Ultrasonic Detection of Segmental Relaxations in Thermoplastic Polyurethanes

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Synopsis

The change in attenuation of longitudinal waves has been measured as a function of frequency and temperature for thermoplastic polyurethanes of different hardness covering a range from rubbery hardness to plastic. Analysis of the results show some segmental relaxations and the activation energies were calculated from the ultrasonic measurements. These activation energies were indirectly related to the fatigue failure of the polymer. This failure was expressed as cut growth.

INTRODUCTION

Thermoplastic polyurethanes are block copolymers formed during the reaction between diisocyanate with hydroxyl terminated polyether or polyester polyol and a short low molecular weight glycol chain extender. This short chain provides the strongly hydrogen bonded hard segment of the polymer. The copolymer consists of amorphous soft segments (polyol) linked to hard segment diisocyanate and medium molecular weight blocks of these two segments are joined together by means of chain extender to form a high polymer. The hard segments act as very minute filler particles and produce a polymer that is self reinforcing and physically cross-linked. The degree of cross-linking must not increase more than a certain ratio to maintain the thermoplasticity of the polymer. The properties of the polymer can be varied by controlling the ratio of the hard to the soft segments in the polymer or the ratio of diisocyanate to the total hydroxyl group or the type of polyol (polyether or polyester). However, the higher hard-to-soft-segments ratio, the harder the polymer.

When a polymer is subjected to heat treatment, physical and chemical changes occur in the polymer. The physical changes take place at the Tg (when the rigidity of the polymer changes) crystallization temperature and at the melting point. The chemical changes happen at oxidizing temperatures.

There are many tools (x-ray diffraction[1-3] and DSC or DTA techniques[4,5]) that can be used to detect phase changes. Recently the ultrasonic technique[6,7] was discovered to be an excellent tool to detect the relaxation in the polymer when it is subjected to heat.

In this paper the ultrasonic technique will be used to study the effect of heat on thermoplastic polyurethanes based on different hardness and degree of cross-linking which are considered to be the two factors that may affect the phase change of the polymer during heating.

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EXPERIMENTAL

Materials

The thermoplastic polyurethanes were supplied by Elastogram UK. The batch number, grades and hardness, are shown (Table 1).

The polymers are basically polycaprolactone/diphenyl methane diisocyanate/1,4-butane diol. The grades vary in shore hardness from 85A representing the elastomeric region to 14D plastic region. These hardness values can be expressed as force, g units and the relation was given previously[8].

Processing

The different grades were injection molded at their optimum temperature determined by DSC[9] and are given (Table 1). The injection machine is a reciprocating screw type, Bipel 70/31 injection molder fitted with $2\frac{1}{4}$ oz shot mold. The molding conditions were (i) screw speed 75 r.p.m. (ii) Injection pressure 15,000 psi (iii) Injection speed pressure moderate (iv) Mold temperature 40°C (v) Injection time 13 sec. (vi) Cooling time 20 sec.

Mechanical Properties (Fatigue test)

The cut growth experiment was carried out using strip samples of approximate dimensions 12.5 cm × 1 cm and about 0.3 cm thick. A cut about 0.5 mm long was made at the center edge of the sample perpendicular to its length. The test piece was clamped into position on a repeated flexing De Mattia Machine such that no strain was applied to the sample. During the test the cut length was measured with a magnifying micrometer eye piece and 3 readings were taken at intervals of 1000 cycles.

Ultrasonic Measurements

The ultrasonic absorption through polyurethanes samples was measured using a conventional pulse-echo technique[10]. For ultrasonic measurements, flaw detector USM2 product by Krautkramer was used. The apparatus is capable of producing high frequency pulse in the frequency range 0.5-12 MHz and usually operates with the same transducer as transmitter and receiver at the same time. If l is the height of a particular echo on the

TABLE I
Polyurethanes Used in these Investigations

Code No.	Batch No.	Grade	Hardness	Universal hardness expressed as force,g. (ASTM D 2240)	Injection Temperature °C
$v1$	1079198	CAP 85 AK	85 Shore A	707.1	185
$v2$	1079199	CAP 90 AK	90 Shore A	745.4	189
$v3$	1079200	CAP 95 AK	95 Shore A	783.7	190
$v4$	37758	CAP 63 DKC	63 Shore D	2731.7	205
$v5$	1079201	CAP 74 DK	74 Shore D	3208.6	207

oscilloscope, d is the distance transversed, lo is the height when d=o and α is the ultrasonic attenuation, so, $l = lo\ e^{-xd}$. Usually, in polymers α is very high comparing with that of metals and only one or two echos are observed in the oscilloscope. So, variation of the ultrasonic attenuation with a certain parameter can be evaluated as seen from the above equation by measuring the change in height of the echo since α has the dimensions of reciprocal height[10,11]. The temperature was achieved by electric furnace. Since the probes delivered with the ultrasonic Flaw Detector could not be used above 40°C, measurements were made with x-cut quartz crystals.

Measurements were carried out at frequency ranging from 1 to 5.7 MHz and a temperature range between 25–140°C. The temperature was achieved using an electric furnace.

The samples were in the form of a disc 20 mm diameter and 7 mm width. The echo height l was measured on the face of cathode ray oscilloscope by means of a calibrated scale having sensitivity of ±0.2 mm. According to this scheme, the change of α with temperature is determined with $\pm1.0\%$ precision.

RESULTS AND DISCUSSION

Effect of Heat Variation on the Ultrasonic Attenuation:

Several investigations were made to detect the effect of heat on the ultrasonic attenuation through all samples used in this study involving: (i) the effect of different bonds (caused by the adhesive used between the sample and the X-cut quartz crystal). (ii) the effect of different frequencies. It was found that for certain samples, frequency and different bonds, the attenuation showed consistent values. That means, the heat variation to the thermoplastic polyurethane has no significant effect on the ultrasonic attenuation. These results are in agreement with those obtained for other polymers[6].

To study the effect of frequency on the ultrasonic attenuation, attempts were made to select three frequencies that give reasonable attenuation with a given urethane. For each frequency the change in attenuation of the longitudinal ultrasonic waves was recorded over a temperature range starting from room temperature up to 140°C. Unfortunately, the temperature device that was used in these investigations cannot supply a temperature higher than this range.

The plots of attenuation for the different grades (expressed as l^{-1} measured in cm.) were made against temperature (expressed in K.). These plots are shown in Figs. 1,2,3,4, and 5. In these figures, for each frequency there are three significant attenuation peaks. These peaks can be attributed to the relaxation of the three main segments which form the polymer. The *1st* attenuation change represents the relaxation of the soft chain entanglements (polyol), the second represents the relaxation of the hard segments, and the third represents the relaxation of the most strongly hydrogen bonded chain extender. These three relaxations may be called segmental relaxations. The polymer U5 clearly showed these three relaxations.

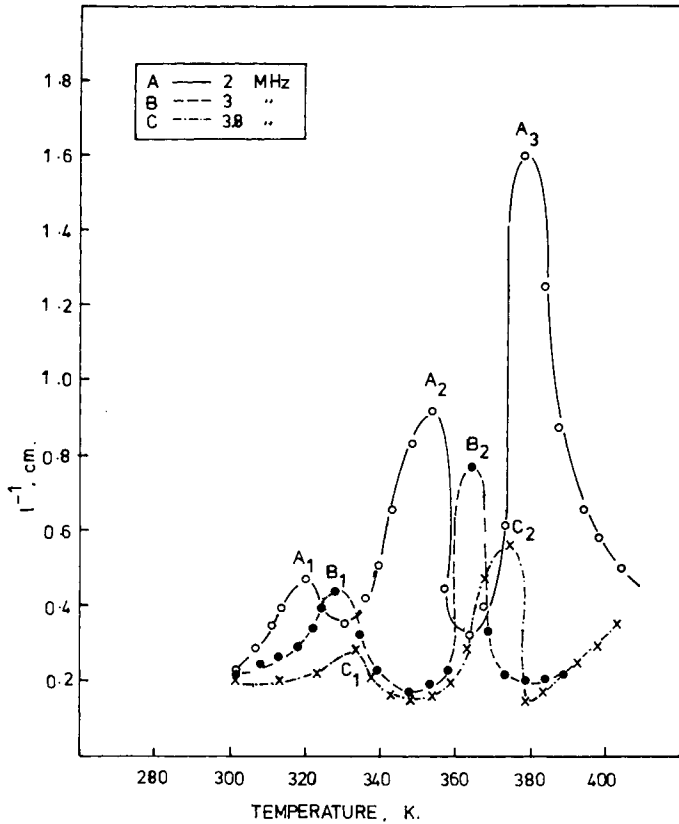By increasing the frequency, there is a shift in the attenuation peaks

Fig. 1. Relation between the attenuation, l^{-1} expressed in cm. vs Temperature given in oK. of polymer U_1.

towards higher temperatures. This may be attributed to the fact that the order of magnitude of molecular motion as affected by temperature is comparable with the ultrasonic wave length used in this experiment. That explains why it was so easy to detect the variation in certain states in a given frequency range and to calculate the activation energy used for such a process. This trend was observed in other polymers[6].

When the logarithm of the operating frequency is plotted vs the reciprocal of absolute temperature ($^{1/T}$Max) a straight line is obtained (Fig. 6). From the slopes of these lines and by using the Arrhenius equation which relates the frequency, f, to the activation energy of the process, W, by the relation $f = f_o e^{-Wkt}$ max, where f_o is the natural frequency of the relaxation process and k is the Boltzmann's constant. The activation energy for the molecules of a segmental relaxation can be calculated. These values were found to be 4.6, 7.6, 12.5, 19.6 and 20k cal/mol. for the grades v_1, v_2, v_3, v_4 and v_5, respectively. These values show an increase with increasing polymer hardness.

By increasing the isocyanate groups in the polymer, the polymer possesses a higher degree of cross- links and hence the mobility of different molecules is very difficult and requires a higher activation energy to cause molecular
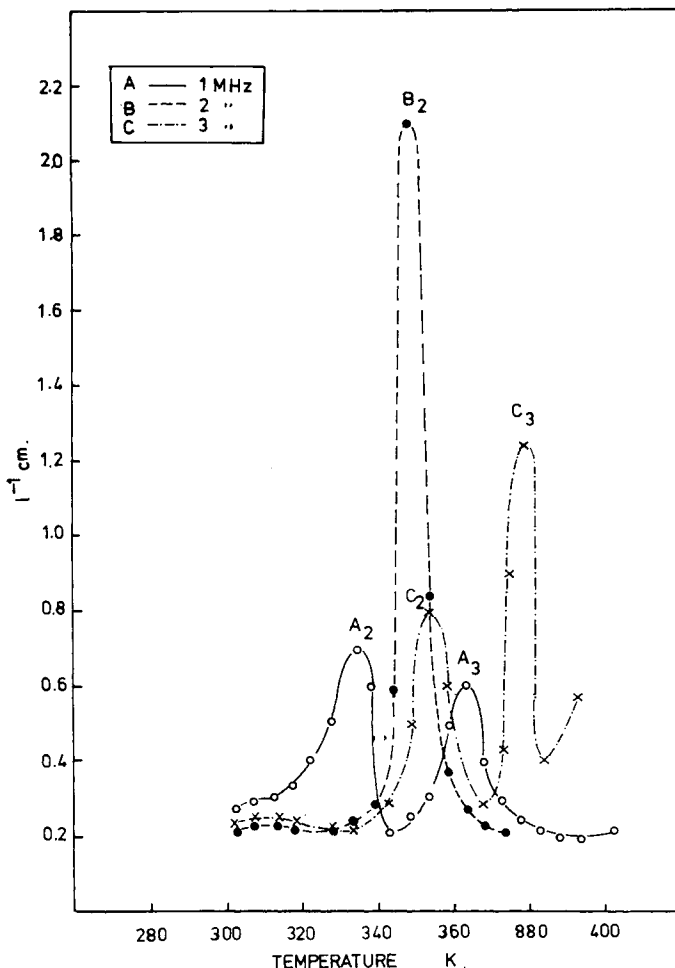
Fig. 2. Relation between the attenuation, l^{-1} expressed in cm. vs Temperature given in oK. of polymer U_2.

motion or molecular disorder. This explain the higher activation energy at higher polymer hardness.

The values of activation energies for segmental relaxation are of the same order of magnitude as the B-relaxation values obtained earlier[12,15]. The polymer showed three relaxations which include B-relaxation or glassy transition relaxations. These are due to the three main groups that form the polymer. These groups are the polcaprolactone, the methyl-disocyanate group and the glycol bonded regions. The latter increases at the expense of the second as the hardness increases. The second relaxation was used to calculate the activation energy. The activation energy is related to the polymer hardness which in turn depends on the diisocyante group in the polymer. The activation energy for most amorphous and crystalline polymers were in the range of 7–26 K. cal/mol.

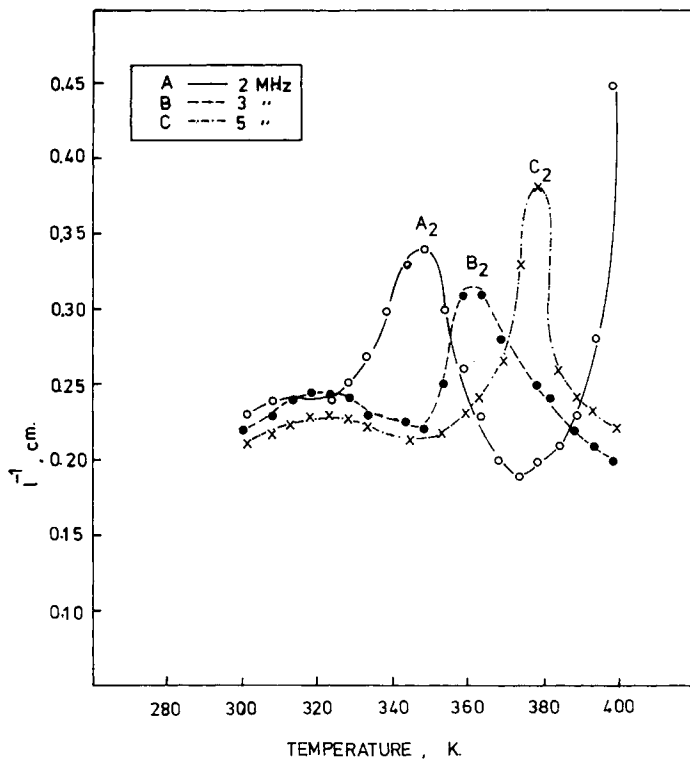When the hardness of thermoplastic polyurethanes was plotted against

Fig. 3.   Relation between the attenuation, l^{-1} expressed in cm. vs Temperature given in oK. of polymer U_3.
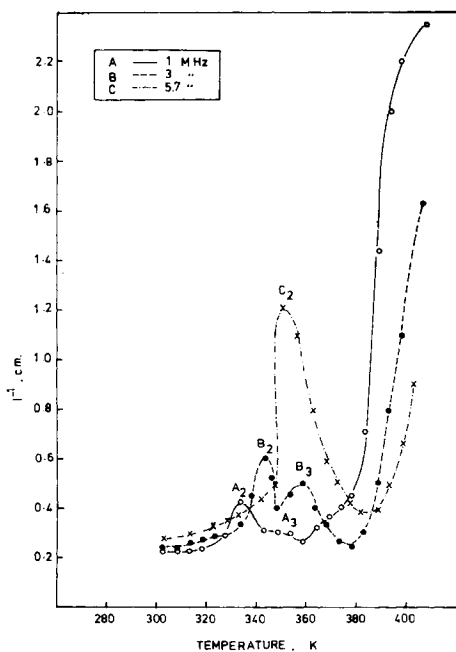

Fig. 4.   Relation between the attenuation, l^{-1} expressed in cm. vs Temperature given in oK. of polymer U_4.
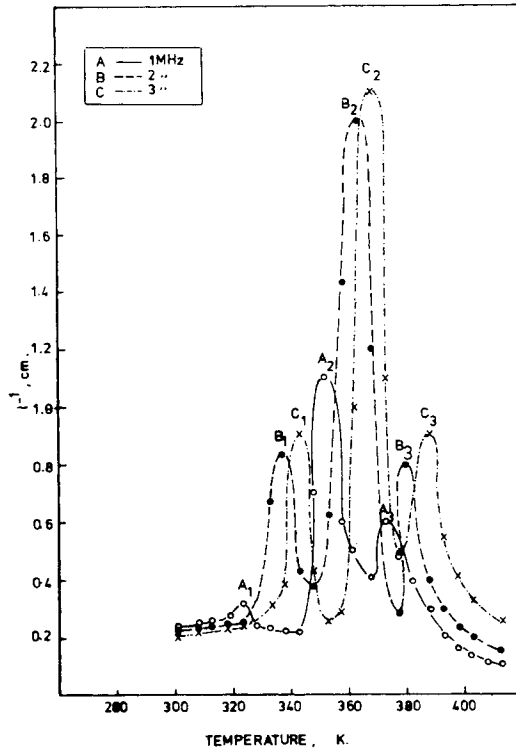
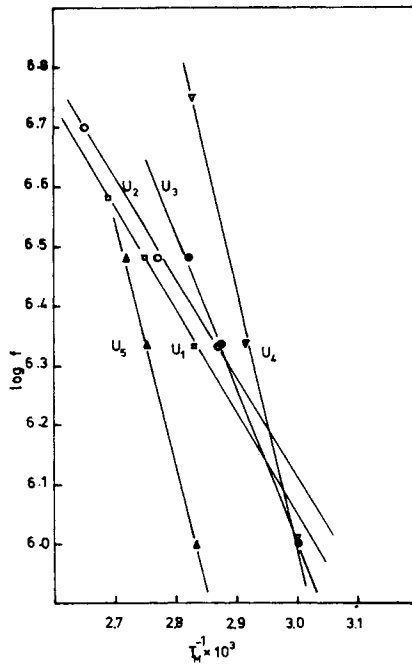Fig. 5. Relation between the attenuation, l^{-1} expressed in cm. vs Temperature given in oK. of polymer U_5.

Fig. 6. Relation between log f expressed in MHZ and $1/T_{max}$, where T is the temperature expressed in K.
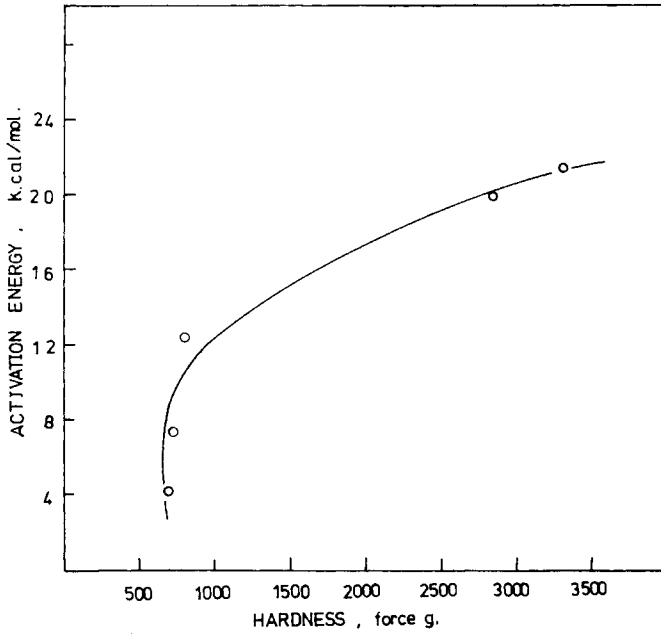
Fig. 7. Relation between the activation energy expressed as K.cal./Mol vs the polymer hardness expressed in force g. units.
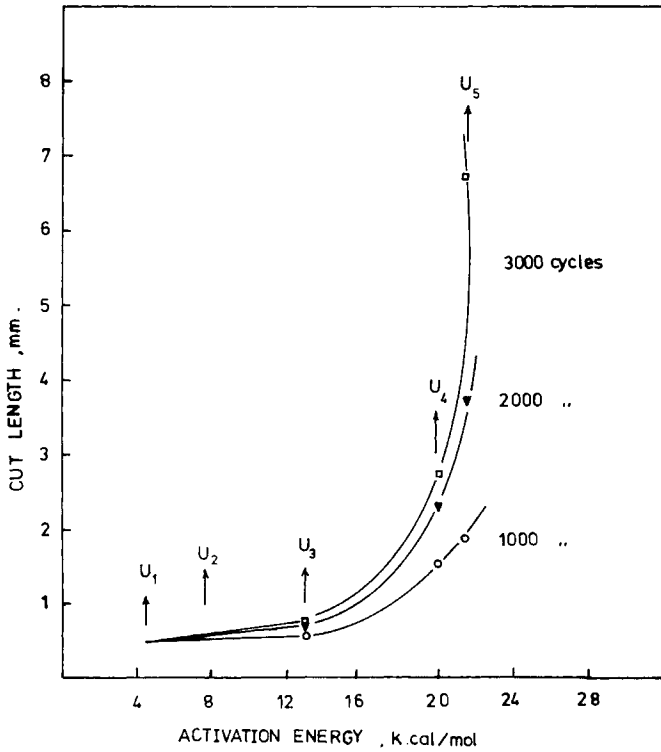

Fig. 8. Relation between the cut length (cut growth due to the fatigue failure) vs. the activation energy of the polymer.

activation energy (Fig. 7), an interesting relation was obtained; The activation energy of the polymer in the elastomeric region varies widely, while at certain hardness (at the plastic region), the activation energy reaches a maximum state. That means there is a point at which the addition of more diisocyanate to the polymer will not be accompanied by an increase in the activation energy. That is why the diisocyanate group must not exceed a certain ratio to maintain the thermoplasticity of the polymer.

The fatigue failure in polymers is one of the most interesting engineering problems in the rubber industry. Many authors related this failure to the mechanical, physical and chemical factors. It may be of interest if this failure can be indirectly related to the activation energy as both are functions of cross linking density of the polymer.

In (Fig. 8) such a relation is shown. In comparing Figs. 7 and 8 one can conclude that higher hardness causes higher activation energy and higher crack growth. This means that polymers of higher activation energy usually possess higher fatigue failure.

CONCLUSION

i. The ultrasonic technique is an excellent non destructive tool to detect the morphology changes in polymers. By this tool one observes the relaxation that happens to the different chemical segments in a certain polymer when this polymer is subjected to heat variation. With other tools such as the thermal analysis and x-ray diffraction techniques, such relaxations can not be easily detected.

ii. By using the ultrasonic technique, it was possible to calculate the activation energy of different thermoplastic polyurethanes. These activation energies increased with increasing polymer hardness.

iii. The fatigue failure of a polymer can be related to the activation energy of a polymer. The lower the activation energy, the better the fatigue resistance.

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