Polyurethane microcellular elastomers: 1. Effect of chemical composition on tensile strength and elongation at break of poly(ethylene–butylene adipate) based systems

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(*Received* 29 *September* 1982; *revised* 20 *January* 1983)

The relationships between tensile strength and elongation at break and the chemical composition of a microcellular elastomer used in shoe sole technology have been calculated using multiple linear regression analysis. Using the statistical Student's test, the importance of the factors that influence the above characteristics have been established. It has been found that the moulded density has the major influence on the tensile strength while the elongation at break depends to a great extent on the hard-segment dispersion into the soft matrix, as indicated by the influence of the water contents and the quasi-prepolymer index (I_{NCO}). Hydroxyl number in the usual range of 52–61 mg KOH/g has no influence on the above characteristics.

Keywords Polyurethane elastomer; microcellular polyurethane; shoe sole material; multiple linear regression; polyurethane mechanical properties; liquid reaction moulding polyurethane

INTRODUCTION

Microcellular polyurethanes for shoe soles are of both the polyester and polyether types. Polyester systems are usually based on quasi-prepolymers (obtained from *p,p'*-diphenylmethane diisocyanate (MDI) and polyester in the molar ratio of 10–13 : 1), polyester, chain extender (diol or diamine), catalyst, surfactants and water to produce CO_2 — the blowing agent.

These materials are block copolymers, consisting of alternating blocks of flexible chains (soft segments) and highly polar, relatively rigid blocks (hard segments). The soft segment is the aliphatic polyester, while the hard segment is formed in the reaction of the quasi-prepolymer's free MDI and chain extender. Because of the incompatibility of hard and soft segments, the material often undergoes microphase separation, clustering into hard and soft domains. Many studies[1–6] have been performed to analyse the nature of domain structures and the factors that influence this morphology. Delides and Pethrick[7], using ultrasonic and dielectric studies, have shown the presence of an 'interfacial' domain between the soft segments and the ordered hard segments.

The presence of crosslinks when the phases are in a mixed state at elevated temperature hinders complete phase segregation at lower temperature, which has an important influence on the material's room-temperature properties[8].

Polyurethane systems using CO_2 as blowing agent assume the existence of crosslinks and/or branches formed by biuret and/or allophanate linkages[9].

In this study, we propose to find the factors influencing the tensile strength and elongation at break of the polyurethane microcellular elastomer systems used in shoe sole technology, and their importance, by multivariable linear regression analysis.

EXPERIMENTAL

The materials used in this study were a linear polyester, poly(ethylene–butylene adipate) (PEBA) with hydroxyl number in the range 52–61 mg KOH/g, PEBA and MDI based quasi-prepolymer (free NCO 19.1%), 1,4-butanediol (BASF) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Houdry–Hüls). The concentration ranges of the reagents are presented in *Table 1.*

The polyol blend (PEBA, 1,4-butanediol, DABCO and water) and quasi-prepolymer have been processed on a two-component metering system with mixing characteristics of 3000 rpm and 2.3 kW, output 50 g s^{-1}, using liquid reaction moulding.

Tensile strength and elongation at break have been measured according to ASTM D 638, on samples cut from plates of 300 × 100 × 8 mm, obtained by pouring into a 40°C mould with the above-mentioned metering system. The free rise density has been measured by pouring into a 600 cm^3 open cup. The free rise hardness has been checked on the upper, freely risen, surface of the foam in that cup.

THE MATHEMATICAL MODEL

We suppose that the tensile strength and elongation at break, which we shall call the dependent known variables (P), depend on the chemical composition (x_k) and cellular

0032-3861/83/101321–06$03.00

Table 1 The concentration ranges of the reagents

Material	Parts by weight
PEBA	100
1,4-Butanediol	13.5–19.8
DABCO	0.6
H_2O	0.4–0.6
Quasi-prepolymer index	92–101

character (y_i) of the microcellular elastomer, as known variables or variates. Thus we can write:

$$f(P)=A_0+\sum A_k f(x_k)+\sum A_i f(y_{i-q}) \tag{1}$$

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

where f represents the linear, reciprocal, logarithmic and minus logarithmic transformations of the dependent known variables (P) and variates (x_k, y_{i-q}); x_k is the kth chemical constituent and x is its concentration; and y_{i-q} is the (i-q)th parameter concerning the cellular structure of the material and y is its value.

The regression coefficients A_k and A_i become the unknown parameters that can be statistically determined, by using the principle of least squares[10], which leads to the system of equations:

$$\mathbf{KQ}=\mathbf{M}$$

where

$$\mathbf{K}=\begin{bmatrix} n\sum f(x_1)_j\sum f(x_2)_j\ldots\sum f(y_1)_j\ldots\sum f(y_{m-q})_j \\ \sum f(x_1)_j^2\sum f(x_1)_j f(x_2)_j\ldots\sum f(x_1)_j f(y_1)_j\ldots\sum f(x_1)_j f(y_{m-q})_j \\ \vdots \\ \sum f(y_1)_j f(y_{m-q})_j \\ \text{symmetric}\qquad\qquad\vdots \\ \sum f(y_{m-q})_j^2 \end{bmatrix}$$

$$\mathbf{Q}=\begin{bmatrix} A_0 \\ A_1 \\ A_2 \\ \vdots \\ A_{q+1} \\ \vdots \\ A_m \end{bmatrix}\quad \mathbf{M}=\begin{bmatrix} \sum^{f}(P)_j \\ \sum f(x_1)_j f(P)_j \\ \sum f(x_2)_j f(P)_j \\ \vdots \\ \sum f(y_1)_j f(P)_j \\ \vdots \\ \sum f(y_{m-q})_j f(P)_j \end{bmatrix}$$

where $j=1,2,3,\ldots,n$.

In every case the symbol $\sum$ indicates summation over all the n measurements according to the chemical composition. The statistical parameters established to estimate the relation are:

(1) The multiple correlation coefficient R, which is a measure of the significance of the linear relationship between the variate functions, $f(x_k)$ and $f(y_{i-q})$, and the dependent known variable function, $f(P)$:

$$R^2=1-\frac{S}{\sum f(P)_j^2-(\sum f(P)_j)^2/n} \tag{2}$$

where

$$S=\sum[f(P)_j-f(\hat{P})_j]^2$$

S is the sum of squared errors or deviations between measured $f(P)$ and calculated $f(\hat{P})$ quantities, over all the n measurements. The equations characterized by $R^2\leqslant 0.4$ represent no relationship between the variates x_k and y_{i-q} and variable P.[11]

(2) The Fisher statistics F, in order to test the significance of the multiple correlation coefficient:

$$F=\frac{n-m-2}{m+1}\times\frac{R^2}{1-R^2} \tag{3}$$

In this case F signifies the F-distribution with $n-m-2$ and $m+1$ degrees of freedom. The quality of the relationship depends on the significance level of F.[12]

(3) The significance level of the regression coefficients A_k and A_i has been estimated by the Student's t statistic:

$$t=\frac{A_{k(i)}}{\sigma\sqrt{d_{ee}}} \tag{4}$$

in which d_{ee} are the diagonal elements of the $\mathbf{K}^{-1}$ matrix, while $\sigma^2=S/(n-m-2)$. A significance level lower than 90% associated with the regression coefficient $A_{k(i)}$ through the t parameter indicates no influence of the variates x_k or y_{i-q} on the variable P, and thus it can be neglected.

RESULTS AND DISCUSSION

The variation of tensile strength (*TS*) and elongation at break (*EB*) depending on the chemical composition (x_k) and foam properties (y_{i-q}) are summarized in *Table 2*. The correlation of *TS* or *EB* with only one parameter x_k (*Table 3*) leads to a meaningless relationship. The R and F values obtained are presented in *Table 4*, taking into consideration all the parameters x_k. In the case of *TS* there is also a meaningless relationship, while in the case of *EB* a poor correlation is obtained. These results suggest that the cellular character influences these characteristics as well. In this context the y_{i-q} parameters have been introduced (*Table 2*) as a potential characterization of the cellular structure. The correlations carried out with the parameters y_{i-q} lead to similar statistical results as in the case of the parameters x_k (*Tables 5* and *6*).

We can therefore state that both tensile strength and elongation at break depend on the chemical composition of the polymer and it's cellular structure. The regression coefficients A_k and A_i and the statistical parameters of the correlational analysis are presented in *Tables 7* and *8*. In both cases, the largest values of R and F indicate that the best fit is obtained for a linear function of the parameters:

$$f(P)=P;\quad f(x_k)=x_k;\quad f(y_{i-q})=y_{i-q}$$

Considering the significance level of the statistical Student's t test, it can be observed that the tensile strength does not depend on the free rise hardness (y_2), free rise density (y_3) or the OH number of the polyester (x_4).

Table 2 Variation of tensile strength (*TS*) and elongation at break (*EB*) according to the chemical composition

n	*TS* (dN cm^{-2})	*EB* (%)	x_1	x_2	x_3	x_4	y_1	y_2	y_3
1	57.1	404	0.40	15.3	95.5	52.0	0.563	42.7	0.349
2	61.6	398	0.40	15.3	99.0	52.0	0.543	38.7	0.313
3	59.6	395	0.44	16.5	94.9	52.0	0.590	43.3	0.323
4	63.7	388	0.44	16.5	98.4	52.0	0.593	44.7	0.373
5	68.5	403	0.44	16.5	99.8	52.0	0.635	45.3	0.361
6	52.1	358	0.56	18.0	92.7	52.0	0.541	50.3	0.296
7	57.6	363	0.56	18.0	96.6	52.0	0.520	44.7	0.316
8	46.9	287	0.56	18.0	95.7	52.0	0.515	44.0	0.296
9	49.5	330	0.56	18.0	99.5	52.0	0.514	41.0	0.278
10	38.8	397	0.47	15.4	92.0	56.8	0.551	52.0	0.361
11	56.9	387	0.47	15.4	94.5	56.8	0.588	50.0	0.360
12	59.7	381	0.47	15.4	96.3	56.8	0.552	45.7	0.322
13	48.9	371	0.47	15.4	98.9	56.8	0.482	40.0	0.307
14	45.8	369	0.49	17.0	94.3	56.8	0.495	42.3	0.276
15	61.0	370	0.49	17.0	99.0	56.8	0.554	41.7	0.327
16	53.6	311	0.49	17.0	99.7	56.8	0.479	40.3	0.293
17	53.8	345	0.52	19.8	96.5	56.8	0.483	50.6	0.291
18	45.5	308	0.52	19.8	98.5	56.8	0.425	45.6	0.305
19	52.2	370	0.47	13.5	95.6	60.8	0.498	41.0	0.321
20	53.0	342	0.47	13.5	98.8	60.8	0.499	42.3	0.294
21	54.9	351	0.47	13.5	101.1	60.8	0.481	44.0	0.302
22	53.4	387	0.49	15.5	95.3	60.8	0.533	49.0	0.351
23	49.3	297	0.49	15.5	98.0	60.8	0.479	43.3	0.299
24	50.9	278	0.49	15.5	99.8	60.8	0.507	40.7	0.297
25	49.0	279	0.59	18.5	97.2	60.8	0.460	49.7	0.270
26	49.7	295	0.59	18.5	98.7	60.8	0.472	45.0	0.291
27	55.1	355	0.48	14.5	96.0	54.0	0.549	41.0	0.340
28	54.7	317	0.48	14.5	98.2	54.0	0.536	39.7	0.327
29	52.2	339	0.48	14.5	101.0	54.0	0.513	39.3	0.303
30	51.6	329	0.50	15.5	95.4	54.0	0.507	38.3	0.306
31	52.8	293	0.50	15.5	97.4	54.0	0.483	37.7	0.297
32	51.3	288	0.50	15.5	100.0	54.0	0.482	38.0	0.291

x_1 = parts by weight water
x_2 = parts by weight 1,4-butanediol
x_3 = quasi-prepolymer index
x_4 = PEBA hydroxyl number (mg KOH/g)
y_1 = moulded density (g cm^{-3})
y_2 = free rise hardness (°Sh A)
y_3 = free rise density (g cm^{-3})

Table 3 Correlation coefficients (R^2) obtained by the correlation of *TS* or *EB* with the parameters x_k

	TS				*EB*			
f	x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Linear	0.229	0.024	0.071	0.130	0.413	0.064	0.131	0.085
Reciprocal	0.197	0.021	0.098	0.108	0.397	0.057	0.127	0.082
Logarithmic	0.218	0.023	0.085	0.119	0.409	0.061	0.135	0.084
Minus logarithmic	0.218	0.023	0.088	0.118	0.408	0.061	0.127	0.082

Similarly, the elongation at break is not influenced by the free rise density (y_3), the 1,4-butanediol contents (x_2) or the OH number of the polyester (x_4).

The correlation parameters obtained by neglecting the above parameters are summarized in *Tables 9* and *10*. Again, the best fit is obtained in the case of a linear function of the parameters. The increase in magnitude of F shows an enlargement of the significance of the relation obtained.

The importance of the influencing factors is estimated by the increasing order of the $t_{k(i)}$ magnitudes. Thus, tensile strength depends to the largest extent on the moulded density, the water contents having the least influence, whereas it has the largest influence on the elongation at break.

Table 4 Correlational data of *TS* and *EB* considering all the parameters x_k

	TS		*EB*	
f	R	F	R	F
Linear	0.631	3.4	0.776	7.8
Reciprocal	0.603	3.0	0.749	6.6
Logarithmic	0.619	3.2	0.770	7.6
Minus logarithmic	0.619	3.2	0.769	7.6

An increase of the water concentration and the quasi-prepolymer index leads to a decrease of the elongation at break. A higher content of water and isocyanate assumes the setting-up of more NH groups liable to build up

Table 5 Correlation coefficients (R^2) obtained by the correlation of *TS* or *EB* with the parameters y_{i-q}

	TS			*EB*		
f	y_1	y_2	y_3	y_1	y_2	y_3
Linear	0.444	0.016	0.217	0.515	0.067	0.490
Reciprocal	0.311	0.027	0.143	0.443	0.062	0.437
Logarithmic	0.378	0.021	0.181	0.496	0.066	0.476
Minus logarithmic	0.377	0.020	0.180	0.494	0.067	0.474

hydrogen bonding and/or chemical crosslinks by allophanate and/or biuret, which leads to impairment of the ability of the material to reach complete phase separation at room temperature[8,13,14], referring to the mixed state of the domains at the reaction temperature (140°–150°C). The dispersed hard blocks in the soft-segment matrix reduce the latter's mobility, lowering the active elongation space, which finally leads to the decrease of the elongation at break.

Table 6 Correlational data of *TS* and *EB* considering all the parameters y_{i-q}

	TS		*EB*	
f	*R*	*F*	*R*	*F*
Linear	0.671	5.5	0.759	9.2
Reciprocal	0.611	4.0	0.725	7.5
Logarithmic	0.663	5.3	0.750	8.7
Minus logarithmic	0.661	5.2	0.749	8.6

It is difficult to attribute physical meaning to the free rise hardness, but considering the formation mechanism of these systems[15], as well as the higher reaction rate of addition rather than of CO_2 formation[16], the assumption that it depends on the cellular structure formed during the reactions is plausible. The increase of the elongation at break with the moulded density and free rise hardness shows an important influence of the cellular structure on this property.

The independence of the elongation at break from the relatively small variation of the hard-segment content, expressed as the negligible influence of 1,4-butanediol, suggests the major role of the soft domains in this phenomenon. The same results were obtained in the case of a polyether based polyurethane[17] in the range of 30–40% hard-segment content.

Table 7 Results of the correlational analysis of the tensile strength (*TS*) (*k* and *i* according to equation (1) with $q = 4$)

f(P)	*k(i)*	$A_{k(i)}$	Standard error	$t_{k(i)}$ (eq. (4))	Significance level of $A_{k(i)}$ (%)	*R* (eq. (2))	*F* (eq. (3))
TS	0	−110.4	0.66	166.3		0.826	6.19
	1	−24.0	14.4	1.67	>90.0		
	2	0.89	0.40	2.23	>97.5		
	3	1.06	0.29	3.66	>99.5		
	4	0.19	0.20	0.97	<90.0		
	5	112.1	15.0	7.47	>99.5		
	6	−0.16	0.17	0.98	<90.0		
	7	−13.2	24.9	0.53	<70.0		
1/*TS*	0	−0.042	0.0003	150.8		0.757	3.87
	1	−0.0018	0.0015	1.20	<90.0		
	2	0.058	0.0445	1.30	<90.0		
	3	4.24	1.15	3.69	>99.5		
	4	0.102	0.265	0.38	<70.0		
	5	0.009	0.00017	5.37	>99.5		
	6	−0.051	0.138	0.37	<70.0		
	7	−0.0003	0.0011	0.31	<70.0		
log *TS*	0	−2.94	0.006	500.2		0.793	4.89
	1	−0.21	0.14	1.46	>90.0		
	2	0.24	0.13	1.83	>95.0		
	3	2.22	0.57	3.87	>99.5		
	4	0.18	0.23	0.79	<80.0		
	5	1.04	0.16	6.51	>99.5		
	6	−0.09	0.15	0.61	<80.0		
	7	−0.073	0.16	0.45	<70.0		
−log *TS*	0	2.91	0.006	496.2		0.793	4.89
	1	−0.21	0.14	1.46	>90.0		
	2	0.25	0.13	1.86	>95.0		
	3	2.20	0.57	3.84	>99.5		
	4	0.19	0.23	0.81	<80.0		
	5	1.05	0.16	6.52	>99.5		
	6	−0.10	0.15	0.65	<80.0		
	7	−0.07	0.16	0.45	<70.0		

Table 8 Results of the correlational analysis of the elongation at break (*EB*) (*k* and *i* according to equation (1) with $q = 4$)

$f(P)$	$k(i)$	$A_{k(i)}$	Standard error	$t_{k(i)}$ (eq. (4))	Significance level of $A_{k(i)}$ (%)	R (eq. (2))	F (eq. (3))
EB	0	625.1	4.28	146.0		0.852	7.63
	1	–497.3	92.6	5.37	>99.5		
	2	0.64	2.56	0.25	<60.0		
	3	–2.62	1.87	1.40	>90.0		
	4	–0.98	1.28	0.77	<80.0		
	5	253.9	96.7	2.62	>99.0		
	6	2.91	1.08	2.69	>99.0		
	7	23.3	160.3	0.15	<60.0		
1/*EB*	0	0.0054	0.00004	132.8		0.825	6.11
	1	–0.0009	0.0002	4.36	>99.5		
	2	–0.0037	0.0065	0.57	<80.0		
	3	–0.199	0.168	1.18	<90.0		
	4	–0.041	0.0386	1.06	<90.0		
	5	0.0005	0.0003	1.85	>95.0		
	6	0.0546	0.02	2.71	>99.0		
	7	0.0001	0.0002	0.48	<70.0		
log *EB*	0	3.82	0.006	670.1		0.840	6.89
	1	–0.69	0.141	4.91	>99.5		
	2	–0.025	0.129	0.19	<60.0		
	3	–0.81	0.556	1.46	>90.0		
	4	–0.021	0.221	0.95	<90.0		
	5	0.33	0.156	2.13	>97.5		
	6	0.39	0.147	2.65	>99.0		
	7	0.05	0.157	0.32	<70.0		
–log *EB*	0	–3.64	0.006	638.9		0.840	6.89
	1	–0.69	0.140	4.92	>99.5		
	2	–0.028	0.129	0.22	<60.0		
	3	–0.73	0.556	1.32	~90.0		
	4	–0.21	0.221	0.97	<90.0		
	5	0.33	0.156	2.15	>97.5		
	6	0.41	0.147	2.77	~99.5		
	7	0.046	0.157	0.29	~60.0		

Table 9 Correlational data of the tensile strength (*TS*) considering the significant parameters (*k* and *i* according to equation (1) with $q = 4$)

$f(P)$	$k(i)$	$A_{k(i)}$	Standard error	$t_{k(i)}$ (eq. (4))	Significance level of $A_{k(i)}$ (%)	R (eq. (2))	F (eq. (3))
TS	0	–111.8	0.63	176.7		0.822	10.85
	1	–22.1	13.7	1.61	>90.0		
	2	0.61	0.38	1.62	>90.0		
	3	1.19	0.28	4.31	>99.5		
	5	96.5	14.3	6.75	>99.5		
1/*TS*	0	–0.0427	0.0003	161.3		0.756	6.94
	1	–0.0016	0.0014	1.16	<90.0		
	2	0.0459	0.0421	1.09	<90.0		
	3	4.43	1.09	4.08	>99.5		
	5	0.0085	0.0016	5.22	>99.5		
log *TS*	0	–2.982	0.0056	535.6		0.791	8.69
	1	–0.187	0.137	1.36	>90.0		
	2	0.175	0.126	1.39	>90.0		
	3	2.364	0.543	4.35	>99.5		
	5	0.916	0.152	6.02	>99.5		
–log *TS*	0	–2.962	0.0056	532.0		0.791	8.69
	1	–0.188	0.137	1.37	>90.0		
	2	0.175	0.126	1.39	>90.0		
	3	2.354	0.543	4.33	>99.5		
	5	0.914	0.152	6.01	>99.5		

Table 10 Correlational data of the elongation at break (*EB*) considering the significant parameters (*k* and *i* according to equation (1) with $q = 4$)

$f(P)$	$k(i)$	$A_{k(i)}$	Standard error	$t_{k(i)}$ (eq. (4))	Significance level of $A_{k(i)}$ (%)	R (eq. (2))	F (eq. (3))
EB	0	576.9	4.08	141.6		0.849	13.42
	1	−465.7	88.19	5.28	>99.5		
	3	−2.86	1.78	1.60	>90.0		
	5	315.5	92.05	3.43	>99.5		
	6	2.60	1.03	2.52	>99.0		
1/*EB*	0	0.0049	0.00003	127.0		0.821	10.73
	1	−0.0010	0.0002	4.81	>99.5		
	3	−0.2316	0.1596	1.45	>90.0		
	5	0.0007	0.0002	2.91	>99.5		
	6	0.00440	0.0192	2.30	>97.5		
log *EB*	0	3.724	0.0054	687.3		0.837	12.17
	1	−0.683	0.134	5.11	>99.5		
	3	−0.907	0.529	1.71	~95.0		
	5	0.460	0.148	3.11	>99.5		
	6	0.327	0.140	2.34	>97.5		
−log *EB*	0	−3.544	0.0054	654.2		0.837	12.17
	1	−0.683	0.134	5.11	>99.5		
	3	−0.827	0.529	1.56	>90.0		
	5	0.462	0.148	3.13	>99.5		
	6	0.341	0.140	2.44	>97.5		

The most important factor that influences the tensile strength is the moulded density, as expected according to the fracture mechanism[18].

The hard-segment concentration has a positive effect on the tensile strength observed by its increasing with the 1,4-butanediol and isocyanate contents, which is in agreement with the widely accepted idea that the rigid domains reinforce the elastomeric matrix by functioning as filler particles[19,20].

The presence of water in the system leads to the formation of urea type hard segments, which form quasi-amorphous domains[21]. Polyurethaneureas exhibit a mixing of hard segments into the soft matrix[22]. Thus, the reducing effect of the water content is due to the decrease of the hard domain crystallinity as well as its dispersion into the soft matrix, which produces stress concentrations in these points, leading to critical fracture regions.

Variation within the usual range of hydroxyl number (50–60 mg KOH/g) influences neither the tensile strength nor elongation at break.

CONCLUSIONS

The important influence of hard-segment dispersion into the soft matrix on the elongation at break, observed by its dependence on the water and isocyanate contents, its independence from the variation of the hard-segment content, as well as the significant effect of the cellular structure, allows us to suppose that this phenomenon is essentially due to the elongation and orientation of the soft segment and cellular system in the stretch direction.

The tensile strength depends to the greatest extent on the moulded density. An important positive effect of the hard-segment content can also be noted. The water content has a less important influence compared to its effect on the elongation at break.

The hydroxyl number of the polyester, in the limits of 52–61 mg KOH/g, has no influence on the properties studied, which is useful information for the industrial application of this material.

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