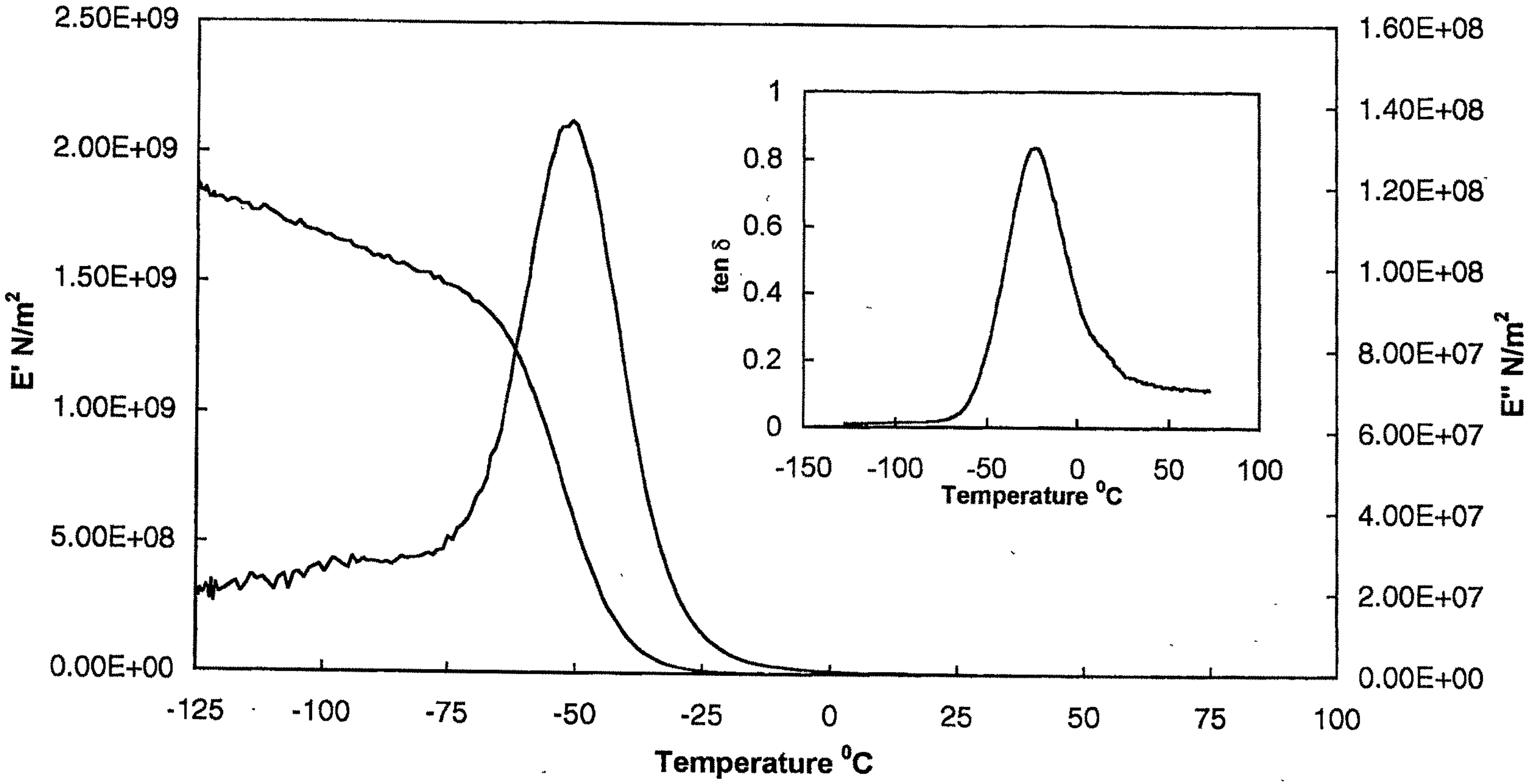


Fig. 1.22 : Variation of E' and E" (A) and tan δ (B) with temperature for P / M B1 at1 Hz .

where ω_1 and ω_2 are the frequencies and T_1 and T_2 are the Tgs obtained at T_1 and T_2 °C respectively. For the HTPB-MDI system the analysis was carried out at 1,2,5 and 10 Hz and the E_A was found to be 36.6 kcal / mole.

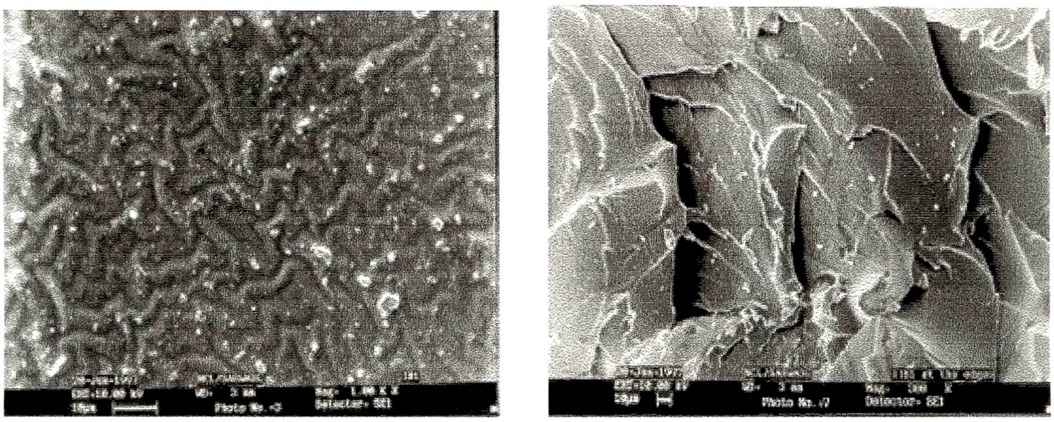
The α relaxation was observed as a sharp peak in tan δ and E' and as a large decrease in E". The Tg values obtained from DMA (Table 1.15) differ somewhat from those obtained from DSC. This may be attributed to the frequency dependence of the transition phenomenon.

Table 1.15 : DMA data at 10 Hz for PUs with R value : 1.3 and diol / triol ratio 1:1.5

PU system	T_g °C (DSC)	T_g °C (DMA)	Tan δ_{max}	E''_{max}
H/T	-66.8	-72.2	0.88	3.30 x 10^8
H/M	-70.8	-65.0	0.83	2.92 x 10^8
P/T	-39.3	-43.1	0.74	2.72 x 10^8
P/M	-43.5	-45.6	0.85	1.37 x 10^8

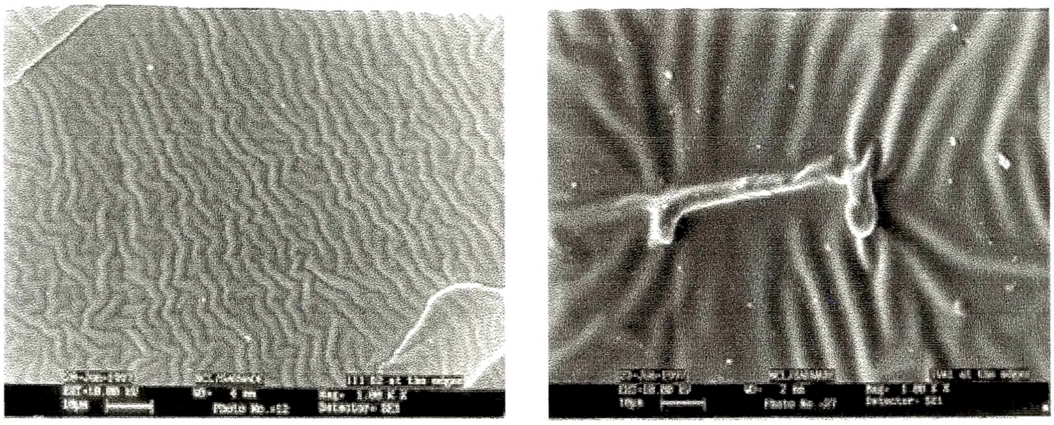
1.4.7 Scanning Electron Microscopy

Figs. 1.23 - 1.25 show the micrographs of the PUs with NCO : OH ratio 1.3 and diol / triol ratio 1:1.5. Macknight et al[129] showed that the heterogeneous nature of the reaction mixture gives rise to a bimodal distribution of the hard segment. On this basis Zawadski et al[66] suggested that hard segment rich regions could coexist and be partially dispersed in the matrix. Thus some of their PUs exhibited two phases while others were monophasic. In the present study H / T



A : H / T (1 K X)

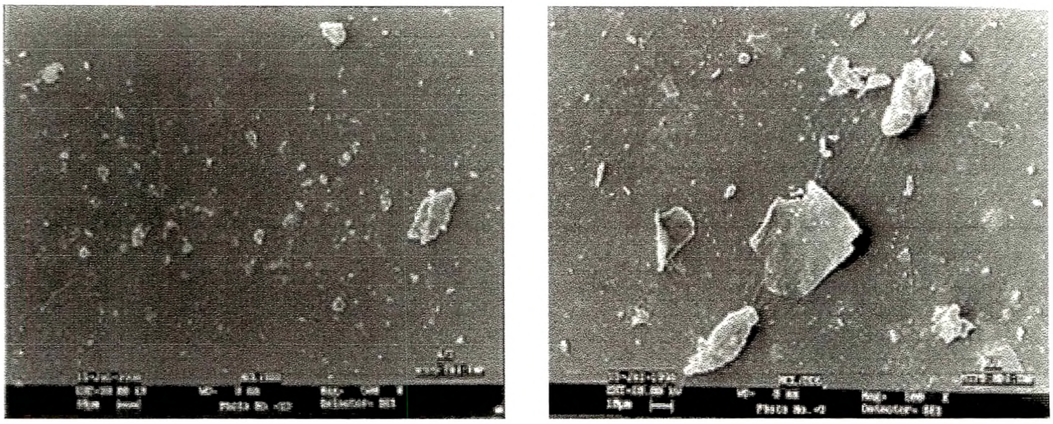
B : H / M (500 X)



C : P / T (1 K X)

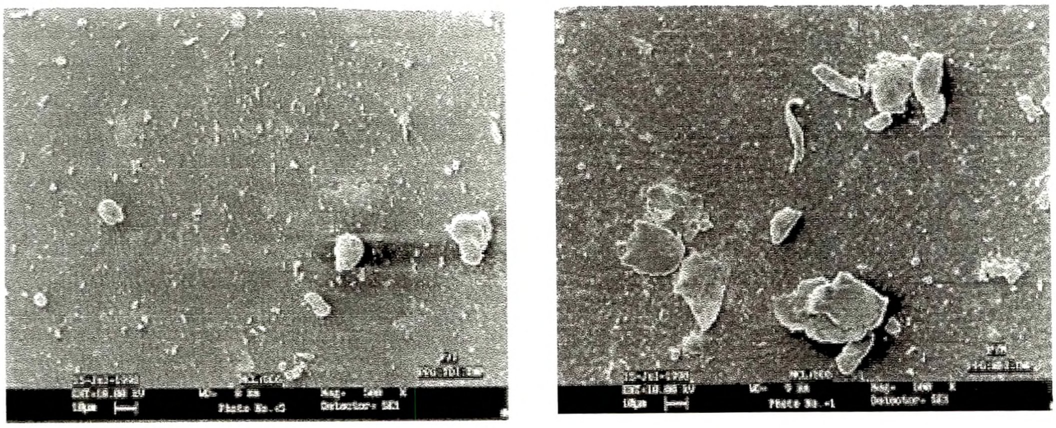
D : P / M (1 K X)

Fig. 1.23 : SE Micrographs of polyurethane films
with NCO : OH ratio 1.3 and diol : triol ratio 1 : 1.5 (B1)



A : H / T (500 X)

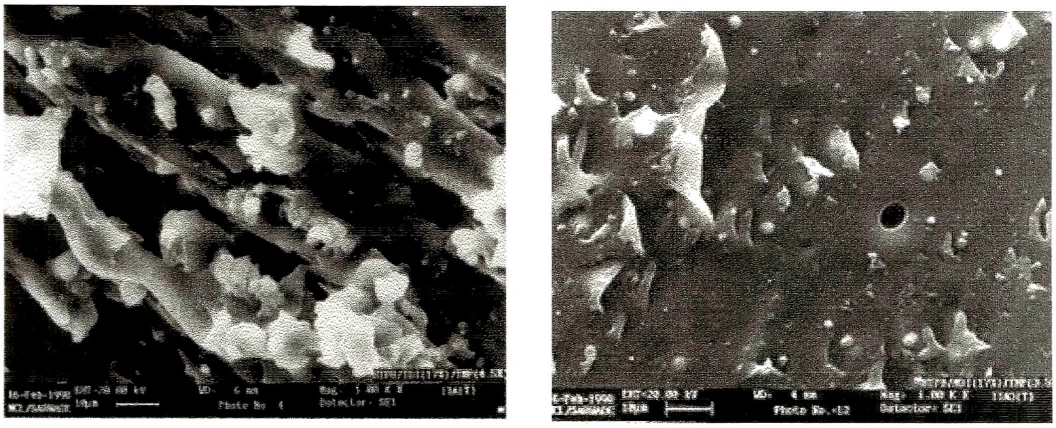
B : H / M (500 X)



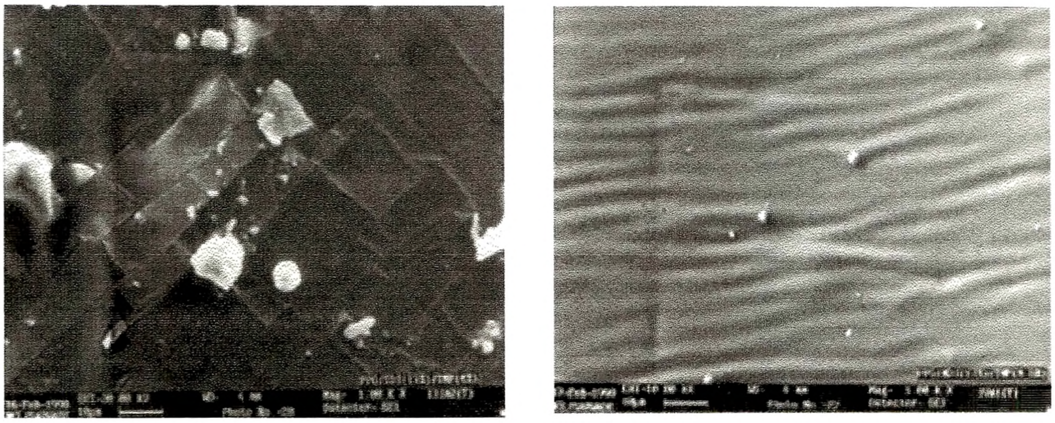
C : P / T (500 X)

D : P / M (500 X)

Fig. 1.24 : SE Micrographs of post - swollen polyurethane films with NCO : OH ratio 1.3 and diol : triol ratio 1 : 1.5 (B1)



A : H / T (1KX)　　B : H /M (1 KX)



C : P / T (1KX)　　D : P / M (1KX)

Fig. 1.25 : SE Micrographs of tensile fractured polyurethanes with NCO : OH ratio 1.3 and diol : triol ratio 1 : 1.5 (B1)

PU (Fig. 1.23 A) shows similar phase segregation, which might be the reason for its better tensile strength.

Micrographs of PU films also show wrinkling which may be due to evaporation of solvents during curing. However, the micrographs of PU films subjected to swelling in 1,4-dioxane (Fig. 1.24) show the disappearance of wrinkles. The particles seen in micrographs may be the gel fraction that may have dissolved and deposited on evaporation of solvent.

Fig.1.25 shows the morphology of tensile fractured PUs. More heterogeneous nature of the fractured surface due to the deformation is observed in H/T specimen (Fig. 1.25A), which is characteristic of samples with higher tensile strength. Whereas the deformation went on decreasing from H/T > H/M > P/T > P/M. This can be attributed to the nature of the diol and isocynate as discussed earlier. The P/T sample showed development of cracks. Thus the behaviour observed in swelling studies was also reflected in the tensile test.

1.4.8 Gel Content

The gel content of the PUs used for swelling studies was found to be in the range of 2 to 5 %. The P/M system had the highest gel content, which is also supported by the SEM study.

1.5 Conclusion

The study on Polyurethanes reviled that the HTPB – TDI system showed greater phase segregation and hence superior thermo – mechanical properties. The common feature of all PU system was the observed higher tensile strength exhibited by the B1 compositions having higher NCO :OH and diol : triol ratios. Hence this composition was selected for the development of IPNs with polymethyl methacrylate (PMMA).

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