THE EFFECT OF CHAIN LENGTH OF POLYETHYLENE GLYCOL ON PROPERTIES OF CASTOR OIL BASED POLYURETHANE ELASTOMERS

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ABSTRACT

Polyurethane (PU) elastomers from castor oil based polyol, polyethylene glycol (PEG) of various molecular weight (200, 400, and 600) and toluene diisocyanate were prepared in the form of transparent sheets. The sorption, mechanical and thermal properties have been studied. The solubility parameter, molecular weight between two crosslinks and degree of crosslinking of PU samples were calculated from equilibrium swelling experiments. The kinetic study of swelling revealed that sorption is anomalous in nature in all the samples. Diffusion coefficient (D) and sorption coefficient (S) were found to decrease with an increase in chain length of PEG. The stress-strain data showed that the elastomers obtained using PEG-200 gave the best mechanical properties. The thermal degradation of all elastomers starts at $\sim 250°C$, regardless of the PEG chain length. The values of activation energy of degradation were in the range of $60-72$ kJ/mole.

Key Words: Polyethylene glycol; Castor oil; Polyurethane elastomers; Solubility parameter

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INTRODUCTION

Polyurethanes are known for their industrial applications due to high strength, resiliency, and good resistance to abrasion. A great number of factors such as extent of crosslinking, nature of polyol and diisocyanate and curing conditions are known to affect the properties of polyurethanes [1−5].

Efforts have been made during the past few decades to replace these expensive polyols with low cost natural vegetable oils or their derivatives in the production of PU products [6−8]. Among the vegetable oils, castor oil stands out for the synthesis of polyurethane elastomers as it possesses double bonds, as well as three hydroxyl groups. Moreover, castor oil possesses good compatibility with polyethylene glycol (PEG) in all proportions so that PEG can be effectively blended with castor oil or its derivatives to obtain castable polyurethane elastomers with improved application properties.

In the present study, we report the synthesis of PU by blending castor oil based polyols and PEG of various molecular weights for producing PU. The effect of molecular weight of polyols on physical, transport, mechanical and thermal properties have been studied.

EXPERIMENTAL

Materials

The castor oil based polyol designated R-60 in the study having hydroxyl equivalent weight 220 and having five hydroxyl groups per mole were supplied by H.K. Agencies, Ahmedabad. Polyethylene glycols (PEG) of molecular weight 200, 400, and 600 used in the study were purchased from Sisco Chem. Industries, India and were dried over anhydrous Na_2SO_4 to remove traces of water. All the solvents used were of analytical grade and were further purified by distillation. Toluene diisocyanate (TDI) and dibutyl tin dilaurate (DBTDL) were purchased from Fluka, Switzerland, and used as received.

Preparation of Prepolymer (PUR-60)

In a four-neck flask, equipped with a mechanical stirrer, thermometer, nitrogen gas inlet and outlet, calculated quantity of R-60 was placed in the flask. The required quantity of TDI was added gradually to R-60, maintaining a temperature of reactants of about 25°C until the addition of TDI was completed. The reactants were stirred for one hour to complete the reaction. The ratio of NCO/OH was maintained at 2.

Preparations of Elastomers (PUP)

Castable polyurethane elastomer was prepared by allowing the reaction of prepolymer PUR-60 with required quantities of PEG-200, PEG-400, and PEG-600, respectively along with the catalyst DBTDL (0.01 wt% total charge) by maintaining the final ratio NCO/OH 1.5. The reactants were weighed in a beaker, stirred well, and degassed under reduced pressure (2−5 mm of Hg.). The resin was then transferred to a previously leveled glass mold kept at 60°C and left overnight for curing. The samples in the form of sheets of about 1 mm. thickness were removed from the mold and finally cured at 80°C for 15 hours.

Swelling Experiments

Equilibrium swelling experiments were performed at 30 ± 0.5°C to determine solubility parameter of polyurethane samples. The swelling was carried out in various solvents ranging their solubility parameter value (δ) from 7.4 to 14.5 $(cal/cm^3)^{1/2}$. From the plots of equilibrium swelling volume Q vs. δ (Fig. 1) acetone gave a maximum value of Q in all three samples and hence, was used for further sorption kinetics studies.

In the kinetic experiments, a so-called pat and weight technique was used for liquid sorption [9]. Samples, after taking the dry weight, were placed in acetone in a standard joint test tube, which was maintained at a temperature of 30 ± 0.5°C. The specimens were taken out at regular intervals, and solvents adhering to the surface was rubbed off, weighed immediately, and replaced in solvent. This procedure was continued till equilibrium swelling was achieved. This was repeated for three specimens from each network in order to ensure the reproducibility of the values. The time taken for wiping out the solvent from the sample surface was kept to a minimum in order to minimize error due to solvent evaporation.

Mechanical Testing

The tensile strength, percentage elongation, and modulus were determined according to ASTM-D 412. Shore A hardness of all the samples were measured by means of a type A Shore Durometer at room temperature as per ASTM- A 2240.

Thermogravimetry

The thermogravimetric analysis of PUP samples were carried out using Shimadzu TG -30 thermal analyzer at a heating rate of 100°C/min in air.
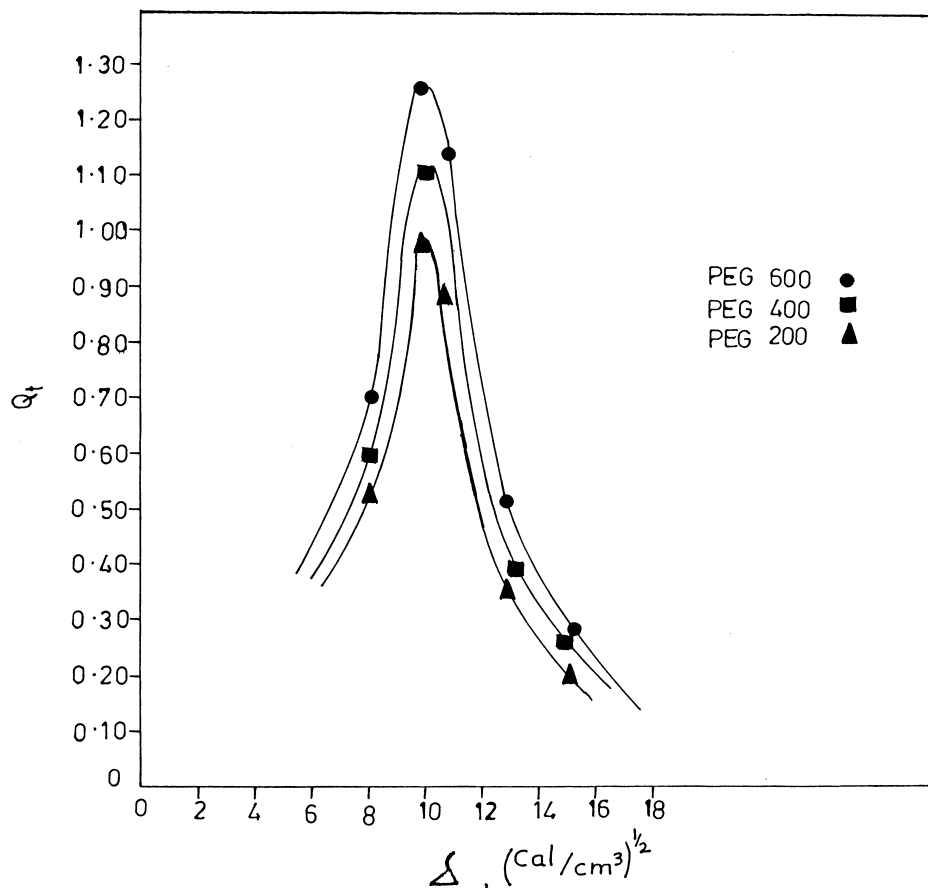
Figure 1. Plot of volume equilibrium of solvents (Q_t) vs. solubility parameter of solvent (δ).

RESULTS AND DISUSSION

Polyurethanes prepared by a transfer molding technique were in the form of yellow transparent films. The densities of polymer films were determined by a floatation method. Results are summarized in Table 1.

Table 1. Physical Parameters of Polyutrethanes

PU	Density g/cm^3	V_p	M_c gm./mole	$N \times 10^3$ mole/cc	$v \times 10^3$ mole/gm.
PUP-200	1.125	0.475	690	1.63	0.73
PUP-400	1.113	0.447	820	1.36	0.61
PUP-400	1.107	0.363	1360	0.81	0.37

The equilibrium degree of swelling (Q), which is the reciprocal of volume fraction of polymer in the swollen state (V_p), was calculated from the swelling data of PUP samples in various solvents using the following relations:

$$Q = 1/V_p$$

$$V_p = \frac{w_p/d_p}{w_p/d_p + w_s/d_s}$$

where,

w_p = dry wt. of polymer
w_s = wt. of solvent taken up at equilibrium
d_p = density of polymer
d_s = density of solvent

In order to determine the solubility parameter of PUP samples, Q was plotted against δ of solvents studied. From the plot (Fig. 1) it was found that acetone = $(9.9 \text{ cal/cm}^3)^{1/2}$ gave a maximum value of Q for all samples studied and hence, was used for further sorption studies. The average molecular weight between two crosslinks (M_c), which is a direct measure of crosslink density, was measured from the well-known Flory-Rehner equation shown below:

$$M_c = \frac{d\,V_1\,(V_p)^{1/3}}{\ln(1-V_p) + V_p + \chi_{12}\,V_p^2}$$

where,

V_1 = molar vol. of solvent
d = density of network
χ_{12} = polymer-solvent interaction parameter which was calculated using the Equation [11]:

$$\chi_{12} = B + \frac{V_1\,(\delta_p - \delta_s)^2}{RT}$$

where,

δ_p = solubility parameter of polymer
δ_s = solubility parameter of solvent
R = gas constant
T = absolute temperature
B = Lattice constant which is generally taken as 0.34 for good solvent.

The degree of crosslinking (v) and number of chains per unit volume (N) were also calculated using the following relations [12, 13]:

$$v = \frac{1}{2M_c} \quad N = \frac{d}{M_c}$$

The values of V_p, M_c and for all samples studied in acetone are summarized in Table 1. It can be seen from the Table that V_p decreases with an increase in chain length of PEG. As the distance between two crosslink points increases with an increase in chain length (for a given NCO/OH ratio) of highly flexible PEG the free volume available also increases and hence, V_p decreases. The increase in chain length increases the distance between two crosslink points resulting in a less dense crosslinked structure and therefore, M_c increases with the increase in molecular weight of PEG incorporated into the network (Table 1).

Kinetics of Swelling

The sorption of penetrating species into polymer matrix is quantified in terms of mole percent uptake. The mole percent uptake (Q_t) at each time interval, from the results of swelling experiments was calculated using the following relation [12]:

$$Q_t = \frac{m_e/m_r}{m_i} \times 100$$

where,

   m_e = mass of solvent taken up at equilibrium
   m_r = relative molar mass of solvent
   m_i = dry mass of sample.

At equilibrium swelling, Q_t was considered to be Q_∞, mole percent uptake at infinite time, the values of which are tabulated in Table 2. The sorption curves of PUP networks which are shown in Fig. 2 were obtained by plotting Q_t vs. $t^{1/2}$. From the curves it is clear that uptake capacity increases

Table 2. Values of Q_∞ and n for PUP

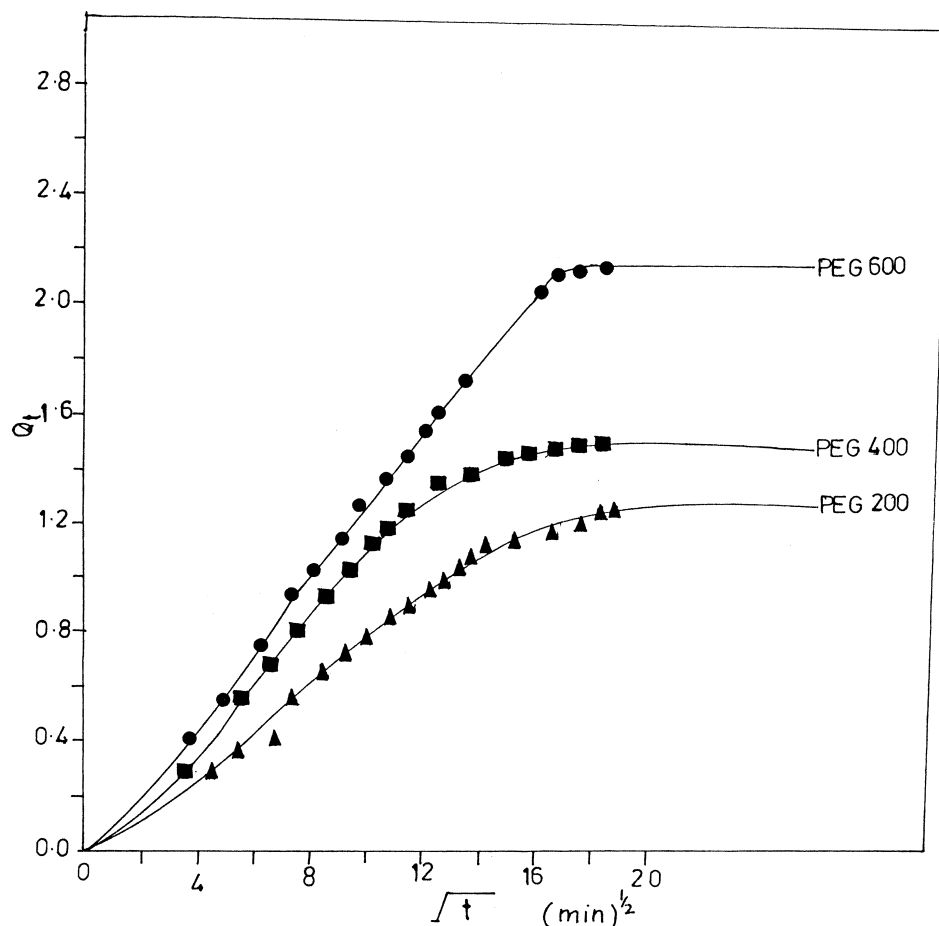| PU	Q^∞	k	n
PUP-200	1.323	0.016	0.58
PUP-400	1.489	0.063	0.54
PUP-600	2.134	0.076	0.45

Figure 2. Sorption curves of PUP samples, (Q_t) vs. $(t)^{1/2}$.

in the order PUP 200 < PUP 400 < PUP 600 at a given time. This shows that the solvent uptake capacity is affected by ethylene oxide chain length. The equilibrium swelling Q_∞ also follows the same trend (Table 2). Incorporation of PEG-600 into R-60 polyol resulted into a PU network of maximum flexibility and thus sorption capacity would be maximum. Decreasing the chain length by introducing PEG-400 and PEG-200, respectively in place of 600, the network structure becomes progressively more rigid and then is less able to accommodate the solvent molecules.

To understand the mechanism of sorption the values of Q_t and $Q\infty$ were substituted into the general expression [14], which describes the transport kinetics.

$$Q_t/Q = kt^n$$

where k is a constant which depends on the structural characteristics of the polymer and its interactions with solvent. The value of n determines the mode of transport. When $n = 1/2$, diffusion obeys Fick's law. Fickian diffusion occurs when segmental mobility of the polymer chain is faster than the rate of diffusion of penetrant molecules. When $n = 1$, the diffusion is said to be non-Fickian, which occurs when diffusion is much faster than polymer chain relaxation processes. In the present system, the values of k and n were obtained from the linear plot of log (Q_t/Q) vs. log t (Correlation coefficient > 0.9) and are presented in Table 2. In all cases, the magnitude of n is nearly 0.5. This suggests that the diffusion process is Fickian in nature.

The transport of penetrant molecules through polymers is also quantified by another term, permeability, P. The permeability of small molecules in polymers usually occurs through the following steps:

(1) sorption of penetrating species into polymer matrix.
(2) diffusion of penetrating species through polymer matrix.
(3) desorption of penetrating species through polymer wall.

The sorption coefficient S which gives an idea about the equilibrium sorption of solvent, was calculated using the Equation [15]:

$$S = \frac{m_\infty}{m_p}$$

where,

m_∞ = mass of solvent taken up at equilibrium.
m_p = initial mass of polymer.

The diffusion coefficient D which is a measure of the penetrant molecules to move among the polymer segment was calculated from the following relation [16]:

$$D = \pi(h\theta/4Q_\infty)^2$$

Table 3. Values of Diffusion Coefficient, Sorption, and Permeability of PUP System

PU	$D \times 10^9$ m^2/sec	S	$P \times 10^9$ m^2/sec
PUP-200	7.4	0.77	5.7
PUP-400	5.2	0.46	2.4
PUP-600	2.4	0.24	0.6

where,

$\theta =$ slope of the linear portion curve (Fig. 2)
h = thickness of sample.

The values of S and D are summarized in Table 3. It can be seen from the results that for the same ratio of NCO/OH, diffusion coefficient, as well as sorption coefficient, increases with an increase in crosslink density and decreases in number of $-CH_2O-$ repeat units. The maximum values of D and S of PUP network having the least number of ethylene oxide units indicate that acetone molecules are absorbed and accommodated mainly by castor oil and isocyanate counterparts, rather than the linear chain molecules of PEG in the network. The permeability coefficient, P which gives the combined effect of both D and S was calculated using the equation:

$$P = D \times S$$

The values of P also follow the similar trend. The values of D, M_c and V_p were used to establish the following relationship proposed for swollen polymer networks [17]:

$$D \sim V_p\beta$$

$$D \sim M_c\gamma$$

where β and γ are empirical constants. Straight lines shown in Fig. 3 represent these power laws.

Mechanical Properties

The tensile properties in terms of tensile strength, modulus and % elongation evaluated from stress-strain curves are tabulated in Table 4. The data show a gradual increase in all mechanical properties studied with a decrease in molecular weight of polyol incorporated with the R-60 polyol. The ratio of NCO/OH, when maintained the same in all PUP samples, the higher molecular weight polyol (PEG 600) which is linear in nature causes formation of a weak polymer network as a result of (1) directly decreases in crosslink density and; (2) indirectly not allowing uniform distribution of load throughout the network due to of its longer chain length. In otherwords, when the load is applied to the network, polyol PEG-600 because of its high flexibility throw away, the load to the rigid part (castor oil and TDI) of the network and creates stress con-
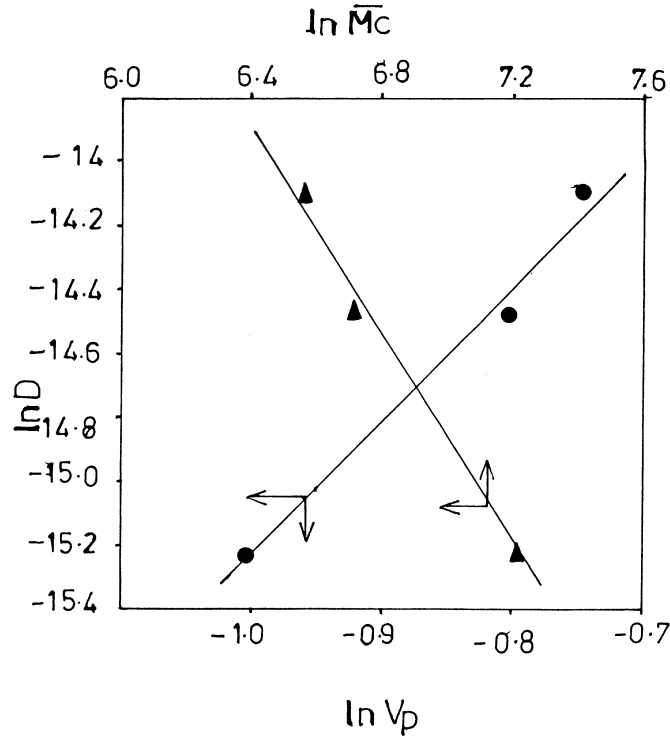
Figure 3. Log-log plot of diffusion coefficient (D) vs. M_c and V_p.

centration at that region. Ultimately, the rupture takes place at low load and elongation values of. Thus, the lack of mutual co-ordination to share the load applied, results in a decrease in tensile strength, elongation, and modulus.

When polyol PEG-200 is used, the shorter length of flexible chain contributes to bare load along with R-60 part coordinately which leads to an increase in tensile properties of the PUP-200 system. Hardness of PUP samples are also shown in Table 4. As can be seen from the Table, hardness

Table 4. Mechanical Properties of PUP System

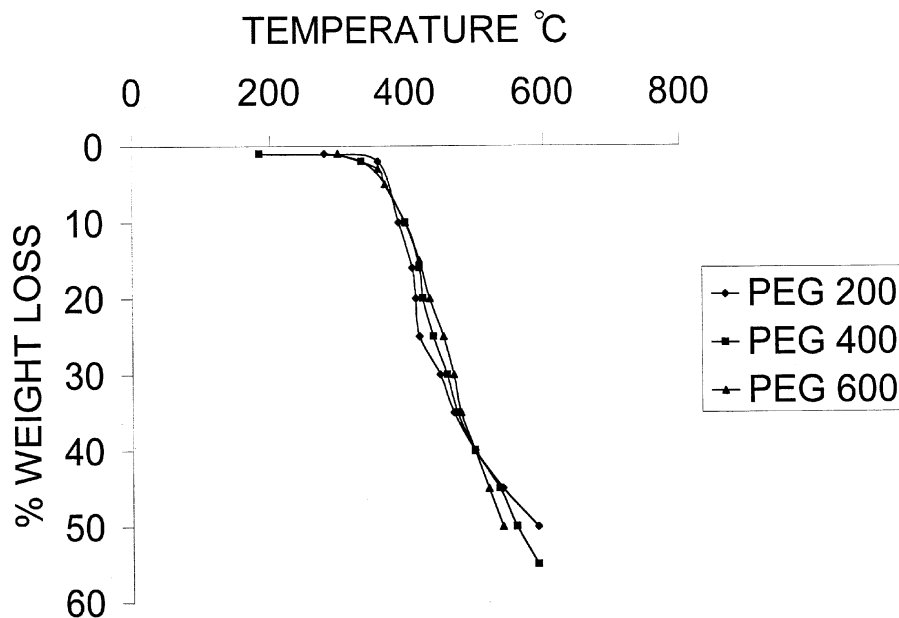|	PUP-200	PUP-400	PUP-600
Tensile strength $\times 10^{-5}(N/m^2)$	133	35	10
% elongation	248	127	48
Modulus $\times 10^{-5}$ (N/m^2)	29.4	24	22
Hardness $\times 10^{-5}$ (N/m^2)	86	64	50

Figure 4. Thermograms of PUP samples.

of PUP increases with a decrease in the chain length of PEG. This is according to expectation. As chain length is decreased, crosslink density increases, which results into more rigid network.

Thermal Analysis

Thermograms of PUP samples are shown in Fig. 4. As can be seen from the thermogram, all the PUP samples, regardless of the chain length of polyol used, undergo spontaneous decomposition at $\sim 270°C$. Once the degradation has started, weight loss is rapid. The initial decomposition may correspond to urethane bond break which starts at $\sim 270°C$ leading to the formation of carbon dioxide, alcohols, amines, carbon monoxide, etc. [18−19]. The decomposition beyond $\sim 350°C$ may be due to polyol. Since one of the polyols used in this study is based on castor-oil, the main chain scission may occur with formation of 10-undecanoic acid and heptanal as evidenced by thermal degradation of ricinoleic acid [20]. Activation energy, which is a quantitative measure of thermal stability, was determined by Broido's method. The values of activation energy lie between 60−72 kJ/mole, indicating reasonably good thermal stability of the polyurethane elastomers.

CONCLUSION

Polyurethane (PU) elastomers synthesized from castor oil based polyol and linear polyethylene glycols(PEGs) were transparent films showing rubbery to tough characteristic behavior depending on the molecular weight of PEG. Diffusion coefficient and sorption coefficient were found to be dependent on the crosslink density and structure of the network. Polyurethane elastomers containing PEG-200 showed the best mechanical properties.

ACKNOWLEDGMENT

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