Polyurethane microcellular elastomers: 2. Effect of chain extender on the mechanical properties

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The influence of ethylene glycol, triethanol amine and a rigid polyol on the tensile strength, elongation at break and tear resistance of a microcellular elastomer (used in RIM technology), have been studied using multiple linear regression analysis. Using the statistical Student-*t* test, the importance of the above parameters has been established. It has been found that the moulded density has the biggest influence on the tensile strength; so that the tensile strength is increased by the ethylene glycol and rigid polyol content, while triethanol amine reduces it. All the chain extenders studied have a negative influence on the elongation at break. Similarly the moulded density and the ethylene glycol content have a beneficial effect on the tear resistance, while triethanol amine and the rigid polyol reduce this property.

(Keywords: polyurethane elastomers; microcellular polyurethanes; multiple regression analysis; RIM materials; chain extender effect; mechanical properties)

INTRODUCTION

The use of polyurethane microcellular elastomers in the automotive industry has increased since the rapid development of the reaction injection moulding (RIM) technology. A complete description of the RIM process is given elsewhere[1,2]. RIM chemistry is based on the reactions of polyols derived from propylene and ethylene oxide, chain extenders and MDI type isocyanates, as well as catalyst and blowing agents.

The polymers obtained are block copolymers consisting of alternating blocks of flexible chains (soft segments) and relatively rigid blocks (hard segments). The soft segments are interconnected by relatively low mobile aromatic urethane hard segments. Because of the incompatibility of these two segments, the material often undergoes microphase separation, with the resultant formation of soft and hard domains. This domain structure is responsible for the unusual mechanical properties of these materials; the degree of phase separation having an important influence on these properties. Many studies[3-7], have been performed to elucidate this morphology and several phase segregation models have been proposed.

A systematic investigation[8] of the effect of aliphatic diols on the final properties of a polycaprolactone based system, shows that the chain extenders affect these properties. The hard segment content also influences the physical, dynamic-mechanical and thermal properties of these systems[9]. O'Connor *et al.*[10] using graphical multiple regression analysis have studied the influence of ethylene glycol and a rigid polyol on the properties of RIM elastomers. The presence of rigid polyols leads to an increase in the hardness and tensile strength but it reduces the elongation at break. It also improves the processing characteristics of the formulation.

In a previous study, using multiple regression analysis[11], we established the influence of constitutional factors on tensile strength and elongation at break of poly(ethylene–butylene adipate) based systems.

The aim of the work presented here was to study the influence of chain extenders on the tensile strength (*TS*), elongation at break (*EB*) and tear resistance (*T*) of the polyurethane microcellular elastomers used in RIM technology, by multivariable linear regression analysis.

EXPERIMENTAL

The materials used in this study were: glycerine, propylene and ethylene oxide based polyether polyol (PPEO) with 33.6 mg KOH g^{-1} and of a functionality ~3, MDI as isocyanate, DABCO 33 LV (Houdry Hüls) as catalyst and Freon 11 (HOECHST) as blowing agent. The rigid polyol was a propoxylated saccharose (PPZ) with 558 mg KOH g^{-1} and of a functionality ~8. Ethylene glycol (EG) and triethanol amine (TEA) were used as chain extenders/crosslinkers. The concentration range of the reagents is presented in *Table 1*.

The accurately weighed quantities of reagents, mixed and the material poured into a mould of dimensions 300 × 150 × 30 mm.

The tensile strength and elongation at break have been measured according to ASTM D638. The tear resistance was determined using specimens (20 × 20 × 100 mm) cut (in the middle) 50 mm along the long axes. The tear force was recorded during the test, and the tear resistance calculated, by dividing the maximal recorded force by the breadth of specimen.

All the mechanical results represent the mean value of 12 measurements. The standard deviation from the mean values was less than 8% in the case of *TS* and *EB* and less

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Table 1 Concentration range of the reagents

Material	Parts by weight
PPEO	100
EG	9–14
TEA	1–5
PPZ	2–7
DABCO 33 LV	0.6
Freon 11	20
MDI	index 100

than 11% in the case of *T*.

The multiple linear regression analysis was used to estimate the PPZ, EG and TEA influence. *TS*, *EB* and *T*, as dependent known variables (*P*) can be expressed as a function of PPZ, EG and TEA composition (x_k) and cellular character (y_{i-q}) of the microcellular system by:

$$P = A_0 + \sum A_k x_k + \sum A_i y_{i-q}$$

$$k = 1,2,3,\ldots,q \qquad i = q+1, q+2, q+3, \ldots, m$$

The moulded density (*d*) was used as cellular characterization parameter. The regression coefficients A_k and A_i were statistically determined using the principle of least squares[11,12]. The statistical parameters to estimate the correlational equation were: multiple correlation coefficient (*R*), the Fischer statistic (*F*)[11] and explained variance coefficient (*EV*)[13]. The statistical 'Students-*t*' test has been used to evaluate the importance of the parameters x_k and y_{i-q}[11].

RESULTS AND DISCUSSION

The variation of mechanical properties (*TS*, *EB* and *T*) and the cellular character (y_{i-q}) with the chain extender quantities (x_k) used, is summarized in *Table 2*. The equations of multiple linear regression analysis are:

$$TS = 0.092\mathrm{EG} - 0.144\mathrm{TEA} + 0.057\mathrm{PPZ} + 0.028d - 1.72$$

$$R = 0.873 \qquad F = 26.9 \qquad EV = 0.74$$

$$EB = -4.34\mathrm{EG} - 9.82\mathrm{TEA} - 1.23\mathrm{PPZ} + 0.264d + 121.3$$

$$R = 0.921 \qquad F = 46.1 \qquad EV = 0.83$$

$$T = 2.14\mathrm{EG} - 3.46\mathrm{TEA} - 0.43\mathrm{PPZ} + 0.0047d - 8.29$$

$$R = 0.819 \qquad F = 17.1 \qquad EV = 0.64$$

The large values of *R*, *F* and *EV* show a high significance level of the obtained relations. The importance of the influence of parameters x_k and y_{i-q} characterized by the statistical 'Student-*t*' test is presented in *Table 3*. The importance of these factors is estimated by the increasing order of the *t* magnitudes[11].

The influence of ethylene glycol which is a bifunctional chain extender, leads to a formation of phase separated hard segments. Thus, as the hard segment concentration increases *TS* increases as well, which is in accordance with the widely accepted idea, that the hard segment domains act as a reinforcing particle in the soft segment matrix[14,15]. The same results were obtained in the case of other polyether urethanes[9,10]. This reinforcing effect also leads to improving tear resistance. It is plausible to suppose that, the negative effect of EG on elongation at break, is due to the building up of a crosslinked graft structure of the hard segments, because of the functionality of PPEO higher than 2. This structure assumes the diminuation and/or reduction of the motion and elongation of the soft segment into the stretch direction, thus lowering the active elongation space.

The influence of triethanol amine has a negative effect on all of the studied properties (*TS*, *EB*, *T*). The tri-

Table 2 Variation of tensile strength (*TS*), elongation at break (*EB*) and tear resistance (*T*) according to the chemical composition and moulded density (*d*)

n	*TS* (dN cm^{-2})	*T* (dN m^{-1})	*EB* %	TEA	EG	PPZ	*d* (kg m^{-3})
1	1.28	42.3	100	1	9	2	89
2	1.42	53.7	88	1	10	2	93
3	2.39	53.6	91	1	12	2	111
4	1.87	48.7	73	1	14	2	81
5	1.43	39.1	83	2	9	2	98
6	1.76	40.3	81	2	10	2	100
7	1.81	54.2	69	2	12	2	94
8	1.96	49.3	64	2	14	2	94
9	1.54	35.2	58	4	9	2	103
10	1.60	34.6	65	4	10	2	101
11	1.83	37.9	45	4	12	2	106
12	1.58	37.2	37	4	14	2	91
13	1.27	36.6	88	1	9	3	71
14	1.40	33.3	81	1	9	4	82
15	1.24	27.9	94	1	9	5	76
16	1.03	29.8	81	1	9	7	67
17	1.30	33.5	88	1	10	3	81
18	1.59	32.3	91	1	10	4	80
19	1.44	36.6	78	1	10	5	81
20	1.41	31.6	61	1	10	7	73
21	1.56	30.1	79	1	12	3	79
22	1.98	37.2	79	1	12	4	88
23	1.86	41.1	75	1	12	5	80
24	1.87	39.3	71	1	12	7	80
25	1.43	31.1	75	2	9	3	89
26	1.83	30.4	83	3	9	3	96
27	1.91	31.0	71	4	9	3	109
28	1.37	26.7	58	5	9	3	93
29	1.72	36.1	79	2	9	5	92
30	1.79	27.1	71	3	9	5	95
31	1.59	25.9	67	4	9	5	95
32	1.38	21.5	54	5	9	5	98
33	1.69	31.0	71	2	9	7	85
34	1.62	30.9	71	3	9	7	92
35	1.95	32.9	71	4	9	7	108
36	1.59	28.9	50	5	9	7	107
37	2.46	36.9	67	2	12	3	113
38	1.82	34.0	71	3	12	3	96
39	1.89	35.3	63	4	12	3	96
40	1.22	30.4	38	5	12	3	90
41	2.26	41.3	71	2	12	5	96
42	2.60	46.0	63	3	12	5	115
43	1.76	32.8	38	4	12	5	108
44	1.32	33.7	38	5	12	5	92
45	2.38	40.6	75	2	12	7	95
46	2.73	46.9	67	3	12	7	109
47	1.86	37.8	48	4	12	7	96
48	1.74	44.3	40	5	12	7	118

Table 3 Statistical 'Student-*t*' test values of EG, TEA, PPZ and *d* on *TS*, *EB* and *T*

	TS (dN cm^{-2})	*EB* (%)	*T* (dN m^{-1})
EG	5.37	7.41	5.08
TEA	7.55	15.08	7.41
PPZ	3.91	2.45	1.30
Moulded density (*d*)	11.98	3.32	6.16

dimensional crosslinkages with TEA, lead to the impairment of the ordered and/or crystalline hard segment domains formation, favouring their dispersion into the soft matrix. This hard segment structure, leads to the formation of stress concentration points, which tend to interfere with the crack propagation step of the failure mechanism[16]. Thus a higher content of TEA has a reducing effect on tensile strength and tear resistance. Furthermore, this dispersed structure of the hard segment domains will reduce the active elongation space of the soft segment domains, which also explains the *EB* diminution with increases in the TEA content. The same results have been reported by Estes *et al.*[17], so that triol crosslinking causes a decrease in *TS* and *EB*. This is because triol may not favour the formation of domain, which appears to be disrupted by such crosslinking. TEA produces a greater diminuation than EG, suggesting that, the reduction produced by the hard segment dispersion, on the soft segment motion or the elongation into the stretch direction, is more important, than the same effect of the hard segments built up on EG. Thus, it is plausible to suppose that the elongation phenomenon of these materials depend on the motion/elongation possibility of the soft segment into the stretch direction.

The influence of the rigid polyol has a positive effect on *TS* but it reduces *EB* and *T*. In the soft matrix the hard segment build up in the PPZ is probably large enough to act as a reinforcing filler, the cyclic structure of PPZ also produces rigidity in the hard segment. But the rigid polyol disrupts the crystallinity (or ordering in the hard segments[10]); favouring crack propagation in the failure mechanism[16]. This leads to an overall increase in the TS which is less important than the influence of EG. The reduction in tear resistance by PPZ is also due to the increase in rigidity (crack propagation becoming more important). The reduction in EB is also shown in TEA where the polyfunctionality of PPZ permits more flexible soft segment motion/elongation in the stretch direction. The same effect of a rigid polyol has been observed with RIM formulations[10].

The influence of the cellular character (*moulded density*) has a beneficial effect on the mechanical properties in all cases, which suggests the important role of the cellular structure. The most important influence is observed with *TS*, which is expected according to the fracture mechanism[18,19]. The less important effect of moulded density on *EB* is in accordance with our previous results[11]. The tear resistance, similarly depends to a great extent on the moulded density, which shows the important effect of the cellular structure on the crack propagation resistance of the material.

CONCLUSIONS

In the case of polyols with a functionality greater than 2, chain extenders have a negative influence on the elongation at break, while the moulded density increases this characteristic. These results suggest that this phenomenon is essentially due to the motion/elongation of the soft segment and cellular system into the stretch direction.

The tensile strength depends to a great extent on the moulded density. The reinforcing effect of the hard segments built up on EG and PPZ, also have a beneficial influence of *TS*. TEA has a negative effect on this property (because it does not favour domain formation), which appears to be disrupted by tridimensional crosslinking.

Tear resistance increases with the moulded density, as well as with the ordered hard segment content observed by the positive influence of EG. TEA, which favours the crack propagation in the material, will reduce this property. Similarly, the rigid polyol reduces *T*, but this influence is less important than that of TEA, which is due to its reinforcing effect as well. The TEA and PPZ effects suggest that the crack propagation is the predominant phenomenon in the tear mechanism.

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