Influence of the Chain Extender Length and Diisocyanate Amount on the Thermal Stability and Mechanical Properties of Some Polyurethanes

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In this study were synthesized some polyurethanes based on polycaprolactone diol (PCL) with Mw=2000g/mol and 4,4’-diphenylmethane diisocyanate (MDI), using as chain-extending agents different linear diols with methylene number between 2 and 6, without adding catalysts. Effect of the diisocyanates concentration and chain extender structures on the polyurethanes has been discussed with reference to the thermal stability and mechanical properties. The physical and mechanical properties (hardness, stress-strain, resilience, abrasion resistance, etc.) of these polymers were measured according to standard methods. All the polymers were characterized by conventional methods. Thermal analysis (TGA and DSC) were used for characterization. The structures were confirmed by infra-red analysis (IR). The results showed that the thermal stability and mechanical properties of the final products can be controlled by the amount of the MDI and/or of the chain extenders nature.

Keywords: polyurethanes, mechanical properties, thermal stability.

Polyurethanes represent a main class of synthetic elastomers. They form a versatile class of polymers, which are used in a broad range of applications as elastomers [1], foams [2], coatings [3], fibers [4] and biomedical materials [5]. The group of polyurethanes comprises all polymers that contain urethane, urea or other isocyanate derived groups. The generally used reagents for segmented polyurethanes are a diisocyanate, a polyol and an extender. Segmented polyurethanes can be considered as multi block copolymers, consisting of a hard and a soft block (segment). The hard segment originates from the diisocyanate and chain extender, while the soft segment usually is the polyol. Polyurethanes are often prepared by one-shot or prepolymer procedure [6]. In the first procedure all reagents are mixed and the resulting polymer is a random distribution of monomer and polyol units. If more control is desired over monomer and polyol distribution along the polymer chain the two-step process is preferred. For this procedure the polyol is first reacted with an excess of the diisocyanate to form a so called prepolymer, which is subsequently reacted with the chain extender and results in the formation of the high molecular weight polyurethane [7-10]. When a diamine is used as chain extender the polyurethane also contains urea groups [11]. Polyurethanes are formed by linear polymeric chains of segmented structure. They are prepared by the addition reaction of bifunctional isocyanates, chain extenders and long chain polyols. Most of conventional PUs are based either on polyester or polyether polyols, 4,4-diphenylmethane diisocyanate (MDI) as an isocyanate component and 1,4-butanediol (BD) as a chain extender [12]. The main interest of researchers is focused on the polyol components saturated [13-16] and unsaturated [17-19]. This study presents the influence of the chain extenders length (saturated diols with 2 to 6 carbon atoms), on the thermal stability and mechanical properties of some polyurethane elastomers.

Experimental part

Materials

The basic materials used in this research were: polycaprolactone diol (PCL, Aldrich) Mw 2000 g/mol; 4,4’-diphenylmethane diisocyanate (MDI); Ethylene glycol (EG, Fluka); 1,3-propylene glycol (PG, Fluka); 1,4-butanediol (BD, Fluka); 1,5-pentane diol (PD, Fluka) and 1,6-hexane diol (HD, Fluka).

PCL and chain extenders were dried under a vacuum until the content of water was below 0.03%. All the chemicals were used as supplied, without further purification.

Measurements

Tensile testing was performed on dumbbell-shaped specimens, cut from thin films at room temperature using a TIRA-test 2161 tensile tester, Maschinenbau GmbH Rauenstein Germany, equipped with a 100 N load-cell, at a cross-head speed of 50 mm/min and the gauge length 40 mm. All samples were measured three times and the averages were obtained.

Infrared Spectroscopy (FT-IR) was done using a Bruker Vertex 70 Instrument equipped with a Golden Gate single reflection ATR accessory, spectral range 600-4000 cm^{-1}.

The thermal stability of polyurethanes was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was 10^oC /min in air. The initial weight of the samples was about 50 mg and the temperature range 30-700^oC.

A Perkin-Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere with a heating rate of 10 ^oC/min and temperature range of -100 ^oC to +150 ^oC.

Hardness was measured on Instron Shore Operating Stand IRHD model 903, using scale A**,** ASTM **D1415-06** Standard Test Method for Rubber Property-International Hardness.

Abrasion test was carried out on a Veb Thuringer Industriewerk Rauenstein abrasimeter, type AP-CI, 1971, Germany, by action of an abrasive paper, set on a rotating drum, following a standard procedure (STAS 6699/89).

Procedure

The polyurethanes from this study were prepared from 4,4’-diphenylmethane diisocyanate (MDI), polycapro-

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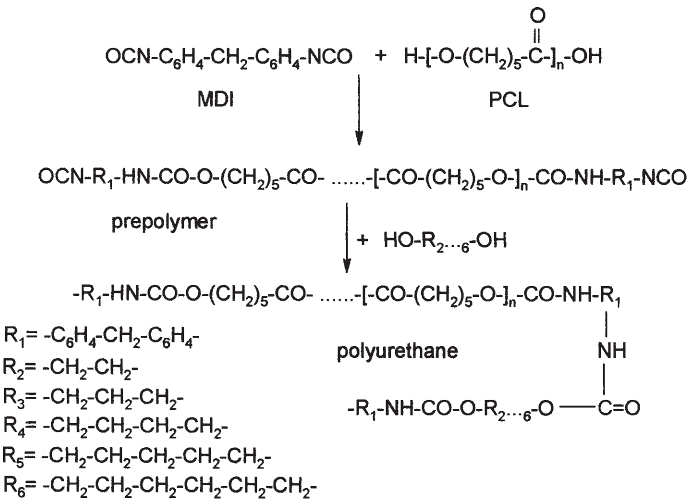
lactone diol (PCL) and diols as chain-extending agents, without adding catalysts. The polymers were prepared in a two-step polymerization process under argon atmosphere by chain extending an isocyanate terminated polycaprolactone diol (PCL) with glycols. The synthetic route for the polyurethane samples preparation is outlined in scheme 1.

Isocyanate terminated polycaprolactone polyester was prepared by a typical procedure. A mixture of polycaprolactone diol (25.00 g; 12.5 mmol) and MDI (6.25 g; 25.00 mmol or 9.4 g; 37.5 mmol) were reacted at 80 °C for one hour under argon atmosphere. The molecular ratio of PCL:MDI were 1:3 and 1:2. The polycaprolactone diol was preheated to 70°C in a glass flask, and dehydrated for two hours under vacuum. For come back to atmospheric pressure an argon blanket was applied over the liquid. The MDI (solid) was then carefully stirred into the polyol, and the reaction was conducted at 80°C for one hour. The prepolymer was then degassed until gas evolution stopped (ca. 10 – 15 min). The reaction is depicted in Figure 1.



Scheme 1

Chain extension of the isocyanate terminated polycaprolactone polyester was performed by a typical procedure. The isocyanate terminated polyester was reacted with diols (EG; PG; BD; PD and HD), to a molar ratio 1:3:2, or/and 1:2:1) without adding catalysts. The chain extender was mechanically stirred (high speed stirrer) for 2 min. The mixture was then degassed until gas evolution stopped (max. 2 - 3 min) and carefully poured into the preheated moulds (80°C). The samples were cured for 16h at 80°C, and 24 h at 100°C. The reaction is depicted in figure 2.

Results and discussion

The polyurethane samples based on PCL, MDI and glycols were characterized using conventional spectroscopic methods. FTIR spectra of the polymer samples showed bands of urethane groups at 3322-3339 cm^{-1} (N-H stretching), 2944-2951 cm^{-1} (CH_2 stretching), 1722-1727 cm^{-1} (NHCOO stretching), and 1530-1533 cm^{-1} (C-N stretching, combined with N-H out of plane bending).

Thermal stability

Thermogravimetric analysis (TGA) has been used to examine the thermal stability of the polyurethanes based on PCL/MDI/Glycols. The results are presented in table 1.

Generally, polyurethanes analyzed decomposed in three steps and the temperature where the weight losses were maximum is 200-550°C (step II). The influence of the chain extender length is not evident. However, the polyurethanes

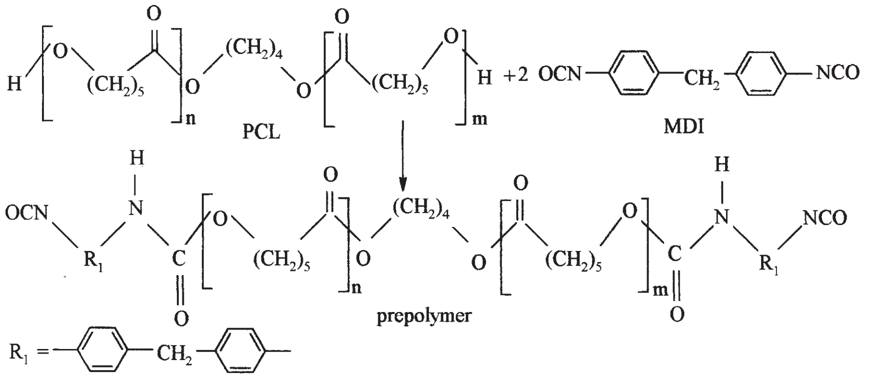


Fig. 1. End-capping of the PCL with MDI

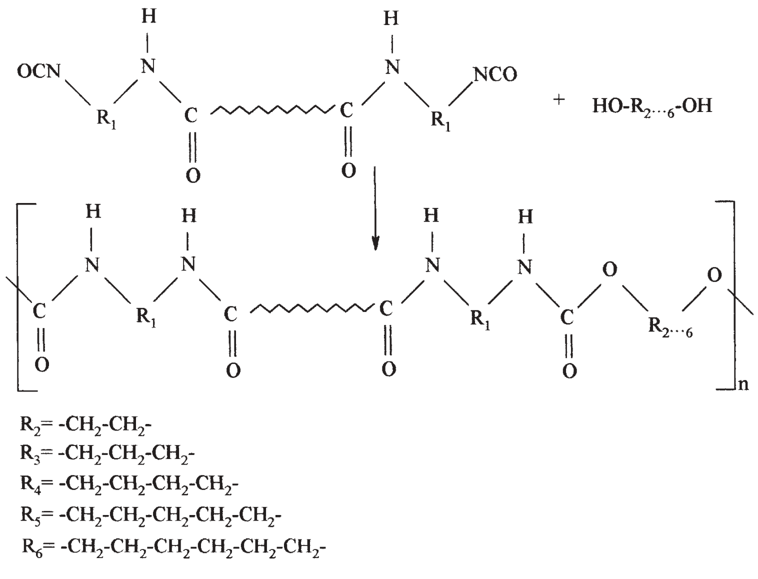


Fig. 2. Chain extension reaction of the end-capped polycaprolactone with diols

Table 1

THERMAL STABILITY OF THE POLYMERS BASED ON PCL/MDI/GLYCOLS

Code	Reaction order*	Weight losses / decomposition temperature ranges				Activation Energy * KJ/mol	*Tg* (°C) *Tmelt***
		Step I % / °C	Step II % / °C	Step III % / °C	Residue %		
PUPCL2	1.6	1/80-270	81/270-535	16/535-685	2	70.57	-39.93 47.78 77.49
PUPCL3	0.6	1.2/75-245	84.4/245-540	13.2/540-660	1.2	60.59	-35.57 49.24 68.01
PUPCL4	2.0	0.8/235-300	83.2/300-550	11.6/550-670	4.4	149.61	-38.40 44.20 64.82
PUPCL5	1.5	0.8/205-298	81.2/298-530	14.6/530-670	3.4	119.76	-39.83 43.86 63.54
PUPCL6	1.2	1.6/75-206	86/206-550	11.4/550-670	1	89.76	-39.12 44.35 64.57
PUPCL2'	1.5	0.8/120-270	82/270-505	13.2/505-655	4	140.91	-39.83 47.78 67.98
PUPCL3'	1.2	0.8/257-294	84.8/294-540	12.4/540-660	2	100.72	-32.96 44.93 62.87
PUPCL4'	1.6	0.8/202-313	83.2/313-540	12.2/540-660	3.8	126.06	-39.80 43.05 65.70
PUPCL5'	1.6	0.8/237-288	84.5/288-530	11.4/530-650	3.8	130.67	-35.49 46.89 68.06
PUPCL6'	1.2	1.2/73-257	81.6/257-540	11.8/540-660	5.4	99.00	-36.19 42.32 70.08

* Calculated through Reich-Levi method.
**Calculated by DSC

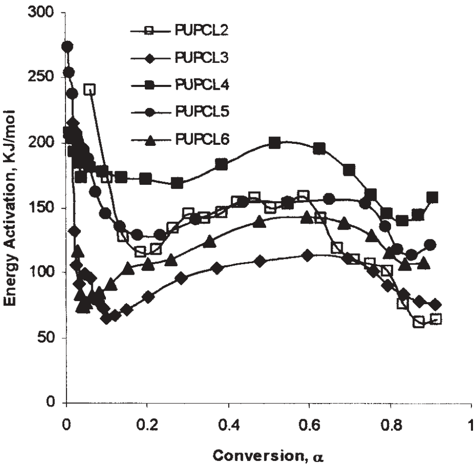


Fig. 3. Activation energy vs. conversion of the polyurethanes based on PCL/MDI/Glycols, ratio - 1:2:1

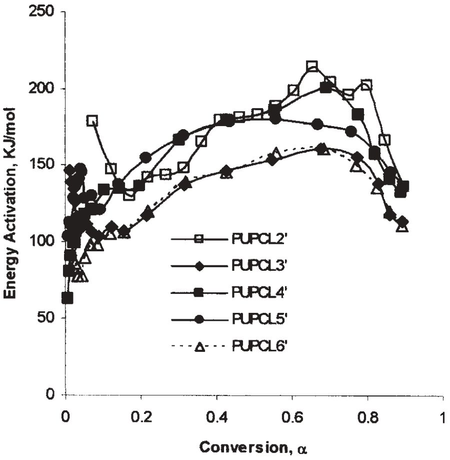


Fig. 4. Activation energy vs. conversion of the polyurethanes based on PCL/MDI/Glycols, ratio -1:3:2

based on PCL, MDI and diols with different length are relatively stable up to 200-300 °C, when maximum 2 % of weight is lost.

The dependence of the activation energy (Reich-Levi method) versus conversion degree is presented in Figures 3, 4. It is can be remarked the fact that the energy of activation decreases until a conversion α=0.15-0.2, after that it increases until at α=0.6-0.7, to finally to decrease again. For α < 0.2 it appears an important depression in activation energy values versus conversion. This suggests that at beginning, the reaction has an autocatalytic behavior. In connection with this, one should note that the oxygen traces in the polymer act as a catalyst for the decomposition process.

Thermal properties of the samples were studied also by means of DSC, which it is one method for determination of glass transition temperature. Thus DSC measurements can be recorded up to 200°C without degradation of the polymers. The polyurethanes based on PCL/MDI/Glycols exhibit *Tg* between -39.93 and -32.96°C. In the negative domain the samples do not present any crystallization temperature, but present two melting endotherms temperature, in the positive domain, first is between 42.32 and 49.24 °C and the second between 62.87-77.49 °C. The *Tg* and lower melting temperature correspond to the soft segments. Since the melting temperature of the polycaprolactone prepolymer is beyond 60 °C, the higher melting temperature corresponds, at least in part to the hard segments.

Mechanical properties

The mechanical properties were discussed in connection with chain extenders length and the amount of the diisocyanate. The syntheses were performed using the prepolymer method. Polyurethanes based on PCL, MDI and diols with different length of chain lead to polymers

Table 2
MECHANICAL PROPERTIES OF POLYURETHANES BASED ON PCL/MDI

Code	Ratio PCL/MDI/Glycols	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)	Hardness (°ShA)	Abrasion mm^3/cm^2
PUPCL2	1:3:2	26.16	5.66	510	90	15
PUPCL3	1:3:2	12.76	4.96	590	90	25
PUPCL4	1:3:2	22.84	3.74	640	85	18
PUPCL5	1:3:2	24.59	3.94	660	80	16
PUPCL6	1:3:2	25.60	4.18	625	70	17
PUPCL2'	1:2:1	21.82	4.31	700	88	19
PUPCL3'	1:2:1	16.36	5.00	725	88	22
PUPCL4'	1:2:1	17.05	4.70	715	83	21
PUPCL5'	1:2:1	11.91	2.96	735	78	30
PUPCL6'	1:2:1	18.74	3.91	750	65	20

with hardness between 65-90 °ShA. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

The increase of the hard segments content in the polyurethane backbone generates an increase of the hardness. By increasing of the hard segment content and/or chain extenders length it was possible to prepare polyurethanes with hardness between 65-90 °ShA. The experimental values of the main mechanical properties are showed in table 2.

Conclusions

In the present study we investigated the effects of chain extender and diisocyanate amount on the thermal stability and mechanical properties of some polyurethanes. The results showed that the thermal stability and mechanical properties of the final products can be controlled by the amount of the MDI and/or of the chain extenders nature. The crystallites of hard segments are very small and not likely to cause problems during degradation. The abrasion resistance depends of the superficial hardness and tensile strength of the sample. These materials seem to be appropriate for medical devices.

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