

## Properties of urethane elastomers

### II. Thermally stimulated depolarization currents from unsaturated polyester urethane elastomers based on 4,4'-dibenzyle diisocyanate

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#### Summary

The thermally stimulated depolarization currents (TSDC) from polyurethanes based on 4,4'-dibenzyle diisocyanate (DBDI) and both saturated and unsaturated polyesters were studied over the temperature range 240-410<sup>o</sup>K. Four relaxation peaks were observed. The structure of the TSDC thermograms, location and intensity of the constituent peaks depend both on the urethane content and thermal history of the polymer. The morphological structure of the samples was evidenced using electron microscopy method.

#### Introduction

In the preceding paper of this series (1) the dielectric relaxation properties of the polyurethane elastomers obtained from DBDI and saturated polyester in connection with their microphase structure were studied by means of TSDC and electron microscopy method. The relaxation processes observed were explained in terms of the multiphase structure model; besides the main hard and soft phases, having ordered and respectively amorphous structures, some other more mixed microphases with intermediate structures exist. The structure of each phase is determined by a specific hard segment concentration which varies from the highest value within hard domains to lowest value within amorphous soft phases.

The purpose of the present article is to analyse the TSDC results for a new type of polyurethane based on DBDI and both saturated and unsaturated polyesters in connection with the thermal history, chemical and microphase structures.

#### Experimental

The polyurethanes used in this study were obtained in dimethylphormamide solution using a mixture of poly(ethylene-adipate) and poly(ethylenefumarate) in the mole ratio of 2:1, DBDI and ethylene glycol. Using different DBDI-ethylene glycol ratios, polymers with various urethane content, ranging from 1.26 to 2.36x10<sup>-3</sup> mole/g, were obtained. Three different urethane concentration polymers were investigated in this study. They were designated as PU-SN-1.26, PU-SN-1.88 and PU-SN-2.36, where SN refers to the saturated and unsaturated polyesters and the numerical code to the urethane concentration times 10<sup>-3</sup>. We will briefly call these polyurethanes series

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as unsaturated polyurethanes based on DBDI.

The polyester used had a molecular weight of 2,000. The duration of the reactions was 6h at a temperature of 60°C, resulting polymers with a molecular weight of approximately 25,000. The dry polymer concentration obtained from reactions was 30%.

Polymer films of about 0.02 mm thick were prepared by casting dilute dimethylphormamide-polymer solutions onto a clean glass plate. After removing from the support, the cast films were dried in a vacuum oven for 2h at 60°C. Samples which were thermal treated were kept for 1h in an oven at 100°C.

The TSDC measurements were performed on films provided with vacuum-evaporated silver electrodes of circular form ( $\phi = 13$  mm). Measurements were carried out in dry nitrogen at normal pressure using a device presented elsewhere (2).

The thermal cycles of polarization and depolarization of samples consisted of the following steps: A sample with a polarization field  $E_p = 15$  kV/cm was warmed up to the polarization temperature  $T_p$  (75°C for original samples and 100°C for annealed ones) which was maintained constant for a polarization time  $t_p = 20$  min.; after cooling to 200°K using liquid nitrogen,  $E_p$  was removed and the sample was short-circuited for 10 min. in order to eliminate the rapid depolarization currents; then the depolarization currents were recorded at a heating rate of 3.5°K/min.

Observation of the microdomain structure of the film specimens was made by transmission electron microscopy on ultrathin sections prepared by cryomicrotomy and staining, using osmium tetroxide technique of Kato (3).

### Results and discussion

Figure 1 shows the TSDC thermograms of the polyurethanes at various urethane concentrations. As a general feature, the spectra are complex consisting of three peaks designated as  $\beta$ ,  $\alpha$  and  $\alpha'$ , followed by a coming high temperature  $\delta$  peak observed for the samples with the lowest urethane content. However, the complexity of these relaxation spectra is not unexpected if the complexity of the chemical and physical structures of these polymers is taken into account.

As shown in Fig.1, the urethane concentration does greatly affect the intensity and location of the TSDC peaks. An increase in urethane content decreases the intensity of the  $\beta$  and  $\alpha$  peaks, and shifts  $\alpha$  peak to higher temperatures. The position of the  $\beta$  peak is scarcely affected by changing urethane content. On the other hand, an increase in intensity accompanied by a shift to higher temperature values were observed for  $\alpha'$  peak.

As the increasing part of the  $\delta$  peak is observed only for polyurethanes with lowest urethane content (PU-SN-1.26), it could be assumed that this peak arises at higher temperatures for samples with higher urethane content. This assumption was further confirmed by TSDC thermograms of the annealed samples recorded at extended high temperatures (Figures 2 and 3).

Figures 2 and 3 show the effects of thermal treatment on the TSDC spectra for the samples with extreme urethane con-

tents. With annealing of the samples, the intensity and location of the constituent peaks are differently affected; the  $\beta$  relaxation process is mostly affected, whereas the  $\alpha$  peak is only slightly increased in intensity. The annealing effects also depend on the urethane content, higher for lower urethane content samples. By annealing, the  $\alpha$  and  $\alpha'$  peaks decrease in intensity and shift to lower temperatures.

In the first paper of this series (1) data on the TSDC relaxation processes in polyurethanes based on DBDI and saturated polyester were reported. Two main relaxation peaks were observed; the  $\alpha$  peak at about 300°K and  $\delta$  peak in the temperature range of 367-380°K. The peak temperatures depended on the precipitation temperature of the polymer. The  $\alpha$  and  $\delta$  processes were associated with the molecular motion within the amorphous portions of the soft polyester segments and respectively with motions within the rigid domains. A small additional peak at 325°K was evidenced only for the polyurethanes precipitated at highest temperature (60°C), which was assigned to the motions of the polyester segments within domains with intermediate hard segments concentration, situated between those of soft and hard domains.

The  $\alpha$  and  $\alpha'$  peaks temperatures of the unsaturated polyurethanes series investigated in this paper are with 10-20°K lower than those of the corresponding peaks of the saturated polyurethanes, whereas  $\delta$  peaks arise at higher temperatures. The lower temperatures for the  $\alpha$  peaks are somehow unexpected if only the elasticity of those two polyesters used are comparatively analysed. Probably, the lower elasticity of the unsaturated polyester determines lower hydrogen bond interactions between soft polyester and hard urethane segments, and therefore the  $T_g$  of these amorphous polyester segments decreases. The increase of the chain elasticity by decreasing hydrogen bond interactions seems to be more important than the opposite effect determined by higher rigidity of the unsaturated polyester. These phenomena could also explain why the  $\beta$  peak was not confirmed for saturated polyurethanes (1). Probably, this peak was coupled with the  $\alpha$  peak due to the high hydrogen bond interactions.

The comparative analysis of the  $\alpha$ ,  $\alpha'$  and  $\delta$  peaks temperatures with those of the saturated polyurethanes, the peak activation energy values (Table 1), the urethane concentration dependence and the annealing effects suggest that these peaks could be associated with the thermal transition ( $T_g$ ) of the domains with various hard segments concentrations. The hard segments concentration increases from domains where from  $\alpha$  peak originates to those corresponding to  $\delta$  peaks. The  $\alpha$  and  $\alpha'$  peaks could be assigned to the motions of the soft polyester segments within domains with low and respectively intermediate hard segments contents, and  $\delta$  peak to segmental motions within hard domains.

Increasing urethane content usually develops a better-ordered structure in the hydrogen bonding polyurethanes. It may be inferred that an increasing urethane content results in a greater size of the hard domains and a higher hard segments concentration of the mixed phases where from  $\alpha$  and  $\alpha'$

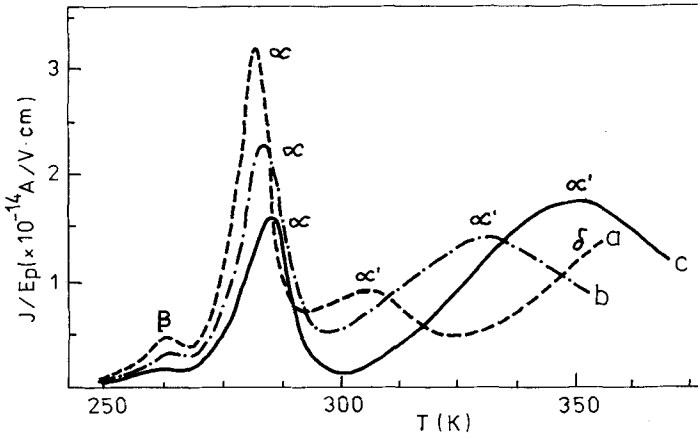


Fig.1. TSDC spectra as a function of urethane content: a-PU-SN-1.26; b-PU-SN-1.88; c-PU-SN-2.36.

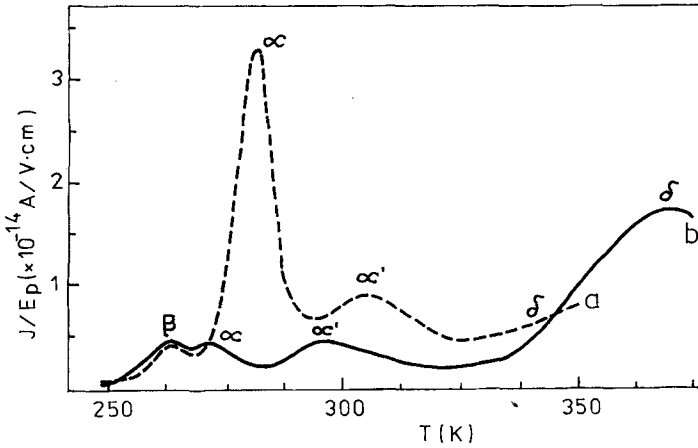


Fig.2. TSDC spectra of PU-SN-1.26: a-original film; b-annealed film.

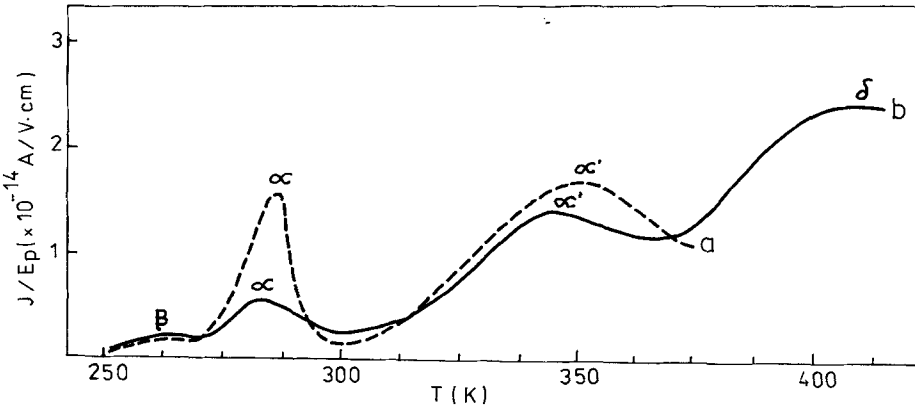


Fig.3. TSDC spectra of PU-SN-2.36: a-original film; b-annealed film

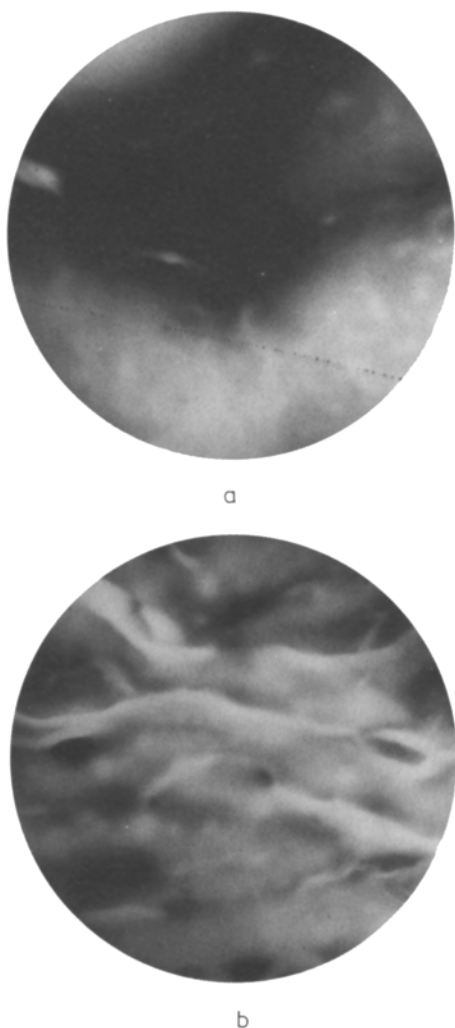


Fig.4. Electron microphotographs of PU-SN-1.26; a-original polymer; b-annealed sample at 100°C for 30 min.

ling the concentration of the hard segments within mixed phases diminishes due to their segregation, and consequently the polyester segment motions became less hindered, moving  $\alpha$  and  $\alpha'$  peaks to lower temperatures. At the same time, the extension of the mixed phases decreases resulting in a corresponding decrease of the  $\alpha$  and  $\alpha'$  peaks intensities.

As shown in Fig.1, the  $\beta$  peak intensity decreased with

originate. This fact favors a greater interaction between the urethane hydrogen and polyester proton acceptor group shifting the  $\alpha$  and  $\alpha'$  peaks to higher temperatures. On the other hand, an explanation of the opposite variation of the  $\alpha$  peak intensity compared to that of the  $\alpha'$  peak as a function of the urethane content (Fig.1) is that with increasing urethane content an extension of the phase with intermediate hard segments content and a diminution of those with lowest hard segments content are developed. The  $\delta$  peak temperature increases with urethane content showing that by annealing a more ordered structure of the hard domains is developed.

The crystallization of the polyurethane elastomers is enhanced by annealing resulting in a smaller size of the soft domains and a corresponding increase of the hard domains (1,4). However, the electron microphotographs taken on the investigated samples proved that by annealing a more ordered structure was developed. An representative example is shown in Fig.4. It may be inferred that by annealing

Table 1. The relaxation characteristics of polyurethanes

Polymer	Peak temperature(K)				Activation energy(eV)			
	$\beta$	$\infty$	$\infty'$	$\delta^*$	$\beta$	$\infty$	$\infty'$	$\delta^*$
PU-SN-1.26	261	274	304	365	0.71-1.52	1.95	2.50	2.92
PU-SN-1.88	261	276	323	382	0.70-1.20	2.05	2.61	2.95
PU-SN-2.36	261	278	350	406	0.66-1.35	2.23	2.70	2.94

\* - From TSDC thermograms of the annealed samples

increasing urethane content. The TSDC thermograms recorded on dry and soaked in water samples, polarized at room temperature, showed no significant change of the  $\beta$  peak intensity. These observations suggest that the  $\beta$  peak may be assigned to the motion of the polyester carbonyl groups. Using dynamic mechanical relaxation method, Jacobs and Jenckel (5) and Huh and Cooper (4) observed a similar secondary peak in polyurethane systems and ascribed it to the motion of water molecules and respectively to the NH or C=O groups to which water molecules were attached by hydrogen bonding.

The relaxation characteristics of the samples derived from TSDC thermograms are presented in Tab.1. The activation energies were determined using the initial current rise method applied to the TSDC spectra obtained by partial heating of the polarized samples. By partial depolarization of the samples, a single value of the activation energy was found for  $\infty$ ,  $\infty'$  and  $\delta$  peaks and a distributed one for  $\beta$  peak. These findings suggest that  $\beta$  process arises from a dielectric relaxation distributed in activation energy, whereas  $\infty$ ,  $\infty'$  and  $\delta$  processes originate presumably from a distribution of the relaxation processes in natural frequency.

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