Determination of Crosslink Density by Swelling in the Castable Polyurethane Elastomer Based on 1/4 - Cyclohexane Diisocyanate and para - Phenylene Diisocyanate

Key Words:

crosslink density, polyurethane, swelling, castable, excess CHDI

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ABSTRACT

Five different series of castable polyurethane elastomers based on the system polycaprolactone /trans 1,4-cyclohexane diisocyanate or paraphenylene diisocyanate and various types of chain extenders were synthesized to study the effect of using excess diisocyanate and three functional chain extender on crosslink density and swollen volume.

Crosslink density was measured by swelling in toluene at room temperature for one week.It was found that the crosslink density significantly increases with increasing amounts of excess diisocyanate in the original gel.It was also found that a higher value of crosslink density is observed on changing from diol chain extenders to a diamine system.

INTRODUCTION

The crosslinking of polymer chains is of primary importance in controlling many polymer properties. Large increases in the degree of crosslinking make amorphous polymers more rigid and cause them to have higher softening points and a higher modulus [1], reduce elongation [2] and swelling by solvents, and raise the glass transition temperatures. Chemical crosslinking in segmented polyurethane elastomers can be produced by:

- The use of an excess of diisocyanate which can react with chain backbone urethane or urea linkages to give allophanate, biuret and isocyanurate groups.
- The use of a branched polyether or polyester having hydroxyl functionality greater than two.
- The incorporation of a low molecular weight triol in the reactions, e. g. Trimethylol propane (TMP).

The effect of percentage excess diisocyanate on the thermal stability of CHDI based polyurethane elastomer has been previously reported [3]. It was recognised that the relative thermal stability of these elastomers was considerably enhanced. In this study the effect of percentage excess diisocyanate and different types of chain extenders on crosslink density of polyurethane elastomers is investigated.

BASIC PRINCIPLES

Swelling measurements are often used to measure the crosslink density of elastomers. The degree of swelling (the amount of solvent imbibed) is known to be dependent upon the crosslink density of polymer networks; the greater the crosslink density, the less the degree of swelling. Percentage swelling by volume of the polymer samples can be determined by using the following formula [4]:

(A)

$$\%\ \text{swelling by volume} = \frac{\text{Gain in weight}}{\text{Specific gravity of solvent}} \times \frac{\text{Specific gravity of specimen}}{\text{Original weight of specimen}} \times 100$$

The number average molecular weight between crosslinks, M_c, can be calculated from the Flory – Rehner [5] equation:

(B)

$$-\text{Ln}\,[(1 - V_r) + V_r + \chi V_r^2] = \rho V_s M_c^{-1} (V_r^{1/3} - V_{r/2})$$

where V_r is the volume fraction of polymer in the swollen gel at equilibrium

χ is the polymer – solvent interaction parameter

V_s is the molar volume of solvent

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M_c is the number average molecular weight between crosslinks (Physical)
ρ is the density of polymer.

The volume fraction of polymer (V_r) can be calculated from the equation:

$$V_r = \frac{V_r}{V_r + V_s} \qquad \text{(C)}$$

$$\therefore \quad V_r = \frac{m_1 d_s}{m_1 (d_s - d_r) + m_2 d_r}$$

where m_1 is the weight of the polymer before swelling
m_2 is the weight of the polymer after swelling
d_s is the density of solvent
d_r is the density of polymer

The polymer-solvent interaction parameter (χ) was determined from the Bristow and Watson semi-empirical equation [6]:

$$\chi = \beta_1 + (V_s / RT)(\delta_s - \delta_p)^2 \qquad \text{(D)}$$

where β_1 is the lattice constant, usually about 0.34
V_s is the molar volume of solvent
R is the universal gas constant
T is the absolute temperature
δ is the solubility parameter and the subscripts s and p refer to the swelling agent and polymer, respectively.

The solubility parameters of polyurethane and the solvent (toluene) are 10.0 $(cal/cc)^{\frac{1}{2}}$ and 8.9 $(cal/cc)^{\frac{1}{2}}$ respectively, according to the data taken from polymer handbooks [7].

The molar volume of solvent is determined from the equation:

$$V_s = \frac{M}{d}$$

where: M is the molecular weight of solvent
d is the density of solvent.

The crosslink density, defined as $\frac{1}{2M_c}$, can therefore be calculated.

EXPERIMENTAL

Synthesis

Polyurethane elastomers used in this study were prepared by bulk polymerisation techniques, where the prepolymer, which can be obtained by reacting a long chain polyol with an excess of diisocyanate, and chain extender, are mixed in the melt state at elevated temperature to yield the final product [8]. Then the product is normally cured in a mould by heating in the temperature range 120–130 °C for several hours. The material used in this study are listed in Table 1.

Test Procedure

Swelling experiments were conducted on small rectangular (approximately 20 x 10 x 2 mm) specimens of the synthesized PU's in toluene at room temperature for one week. A swelling time of one week was chosen as the basis of the test results on several samples which showed no significant changes after one week of immersion in toluene. At the end of the immersion period the sample was removed, rapidly blotted with tissue and transferred to the weighing bottle to obtain the swollen weight of the sample. The crosslink density was calculated, based on the values of V_r and V_s obtained, using equation (B). Crosslink density was expressed as moles of crosslink per gram of insoluble network.

RESULTS AND DISCUSSION

As the polymer - solvent interaction parameter χ was necessary to calculate the crosslink density from the swelling data, it was determined (χ = 0.56) from equation (4).

The results of swelling tests for five series of prepared polyurethane elastomers are given in Tables 2 to 6 and Figure 1. The results indicate that:

- The crosslink density values of the polyurethanes significantly increased with increasing amounts of excess diisocyanate in the original gel.
- The swelling capacity (or ability of the network to imbibe solvent) decreases with increasing the degree of crosslinking (Figure 2-3).
- Swollen volume of polyurethanes based on 1/2/1 block ratio was greater than the swollen volume of urethanes based on 1/3/2; this means samples with lower block ratio have lower crosslink density.
- Swollen volume of the polacure urethane was greater than the swollen volume of the 1,4 - BD+1,4 - CHDM based urethanes (as is clear from Tables 3 and 4).
- Crosslink density of polyurethanes cured by polacure exhibited higher values than the polyurethanes cured with the 1,4 – BD+1,4- CHDM chain extension agent (Figure 1 - 2).
- Polyurethanes extended by the dianol (22+33) chain extension agent showed a lower crosslink density than those extended by dianol (22+33)+ TMP (1/1) or TMP alone. These results illustrate that more crosslinks were formed during the chain extension of polyurethane with TMP chain extender (Table 6) than where it was not used in the chain extension system.

Table 1: Materials used in the synthesis of these polyurethane elastomers.

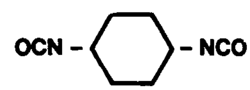
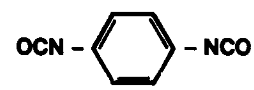
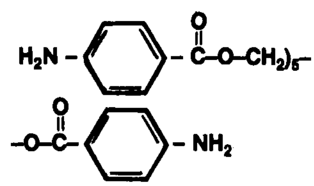
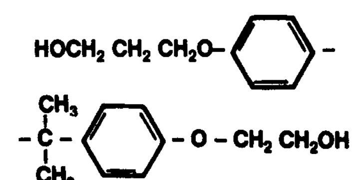
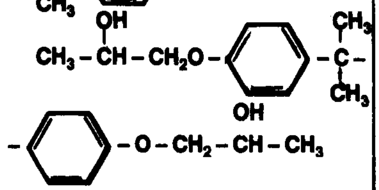
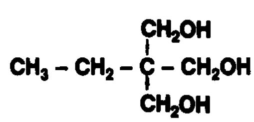
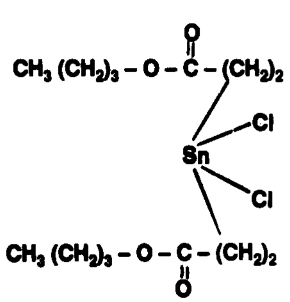
Materials	Abbre - viation	Chemical formula	Molecular Weight	Melting Point	Suppliers
Polyol Polycaprolactone	Capa 225	$HO[(CH_2)_5-\overset{O}{\overset{\parallel}{C}}-O]R[O-\overset{O}{\overset{\parallel}{C}}-(CH_2)_5]_n OH$	2000	60	Interox Che - mical Ltd.
«	Capa 305		540		«
Diisocyanate Trans 1, 4-cyclohexane diisocyanate	CHDI		166.16	64	AKZO Chemie
P - Phenylene diisocyanate	PPDI		160	94 - 95	AKZO Chemie
Chain extender 1,4 Butanediol	1,4 - BD	$HO-CH_2CH_2CH_2CH_2-OH$	90	16	GAF*
Trimethylene glycol di - p - aminobenzoate	Polacure		314	125 - 128	Polaroid cor- poration, U.S.A
[1, 1' - isopropylidene bis - (p - phenylene - oxy) di - ß ethanol]	Diano122		316	—	AKZO Chemie
[1, 1' - Isopropylidene bis - (P - phenylene - oxy) di - ω - propanol - 2]	Diano 133		344	70 - 80	«
Trimethylol propane	TMP		134	56 - 58	BDH Chemical Ltd.
Catalyst Dicarbobutyloxy ethyl tin dichloride	T 220				AKZO Chemie

***Table 2:** Crosslink density and swollen volume of polyurethane elastomer based on Capa 225/CHDI/1,4-BD (Block ratio 1/2/1).*

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mole/kg)
Capa 17,1	2	0.4862	235	72.7×10^{-2}
B59	5	0.4939	232	77.4×10^{-2}
B60	10	0.5049	228	84.7×10^{-2}
B61	15	0.5200	222	95.5×10^{-2}
B62	20	0.5295	219	103.0×10^{-2}
B56	25	0.5512	211	121.9×10^{-2}
B63	30	0.5601	209	130.3×10^{-2}
B64	35	0.5690	206	139.1×10^{-2}
B65	40	0.5860	201	157.7×10^{-2}
B66	45	0.5882	201	160.2×10^{-2}
A'6	50	0.5929	199	165.8×10^{-2}

***Table 3:** Crosslink density and swollen volume of Polyurethane elastomer based on Capa 225/CHDI/1,4-BD + 1,4 - CHDM (Block ratio 1/3/2)*

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mol/kg)
Capa 18,6	0.2	0.5751	204	146.47×10^{-2}
B74	5	0.5895	200	167.14×10^{-2}
B75	10	0.5966	197	170.49×10^{-2}
B76	15	0.6024	197	177.72×10^{-2}
B77	20	0.6066	196	182.46×10^{-2}
B78	25	0.6159	194	194.97×10^{-2}
B79	30	0.6251	191	208.15×10^{-2}
B80	35	0.6382	188	228.16×10^{-2}
B81	40	0.6398	188	230.71×10^{-2}

***Table 4:** Crosslink density and swollen volume of polyurethane elastomer based on Capa 225/CHDI/polacure (Block Ratio 1/3/2)*

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mole/kg)
B142	0.2	0.6067	200	177.61×10^{-2}
B143	5	0.6362	192	227.12×10^{-2}
B144	10	0.6502	189	241.78×10^{-2}
B145	15	0.6623	186	262.23×10^{-2}
B146	20	0.6642	185	266.32×10^{-2}
B147	25	0.6879	180	314.59×10^{-2}
B148	30	0.6962	179	332.10×10^{-2}

***Table 5:** Crosslink density and swollen volume of polyurethane elastomer based on Capa 225/PPDI/1,4-BD (Block Ratio 1/2/1)*

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mol/kg)
B119	0.2	0.5637	210	131.79×10^{-2}
B120	5	0.5639	209	132.32×10^{-2}
B121	10	0.5676	208	136.05×10^{-2}
B122	15	0.5773	205	146.08×10^{-2}
B123	20	0.5789	204	147.30×10^{-2}
B124	25	0.5882	203	157.79×10^{-2}

***Table 6:** Crosslink density and swollen volume of soft polyurethane elastomer (Block Ratios 1/3/2)*

Sample No	Polyol	Diisocyanate	Chain Extender	V_r	%Volume Swollen	Crosslink Density (mol/kg)
B103	Capa 225	PPDI	Dianol (22 + 23)	0.4851	241.41	69.27×10^{-2}
B106	Capa 225	PPDI	Dianol (22 + 33)	0.5409	219.84	108.94×10^{-2}
	Capa 225		+ TMP			
B108	Capa 240	PPDI	TMP	0.7227	208.74	400.64×10^{-2}
B131	+Capa 305	PPDI	TMP	0.4806	240.95	678.80×10^{-2}
	(3/1)					
B133	Capa 225	CHDI	TMP	0.5663	207.97	135.86×10^{-2}
B155	Capa 231	CHDI	Capa 305	0.4014	278.83	33.55×10^{-2}

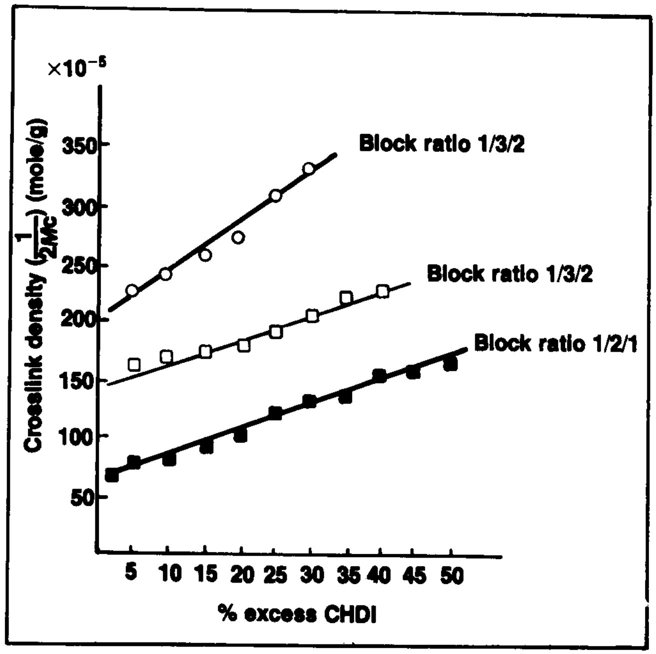


***Figure 1:** Crosslink density vs % excess CHDI for the polyure – thane elastomer based on Capa 225/CHDI/chain extender:*

(0) Polacure; (□) 1,4 – BD + 1, 4 – CHDM; (■) 1, 4 – BD

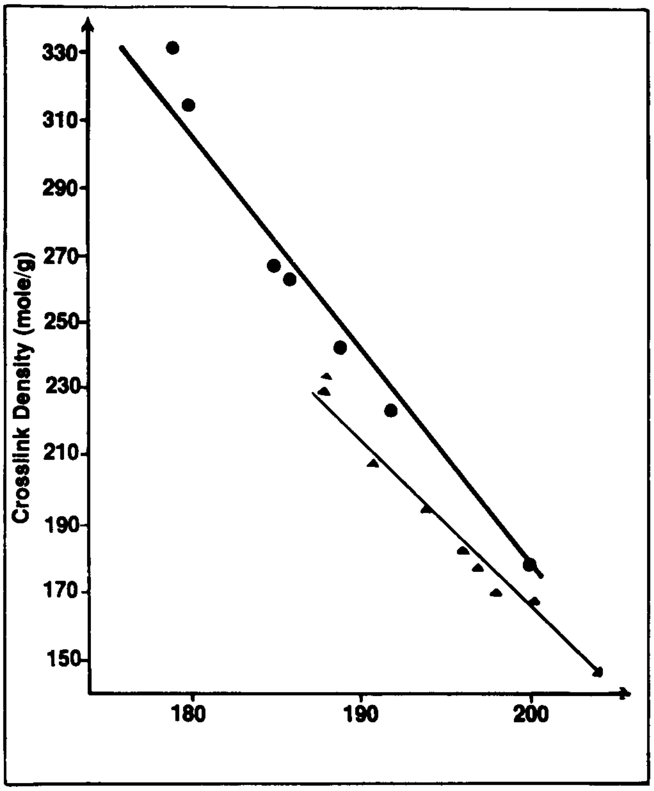


Figure 2: Crosslink density vs % swollen volume for the polyurethane elastomers.

● Polyurethane Elastomer Based on Capa 225/CHDI/Polacure (Block ratio 1/3/2)

▲ Polyurethane Elastomer Based on Capa 225/CHDI/1, 4 – BD + 1, 4 – CHDM

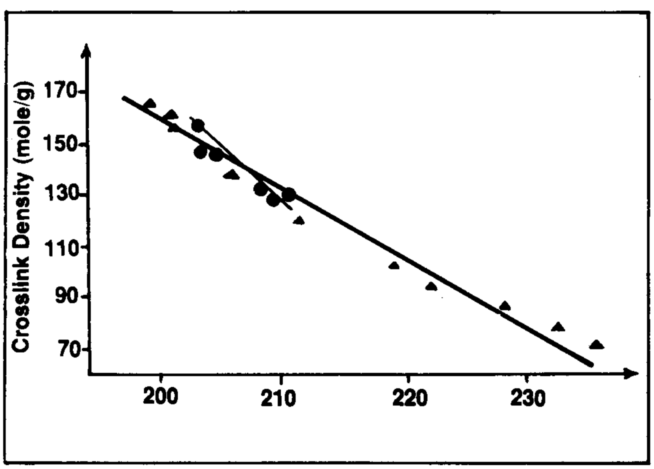


Figure 3: Crosslink density vs% swollen volume for polyurethane elastomers

● Polyurethane Elastomer Based on Capa 225/PPDI/ 1,4 – BD

▲ Polyurethane Elastomer Based on Capa 225/ CHDI/ 1,4 – BD

CONCLUSION

The crosslink density of polyurethanes was measured experimentally using the swelling method and it was found that the crosslink density values of the polyurethanes significantly increased with either an increase in the amount of excess diisocyanate in the original polymer or the presence of a trifunctional chain extension agent i.e. TMP. It was also found that a higher crosslink density was found to be present in diamine (Polacure) based polyurethane than in diol (1, 4 – BD or 1, 4 – BD + 1, 4 – CHDM) based materials. Samples with higher block ratios also showed relatively higher crosslink densities.

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