

# Mechanical, Thermal, and Electric Properties of Polyurethaneimide Elastomers

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## Synopsis

Linear polyurethaneimide elastomers (PUI) were obtained from polyether- or polyester-diols, diphenylmethane diisocyanate or bitolyene diisocyanate and pyromellitic acid dianhydride. It was found that these polymers have considerably better mechanical properties than typical linear polyurethanes (PU). The elastic modulus and stress at break increase with contents of the hard polyimide segments. The softening temperatures and thermal stability of the PUI at 500°C were higher than the ones of PU with similar hard segment contents. Electric properties of PUI were close to the ones of conventional PU. It was shown that cellular PUI had considerably lower dielectric constant.  $T_g$ 's of the soft segments PUI were less than  $T_g$ 's corresponding to PU. It is connected with greater phase separation of the hard imide segments from the soft polyether- or polyester-urethane matrix.

## INTRODUCTION

The conventional urethane elastomers (PU) are known to exhibit small resistance to heat, e.g., the acceptable mechanical properties (strength, moduli, etc.) disappear from about 80–90°C and thermal degradation takes place at processing temperatures above 200°C.<sup>1,2</sup> This low heat resistance is the main reason of relatively limited technical applicability of this class of polymers. One of the reported methods to improve the thermal stability of PUs is a chemical modification of their structure by heterocyclic groups, e.g., ring imide groups obtained from isocyanates.<sup>3</sup> The imide rings conjugated with the aromatic benzene rings form coplanar, rigid structures so that the rotation of the imide groups with respect to the benzene rings is greatly hindered. The segments of the aromatic polyimides (PI) tend to aggregate into domains, which results in valuable mechanical properties and high thermal stability reaching as high temperatures as 500–550°C.<sup>4-6</sup>

One- and two-step methods of preparation of polyurethane-imides (PUI) have been already claimed by several patents.<sup>7,8</sup> The one-step method consists in the reaction of a polyisocyanate with a polycarboxylic acid or diaryl sulphone polycarboxylic acid in the presence of polyether- or polyester-diols. The two-step procedure involves the reaction of a PI prepolymer obtained from the polycarboxylic acid and polyisocyanate with a diol. No exact temperature details concerning the synthesis and properties of the obtained products are given in the patent descriptions. However, the suggested temperature of at least 100°C for PI synthesis may result—as was found in this laboratory—in an insoluble precipitate giving rise to inferior properties of the films, obtained after evaporation of the solvents.

In our previous work<sup>9</sup> the synthesis and some thermal properties of the polymers obtained from the reaction of a hydroxyl-terminated PU prepolymer with a NCO-terminated PI prepolymer and from the reaction of the pyromellitic dianhydride PMDA with an NCO-terminated PU prepolymer—both in bulk and in solution—were presented. In this work more data on the properties of solution synthesized PUIs from NCO-terminated PU prepolymers and PMDA are given. Also, for a selected composition, PUI was obtained by the two-step method from the reaction of a NCO-terminated PI prepolymer with a polyesterdiol and by the one-step method in the reaction of a tetracarboxylic acid, polyesterdiol, and diisocyanate. The properties of the obtained PUIs are compared with the properties of soluble, linear PUs that were described earlier.<sup>10</sup> In addition, the behavior of a cellular PUI blown by carbon dioxide evolving during the reaction and stabilized with silicone oil is presented.

## EXPERIMENTAL

### Materials

The following substrates were used in the synthesis:

(a) poly(ethyleneadipate)glycol (PEA) of MW 2000 and the hydroxyl number 56, delivered by Organika-Zachem, Poland;

(b) poly(oxytetramethylene)glycol (PTMG) of MW 930 and the hydroxyl number of 120, produced by DuPont, USA;

(c) 4,4'-diphenylmethane diisocyanate (MDI) distributed by Bayer A.G. as Desmodur 44 MS;

(d) bitolylene diisocyanate (TODI) distributed by Rahn Co. as Isonate 136 T;

(e) pyromellitic dianhydride (PMDA) distributed by Fluka A.G.

Dimethylformamide (DMF) was used as the solvent; prior to synthesis it was purified by distillation. L-546 silicone oil produced by Union Carbide was used as a pore stabilizer.

The purification of the reagents and the details of the two-step synthesis from NCO-terminated PU prepolymers and PMDA (in 60–70% solution) were described in our previous work.<sup>9</sup> In this way the polymers PUI-1 ÷ PUI-7 and PUI-10 ÷ PUI-11 were obtained. The polymer PUI-8 was synthesized by the two-step procedure that differed from the one given above mainly in the nature of the reagents: the PI prepolymer was obtained from the reaction of 10.7 g (0.049 mol) of PMDA (in 50 cm<sup>3</sup> DMF) with 19.4 g (0.077 mol) of MDI at 25–35°C for 3 h. Subsequently, this prepolymer was reacted with 50 g PEA at 45–65°C for 1.5 h and poured onto a plate to obtain 0.3 mm thick layer. The film was annealed for 12 h at 60°C under vacuum of 40 mm Hg, then heated up to 170°C, and kept in this temperature for 2 h. The one-step synthesis was carried out in the following way: To a solution of 10.7 g (0.049 mol) of PMDA in 50 cm<sup>3</sup> of DMF, 1.7 g (0.094 mol) of H<sub>2</sub>O was added, and subsequently 50 g (0.025 mol) of PEA and 19.4 g (0.0776 mol) of MDI were introduced at 35°C. The temperature of the reaction mixture went up spontaneously to 60°C. (At this temperature the solution gets turbid of PI macromolecules.) Then the mixture was heated

up to 120°C for 1 h and poured onto a plate to obtain a 0.3 mm thick layer. The film was subject to the same heat treatment as in the case of the two-step method employed for PUI synthesis. All such received PUI polymers were insoluble in DMF in spite of their linear structure.<sup>9</sup>

### Experimental Methods

The tensile strength measurements were done on an Instron 1112 tester at a room temperature; the specimens had dimensions of  $50 \times 10 \times 0.07 \div 0.12$  mm and the extension rate was 50mm/min.

Thermogravimetric analysis (TGA) was carried out in air by means of a OD 104-MOM (Hungary) Derivatograph at a heating rate of 6 deg/min and sensitivity of 200.

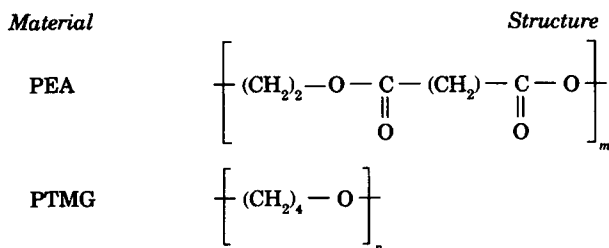
The temperature indices (TI) were determined by graphical extrapolation in the way recommended by ICE standards 216-1, 216-2, 1974 (PN-76/E-04401). The 5% loss of weight was taken as the critical level and the temperatures selected for annealing were: 170, 190, and 210°C.

Thermomechanical analysis (TMA) was carried out in compression by means of a DuPont's analyzer TMA 943 at a heating rate of 5 deg/min and in tension by means of TMA-Politechnika Lodzka analyzer at a heating rate of 2 deg/min.

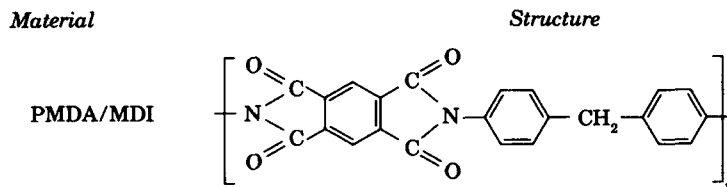
The conductance  $G$  and capacity  $C$  were measured by means of a semi-automatic bridge BM 484, Tesla, at a frequency of 1592 Hz. The real part of the dielectric constant  $\epsilon'$  and the loss factor  $\tan \delta$  were calculated as follows:  $\tan \delta = G/C$  and  $\epsilon' = C/C_0$  with  $C_0 = \epsilon_0 S/d$ , where  $S$  is the surface and  $d$  is the thickness of the investigated sample. The samples were of 20 mm diameter and coated with silver electrodes. The measurements were recorded in the temperature range from  $-40$  to  $+160^\circ\text{C}$  in inert gas (argon).

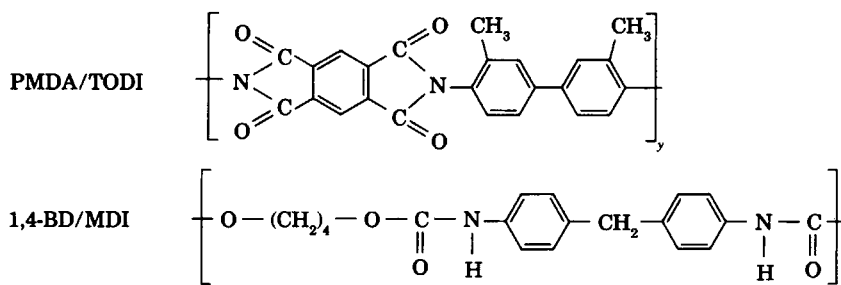
The structure of the flexible and hard segments that constitute the investigated polymers is shown below:

*Flexible segments:*



*Hard segments:*





## RESULTS AND DISCUSSION

In Table I the composition, hard segment content and basic mechanical properties of the investigated polymers are collected. The hard segment content is expressed by weight percent and was calculated as the ratio of PMDA + MDI or BD + MDI to the total weight of the reagents involved in the synthesis. The complete evolution of CO<sub>2</sub> in PUI synthesis was taken into account in these calculations.

From the table and Figure 1 it is clearly seen that PUI are remarkably more rigid than PU of similar hard segment content. Such magnitudes as elastic modulus taken from the stress at 5% elongation, the stress at 100% and 300% elongation and at break are higher for PUI and increase rapidly with increase of PI segment content. It is also seen that the strength of PUI based on PTMG and MDI or TODI is smaller in the case of TODI based polymers, which certainly is due to lower molecular order and weaker molecular interactions within the hard segments, caused by the presence of methyl groups in the structure of this diisocyanate.

TABLE I  
Composition and Mechanical Properties of the Investigated PUI and PU

Polymer symbol	Polymer composition and weight fraction of hard segments	%	Elastic modulus (MPa)	$\sigma_{100\%}$ (MPa)	$\sigma_{300\%}$ (MPa)	$\epsilon_b$ (%)	$\sigma_b$ (MPa)
PU-1	PTMG/MDI/PMDA	31.7	—	13.1	21.5	570	56.4
PUI-2	PTMG/MDI/PMDA	35.2	36	21	39	470	73.1
PUI-3 cell.	PTMG/MDI/PMDA	30.9	—	5.9	7.7	740	17.3
PUI-4	PTMG/TODI/PMDA	32.7	15.1	10	16	590	41.5
PUI-5	PTMG/TODI/PMDA	40.8	50	14.5	24.6	560	70.4
PUI-6	PEA/MDI/PMDA	26.8	—	3.2	6.8	890	40.5
PUI-7	PEA/MDI/PMDA	34.0	53.8	8.5	14.7	820	46.7
PUI-8 <sup>a</sup>	PEA/MDI/PMDA	34.0	23.2	5.5	10.6	715	31.1
PUI-9 <sup>b</sup>	PEA/MDI/PMDA	34.0	29.8	5.6	10.1	710	25
PUI-10	PEA/MDI/PMDA	40.8	174.6	16.4	24.7	720	59.2
PUI-11	PEA/MDI/PMDA	46.7	293	23.7	33.6	430	44.2
PU-A	PTMG/MDI/1,4BD	43.1	12	3.9	6.1	770	27
PU-B	PEA/MDI/1,4BD	48.1	79	10.5	17.5	780	37.5

<sup>a</sup> PUI obtained by two-step method from the PI prepolymer.

<sup>b</sup> PUI obtained by one-step method.

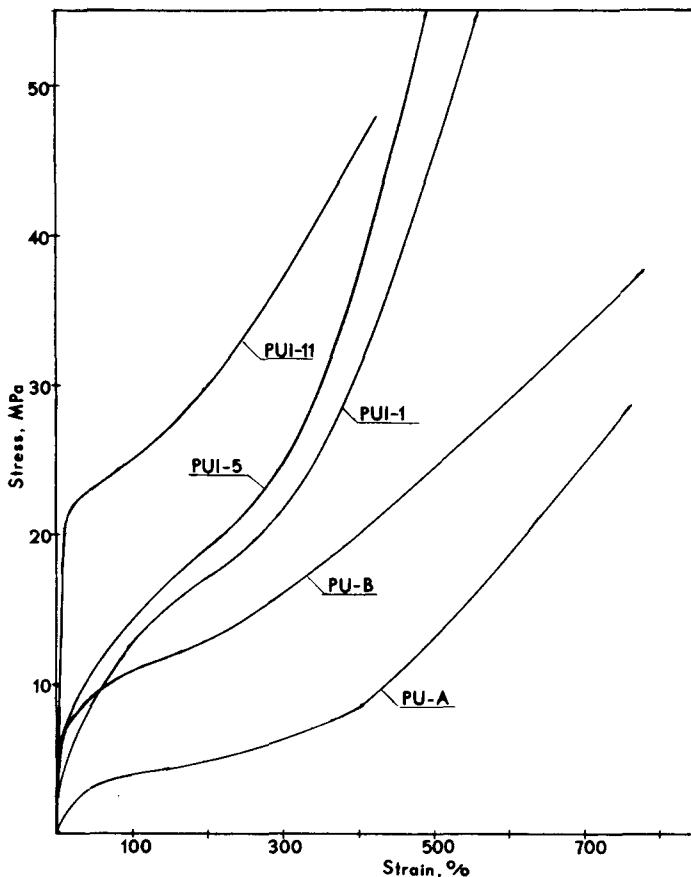


Fig. 1. Stress-strain relations for some investigated PUIs and PUs.

Comparing PUI obtained by different methods (PUI-7,8,9), one finds that higher strength is achieved when the NCO-terminated PU prepolymer is used in the synthesis. This is probably due to its highest molecular weight. On the other hand, in the one-step method (PUI-9) pyromellitic acid is present in the reaction mixture. This may degrade<sup>11</sup> the macromolecules of PUI and lead to lower strength.

It should be noted that the cellular PUI-3 is more rigid at 100% and 300% elongation than the solid PU-A of similar hard segment content.

With increase of PI segment content also the heat distortion temperature (HDT) is increased, as it follows from TMA measurements. In the case of PEA based polymers it is seen that the same flow temperature require much higher hard segment concentration for PU than for PUI (e.g., PU-B and PUI-7, Fig. 2).

Similarly to the strength data, TODI-based PUI exhibit lower HDT values than their MDI analogs (Fig. 3). It should be, however, noted that in the series of PI with diphenyl structure without methyl groups the thermal stability is higher than for polymers containing diphenyl methane structure.<sup>5</sup>

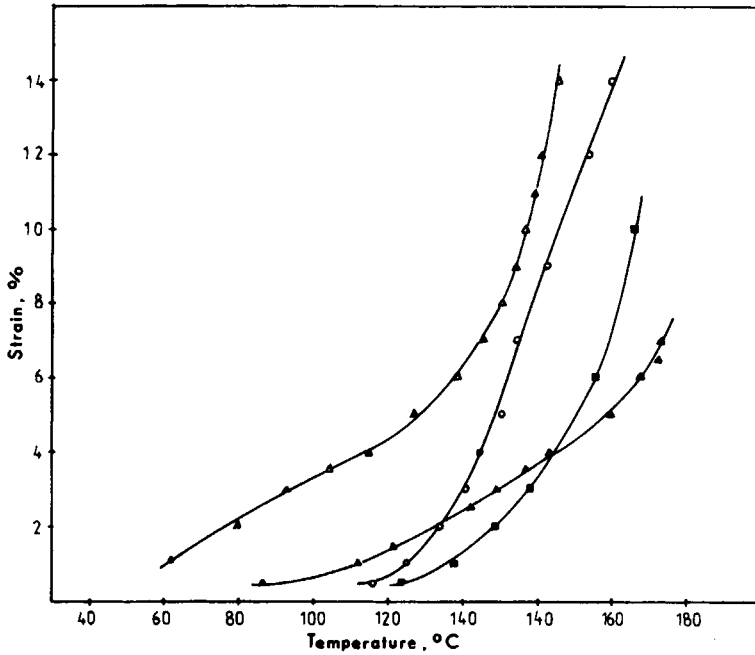


Fig. 2. Thermomechanical curves for PUI from PEA; measurements taken on a TMA-Politechnika Lodzka instrument; scan rate 5 deg/min; load (MPa): ( $\Delta$ ) PU-B, 0.3; ( $\circ$ ) PUI-7, 0.1; ( $\blacktriangle$ ) PUI-10, 1; ( $\blacksquare$ ) PUI-11, 1.5.

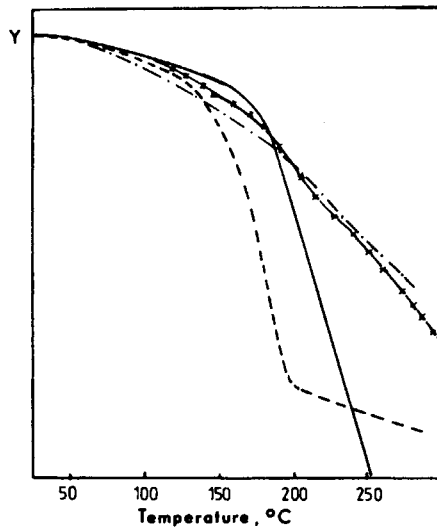


Fig. 3. Thermomechanical curves for PUI from PTMG; measurements taken on TMA-943 DuPont instrument; scan rate 5 deg/min; load 5 g; simple thickness (mm): ( $\cdots$ ) PUI-2, 0.16; ( $\text{---}$ ) PUI-4, 0.12; ( $\text{-- --}$ ) PUI-5, 0.24; ( $\text{---}$ ) PU-A, 0.28; sensitivity for curve showing the probe displacement ( $y$ ), 20 mV/cm.

TGA measurements show that the initial decomposition temperatures of obtained PUI are higher than for PU. Also, the loss of weight at 500°C is much smaller for PUI than for PU. The differences in thermal stability between PUI and PU is specially seen for PUI based on polyester (PEA) segments (Fig. 4), although for PUI with much less thermally stable polyether segments is also noticeable (Fig. 5).

The obtained changes in the loss of weight for samples of PUI-10 annealed for different periods of time at temperatures of 170, 190, and 210°C made possible to determine by extrapolation the temperature indices (TI) corresponding to the stability of 20,000 h and TI 5 kh. As follows from Figure 6, the results are: TI/145 and TI 5 kh/158.

After the isothermal aging at 210°C for 173 h in air, 12% loss of weight for PUI-10 and 29% loss of weight for PU-B was found. After 216 h in this temperature the PUI-10 samples were still red-brown and elastic while the PU-B samples were easy to break and almost black.

As it is shown in Table II the annealing of PUI-10 for about 180 hrs at 170–210°C causes nearly 50% loss of the initial  $\sigma_b$  (Table I). The elongation at break is reduced to 60% of the initial  $\epsilon_b$  after annealing at 170°C and to about 10% of the initial value—at 210°C. These changes in the stress-strain behavior are connected with partial decomposition of the urethane groups in the soft polyesterurethane segments<sup>1</sup> and with final imidization in the hard PI segments<sup>9,12</sup>; moreover, the annealing at 210°C leads to reinforce-

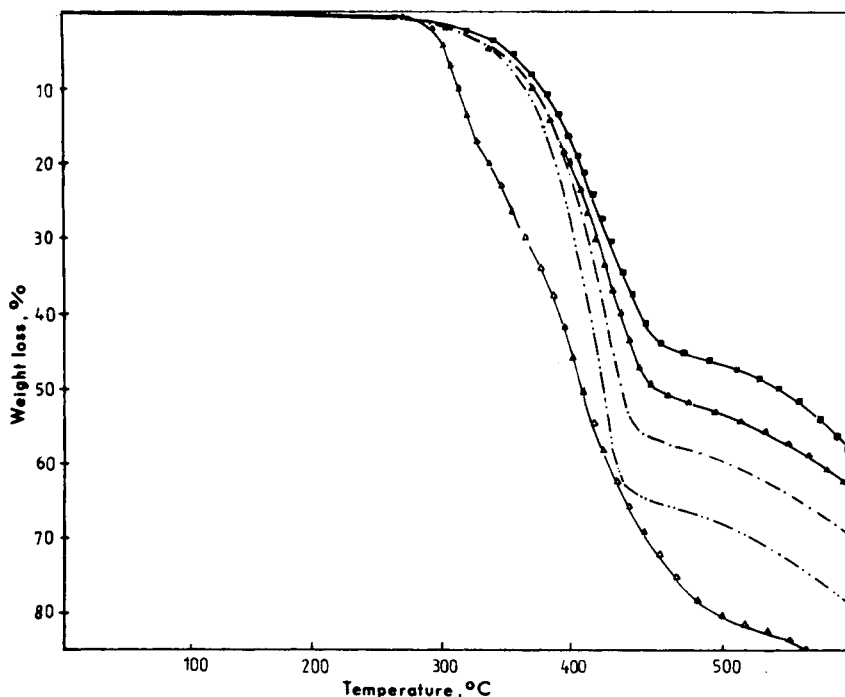


Fig. 4. Thermogravimetric traces for PUI from PEA: (■-■-■) PUI-11; (▲-▲-▲) PUI-10; (.....) PUI-7; (-·-·-·) PUI-6; (-△-△-△-) PU-B.

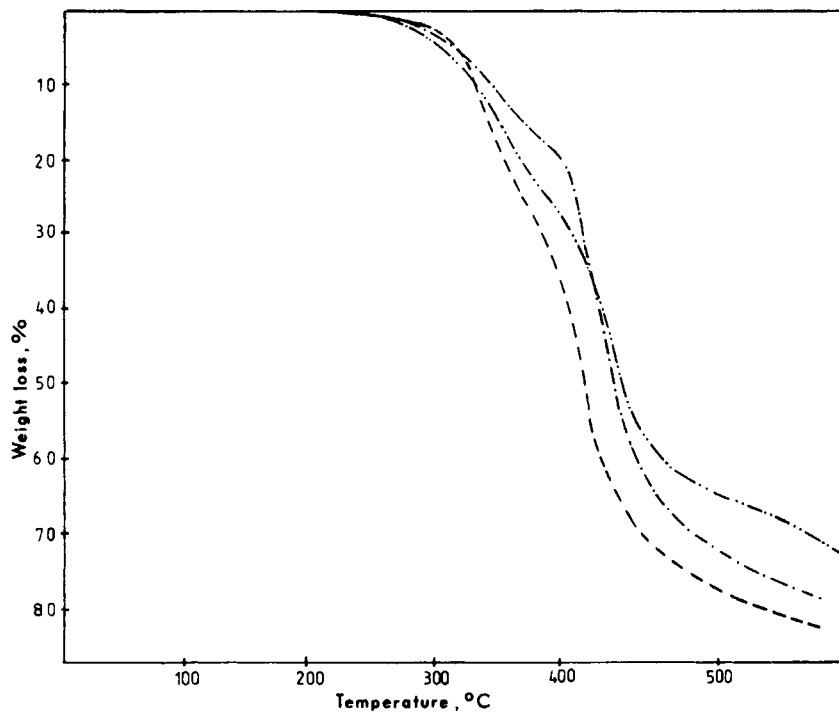


Fig. 5. Thermogravimetric traces for PUI from PTMG: (- · - · - ·) PUI-2; (· · · · ·) PUI-5; (- - -) PU-A.

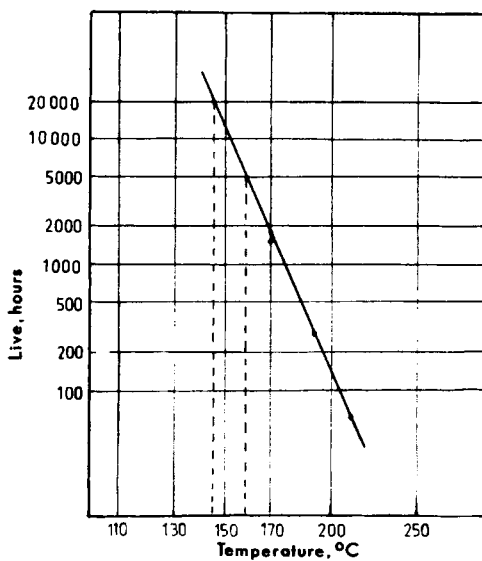


Fig. 6. Temperature index for PUI-10, determined from the loss of weight.



TABLE II  
 Isothermal Aging of the PUI-10 in Air

Temperature (°C)	Time (h)	Elastic modulus (MPa)	Stress at break		Elongation at break	
			MPa	Loss %	%	loss %
170	50	106	49	16	640	11
	140	103	35	41	450	37
	182	115	32	46	430	40
190	25	90	41	31	650	9
	75	121	31	47	424	41
	315	183	23.6	60	137	81
210	77	174	24	59	160	78
	173	311	31	47	87	88
	216	369	31.4	47	44	94

ment of the domain structure which is reflected in the increase of the elastic moduli.

For several investigated PUI and PU the real part of the dielectric constant,  $\epsilon'$ , and the dielectric loss,  $\tan \delta$ , were measured in the temperature range from  $-40$  to  $+160^\circ\text{C}$ . As is seen from Figure 7, there are no essential differences between PUI and PU, if the polymers are derived from the same polydiol and are of similar concentration of the flexible segments. The high and stable value of  $\epsilon'$  for PUI on a broad temperature range qualifies these materials as the proper for use in dielectric capacitors.<sup>13</sup> The real part of the dielectric constant depends strongly on whether the polymer is solid or cellular. This effect is presented in Figure 8, and one finds that the cellular

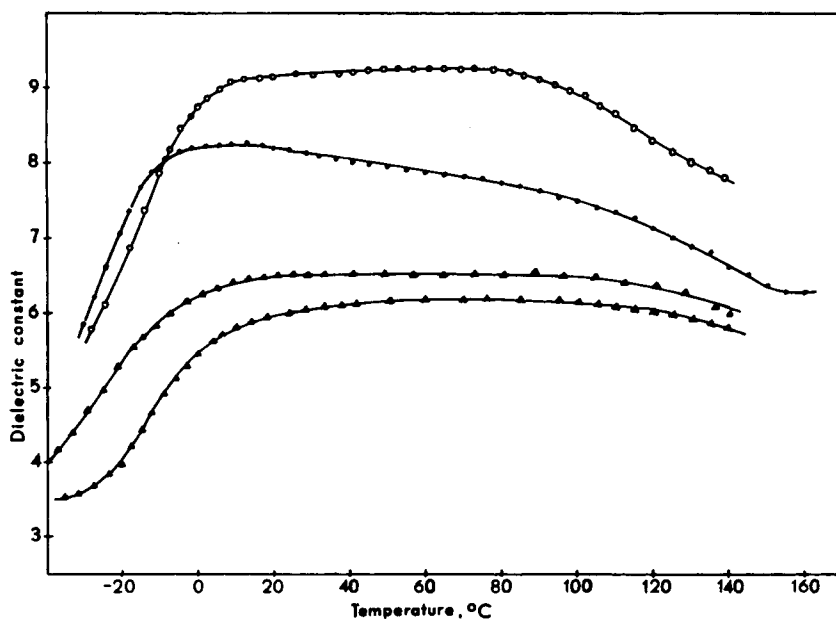


Fig. 7. Temperature dependence of the dielectric constant ( $\epsilon'$ ) for PUI and PU: (○-○-○) PU-A; (●-●-●) PUI-3; (▲-▲-▲) PUI-10; (△-△-△) PU-B.

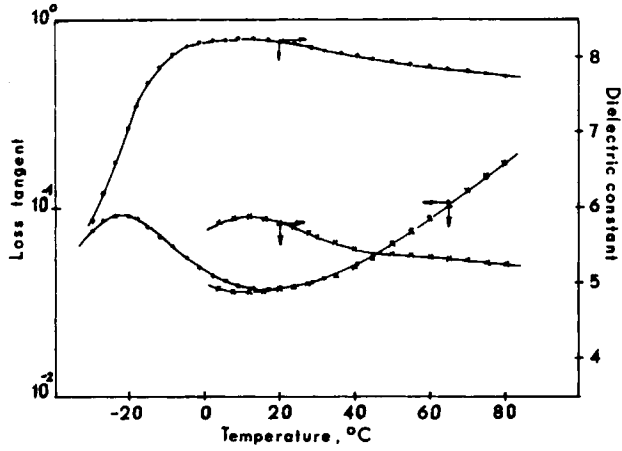


Fig. 8. Temperature dependence of the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) for PUI-3 (film and cellular): (●●●) PUI-3; (×××) PUI-3 cell.

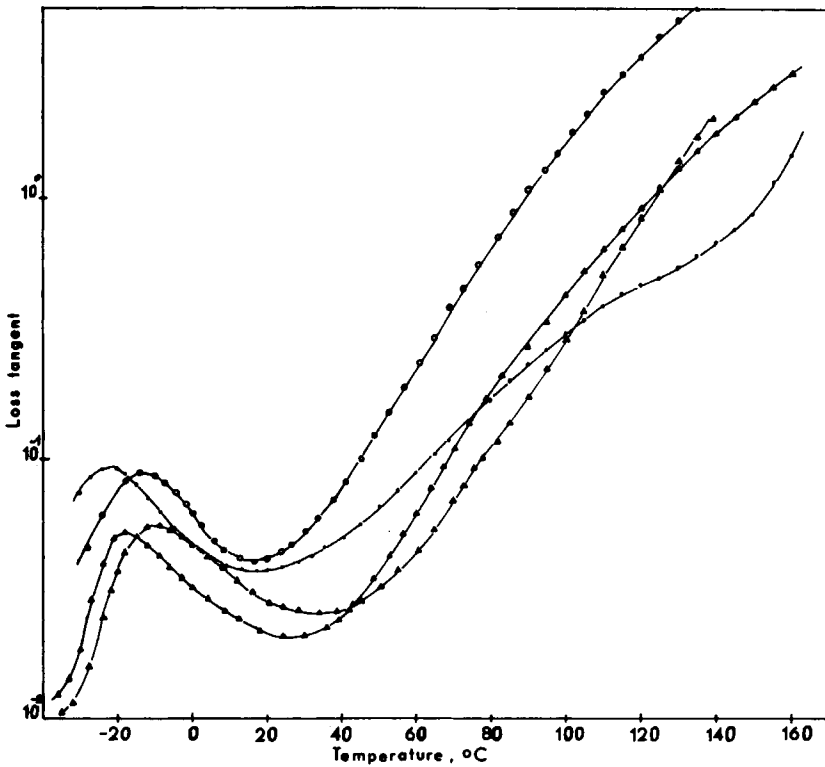


Fig. 9. Temperature dependence of the dielectric loss ( $\tan \delta$ ) for PUI and PU: (○○○) PU-A; (●●●) PUI-3; (△△△) PU-B; (▲▲▲) PUI-10.

structure leads to much smaller values of  $\epsilon'$ . As a matter of fact, this trend is in agreement with other findings<sup>13</sup> stating the  $\epsilon'$  drops down with decrease of the apparent density. For the investigated cellular PUI the density is 0.81 g/cm<sup>3</sup>, while for the solid analog the value is 1.14 g/cm<sup>3</sup>.

Figure 9 presents the dielectric loss vs. temperature. The glass transition of the flexible segments is seen to be remarkably lower for PUI than for the corresponding PU. This can be explained by better phase segregation of stiff PI segments from the soft, flexible polyether- or polyester-urethane matrix. In the case of PUI and PU obtained from PTMG, the dielectric loss is higher than for the polymers synthesized from PEA. It is due to a higher content of the flexible segments in PTMG systems and due to higher mobility of the polyether chain vs. the polyester one. These factors are also—at least partly—responsible for the lower glass transition of PTMG derived systems in comparison with PEA based PUI, just as it is in typical PU.<sup>14</sup>

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