

Effect of Crosslinking Agents on the Structure and Properties of Polyurethane Millable Elastomer Composites

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SYNOPSIS

A study of the effect of crosslinking agents on the structure and properties of the millable polyurethane (PU) elastomer is reported here. Effects of the conventionally used dicumyl peroxide (DCP) and tolylene diisocyanate dimer (TDID) on the curing characteristics, mechanical properties, and relative thermal stabilities of the PU composites have been compared. Use of X-ray diffraction as a supportive evidence helps in understanding the nature of crosslinking. The mixture of DCP and TDID is also evaluated as crosslinking agents. A dramatic improvement in the mechanical properties and thermal stability is observed because of the mixed type of crosslinking obtained by the combined use of DCP and TDID. Effect of carbon black loading shows an increase in the mechanical strength with a decrease in the elongation. The results obtained from various properties measurements have been satisfactorily explained with a general model of crosslinking.

INTRODUCTION

Polyurethane (PU) elastomers are now widely utilized as engineering materials in various industries and are well known for their outstanding properties such as superior abrasion resistance, water and oil resistance, and excellent mechanical properties.

Millable, cast, and thermoplastic are three main classes of PU elastomers. Millable PU elastomers have an advantage over the other two in that they have higher heat resistance and good storage stability.

The effect of structural changes on properties for cast polyurethane elastomers has been reported earlier.¹ The present work describes the synthesis of PU millable elastomer and the effect of filler and crosslinking agents on the mechanical and thermal properties of the final composites prepared.

EXPERIMENTAL

Material

Hydroxy-terminated poly(tetramethyleneether glycol) (PTMEG) with the characteristic features given in Table I was synthesized in our laboratory.

4,4'-Diphenylmethane diisocyanate (MDI), toluene diisocyanate, (TDI), a 80 : 20 mixture of 2,4 and 2,6 isomers, were used as received. The structure, source, and purity of each chemical are described in Table II.

Synthesis of Polyether Polyol

PTMEG was synthesized by ring-opening polymerization of tetrahydrofuran, (THF).² The dry and purified monomer, THF (72 mL) and catalyst SbCl₅, 0.1 M solution in CH₂Cl₂ (0.2 mL) were placed in a closed round-bottom flask under dry nitrogen atmosphere. The reaction was carried out at 0°C for 24 h with occasional shaking. The liquid monomer turns into a waxy solid polyol at the end of the re-

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Table I Characteristics of PTMEG (at 25°C)

Appearance	Colourless semisolid
Acid number	0
Hydroxyl number	37
Molecular weight (end group analysis)	3030
Molecular weight (vapor pressure osmometry)	3100

action. The polyol thus obtained was treated under vacuum to remove the unreacted monomer and was characterized.

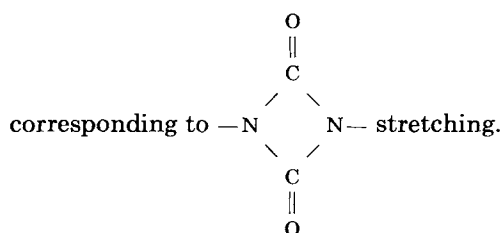
Characterization of Polyol

The acid number was determined by the usual titrimetric method (ASTM D1638-61T) using 0.2N KOH. The hydroxyl number was determined by acetylating the hydroxyl group of the polyether and titrating the hydrolyzed excess acid with 0.2N KOH (ASTM D1638-61T). Molecular weight was obtained using Kanaur Vapour Pressure Osmometer and also by end group analysis.

Synthesis of Crosslinking Agent (TDID)

The dimer of TDI (TDID) was synthesized by taking 25 mL of TDI in a round-bottom flask and adding 0.5 mL of freshly distilled pyridine to it under a nitrogen atmosphere. The reaction mixture was left

overnight to obtain white crystals of TDID, which showed characteristic IR absorption at 1775 cm^{-1}



Synthesis of Millable Polyurethane Elastomers

The polyol (PTMEG) 1 mol, degassed under vacuum, was reacted with 1.05 mol of MDI at 50°C to give isocyanate-terminated prepolymer. The reaction was carried out in a nitrogen atmosphere for 30 min. The diisocyanate was injected with a hypodermic syringe with constant stirring. The prepolymer formed was further reacted with 0.1 mol of chain extender, 4,4'-diaminodiphenyl sulfone, for 15 min. The mixture was then transferred to stainless steel plates and was heated for 2 hr at 100°C to ensure the completion of reaction. Silicone release agent was applied to the plates for an easy removal PU.

Processing of Polyurethane Millable Elastomers

PU was masticated in an open twin roller mill. This was followed by the addition of fillers, curing agents, i.e., dicumyl peroxide (DCP) and/or TDID. During this mastication process the temperature was kept below 70°C by circulating cold water through the

Table II Materials Used

Materials	Structure	Remarks	Source
Diphenyl methanediisocyanate (Crude MDI)		Mixture of di- and triisocyanates Dark brown viscous liquid	EMERK
2,4-Toluenediisocyanate (TDI)		80% 2,4- +20% 2,6- isomeric mixture	FLUKA AG, Switzerland
4,4-Diaminodiphenyl sulfone		—	CHEMISCH, Germany

rollers. The recipes of various compounds prepared are described in Table III.

For molding, fly wheel press and plate and disk molds were used. The curing temperature and time were determined from the rheometric results (Fig. 1).

Characterization of Polyurethane Elastomers

Rheometric studies on the compounded elastomers were made on a Monsanto moving die rheometer. Samples weighing 10 g were placed in the die, and the increase in torque with respect to time at constant temperature was studied.

Mechanical properties such as modulus, tensile strength, and elongation at break were measured on a universal tensile testing machine (Instron), with a crosshead speed of 500 mm/min as per ASTM D412 using dumbbell-shaped specimen of 2 mm thickness. Hardness was measured with a durometer on a Shore A scale following ASTM D2000. Thermogravimetric analysis was carried out at a heating rate of 5°C/min under oxidative atmosphere from 25–500°C on DuPont 9900 computerized thermal analyzer. Wide-angle X-ray diffraction study was carried out on a Philips PW 1729 model with PW 1820 diffractometer using 1 × 1 × 0.2 cm pieces with Cu target.

RESULTS AND DISCUSSIONS

Rheometric Studies

Rheometric study for the curing characteristic of elastomer is an important technique. The effect of curing agents on rheometric curves of compounds is shown in Figure 1. The TDID cured system, sam-

ple 1, indicates the lowest curing time among the three curing systems. This is attributed to the formation of free TDI and its reaction with active protons yielding crosslink between two polymer chains. Whereas in the DCP-cured system, sample 2, because a higher temperature is required for decomposition of dicumyl peroxide, it indicate the higher cure time. Sample 3, which is cured by a mixture of TDID and DCP, has a shorter cure time compared with sample 2 due to the additional crosslinking by TDID. Higher stiffness is observed in sample 3, which is a manifestation of an increase in the total crosslink density. In samples 2 and 3 marching modulus is observed due to the continuing crosslinking reactions of TDID over a period of time. Due to this reason all TDID-cured systems were subjected to the postcuring at 110°C for one hour.

Mechanical Properties

The mechanical properties of all the samples are given in Table IV.

The moduli and tensile strength of sample 1 are significantly higher than those of sample 2. This can be explained on the basis of the structure of the diisocyanates used in the synthesis of PU and position of the various crosslinking sites generated there (Fig. 2). The major crosslinking sites for the TDI (generated from TDID) are in the hard segments. Chiefly these include the active hydrogen atoms present in urea and urethane linkages. When TDID is used for crosslinking, the weak hydrogen bonds in the hard segments of PU are replaced by the allophanate and biuret linkages. This reorganizes the ordered structure of the hard segments. Whereas in DCP-cured sample 2 the major crosslinking sites are the $-\text{CH}_2-$ groups in the MDI

Table III Recipes of Polyurethane Composites Prepared

Components	Recipe Number							
	1	1a	2	2a	3	4	5	6
Polyurethane	100	100	100	100	100	100	100	100
HAF-carbon black (phr)	10	10	10	10	10	20	30	—
Aluminum silicate (phr)	—	—	—	—	—	—	—	10
BC-40 ^a (phr)	—	—	5	10	5	5	5	5
TDI dimer (phr)	5	10	—	—	5	5	5	5
Cure temperature (°C)	150	150	170	170	170	170	170	170
Cure time (min)	4.5	—	9	—	9	9	9	9

^a 40% DCP coated on kaolin.

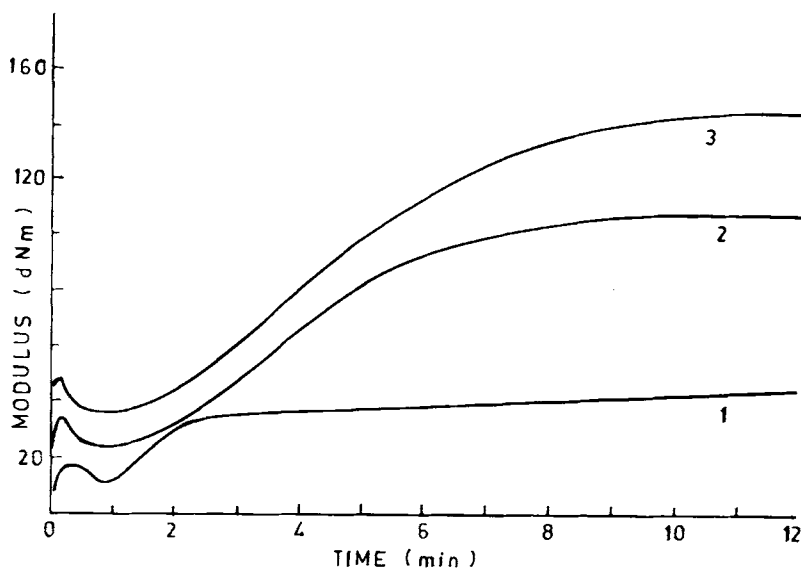


Figure 1 Rheometric curves for sample 1 (at 150°C): samples 2 and 3 (at 170°C).

and $-\text{CH}_2-$ adjacent to the urethane linkages.³ The later type of sites are preferred for forming covalent bonds between the adjacent chains. This is usually formed at the periphery of the hard segments because of the steric hindrance. This forces the hard segments to segregate. The hardness and rebound resilience and percent elongation are higher in the case of sample 2 than those in the case of sample 1. The segregation of hard segments accounts for the higher hardness in sample 2. The formation of TDI bridges between the main chains in sample 1 results in smaller fragments on application of stress and explains the reduction in ultimate percent elongation.

In sample 1a where the TDID content is double that in sample 1, the moduli and tensile strength are increased whereas the percent elongation is decreased. This can simply be attributed to the in-

crease in the total number of crosslinks. However, attempts to make the samples with 10 phr DCP resulted in the very hard and brittle material because of the excessive crosslinking. Comparing sample 3 with sample 1a and sample 2a points out that although the concentration of the crosslinking agents remain same, sample 3 has superior strength coupled with elasticity. This can be explained by the mixed kind of crosslinking present in the case of sample 3. The main chains in sample 3 are separated by the TDI bridges formed earlier in the process. Also, $-\text{CH}_3$ of TDI represents an additional site for generation of the stable free radical by DCP.³ Thus free radicals are available on the main chains as well as on the TDI bridges, resulting in the inter- as well as intrachain bonding.

Increase in the filler loading increases the moduli, tensile strength, and hardness, whereas it decreases

Table IV Mechanical Properties of Millable Polyurethane Composites

Sample	Tensile Strength (MPa)	Elongation at Break (%)	Moduli at			Hardness Shore A	Rebound (%)
			100% (MPa)	200% (MPa)	300% (MPa)		
1	8.55	270	3.0	6.2	—	48	15
1a	10.6	220	4.2	8.5	—		
2	6.9	310	2.2	4.5	6.5	60	30
2a	—	—	—	—	—	88	10
3	11.2	520	2.5	5.1	8.0	68	25
4	11.6	370	2.8	6.2	9.2	72	20
5	11.9	270	4.2	8.5	—	80	18
6	9.8	530	2.1	4.6	6.8	60	17

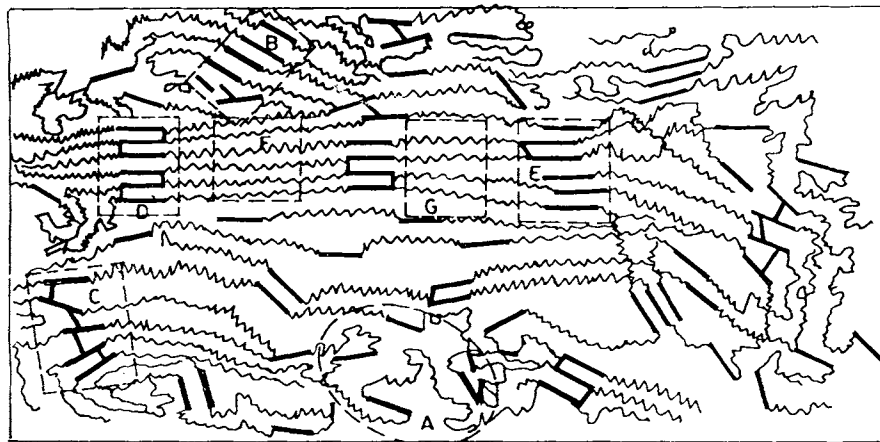


Figure 2 Schematic presentation of PU bulk structure. A: Amorphous solution of Hard and Soft segments; B: Segregation of Hard segment to have Long and Short order structures; C: Crosslinking by TDI Bridge across hard segments; D: Crystalline hard segments formed by crosslinking at the periphery of Hard segments; E: Paracrystalline hard segments formed because of forced segregation; F: Stress induced crystalline soft segments; G: Stress induced paracrystalline soft segments. In the gumstock only A and B type are present. In sample 2: A, B, D, E, F, and G type are present. In sample 1: A, B, and C type are present. In sample 3: A, B, C, D, E, F, and G type are present.

the percent elongation at break and rebound resilience (samples 3, 4, and 5). This can be attributed to the increase of hard filler particles, which are evenly dispersed. This reduces the flexibility of polymeric chains explaining the reduction in elongation and rebound resilience.

A comparison between the data of sample 3 and sample 6 indicates the inferior reinforcing nature of the aluminum silicate as compared to carbon black.

Thermal Analysis

The DSC curve of polyurethane gum stock, shown in Figure 3, exhibits several endotherms associated with disordering processes that occur in the hard domains. The three characteristic endothermic transitions observed in general agree with the studies by Seymour and Cooper.⁴⁻⁶ The endotherm centered at approximately 70°C is attributed to the disruption of domains with limited short-range order. The next transition at 130–225°C represents the dissociation of the domains containing long-range order. The third transition above 300°C is due to melting of the crystalline hard segments. These endotherms are very shallow but distinct in the gum stock, indicating a very small amount of the segregation of the hard domains as well as a good dispersion of the hard segments and the soft segments in the bulk. These three transitions are masked in the samples 1, 2, and 3 due to the presence of filler in the bulk.

The details of thermogravimetric analysis done on samples 1, 2, and 3 are given in the Table V. Integral procedural decomposition temperature (IPDT) as proposed by Doyle⁷ provides a semi-quantitative measure for the comparison of relative thermal stabilities. Crosslinks in sample 1 are the weakest sites⁸ and are broken first, during the degradation process. Once these crosslinks break down at comparatively lower temperatures, the resultant main chains undergo fragmentation at a rapid rate (Fig. 4). The relative stability can also be compared by the temperatures at which 10, 30, 50, and 70% degradation take place (Table V). In sample 3, which is mixture cured, the polymer is comparatively stable due to the mixed kind of crosslinking. The breaking away of crosslinks due to TDID at lower temperature do not generate the free main chains as they are joined by the crosslinks due to DCP. This retards the process of fragmentation, which in turn reduces the rate of degradation. Though the intermediate stability is more in the case of sample 2, IPDT values indicate that sample 3 has better overall thermal stability.

Wide-Angle X-ray (WAX) Diffraction Studies

Schematically any kind of polyurethane bulk structure can be represented as shown in Figure 2. According to Chang and Wilkes,⁹ in WAX diffraction of diamine-extended polyurethanes, the peaks ap-

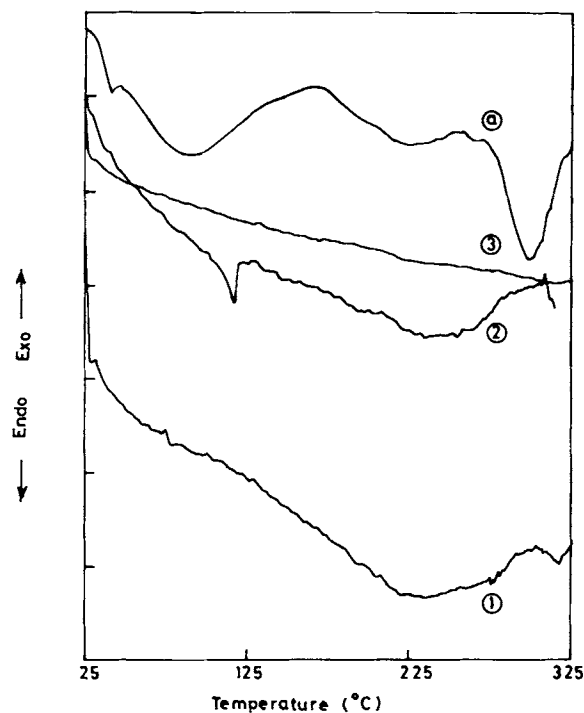


Figure 3 DSC curves of PU samples. (A) Gum Stock; (1) Sample 1; (2) Sample 2; (3) Sample 3.

peaking at 18° – 28° of 2θ correspond to either supramolecular structure of bulk and/or stress crystallized and paracrystalline soft segments. In a study by Minoura et al.¹⁰ it was shown that the diffraction intensity of the peaks at 9° and 28° of 2θ vary with the nature of the chain extender, which was corroborated in our earlier studies on the cast polyurethanes.^{1(a-c)} Thus it can be said that the peaks around 9° and 28° represent the formation of an overall ordered structure or at least stress-induced ordering of soft segments. The other important characteristic of WAX diffraction pattern of polyurethane is the halo appearing over a range of 2θ . This is attributed to the amorphous solution of the hard and soft segments to give an evenly distributed bulk.¹¹ In our earlier studies it was observed that

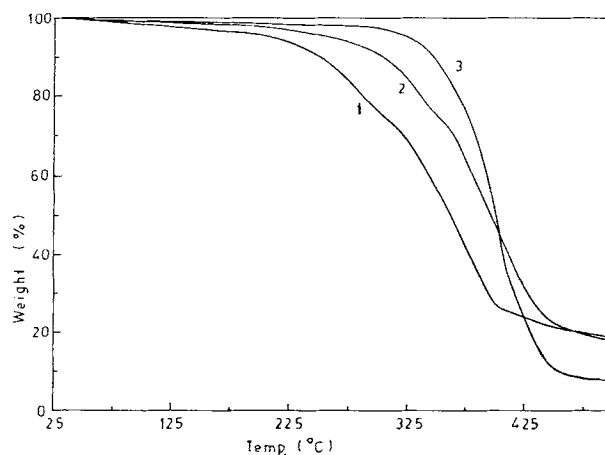


Figure 4 Thermogravimetric curves for samples 1, 2, and 3.

with the increase in crystallinity, the intensity of the peaks increased along with the reduction in the span of halo.

As can be seen from Figure 5, the gum stock and samples 1, 2, and 3 show a broadened peak with a maximum at 20° and spanning over 10° to 30° of 2θ . Additionally, gum stock exhibits a halo spreading over 35° to 50° of 2θ . This result corroborates the observation made in DSC curves that there is no stress-induced crystallization of soft segments in the bulk. The broadened peak can be attributed to the segregated hard segments whereas the halo represents the ordering because of hydrogen bonding. The same observation for sample 1 indicates the presence of segregated hard segments but well dispersed in the bulk because of TDI bridge between the main chains. This inference corroborates the results obtained from the mechanical and thermal properties.

In sample 2 additional peaks appear at 9° , 12° , 18° , 28° , and 29° of 2θ . This clearly indicates that a specific crystalline structure is formed when the crosslinking is done using DCP. This may be due to the crosslinking taking place at the periphery of hard segments thereby forcing them to undergo segre-

Table V TGA Data of Polyurethane Composites

Composite	Temperature at % Wt Loss				IPDT (°C)	% Residue at 500°C
	10	30	50	70		
1	285	325	415	415	330	20
2	285	290	410	435	376	17
3	275	365	395	444	400	19

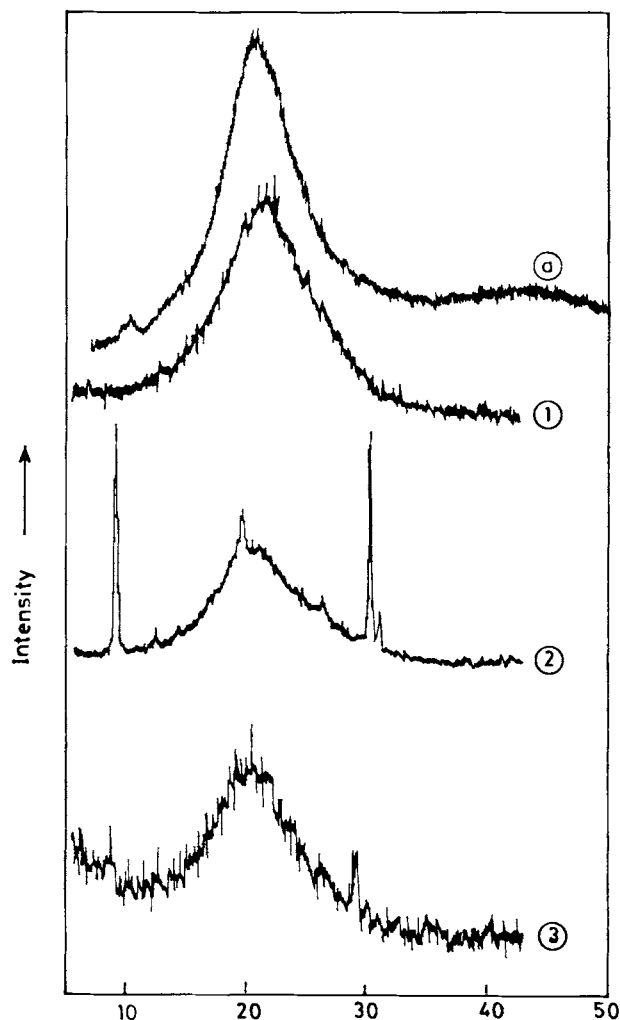


Figure 5 Effect of crosslinking agents on the X-ray diffraction pattern. (A) Gum stock; (1) Sample 1; (2) Sample 2; (3) Sample 3.

gation and consequently a distinct phase separation. This may also induce the soft segments to undergo stress-induced crystallization. Thus in sample 2 a definite supramolecular structure is formed.

In sample 3 where a mixed kind of bonding is present, it has an intermediate kind of diffraction pattern. The less intense but distinct peaks at 9° and 28° of 2θ indicate that though segregation of hard segments takes place, the extent of phase separation is considerably less than that present in sample 2.

CONCLUSION

The crosslinking by TDID is rapid and gives a very even distribution of hard segments in the bulk. This is because of the preference of TDID to form the links of TDI in between the hard segments. The crosslinking by DCP is comparatively slow but yields segregated hard segments because of the crosslinking reactions occurring at periphery of hard segments. However, the use of a mixture of TDID and DCP gives an intermediate kind of crosslinking at periphery as well as in between the hard segments. This results in a dramatic improvement in the mechanical properties and thermal stability. The addition of carbon black improves the mechanical strength of the vulcanizates as expected.

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