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Poly(ester-siloxane)urethane network structure from tensile properties

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Abstract

New poly(ester-siloxane)urethane structures, which exhibit the alternation of the flexible and hard segments in the polymer chain, using the 'prepolymer' polyaddition procedure were obtained. These networks were analyzed on the basis of molecular theory of rubber elasticity from stress–strain data. The cumulated effect of the physical and chemical crosslinkings induced by a tetrafunctional compound was pointed out by the average critical molecular weight of the linear segments existing among the junctions of copolymer networks. The correlation between the structure of soft and hard segments and tensile properties, density of chemical crosslinks and the hardness of these polymers was established. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ester-siloxane)urethane copolymers; Crosslinked networks; Tensile properties

1. Introduction

As promising functional polymer materials, the polymer networks made up of two (more than) kinds of components having different physico-chemical properties have been developed [1,2]. The attempts to link various components by chemical bonds were firstly carried out for copolymers made of multicomponent systems with block- and random sequences [3,4]. The introduction of crosslinking affords to the polymer systems rubber elasticity and swelling ability, which cannot occur in the uncrosslinked systems. It is well known that the physico-chemical properties of multicomponent polymer systems are strongly influenced by the morphology and structure of the components. In the case of copolymer networks, the methods of preparation may influence the characteristics of the resulting networks, namely, composition and component sequences. The preparation procedures of the copolymer networks can be divided into the following two groups: reactions between bifunctional telechelic polymers and polymers containing multifunctional sites at the side chains [5,6] and reactions between bifunctional and multifunctional telechelic polymers [7].

The structural and compositional diversity of polyurethane elastomers represents a useful way to investigate the properties and supramolecular structure of these materials. Polydimethylsiloxane can be employed in the synthesis of polyurethane block copolymers as flexible segments improving the physical characteristics of polyurethane–polydimethylsiloxane copolymers [8–10]. The incorporation of the siloxane segments in linear polyester urethane chains leads to the thermodynamic incompatibility of hard and soft segments proved by phase separation [11]. The polydimethylsiloxane–polyurethane copolymers containing about 12% siloxane segments have higher thermal stability and improved mechanical properties [12].

In the present study, crosslinked poly(ester-siloxane)-urethanes based on 4,4′-methylene diphenylene diisocyanate/diglycerin maleate tetrol (MDI/DGMA) and 2,4-tolylene diisocyanate/DGMA (TDI/DGMA) were synthesized. The influences of the network structure and the crosslinking degree on the mechanical properties of these polyurethane–polydimethylsiloxane networks were discussed.

2. Experimental

2.1. Materials

MDI (Suprasec ICI) and TDI (Riedel) were purified by vacuum distillation and stored in darkness at 10°C. Dibutyl tin dilaurate (Bu_2SnL_2, Aldrich), poly(ethylene glycol adipate)diol (PEGA, Fibrex Savinesti) were used as received.

2.2. Synthesis of polyols

Poly(dimethylsiloxane)diol (PDMS) with molecular weight $M_n = 10,000$ was obtained by ring opening polymerization of octamethylcyclotetrasiloxane in tetrahydrofuran

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Table 1
Chemical composition of poly(ester-siloxane)urethanes based on MDI

Sample	Soft segment ($g_{polyols}$/100 g_{sample})			Hard segment (g/100 g_{sample})		NCO groups (mole/g × 10^2)	SSC (%)	HSC (%)
	PEGA	PDEGA	PDMS	DGMA	MDI			
1	66.135	–	–	8.839	25.026	20.0	65.0	35.0
2	53.448	–	12.0	9.526	25.026	20.0	64.5	35.5
3	–	65.21	–	9.764	25.026	20.0	64.0	36.0
4	–	52.702	12.0	10.272	25.026	20.0	64.0	36.0
5	48.338	–	12.0	11.508	28.154	22.5	59.5	40.5
6	–	47.665	12.0	12.181	28.154	22.5	59.0	41.0

solution, in the presence of benzyltrimethylammonium siloxanolate and water, at 35°C for 12 h [13].

Poly(diethylene glycol adipate)diol (PDEGA) was prepared by melt polycondensation between adipic acid and diethylene glycol (DEG) (molar ratio 1:2). In the first stage of the reaction (150–180°C) a hydroxy-terminated low molecular weight ester was formed and water was removed. In the second stage, the transesterification reaction took place at 200°C and 2 mmHg with glycol elimination. In these conditions, PDEGA having $M_n = 2500$ and C_{OH} (OH number) = 45 mg KOH/g, was obtained [14].

The low molecular weight polyol-DGMA having $C_{OH} = 850$ mg KOH/g was synthesized by esterification of maleic anhydride with glycerol at 160–180°C (molar ratio 1:2) in the presence of *p*-toluenesulfonic acid [15].

2.3. Synthesis of crosslinked elastomers

Crosslinked polyurethane–polysiloxane elastomers were obtained by melt polyaddition using a ‘prepolymer’ procedure [11]. In a reactor fitted with a mechanical stirrer, a nitrogen inlet tube and a vacuum line, 53.448 g of PEGA were placed and heated under stirring at 125°C and 2–3 mmHg residual pressure for 4 h to remove the water traces. Then, the temperature was reduced to 80°C and 13.376 g of MDI and 0.001 g of Bu_2SnL_2 were added under nitrogen flow. In another reactor, 12.00 g of PDMS and 0.60 g of MDI were introduced and the reaction was conducted in the same way. The resulting MDI/PEGA/MDI and MDI/PDMS/MDI prepolymers were then mixed for 0.5 h. Subsequently, 9.526 g of DGMA were put into in the reaction mixture. Finally, after 30 min 11.05 g of MDI were introduced in the reactor. After 30 min, the content of reactor was poured in a mould and maintained there at 80°C for 8 h to complete the reaction. Thus, 300 × 200 × 1 mm^3 plates were obtained, which were then treated at 65°C for 6 h.

The chemical compositions of all materials synthesized for this study are shown in Tables 1 and 2.

2.4. Measurements

Tensile properties were evaluated from stress–strain curves recorded on a TIRA-Test 2161 apparatus at room temperature and an elongation rate of 9 mm/min. Samples in the form of films of constant thickness (0.96–1.07 mm) were cut into strips of 65.3 × 6.0 mm. At least six measurements were made to report the average.

Hardness was measured using a Durometer Instrument type I (scale 0–100° Shore A), at room temperature on the samples of 6 mm thickness.

3. Results and discussion

Taking into account the alternation of the flexible and hard segments in the polymer chain, much more uniform polyurethane structures were obtained using the prepolymer polyaddition procedure. In these polymerization reactions the molar ratio NCO/OH was approximately 1:1. The

Table 2
Chemical composition of poly(ester-siloxane)urethanes based on TDI

Sample	Soft segment ($g_{polyols}$/100 g_{sample})			Hard segment (g/100 g_{sample})		NCO groups (mole/g × 10^2)	SSC (%)	HSC (%)
	PEGA	PDEGA	PDMS	DGMA	TDI			
7	74.274	–	–	8.310	17.416	20.0	73.0	27.0
8	61.600	–	12.0	8.984	17.416	20.0	72.5	27.5
9	–	73.243	–	9.341	17.416	20.0	72.0	28.0
10	–	60.741	12.0	9.843	17.416	20.0	72.0	28.0
11	70.181	–	–	10.226	19.593	22.5	69.0	31.0
12	57.507	–	12.0	10.900	19.593	22.5	68.5	31.5
13	66.075	–	–	12.155	21.770	25	65.0	35.0
14	–	52.661	12.0	13.569	21.770	25	64.0	36.0
15	60.997	–	–	14.533	24.470	28.1	60.0	40.0

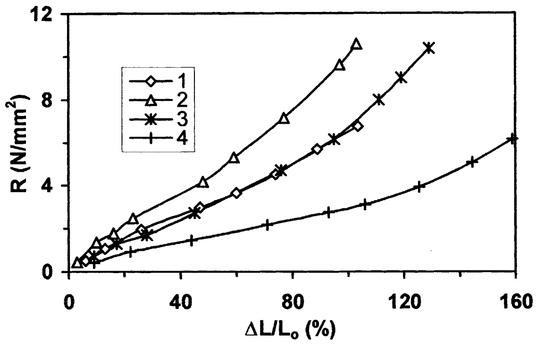


Fig. 1. Stress–strain curves of polyurethane elastomers based on MDI.

structure of the crosslinked polydimethylsiloxane–polyurethane copolymers as well as the steps involved in their synthesis are shown in Scheme 1.

The resultant polyurethane–polydimethylsiloxane copolymers contain about 12% siloxane segments, which were found to be the optimum concentration to obtain linear polyurethane structures with siloxane units in the backbone [16].

These poly(ester-siloxane)urethanes subjected to a mechanical deformation exhibit an elasto-plastic behaviour in static conditions. The mechanical characteristics depend both on the structure and the defects of the samples under the study. The hard domains of the elastomers are responsible for their strength. These domains are found to be effective reinforcing agents provided their volume fraction exceeds 0.20, their size is less than 0.1 μm and their softening temperature is substantially above the test temperature [17]. They are more effective than particulate fillers because they are deformable and uniformly distributed throughout the sample volume. The plastic deformation of the hard domains reduces the concentration of the internal energy, and thus the strength and hardness of tested materials. At room temperature, linear polyurethanes have a network behaviour, which is generated by the hard domains and this behaviour becomes ineffective over the softening point. In the crosslinked polyurethanes, the bonds between polymer chains assure the network stability until the thermal degradation occurs.

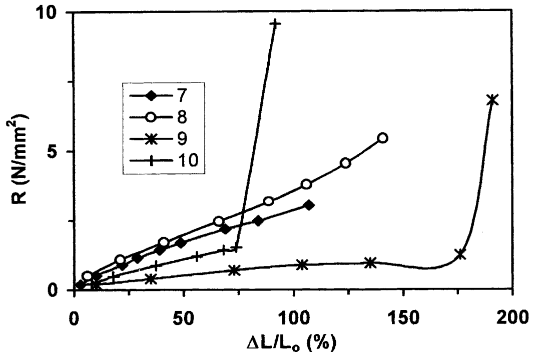


Fig. 2. Stress–strain curves of polyurethane elastomers based on TDI.

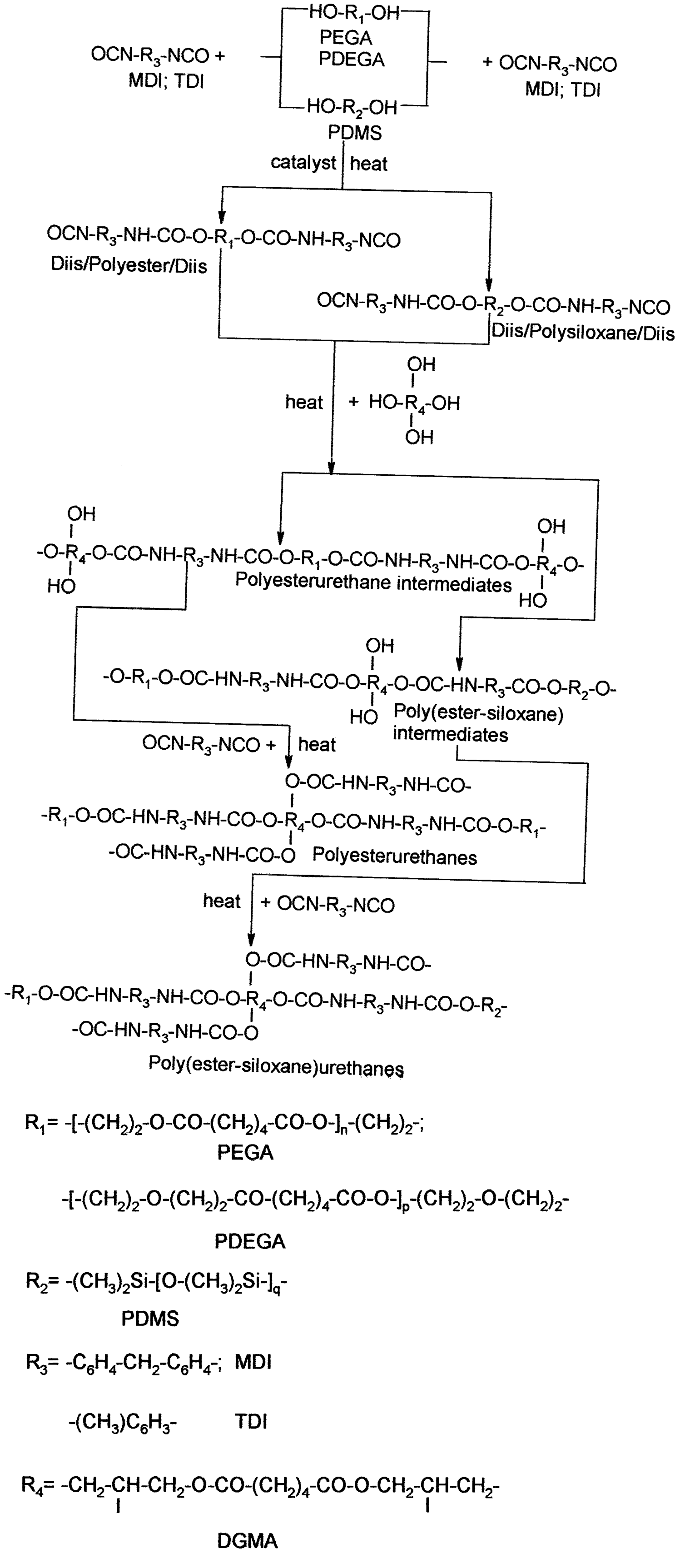
Typical, stress–strain curves of some poly(ester-siloxane)urethanes are presented in Figs. 1 and 2. The mechanical parameters derived from these curves are summarized in Table 3.

For the chemically crosslinked copolymers based on MDI/DGMA segments (1–4), the variation of mechanical parameters was correlated with the crosslinking degree (the concentration of NHCOO groups). Generally, together with the increasing of the crosslinking degree, the tensile strength at break, Young's modulus and hardness at break will increase, while the elongation at break will decrease.

Depending on the density of urethane groups, polyurethane elastomers having a hardness between 65 and 90° Shore A were obtained. Chemically crosslinked elastomers based on TDI/DGMA as hard segments reveal the same

Table 3
Ultimate mechanical parameters and hardness of crosslinked polyurethane elastomers

Sample	Ultimate mechanical parameters			Hardness (°Shore A)
	Elongation (%)	Strength (MPa)	Modulus (MPa)	
1	103.54	6.74	7.54	65
2	102.72	10.55	14.18	70
3	136.36	8.70	12.86	80
4	158.80	6.16	4.81	65
5	53.64	9.45	33.49	87
6	103.96	15.51	30.49	90
7	106.91	3.03	5.08	55
8	140.81	5.39	6.94	45
9	191.40	6.79	1.79	65
10	92.22	9.55	3.71	55
11	115.08	10.61	25.45	85
12	108.57	6.23	8.10	80
13	107.51	10.83	26.59	90
14	134.66	7.77	21.38	85
15	77.26	15.63	32.15	95



Scheme 1. Preparation of PDMS–polyurethane elastomers.

behaviour as the above-mentioned polymers, but they are more flexible and have a reduced strength at break.

The structure of polyurethane networks can be discussed on the basis of the molecular theory of rubber elasticity using the stress–strain data [18]. The stress–strain data were interpreted in terms of the reduced stress $|f^*|$ and the Mooney–Rivlin semiempirical equation:

$$|f^*| = \frac{b}{A(\alpha - \alpha^{-2})} \tag{1}$$

and

$$|f^*| = 2C_1 + 2C_2/\alpha, \tag{2}$$

where f is the applied force, α the elongation ($\alpha = L/L_i$, L and L_i are the stretched and unstretched lengths, respectively), A the cross-sectional area of the unstressed sample and C_1 and C_2 are constants.

The reduced stress can be plotted as a function of reciprocal elongation to determine the crosslink density of the sample. The empirical Eq. (2) provides a linear relation between $|f^*|$ and $1/\alpha$.

If one compares reduced stress for $\alpha \to 1$ according to Eq. (2) and Flory expression for the modulus [19] we obtain

$$2C_1 + 2C_2 = \frac{\rho}{M}[(1 - 2/\phi)(1 + f_c/f_{ph})]_{\alpha\to 1}RTV_{2c}^{3/2} = A'_\phi \frac{\rho}{M}RTV_{2c}^{2/3}, \tag{3}$$

where A'_ϕ represents the term in square brackets, M means the molecular weight between crosslinks, ρ is the sample density, ϕ the crosslink functionality, f_c the contribution due to the constraints imposed by the junction fluctuations in the polymer coils, and f_{ph} the contribution due to the assimilation of the polymer network with a 'phantom' network, $V_{2c} = V/V_0$ (V_0 is the initial volume of the sample, and V is the volume of the sample strained with a force f).

One can consider that $|f^*|$ corresponding to $\alpha = 1$ calculated by Eq. (2) does not differ from the value calculated by the Flory equation for an 'affine' network. In this case, A'_ϕ should be unity and should not depend on ϕ. If the network behaviour is not affine, A'_ϕ will be sensibly different from unity. Because all reactants were included in the polymer network, an average value of 0.45 was used [19].

The plots of $|f^*|$ versus $1/\alpha$, determined by Eq. (3), show a linear dependence for all samples under the study (Figs. 3 and 4). From these plots the constants $2C_1$ and $2C_2$ were determined and then using Eq. (3) the molecular weight

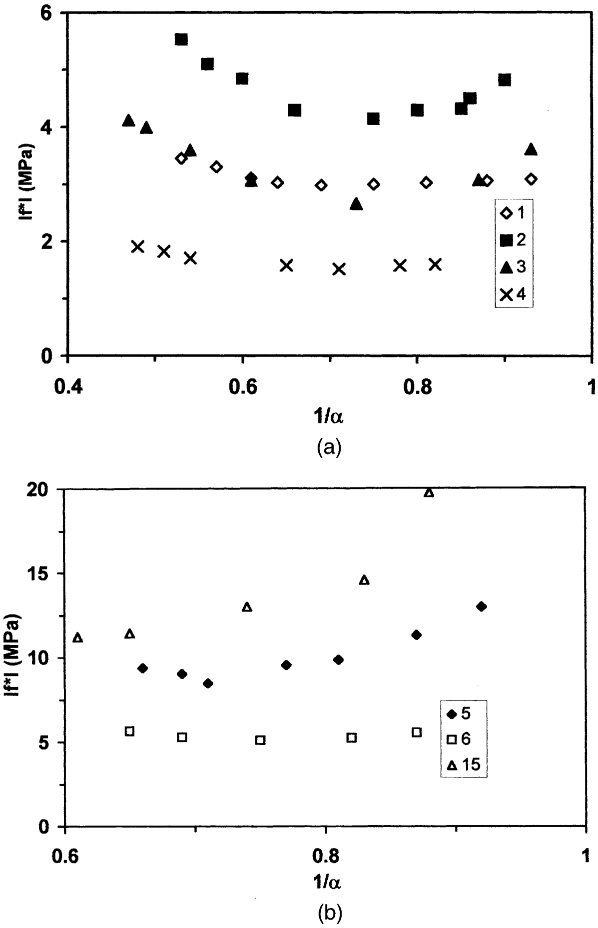


Fig. 3. Mooney plots of polyurethane–polydimethylsiloxane networks based on MDI: (a) 1–4: 2×10^{-3} mole NCO/g; (b) 5, 6: 2.25×10^{-3} mole NCO/g; and 15 (TDI): 2.81×10^{-3} mole NCO/g.

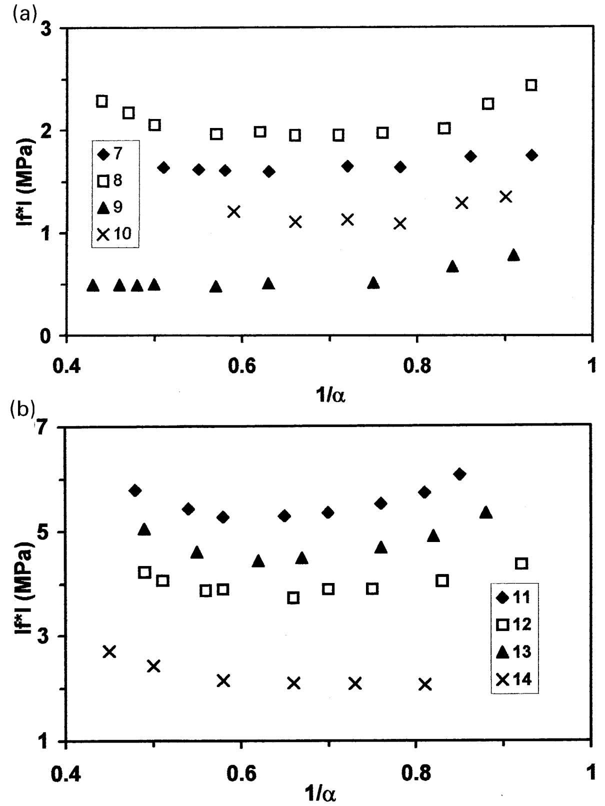


Fig. 4. Mooney plots of polyurethane–polydimethylsiloxane networks based on TDI: (a) 7–10: 2×10^{-3} mole NCO/g; (b) 11, 12: 2.25×10^{-3} mole NCO/g; and 13, 14: 2.5×10^{-3} mole NCO/g.

Table 4
Molecular weights of elastomeric networks for 'affine' and 'phantom' models

Sample	Moles OH/g × 10^3		NCO groups (mole/g × 10^3)	Density (g/cm^3)	$2C_1 + 2C_2$ (MPa)	Calculated M (Eq. (3))	
	Primary	Secondary				Affine model ($A'_\Phi = 1$)[a]	Phantom model ($A'_\Phi = 1 - 2/\Phi$)[b]
1	1.331	0.669	2.00	1.101	2.20	730	365
2	1.279	0.721	2.00	1.160	4.27	395	198
3	1.261	0.739	2.00	1.231	3.22	367	184
4	1.2225	0.7775	2.00	1.187	1.68	1,052	526
5	1.379	0.871	2.25	1.069	13.67	114	57
6	1.328	0.922	2.25	1.202	4.54	376	188
7	1.371	0.629	2.00	1.205	1.77	990	495
8	1.32	0.680	2.00	1.075	2.05	763	381
9	1.293	0.707	2.00	1.216	0.56	3,159	1,580
10	1.255	0.745	2.00	1.096	1.27	1,256	628
11	1.476	0.774	2.25	1.047	5.84	302	151
12	1.425	0.825	2.25	1.157	4.29	392	196
13	1.580	0.920	2.50	1.203	5.04	300	150
14	1.473	1.027	2.50	1.121	2.22	735	367
15	1.710	1.100	2.81	1.137	15.67	106	51

[a] Affine model.
[b] Phantom model.

between crosslinks both for affine models ($A'_\Phi = 1$) and for phantom models were evaluated (Table 4).

The cumulated effect of the physical crosslinkings (hydrogen bonds) and chemical crosslinkings induced by the tetrafunctional compound (DGMA) is evidenced by the average critical molecular weight (M) of the linear segments existing among the junctions of copolymer network. Also, the influence of the polyol length and the structure of polyols, which form the architecture of the soft segments as well as of the diisocyanates from the hard segments on the mechanical properties of copolymers, were discussed. Two ester oligomers were used: PEGA with $M_n = 2000$ and which crystallize to room temperature and PDEGA with $M_n = 2500$, which is noncrystallizable.

As TDI leads to less rigid structures than MDI, in order to compare the two types of copolymers obtained, we synthesized samples having a higher content of isocyanate groups (2.50×10^{-3} mole NCO/g, samples 13 and 14, and 2.81×10^{-3} mole NCO/g, sample 15, respectively).

The samples 1–3 have almost the same concentration of soft segments (SSC) and hard segments (HSC). In this case, the molecular weight decreases from 730 to 367, while the concentration of secondary hydroxyl groups that mainly determines the formation of urethane networks increases from 0.669×10^{-3} to 0.739×10^{-3} mole OH/g.

It is surprising that the molecular weight of sample 1 is greater than that of 2, which contains both PDMS and PEGA. This effect is probably due to the presence of a higher number of urethane bonds which annihilate practically the influence of polydimethylsiloxane units from the soft segments and also to the fact that sample 1 does not develop a well outlined network (R decreases very much (Fig. 1)). However, the copolymer PDEGA–PDMS/MDI/DGMA (sample 4), which should possess an enhanced crosslinking degree, exhibits the greatest value of the molecular weight among the samples having 2.00×10^{-3} mole NCO/g.

This behaviour can be related to the greater length of PDEGA segments and their reduced ability to form hydrogen bonding as compared to PEGA. Also, the PDMS segments, which practically do not form hydrogen bonds with urethane groups, influence this behaviour in the same way. In these conditions the final result could be the incomplete reaction of the secondary hydroxyl groups.

The samples 5 and 6, which are differentiated only by the nature of the ester oligomers from soft segments have different molecular weights. This difference confirms once more the influence of the length of PDEGA segments and its ability to form hydrogen bonds on the molecular weight of copolymers. Thus, the hardness of sample 6 decreases and its molecular weight increases about four times. One can conclude that PDEGA leads to more flexible copolymers.

The crosslinked copolymers having hard segments based on TDI/DGMA and the same concentration of NCO groups (samples 7–10) as well as those based on MDI/DGMA (samples 1–4) exhibit similar characteristics, with the exception of molecular weight (Table 4).

The molecular weights, calculated by Flory equation, helped to find some relationships between the influence of soft and hard segments of the resulting copolymers and the initial composition of the starting materials. For example, the influence of PDMS segments on the characteristics of the poly(ester-siloxane)urethanes copolymers can be evidenced by analyzing the samples 11 and 12 (Table 4). Although, the sample 12 has a greater HSC than sample 11 (Table 2), its molecular weight is higher due to the decrease of hydrogen bonding density and increase of phase separation. The molecular weight of sample 12 is practically equal with that of 2, although former has more NCO groups than 2. This fact is determined by the higher HSC of the copolymer 2. In order to obtain two copolymers having the same hardness but different isocyanates in the hard segment (MDI and TDI), it is necessary for samples based on TDI to multiply the NCO group concentration by 1.125, DGMA content by 1.144, PEGA content by 1.076, while the PDMS content remains unchanged.

If the structure of soft and hard segments is unchanged and the content of the urethane groups increases with 0.5×10^{-3} mole NCO/g, the molecular weight diminishes to a half by comparison of samples 10 and 14. This finding suggests that to obtain an increase of the hardness by two times, using the samples with the same structure (PDEGA–PDMS/TDI/DGMA), we must make the following correction for sample 10: 1.25 × NCO group concentration, 1.379 × DGMA content, 0.867 × PDEGA content and 1.000 PDMS content, respectively.

A good agreement between the increasing of NCO group concentration and the decreasing of critical molecular weight was observed for samples 7, 13 and 15. Adding 0.80×10^{-3} mole NCO/g results in molecular weights that are nine times lower (correction for sample 7: 1.405 × NCO group concentration, 1.749 × DGMA content and 0.821 × PEGA content, respectively).

4. Conclusions

Much more uniform poly(ester-siloxane)urethane structures which contain about 12% siloxane units were obtained, taking into account the alternation of the flexible and hard segments in the polymer chain, using the prepolymer polyaddition procedure.

These poly(ester-siloxane)urethanes subjected to a mechanical deformation exhibited an elasto-plastic behaviour in static conditions. In these polyurethane networks, the chemical crosslinks assure the network stability until the thermal degradation occurs.

The copolymer samples that differ only by the nature of the ester oligomers from soft segments have different molecular weights. This difference confirmed once more the influence of the length of PDEGA segments and their lower ability to form hydrogen bonds on the molecular weight of copolymers. The incorporation of PDEGA units in the polymer chain leads to more flexible copolymers. The influence of PDMS units, long and very flexible segments, on the tensile properties of the resulting copolymers were evidenced by greater molecular weights due to the decreasing of hydrogen bonding density and increasing of the phase separation.

The molecular weight decreased directly proportional to the increasing of crosslinking degree, and it did not depend significantly on the structure of the partners, which participated in the building of the urethane–siloxane elastomer networks. A good agreement between the increasing of density of chemical crosslinkings and the increasing of the polyurethane hardness was established.

Finally, one can affirm that the oligomer segments with increased flexibility and greater dimensions as well as diisocyanates with reduced hardness and crystallization ability led to more flexible polyurethanes.

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