Properties of urethane elastomers

I. Dielectric relaxation in saturated polyester urethane elastomers determined by thermally stimulated depolarization currents

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Summary
        The dielectric relaxation processes in polyurethanes based on
4,4'-dibenzyle diisocyanate and saturated polyester in the temperature
range of 250–400°K using thermally stimulated depolarization currents
method have been investigated. The structure of the relaxation thermo-
grams, location and intensity of the constituent peaks depend both on the
precipitation temperature and thermal history of the polymer. The rela-
xation processes have been associated with the molecular motions within
domains with distinct morphological structures. The morphological struc-
ture of the samples was evidenced using electron microscopy method.

Introduction
        The polyurethane elastomers are molecular systems with a block
structure composed of rigid and soft segments. Owing to the relative
thermodynamic incompatibility of the hard and soft segments, a demixing
process occurs during polymerization reaction and postannealing of the
polymer, which leads to at least two main phases: ordered domains formed
by clustering the hard segments and amorphous domains mainly composed of
soft segments. The heterogeneous supramolecular structure explains many
of the particular properties of the elastomeric polyurethanes.
        Recent works (1,2) explained the thermal transitions in polyure-
thanes in terms of the multi-phase model; besides the main hard and soft
phases some other microphases with intermediate structures exist.
        The purpose of this paper is to investigate the molecular relaxa-
tion mechanisms and microphase structure of the elastomeric polyurethanes
obtained from 4,4'-dibenzyle diisocyanate(DBDI) and saturated polyester,
using thermally stimulated depolarization currents (TSDC) and electron
microscopy methods.

Experimental
        The investigated polyurethanes have been obtained in dimethyl-
phormamide solution using poly(ethyleneadipate) with OH end groups having
a molecular weight of 2,000, DBDI and ethylene glycol in a such ratio
that the urethane concentration was 2.45×10^{-3} urethane mole/g. The con-
centration of the obtained dry polymer was 30%. The working temperature
was 60°C for a reaction time of about five hours, during that the vis-
cosity of the polymer solution reached a value of 30.000 cP at 20°C.
This value corresponds to a molecular weight of aproximatively 25.000.
        The polymer were precipitated in water as follows: Onto a clean
glass plate, a polymer solution was cast. Before casting, the air from
polymer solution was removed at a pressure of 70–90 torr. Then, the po-

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lymer solution films were kept in water at 35°C and 50°C respectively
for 25 min. After that, the films were removed from the support, washed
with water and dried in a vacuum desicator at a pressure of 3-4 torr at
room temperature until use. The polyurethanes precipitated at 35°C and
50°C are designated as PU-35 and PU-50 respectively.

The TSDC measurements were performed on films provided with
vacuum-evaporated silver electrodes of circular form ($\phi = 13$ mm). Mea-
surements were carried out in dry nitrogen at normal pressure using a
device presented elsewere (3).

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 thermal treated ones), which was main-
tained constant for a polarization time $t_p = 30$ min; after cooling to
250°E 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 pre-
pared by cryomicrotomy and staining, using osmium tetroxide technique(4).

Results and discussion

In Fig.1 and 2, TSDC thermograms of the saturated polyurethanes
(original and thermal treated samples) precipitated at 35°C and 50°C
respectively are presented. The structure of the thermograms depends both
on the precipitation temperature and thermal history of the sample. The
TSDC spectra of the polyurethane precipitated at 35°C consist of two
peaks designated as α and δ whereas, the polyurethane precipitated at
50°C contains one additional peak α', located between the main peaks α
and δ . By annealing at 100°C for 30 min., the intensity and location
of the constituent peaks of the TSDC spectra are affected, mostly for α
peak; the α and α' peaks decrease in intensity and shift to lower tem-
peratures,and δ peak increases and shift to higher temperatures.

Many papers in the literature are dealing with the thermomechani-
cal, dynamic mechanical, DSC, NMR and dielectric relaxation analysis on
polyurethanes, but few workers used TSDC method (5,6). The majority of
these papers mention the presence of certain phenomena associated with
the thermal transitions (T_g) of the amorphous and rigid phases.

The temperatures found for α and δ relaxation processes
(Fig.1 and 2) are close to those glass-transition temperatures of the
soft and rigid domains respectively reported in the literature on simi-
lar polyurethane elastomers (7-10).

On the other hand, the crystallization of the polyurethane elas-
tomers is enhanced by annealing, resulting in a smaller size of the soft
domains and a corresponding increase of the hard domains. However, the
electron microphotografs taken on the investigated samples showed that
by annealing a better ordered structure was developed. An representative
example is presented in Fig.3.

The temperature values of the α and δ peaks, the decrease of
the α peak intensity and the increase of the δ peak with annealing,
may suggest that these peaks originate from the soft and hard domains; α
process involves motions within the amorphous portions of the flexible
polyester segments and δ process involves motions within the rigid do-
mains. Probably, the higher temperature shift of the δ peak by annea-
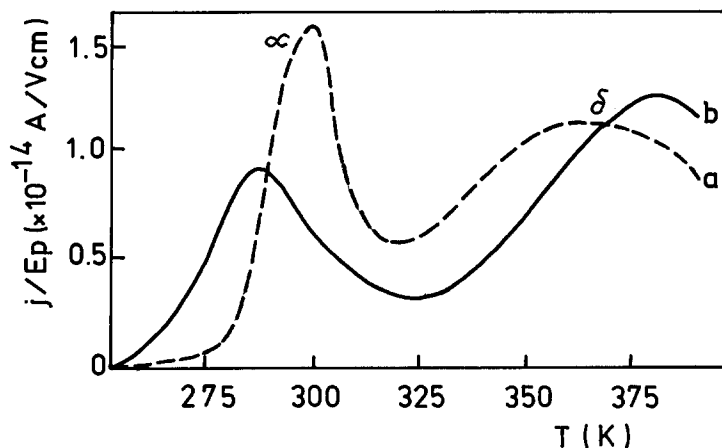ling is due to a dependence of the T_g on phase size, or/and to

Fig.1.
TSDC spectra
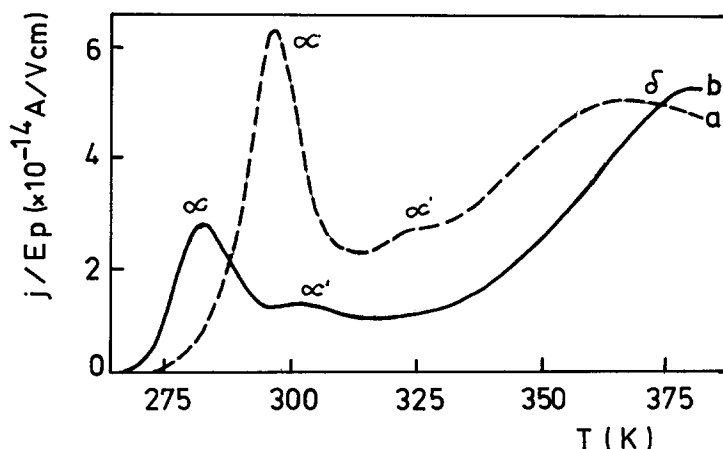of PU-35:
a-original
film; b-ther-
mal treated
film.

Fig.2.
TSDC spectra
of PU-50:
a-original
film; b-
thermal
treated film

a better-order of the hard domains.

It may be expected that the annealing restricts the molecular
motions of the polyester regments due to the increase of the crystalli-
nity. This phenomenon was observed in semicrystalline homopolymers
(11,12), where increasing the crystalline fraction usually decreases
and shifts the main relaxation processes to slightly higher temperature.
The lowered temperatures of the $\propto$ and $\propto'$ peaks (Fig.1 and 2) seems
to be contradictory to previous finding.

More recent investigations (1,2) suggested that thermal transi-
tions in polyurethane elastomers could be explained in terms of the
multiphase structure model. According to this approch, the lowered tem-
perature of the $\propto$ peaks (Fig.1 and 2) is due to that by annealing the
concentration of hard segments within soft domains diminishes and con-
sequently the polyester segment motions became less hindered. The simi-
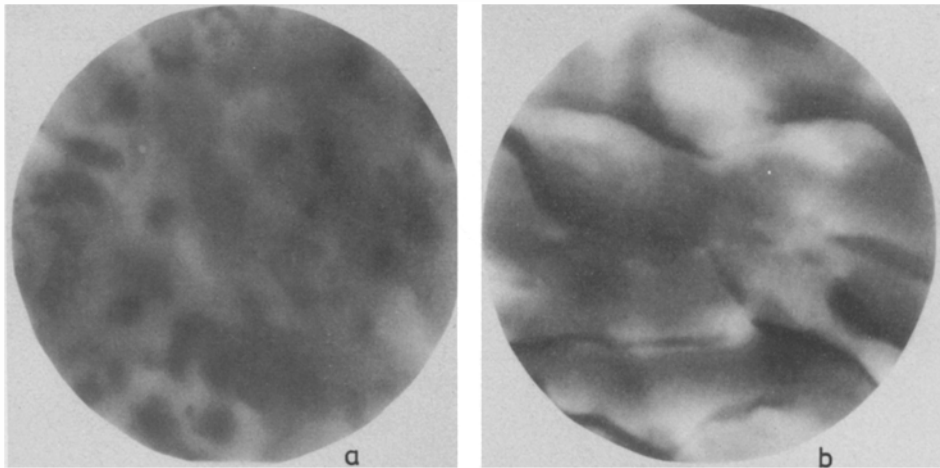lar behaviour of the $\propto'$ peak and its higher temperature comparatively

Fig.3. Electron microphotografs of PU-50:
a-original polymer; b-thermal treated polymer at 100°C for 30 min.

Table 1. The relaxation characteristics of polyurethanes

Polymer	Peak temperature (K)			Activation energy (eV)		
	α	α'	δ	α	α'	δ
PU-35	301	—	367	1.0-1.3	—	2.5
PU-35^x	288	—	372	—	—	—
PU-50	296	324.5	369	0.9-1.36	1.5	2.6
PU-50^x	282	299.5	380	—	—	—

x - thermal treated samples.

with α peak suggests that this relaxation process could be assigned to the motion of the polyester segments within domains with intermediate hard segments concentration, situated between those of soft and hard domains.

The relaxation characteristics of the polyurethanes derived from TSDC spectra are presented in Tab.1. The activation energies were determined using the initial current rise method applied to the thermograms obtained by partial heating of the polarized samples. By partial depolarization of the samples, a single value of the activation energy was obtained for α' and δ peaks and a distributed one for α peak. This finding suggests that α process arises from a dielectric relaxation distributed in activation energy, whereas α' and δ processes originate presumably from a distribution of the relaxation processes in natural frequency.

The calculated activation energies of the α and α' relaxation processes are smaller than the tipical values found for major glass transition phenomena (2.0 eV). This diminutions are due to the electrical conductivity, which in polyurethanes is usually quite high owing to proton transfer along hydrogen bond chains.

In conclusion, the existence and the origin of the α , α' and δ relaxation processes can be easily understood if a multi-phase structure differentiated by various hard segment concentration is admited.

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