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Investigation into the network structure of plasticized rocket propellant

J. Akhavan
School of Engineering and Applied Science, Cranfield University, RMCS, Shrivenham, Swindon SN6 8LA, UK
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To improve the dimensional stability of a solid rocket propellant and to allow it to deform under stress a rubbery polymeric network is incorporated into the composition. Energetic plasticizers are also added to the propellant to improve its performance. However, migration of the plasticizer has been observed. This can lead to irregularities in the propellants ballistic properties and may sometimes lead to premature detonation. It is important therefore to be able to understand the effect the plasticizer has on the network structure of the polymer in solid rocket propellant. In order to look at this problem compositions containing polycaprolactone crosslinked with excess isocyanate were formulated. Varying amounts of plasticizer [glycerol triacetate $(CH_3COO)_3C_3H_5$)] were incorporated into the compositions. The network structure of polycaprolactone crosslinked with an isocyanate was found to be dependent on the quantity of plasticizer present during curing. A reduction in plasticizer results in a reduced mobility of the free isocyanate molecules, thus leading to a tighter polymeric network. The average number of polycaprolactone chains between each crosslink unit increases from 14 to 77 as the amount of plasticizer is increased. This leads to the polymeric network having a more open structure. On crystallization the looser networks were able to form structures with higher degrees of crystallinity. On total removal of the plasticizer by extraction, the network structure collapsed and formed structures with a high crystalline content. The networks were able to regain their integrity by reintroducing the samples back into plasticizer above the crystalline melting temperature. The more open networks could absorb more plasticizer. When allowing the samples to crystallize again the same amount of plasticizer was expelled, thus suggesting that plasticized network structures have a memory. © 1997 Elsevier Science Ltd.

(Keywords: plasticizer; network; propellant)

INTRODUCTION

Solid rocket propellants containing elastomeric binders are employed in most modern rocket propellants. The mechanical properties of the rocket propellant are largely determined by the mechanical properties of the polymeric network. The propellant must be able to expand and contract within the rocket shell without cracking or detaching itself from the inner walls of the casing. Cracking of the propellant can lead to irregular burning and an increase in pressure resulting in the propellant exploding.

Solid rocket propellants can be regarded as highly filled polymers. The propellant generally consists of ~85% wt of explosive particulates embedded in ~15% wt of an elastomeric binder. To improve the performance of this highly filled elastic propellant an energetic plasticizer[1] can be incorporated, such as nitroglycerine or a nitrated ester. The plasticizer acts as a lubricant within the polymeric network, reducing the elastic modulus and lowering the glass transition temperature of the polymer. Large amounts of energetic plasticizer can increase the specific impulse of the propellant and reduce the possibility of cracking.

The migration of plasticizers in polymers is well known and has been thoroughly investigated[2–13]. In some cases this migration can be advantageous, however in rocket propellants it can be extremely hazardous. Migration and leakage of an energetic plasticizer in a rocket propellant produces an inhomogeneous composition[14], which can lead to premature detonation, change in ballistic characteristics, etc. It is therefore important to be able to predict the behaviour of the energetic plasticizer and to control the leakage of plasticizer from the propellant.

An investigation was carried out to determine the effect plasticizer has on the structure of the polymeric network used in high energy rocket propellant.

EXPERIMENTAL

The formulations chosen represent as closely as possible the actual formulations used for modern high energy, plasticized propellants. The energetic plasticizer nitroglycerine was replaced with glycerol triacetate $[(CH_3COO)_3C_3H_5]$. In this study the polymeric binder was a hydroxyl-terminated polycaprolactone. This was obtained from Union Carbide under the trade name of TONE 0260 Polyol. The approximate molecular weight of the polymeric binder was 3000 $gmol^{-1}$. The binder was crosslinked with a polyfunctional isocyanate called Desmodur N-100 (molecular weight = 478), this was supplied by Bayer (UK) Ltd. The cure was assisted by a small amount of cure catalyst, triphenyl bismuth supplied by Unichem Ltd. The plasticizer glycerol triacetate, was supplied by Eastman Chemical Products under the trade name of 'Kodaflex'.

Polycaprolactone, glycerol triacetate and the isocyanate were mixed together in a beaker using the formulae given in *Table 1*. The mixture was then left in an oven at 60°C for 10 minutes to melt the polycaprolactone before triphenyl

Table 1 Formulations of network polymers containing different amounts of plasticizer

Plast:polymer	1:1	1.25:1	2:1	2.5:1	3:1	4:1	5:1	6:1	7.5:1
% wt of plast	45%	51%	62%	68%	71%	77%	80%	83%	86%
Polycaprolactone	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Glycerol triacetate	9.2	11.5	18.4	23.0	27.6	36.8	46.0	55.2	69
Isocyanate	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Triphenyl bismuth	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

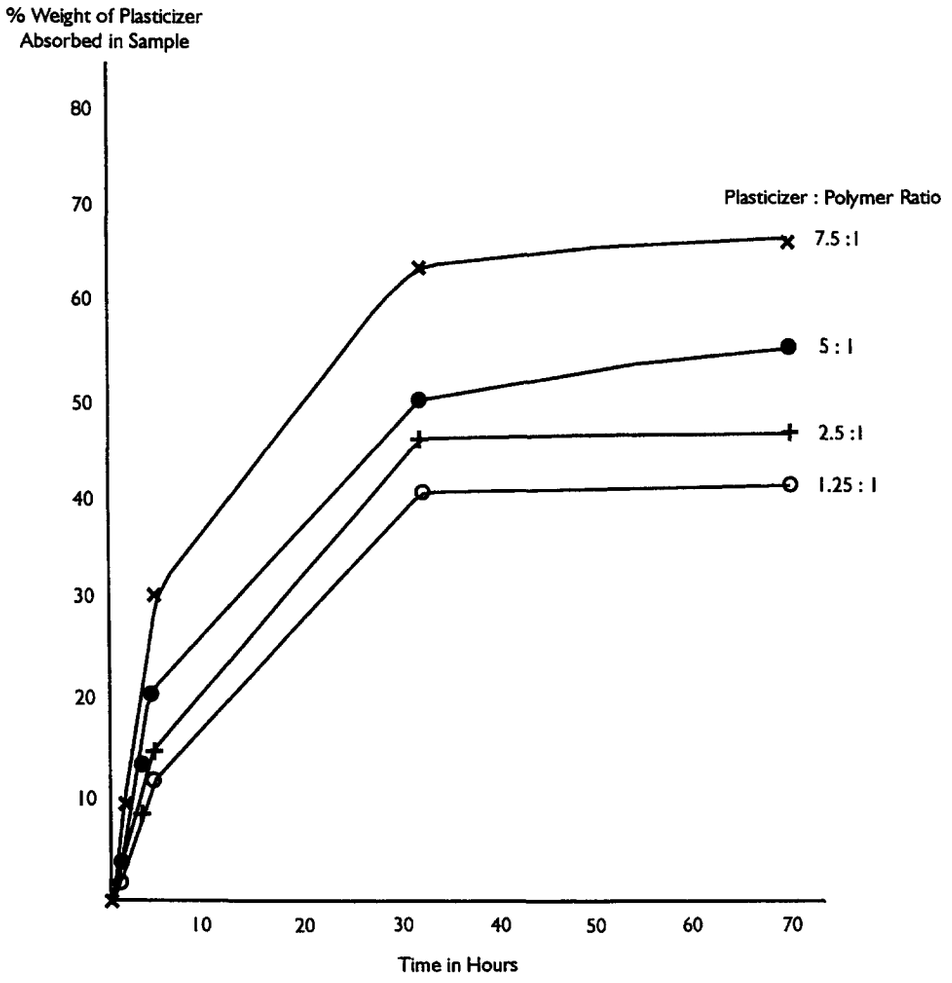

Figure 1 Reabsorption of plasticizer into extracted polymeric networks at 50°C

bismuth was added. The mixture was then poured into a Teflon-coated mould of dimensions 100 mm × 100 mm × 2 mm, and left to de-gas at 60°C for 20 minutes in a vacuum oven. After de-gassing the lid was clamped onto the mould and placed into an oven at 100°C for 24 hours to allow the polymer to cure.

To study the effect plasticizer has on the network polymer, the quantity of plasticizer to polymer ratio was increased from 1:1 to 7.5:1. The formulae for these compositions are shown in *Table 1*. After the samples had cured, the moulds were removed from the oven and left to cool to room temperature. The cured compositions were carefully removed from the moulds and cut into samples of dimensions 15 mm × 15 mm × 2 mm. The samples were then weighed on an analytical balance (with an accuracy of ± 0.005g) to establish the initial weight at zero time.

To investigate the network structure of the samples, the plasticizer was removed by solvent extraction using methanol. The methanol extracts were analysed to see if any other material was extracted using a Carlo Erba Strumentazione HRGC 3300 Gas Chromatograph (GC). Only the plasticizer was found to be extracted. The samples were then dried in a vacuum oven at 50°C for 7 days to remove any residual methanol. The extracted samples were then reimmersed in excess plasticizer and held at 50°C* in a sealed container. The rate of adsorption of plasticizer was determined by weighing the samples at regular intervals. The results are presented in *Figure 1*.

The degree of crosslinking in the network polymers were calculated from swelling experiments using the plasticizer as the swelling agent. The swelling experiments were conducted on the compositions given in *Table 1* with the removal of plasticizer by methanol extraction. The extracted samples were immersed in excess plasticizer and the degree of swelling was measured at regular intervals. The molecular weight per crosslinked unit (M_x) was calculated

* Elevated temperatures were used to prevent the polycaprolactone from crystallizing and expelling the plasticizer.

using the equation[15] below and the results are presented in *Table 2*:

$$-[\ln(1-c)+c+x_1c^2]=(V_1\rho_2/M_x)(c^{1/3}-c/2)$$

where c = concentration at equilibrium, x_1 = polymer–solvent interaction parameter of the Flory-Huggins theory, V_1 = molar volume of the solvent, ρ_2 = density of the polymer, and M_x = molecular weight per crosslinked unit.

RESULTS AND DISCUSSION

On extraction of the plasticizer by methanol and reimmersion of the extracted samples in excess plasticizer, the uptake of plasticizer was found to be dependent on the quantity of plasticizer originally incorporated in the compositions as shown in *Figure 1*. An increase in the plasticizer content in the original compositions resulted in an increase in the uptake of plasticizer after extraction, suggesting that a high degree of plasticization in the curing process produces a network structure that is more open. The molecular weight per crosslinked unit (M_x) was calculated from swelling experiments. The results are given in *Table 2*. The degree of crosslinking in the network polymer was found to be reduced as the quantity of plasticizer increased. This suggests that the plasticizer is somehow affecting the way the polymer crosslinks during curing.

Hydroxy end groups on the polycaprolactone react with the NCO groups on the isocyanate to form a crosslinked network, as shown in *Figure 2*. The number of polycaprolactone chains between each crosslink unit was found to increase as the plasticizer content increased as shown in *Table 2*. This suggests that an increase in plasticizer content effects the size of the network creating larger gaps between each crosslink. These larger gaps would allow the polymer to have more mobility. If network structures are allowed to crystallize then it would be expected that higher degrees

Table 2 Calculation of the molecular weight per crosslinked unit (M_x) from swelling experiments; calculation of the average number of polycaprolactone chains in the network (M_x/M), where M for the perfect network is taken as $[M_{polymer} + (2/3)M_{isocyanate}]$

Plasticizer:polymer	M_x($\times 10^5$)	(M_x/M)
0:1	0.46	13.9
1.25:1	0.84	25.3
2.5:1	1.39	41.9
5:1	2.30	69.3
7.5:1	2.54	76.5

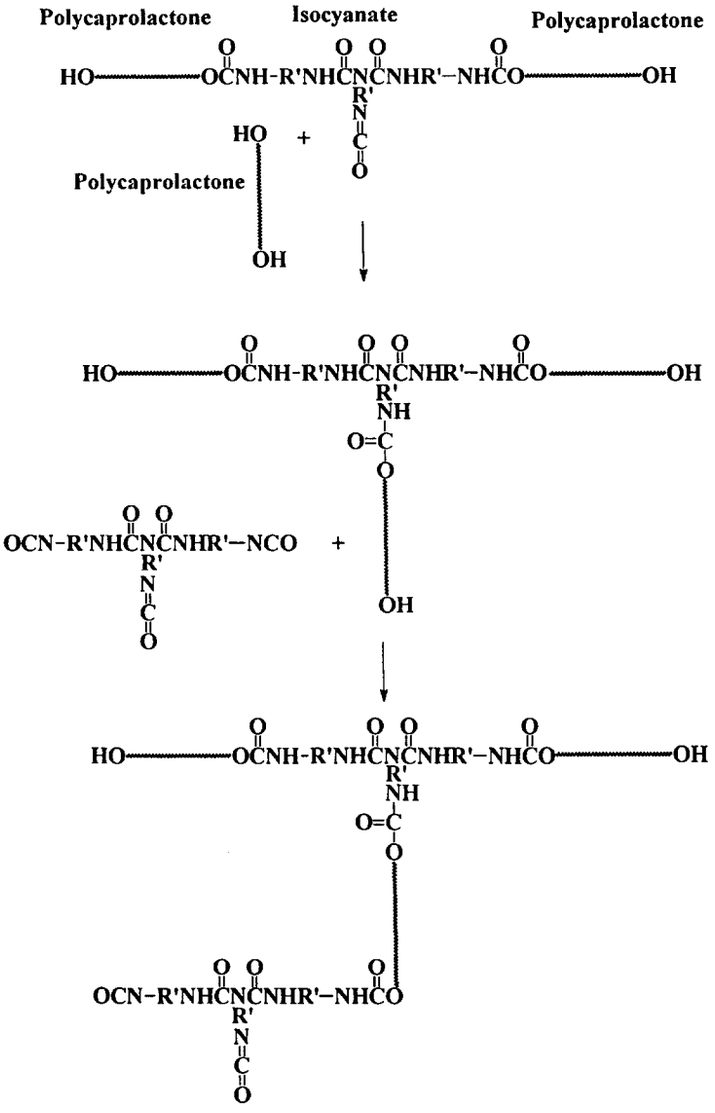

Figure 2 Schematic diagram showing how the polymeric network structure is formed

of crystallinity should occur in samples with higher concentrations of plasticizer.

In order to study this effect, more samples were prepared using the formulations given in *Table 1*. The prepared samples were weighed and left at room temperature. After 3 days the transparent samples had become opaque and a quantity of plasticizer expelled. The samples were dried and reweighed. Differential Scanning Calorimetry (DSC) was carried out on the opaque samples using a Mettler 4000 DSC. As expected the opacity was found to be due to the onset of crystallinity. The results are presented in *Figure 3*. The amount of plasticizer expelled from the samples (due to the onset of crystallinity) is shown in *Figure 4*. From *Figure 4* it can be seen that the loss of plasticizer from the samples is related to the degree of crystallization. An increase in crystallization results in an increase in the loss of plasticizer. *Figure 3* also relates the change in (M_x/M) and degree of crystallinity as the plasticizer:polymer ratio increases. Again there is evidence that the plasticizer is somehow effecting the size of the interstices in the polymer network during curing of the polycaprolactone with isocyanate. The looser network structures are able to form more ordered structures on crystallization.

The degree of crystallinity calculated from DSC were also carried out on samples that had undergone (i) extraction with methanol and left to crystallize at room temperature for 3 days, and (ii) reimmersion of the extracted samples into excess plasticizer for 1 week at 50°C and then left to crystallize at room temperature for 3 days. The degree of crystallinity and the loss of plasticizer are presented in *Tables 3* and *4*, respectively. The removal of plasticizer from the samples by extraction results in an increase in crystallinity far higher than the value calculated for the original network containing no plasticizer. On immersion into excess plasticizer the network structure of the samples were able to regain 75% of their original integrity and absorb the plasticizer as shown in *Figure 1*. Plasticizer was again expelled from the network structure when the samples

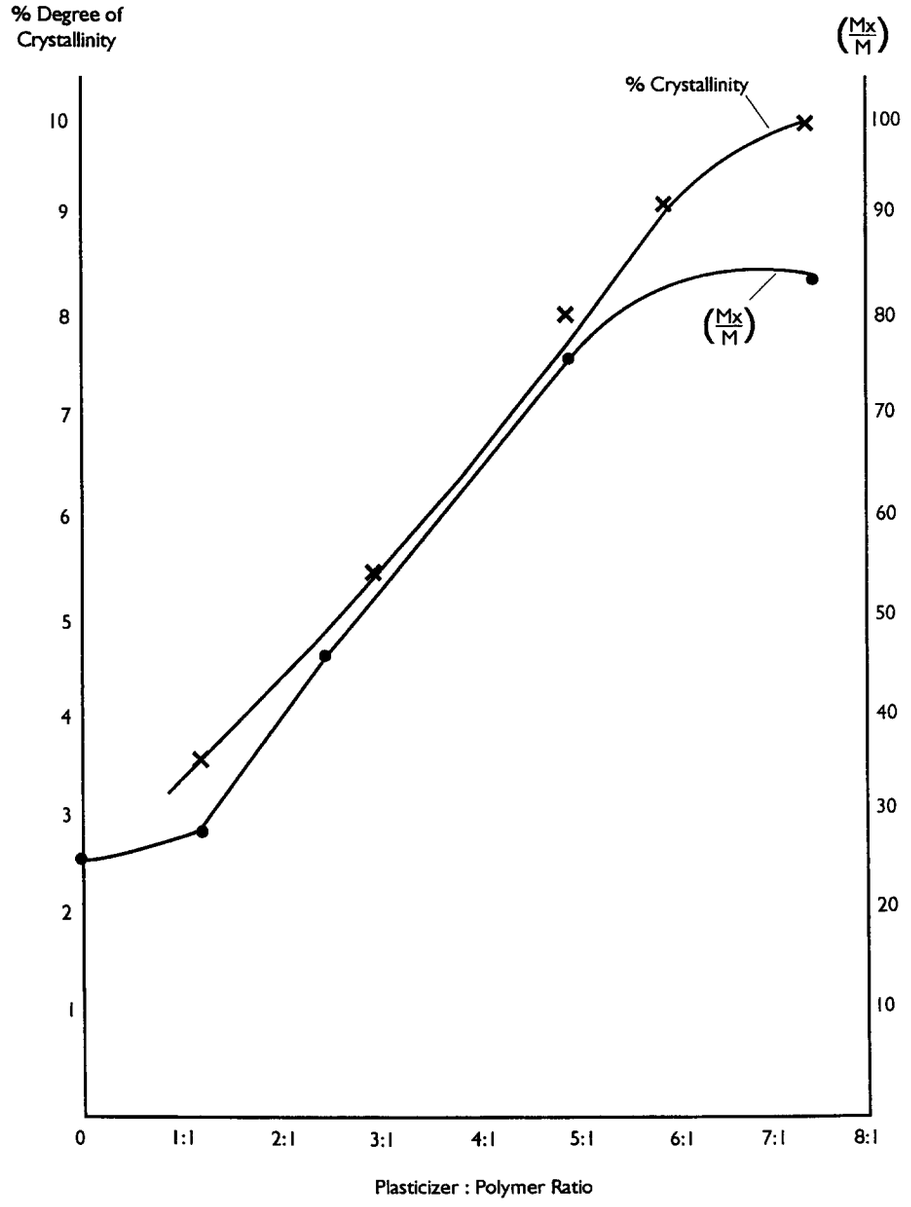

Figure 3 The relationship between the concentration of plasticizer incorporated in the compositions during curing with the average number of polycaprolactone chains between each crosslink (M_x/M) and the degree of crystallinity of the network at room temperature, calculated from Differential Scanning Calorimetry (heating rate 20g/min, ref $\Delta H = 148$ J/g for 100% crystalline polycaprolactone)

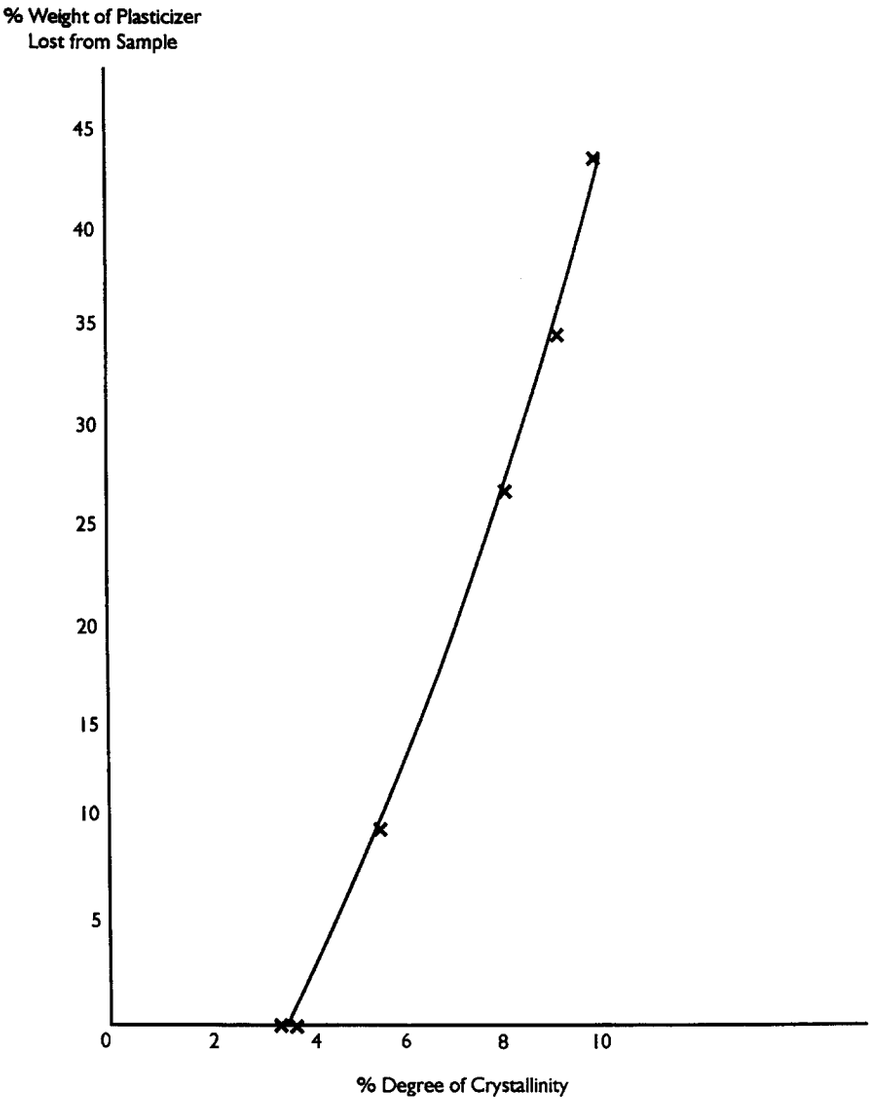

Figure 4 Percent weight of plasticizer lost from the polymeric network during crystallization

Table 3 Calculated degree of crystallinity from Differential Scanning Calorimetry (heating rate 20g/min, ref $\Delta H = 148$ J/g for 100% crystalline polycaprolactone)

	Degree of crystallinity		
Plasticizer:polymer	Left at room temp	Plasticizer extracted and cooled to room temperature	Left in excess plasticizer for 1 week at 50°C and cooled to room temperature
0:1	16.0%		
1:1.25	3.6%	28.7%	3.0%
3:1	5.5%	35.1%	6.0%
5:1	8.1%	34.9%	8.0%
6:1	9.2%	36.0%	10.2%
7.5:1	10.0%	36.6%	11.1%

Table 4 Percent weight of plasticizer loss from the samples when cooled to room temperature due to the onset of crystallization

	% weight of plasticizer expelled from samples	
Plasticizer:polymer	Left at room temp	Left in excess plasticizer for 1 week at 50°C and cooled to room temperature
0:1		
1:1.25	0%	0%
3:1	10.1%	10.7%
5:1	24.2%	24.0%
6:1	35.1%	36.2%
7.5:1	44.2%	44.9%

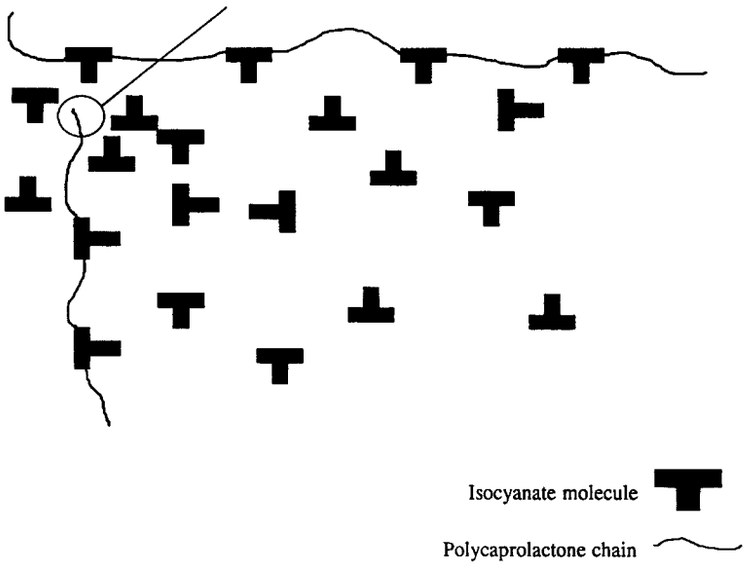

Figure 5 Schematic diagram of polycaprolactone reacting with free isocyanate molecules; the degree of mobility of the isocyanate will increase with increasing plasticizer

were allowed to cool to room temperature and recrystallize. These results suggest that the loss and uptake of plasticizer from the network polymer is a reversible process. The network will expel plasticizer on crystallization and reform its plasticized structure if warmed to above its crystallization temperature and held in excess plasticizer.

SUMMARY AND CONCLUSIONS

On curing polycaprolactone with a crosslinking agent (isocyanate) in the absence of a plasticizer, a network polymer is formed. If allowed to cool to room temperature the network polymer will order itself and form a semicrystalline polymer containing ~16% crystallinity. When polycaprolactone is cured with a crosslinking agent in the presence of a plasticizer (glycerol triacetate) a polymeric network is formed with a more open structure. The degree of 'openness' depends upon the quantity of plasticizer present during curing. Doubling the quantity of plasticizer will increase the chain length between each cross link by ~20 polycaprolactone chains. The plasticizer is able to influence the morphology of the network structure up to a level of saturation (7.5 plasticizer:1 polymer). At this high value of plasticization, network structures can no longer incorporate any more plasticizer. Here the network structure has ~77 polycaprolactone chains between each crosslink unit.

The reaction between the isocyanate and the polycaprolactone is a chemical reaction. The mixing ratio can be calculated from the number of functional groups in the coreactants, which is given by†:

$$\text{equivalent weight of isocyanate} = \frac{42 \times 100}{\%\text{NCO}} = \frac{42 \times 100}{22.00} = 191\text{g}$$

† Values obtained from Bayer and Union Carbide data sheets.

$$\text{equivalent weight of polycaprolactone} = \frac{17 \times 100}{\%\text{NCO}} = \frac{17 \times 100}{1.121} = 1516\text{g}.$$

If we assume the stoichiometric relationship of NCO/OH = 1:1 then for every 8 g of polycaprolactone we need 1 gram of isocyanate to give a fully crosslinked system. The compositions studied in this investigation used 2 g of isocyanate to 9 g of polycaprolactone (see *Table 1*), therefore giving an excess of isocyanate which should in theory produce a highly crosslinked structure. Vargo and Kelley[f4] in 1991 carried out research on the same compositions as studied in this paper. They reported that an increase in the plasticizer content results in an increase in the degree of crosslinking due to the increase in the mobility of the polycaprolactone chains. However, further on in their investigation they observed the reverse effect with the crosslinking density of their network structures decreasing as the ratio of plasticizer increased from 0 to 2.5.

Incorporation of the much-less-viscous glycerol triacetate decreases the viscosity of the crosslinking medium and increases the mobility of the isocyanate molecules. The mobile free isocyanate molecules in solution will be attracted to the OH groups on the ends of the polycaprolactone chains. Thus aiding the production of long linear chains. The reduction in plasticizer will therefore result in a reduced mobility of the free isocyanate molecules allowing the OH on the polycaprolactone chain to react with NCO on an isocyanate that is already incorporated in a polycaprolactone backbone as shown in *Figure 5*. This in turn will lead to a tighter network structure.

The addition of the glycerol triacetate plasticizer will also dilute the reactive groups, which results in an increase in intramolecular reactions. This will lead to a reduction in junction-point density and give a more 'open' network structure[f6].

On crystallization the chains pack close together and squeeze out some of the plasticizer. A more open structure

allows the chains to have more mobility and subsequently leads to a higher degree of crystallinity (i.e. 10%). An increase in crystallinity by 1% results in ~7–10% of plasticizer being expelled from samples with crystallinities greater than 4%. At lower crystallinities the network is able to order itself and still retain the plasticizer. On removal of the plasticizer by extraction the polymeric networks will have an open structure without integrity. The regions between the crosslinks would have collapsed. When cooled below the crystalline temperature the network structures crystallize. With the plasticizer removed the networks form crystalline structures with higher degrees of crystallinities (i.e. 29–37%). This suggests that the presence of plasticizer hinders crystallization. The looser networks are more mobile and as expected form structures with high degrees of crystallinity.

When the collapsed crystallized network is reintroduced to the plasticizer (above its crystallization temperature) the network is able to regain 75% of its original structure. The more open networks being able to absorb more plasticizer. On cooling these samples to room temperature and allowing them to crystallize once again, the same quantity of plasticizer was found to be expelled from the samples and the degree of crystallinity was found to be very similar to the initial values. These results suggest that the network structure has a memory. The 'openness' of the network structure is dependent on the quantity of plasticizer in the original composition up to a level of 7.5 plasticizer:1 polymer. The removal of plasticizer from the network, its subsequent collapse and crystallization does not deter the polymeric network from gaining some of its original integrity when left in excess plasticizer at temperatures above its crystallization temperature.

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