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DMTA STUDY OF THE URETHANE NETWORK IN RUBBER WASTE–URETHANE COMPOSITES

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The supermolecular structures of rubber waste–urethane composites based on results of mechanical spectroscopy are discussed. The results give a broader understanding of the relation between the processing history and the morphology in the resultant engineering products. The effect of the kind and amount of urethane prepolymers on the formation of the urethane network, and hence on the properties of potential commercial products, is presented. DMTA study showed some differences in the measured parameters of all studied samples. The real and imaginary parts of Young's modulus reflected the contents variety. Simple statistic methods were applied for the description of the behaviour of the measured parameters.

Keywords: *DMTA, rubber waste–urethane composites, structural relaxation, tyre waste*

Introduction

Every year used tyres constitute about 75% of the rubber material waste in Poland, that is more than 100000 tons. Used rubber may replace conventional fuel and owing to its low price, it can improve the economic effectiveness of combustion. Energy recovery by combustion of car tyres allows for rapid management of rubber waste. However, it is well-known that all kinds of waste including rubber tyre waste are better modified and reused. This modification does not much extra energy, work and materials. Moreover, that such a proceeding does not limit the possibility of combustion of the modified waste in general. One possible way of rubber waste management is to break up the waste rubber and to use the obtained fine rubber, rubber granulate or rubber dust as a valuable additive to raw materials for production of composites made from rubber and different kinds of elastomers [1–4].

An attempt to solve the problem of the rubber waste management has been made by studying the properties of rubber waste–urethane composites in our laboratory [1, 5, 6]. The composites were obtained from car tyre granulate, fine rubber and polyurethane: unary (one-component) prepolymers with similar hardness, i.e. Monothane A50, Monothane A60, and binary (two-component) prepolymer Chemolan M. The obtained results pointed to the non-homogenous structure of the composites and their good mechanical properties. It was also found that a probable reaction of polyurethane with rubber could also occur. This conclusion was based on the changes of the T_g values of rubber and polyurethanes in comparison with their T_gs values found in the composites. However, the postulate concerning this reaction would require a more detailed study, e.g. investigations of the mechanical properties of the composite with the use of a DMTA method. This method could give a broader understanding of the relationship between the processing history and the morphology of the resultant engineering products. A wide range of conditions applied to the material preparation make it possible to obtain specimens of different morphology, resulting from the arrangement of macromolecules and the various composite contents.

Investigations of polymers in a wide temperature range show that these materials exhibit a complex dynamic mechanical behaviour. This behaviour becomes more complex for a polymeric system composed of several polymer components. One possibility is to form a heterogeneous structure with a phase separation of the components. Hence, the formation of domains takes place and the material exhibits the feature of each component. However, homogenous polymeric material might also be obtained. Then, one supermolecular structure is formed due to either a chemical reaction (copolymers) or a physical process (blends). It is very easy to recognise which structure has been obtained. Heterogeneity is characterised in experiments by several glass transitions and structural relaxations. The number of relaxations and transitions

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depends on the number of components. Homogeneity, on the other hand, has one glass transition and one structural relaxation [7–9]. However, in the last decade it has been shown that semi-crystalline or liquid-crystalline polymeric systems, being chemically homogenous, also exhibit two glass transitions and two structural relaxations due to the existence of two amorphous fractions (‘real’ and ‘semi-ordered’) in one polymeric system [10–12].

It seems to be commonly accepted that calorimetry is the easiest and cheapest method for studying material homogeneity, as calorimetry reflects the phase situation of the specimen. Unfortunately, this method is only a relative one and can only be applied when the processes occurring in the studied specimen are well diagnosed by other techniques [13–15]. Therefore we should use at least two complementary techniques. However, one of the most valuable tools for characterising the behaviour of a polymer system is dielectric or mechanical spectroscopy. The characterisation of the structural and local relaxations is usually obtained in terms of relaxation times and activation enthalpies [16–18].

In this paper, we report on the results of mechanical measurements of rubber waste–urethane composites with a various composition of the urethane agent. The concept of chemical reaction between rubber (e.g. disulfide bridges or double bonds) and isocyanate free groups, present in polyurethane prepolymers, is considered. We show that simple statistics can be a useful tool for describing the properties of the resultant engineering products.

Experimental

Materials and methods

For synthesis of rubber waste–urethane composites the following substrates were used:

- rubber granulate of 1.5–2.0 mm granularity and rubber granulate below 1.5 mm granularity (fine rubber) from car tyre waste obtained from natural rubber (NR), styrene–butadiene rubber (SBR) and/or butadiene rubber (BR) [1, 5, 6]
- Chemolan M urethane two-component prepolymers (urethane A), with 5.6–5.9% free –NCO groups (obtained from the mixture of toluene 2,4-diisocyanate – 80%, toluene 2,6-diisocyanate – 20% and polyoxypropylene 2000), and crosslinking agent CPP – 100 amine (from Interchemol sp. z o.o., Oborniki Śląskie, Poland)
- Monothane A50 and Monothane A60 urethane unary (one-component) prepolymers (from Compounding Ingredients Limited, Bamber Bridge, Preston, England), urethane B and C, respectively

The rubber–urethane samples were tested in a dynamic mechanical thermal analyser (DMTA) Qualimeter Eplexor 150N. The temperature range was –140 to 120°C. Cooling conditions of the samples in the analyser were: room temperature to –60°C with a cooling rate 10° min^{-1}; –60 to –120°C with 3.5° min^{-1}; –120 to –140°C with 2° min^{-1}. The samples were tested in a pressure mode (cylindrical samples) in the temperature range, mentioned above, with a heating rate 1° min^{-1} at frequency of 1 Hz.

Results and discussion

Figure 1 shows a set of representative data from the rubber waste-urethane composites, for which Chemolan was the urethane agent. The amount of 10% of the urethane prepolymer was used for the preparation of the composites, K–M and K–A, presented in Fig. 1. The results for the K–M sample, published earlier [1, 5, 6], did not exhibit the relaxation of the urethane agent distinctly. It was concluded that the structure was homogenous and a better dispersion of the agent took place. In other words, no urethane domains were formed in the composites. It was also found that the structural relaxation was very sensitive to the composite production process, i.e. pressure, temperature, amount and kind of urethane prepolymer. In this study three other urethane agents were used for the preparation of the composites: Chemolan (sample K–A); Monthane A50 (sample K–B); Monothane A60 (sample K–C). In order to study the effect of the urethane content on the binding effect of the composites, the amount of the urethane prepolymer in the composite varied from 10 to 20 mass%. The mechanical data for the 20 mass% urethane samples are presented in Fig. 2 and three relaxation peaks can be observed. According to the labels proposed in Fig. 1, the composites exhibited similar features as the ones studied previously [18]. The first peak (the lowest temperature) reveals the structural relaxation which occurred in the rubber domains. During this study it was impossible to find distinct peaks reflecting the relaxations of natural rubber (NR) and styrene-butadiene rubber (SBR). Only one rather broad peak representing the relaxation of the NR and SBR supermolecular structures was found. Owing to the fact that the thermogravimetric measurements showed the existence of both rubber components in the studied waste rubber one should assume that the contents is preserved after the preparation of the composite [19]. Since one structural relaxation of the rubber component has only been observed, one can conclude that the homogenous structure of the rubber domains was achieved in the process. The second and the third peak recorded for the tgδ curve, Fig. 2, should be assigned to the polyurethane component. The study of the pure polyurethane components exhibited

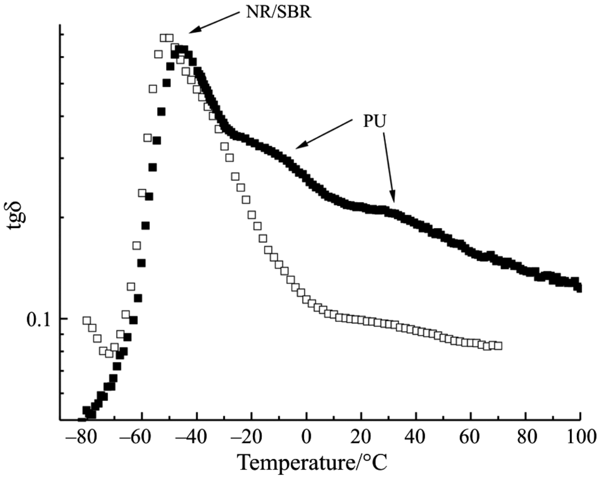

Fig. 1 Loss tangent (tgδ) as a function of temperature. The samples contain 10 mass% Chemolan □ – K–M, data taken from [18] and ■ – K–A. The peak labels are the same as in our previous paper [18]

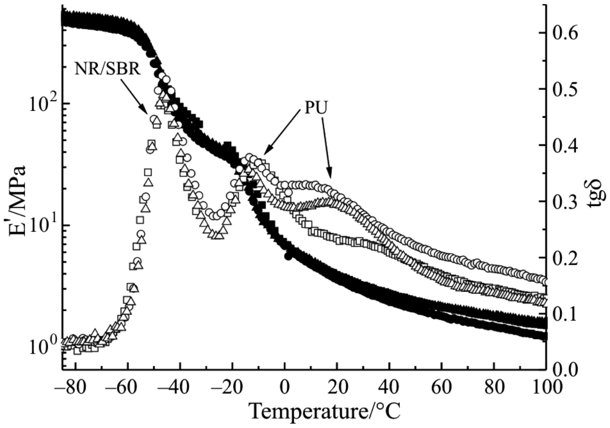

Fig. 2 Representative dynamic mechanical data showing elastic modulus (E') and tgδ as functions of temperature. The data were obtained for the pure urethane samples; ■ – K–A, ● – K–B, ▲ – K–C

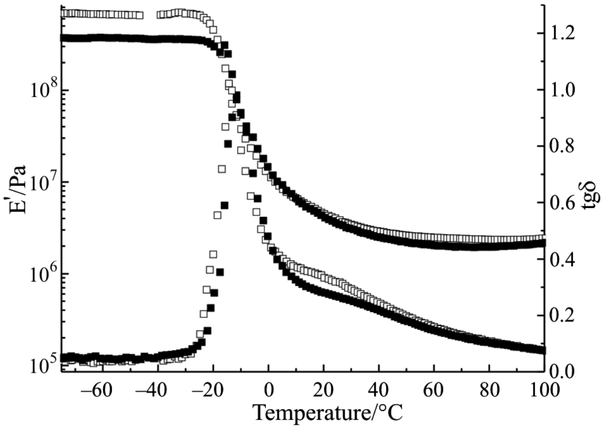

Fig. 3 Representative dynamic mechanical data showing elastic moduli and loss tangents for the studied composites; □ – urethane B and ■ – urethane C

both relaxations, Fig. 3. A strong peak with the maximum at –13°C was found for both polyurethanes. This peak corresponds to the second one observed in the mechanical spectrum of the composites. Also, a weak and broad peak, corresponding to the third one in the composites, was recorded for both polyurethanes at different temperatures. The temperatures were 29 and 18°C for urethane C and B, respectively. It can also be seen that the position of the second peak in the composites did not shift in comparison with the peak for the pure urethane samples. However, the third peak in composites shifted towards lower temperatures for K–B and K–C that is to 10 and 18° C, respectively. It must be emphasised that it was not possible to determine either the precise temperature or the intensity of the peak maximum since the peaks overlapped in a very narrow temperature range. The most sensitive peak to the change of the urethane agents seemed to be the third one. Although this peak was very weak in the studied pure urethanes, its intensity drastically increased with the rise of the urethane content in the composite from 10 to 20 mass%. This could mean that it was easier to activate the relaxation, reflected in the third peak, in the composite materials than in the pure urethane samples. An easier activation of the process must be the consequence of a new supermolecular structure in the composite. It is well known that one of the possible ways of the forming a new supermolecular structure is a chemical reaction requiring adequate thermodynamic parameters, e.g. high temperature and high pressure in some cases. Both parameters were applied for composite preparation in this study. Hence, one can conclude that the postulated reaction between the polyurethane prepolymer and rubber might occur. The Young's moduli measured for the composites exhibited different sensitivities to the urethane agents. It might be connected with the chemical constitution of the urethane prepolymers and their different reactivity.

In order to find some correlation between the amount of the urethane prepolymer in the composite and its thermomechanical properties, two contradictory concepts were considered. The first one assumed that no reaction occurred whereas the second one assumed that the chemical reaction took place. Both cases should give different mechanical and thermodynamic behaviour of the measured parameters of the studied materials. When the reaction takes place the temperature of the maximum of the relaxation peak should shift on the temperature scale, towards higher or lower temperatures. However, if the reaction does not occur, the position of the peak maximum should be stable, with only the intensity varying due to the quantity effect. Such obvious mechanical behaviour results from the changes of the supermolecular structures, which might be modified by new chemical bonds originating from the chemical reaction between moieties of the macromolecules, for example, the moieties of rubber and urethane components in a composite. In general, the structure might also be modified due to physical process, however, such a process should not have changed the thermogravimetric curves obtained for the studied composites [19]. Using simple statistic methods, the mean values of the adequate parameters were calculated or the linear regression approach to the measured parameters was applied. The results are presented in Table 1.

The first peak – structural relaxation of the rubber component, $E''_{max}(1)$ and $T_{max}(1)$

There were no linear correlations for $E'' \rightarrow f(n)$ in the case of all composites, where n is the amount of rubber concentration in the composites, calculated in %. Considering the calculation errors, Table 1, only one value of E'' should be taken into account for all composite materials. However, the experimental points are widely spread around the average values (Fig. 4a).

The position of the peak on the temperature scale, $T_{max}(1)$, seems to be stable in the case of the K–B and K–C composites. The average values, calculated for the studied range of urethane content in the composites (10–20%) are –50.9 and –50.8°C, respectively. Linear regression did not give a good correlation between the amount of urethane and the temperature in both cases, Table 1 and Fig. 4b. This would mean that the modification of the structure was only quantitative in the studied concentration range of the B and C urethanes. The temperatures are similar to the temperatures found for other composites [18]. A different situation was observed for the K–A composite. The temperature increased with the decrease of the amount of urethane. Extrapolation to 100% of rubber gave the temperature of –50.9°C. This value confirms the qualitative effect for the first peak of K–A. Moreover, it suggests that the structure of pure rubber components was still present in the composites in the form of small domains. This means that the urethane agents were not able to penetrate the interior of the granulates. Hence, the effect of binding of granulates occurs only on their surface.

The second peak – structural relaxation of the urethane component, $\mathrm{tg}\delta_{max}(2)$ and $T_{max}(2)$

The analysis of data was performed with the use of the tgδ curves, in which the second relaxation peak was pronounced better in comparison with the E'' curves. The analysis of $\mathrm{tg}\delta_{max}(2) \rightarrow f(n)$ for the studied composites did not give a linear correlation, hence only the average value in all cases should be considered, Fig. 4c. The mean values for K–A, K–B and K–C are 0.34, 0.37 and 0.37, respectively. The temperature of the peak maximum, $T_{max}(2)$, increased in a linear manner with rubber concentration, in the case of the K–A composite, Fig. 4d. However, the calculation of average values for

Table 1 Fitting parameters obtained in the peak analysis: E'' (MPa), T (°C), tgδ (dimensionless). The dimensions of the parameters used in the statistics are related to the adequate measured parameters

Parameter	PU	Linear regression $y=a+bx$					Mean value	
		$a \pm \Delta a$	$b \pm \Delta b$	R	SD	P	$<Y>$	SD
$E''_{max}(1)$	A	198±70	–1.24±0.81	–0.55	7.88	0.260	93.5	8.5
	B	75±82	0.21±0.97	0.11	8.14	0.836	94.1	7.3
	C	90±114	0.07±1.34	0.03	11.2	0.960	95.9	10.1
$T_{max}(1)$	A	–61.9±1.7	0.11±0.02	0.94	0.17	0.005	–51.7	0.4
	B	–52.7±2.1	0.02±0.02	0.39	0.21	0.447	–50.9	0.2
	C	–51.6±2.2	0.01±0.03	0.16	0.22	0.764	–50.8	0.2
$\mathrm{tg}\delta_{max}(2)$	A	1.1±0.3	–0.01±0.004	–0.77	0.03	0.072	0.34	0.04
	B	0.1±0.4	0.003±0.005	0.29	0.04	0.581	0.37	0.04
	C	0.1±0.4	0.003±0.005	0.29	0.04	0.581	0.37	0.05
$T_{max}(2)$	A	–35.8±2.6	0.32±0.03	0.98	0.26	$5 \cdot 10^{-4}$	–8.6	1.2
	B	–24.2±8.9	0.15±0.10	0.61	0.87	0.201	–10.3 (–12.3)	0.5
	C	–36.6±17.5	0.31±0.21	0.61	1.73	0.198	–8.8 (–13.5)	0.3
$\mathrm{tg}\delta_{max}(3)$	A	–	–	–	–	–	0.24	0.02
	B	1.15±0.20	–0.011±0.002	–0.91	0.02	0.011	0.26	0.04
	C	0.77±0.19	–0.006±0.002	–0.82	0.02	0.046	0.24	0.03
$T_{max}(3)$	A	–	–	–	–	–	26.8	0.5
	B	–	–	–	–	–	22.2	0.5
	C	–	–	–	–	–	19.8	0.6

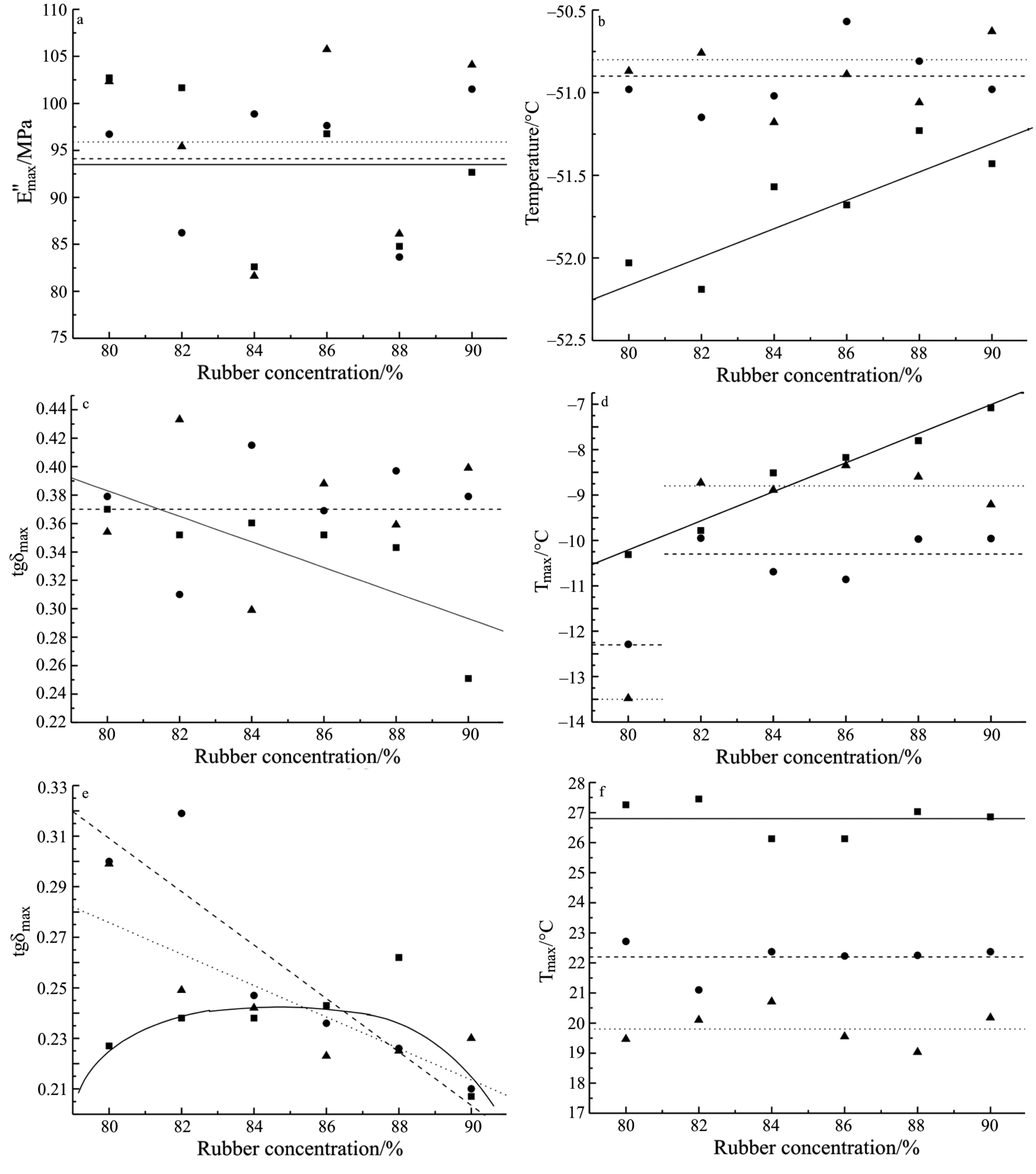

Fig. 4 The fitting procedure of experimental points obtained from the measured mechanical spectra of the composites (as indicated in the figure). The lines are added to guide the eye: — – A, --- – B, ··· – C. A mean value of the tested parameters or the linear regression applied to the points were taken into consideration: a – the first peak points – maximum of the viscous moduli; b – the first peak points – temperature of the maximum of the viscous moduli; c – the second peak points – maximum of loss tangent; d – the second peak points – temperature of the maximum of loss tangent; e – the third peak points – maximum of loss tangent; f – the third peak points – temperature of the maximum of loss tangent; ■ – A, ● – B, ▲ – C

K–B and K–C gave lower errors than the linear regression. It is worth noticing that two values in each case were calculated in order to improve the calculation error, Table 1. The higher temperatures, i.e. –10.3 and –8.8°C, for the urethane concentration of 10–18% were calculated for K–B and K–C, respectively. When the concentration of the urethane prepolymer increased up to 20%, the values of –12.3 and –13.5°C were found, respectively. Latter values are close to the temperatures of pure urethane. This may indicate that phase separation had occurred. In other words, some portions of the urethane prepolymer reacted with the rubber grains on their surfaces whereas the rest of the unbound urethane had formed separated domains. Most likely, the supermolecular structure in such domains was identical with the pure urethane structure. Moreover, the size of the domains was sufficient to exhibit their properties in the whole sample, i.e. in the sample composed of rubber grains (80%), the reacted urethane and pure urethane domains. Hence, the mechanical properties of the domains should be predominant for the rubber–urethane composite.

The third peak – structural relaxation of the urethane component, tgδ_{max}(3) and T_{max}(3)

Linear tendencies of tg$\delta_{\max}$(3) intensities were observed for K–B and K–C whereas the mean value for K–A seemed to be more adequate. It is opposite to the tendencies found for the second peak. Also, a parabolic interpolation for data of K–A, with a maximum of 14% of urethane in the composite (Fig. 4e), gave very low fitting errors. However, the mean values for K–B and K–C should also be considered. The facts mentioned above indicate that no quality effect occurred for this relaxation in the studied urethane concentration range. The constant temperatures, $T_{\max}$(3), found for the maximum peaks in all cases, i.e. 26.8, 22.2 and 19.8°C for K–A, K–B and K–C, respectively, seem to confirm this reasoning. This indicates that there was no structural changes in the areas occupied by the relaxing segments.

Elastic modulus analysis at chosen temperatures

The imaginary part of Young's modulus reveals the dumping effects whereas the real one is a measure of the elasticity of the sample. The same statistic approach was applied to the elastic moduli taken at four temperatures. The temperatures were chosen arbitrary at points where relaxations did not occur. It must be emphasised that the mentioned above procedure was applied to the curves which were obtained for measurements performed at 1 Hz. It is well known that lower or higher measurement frequencies shift the relaxation processes [7]. Owing to the fact that three relaxations were found in the studied temperature range, only four temperatures were considered: – 70, –30, 5 and 45°C. The first temperature was below the DSC glass transition of the rubber component whereas the last one was above the DSC glass transition of the urethane components. Hence, we can conclude that $E'(-70)$ and $E'(45)$ revealed the mechanical properties of the composites in the glass-like and the rubber-like states, respectively. The temperature zone corresponding to the transition from glass (energetic) to rubber (entropic) behaviour includes two of four points at which E' was analysed, i.e. $E'(-30)$ and $E'(5)$. The results of the analysis are presented in Table 2. One can easily see that in all cases except for the $E'(45)$ analysis, the concept of linear relationship might be considered and the negative correlation coefficients were obtained. Therefore, with the increase of rubber concentration in the composite the E' modulus decreased linearly. Almost all fittings were characterised by low errors, see the SD values presented in Table 2, and the correlation coefficients were much higher than 0.60. In spite of these results, there were several cases for which this procedure did not give satisfactory results from the statistical point of view. However, it must be emphasised that the investigations were performed on composite specimens which were not obtained in model reactions but were made from waste materials. Therefore, from the physical point of view, the results which gave a linear

Table 2 Fitting parameters obtained in the analysis of the elastic moduli: E' (MPa). The dimensions of the parameters used in the statistics are related to the corresponding measured parameters. The numbers in the parenthesis give the temperature at which the E' values were indicated

Parameter	PU	Linear regression *y*=*a*+*b*x					Mean value	
		a±Δ*a*	*b*±Δ*b* MPa	*R*	*SD*	*P*	<*Y*>	*SD*
$E'(-70)$	A	1504±324	–13.0±5.2	–0.87	31.9	0.024	357	60
	B	1492±311	–13.1±3.7	–0.87	30.6	0.023	382	56
	C	1502±682	–13.0±7.9	–0.73	46.6	0.178	400	77
$E'(-30)$	A	347±47	–3.59±0.55	–0.96	4.6	0.003	41.2	14.1
	B	181±64	–1.65±0.75	–0.74	6.28	0.092	40.6	8.3
	C	158±62	–1.32±0.73	–0.67	6.14	0.146	45.7	8.2
$E'(5)$	A	29.9±6.3	–0.31±0.07	–0.89	0.62	0.014	3.91	1.27
	B	26.5±6.4	–0.26±0.07	–0.86	0.63	0.026	4.48	1.12
	C	19.3±5.0	–0.16±0.06	–0.81	0.49	0.049	5.24	0.76
$E'(45)$	A	–	–	–	–	–	2.52	0.19
	B	–	–	–	–	–	1.42	0.17
	C	–	–	–	–	–		

correlation between a rubber concentration and an E' modulus are worth noticing. Considering $E'(-70)$, it was observed that the fitting lines were almost parallel to each other and only slightly shifted, Fig. 5a. Analysis of $E'(-30)$ and $E'(5)$ gave intersecting straight lines, Figs 5b and c, respectively. In the case of $E'(5)$ the values of 29.9, 26.5 and 19.3 MPa were obtained by line extrapolation to zero percentage of rubber content. All of these values are much higher than the one for pure urethane (8.75 MPa). This might also confirm the suggestion that a reaction between sulfate groups from waste rubber granulate and free isocyanate groups from polyurethane prepolymer take place.

A linear correlation tested for the $E'(45)$ case gave very high fitting errors. Therefore, the concept of linear relationship between the value of E' modulus taken at 45°C and the urethane amount in the samples was rejected. However, two mean values were calculated for the $E'(45)$ moduli, taken from all composites and treated as one set of data, 2.52 and 1.42 MPa. The former one might reveal the existence of pure urethane probably in the form of domains in the composites. The E' value at 45°C for pure polyurethanes, Fig. 3, was of the range from 2.72 to 2.33 MPa. Hence, the property of the pure polyurethane would be observed in the composites at this temperature. The latter mean value might reflect the viscous-elastic property of the rubber component. One can easily see from Fig. 5d that both properties are exhibited by the composites with different urethane agent concentration. In other words, the Chemolan amount of about 18 mass% is sufficient in the composite to form pure urethane domains. This is reflected in the mechanical properties of the studied composite by the properties characteristic for pure polyurethane. It would indicate that the properties of polyurethane are predominant. For K–B and K–C the value of 14 mass% of prepolymer would be sufficient to form the urethane domains in the composites.

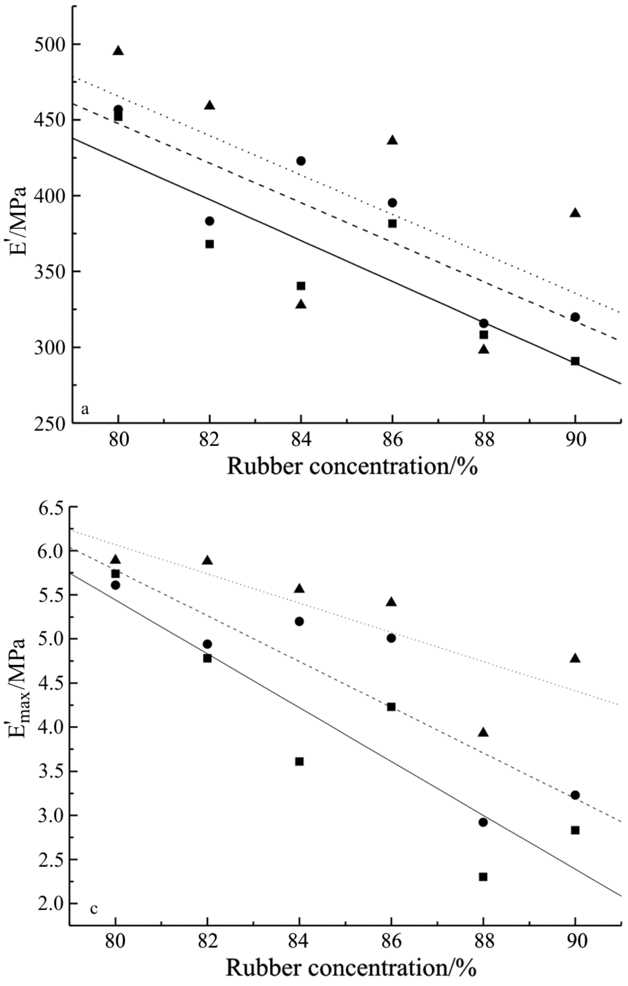

Fig. 5 The fitting procedure of experimental points of elastic moduli obtained for the studied composites at chosen temperatures: a – 70°C, b – 30°C, c – 5°C, d – 45°C; ■ – A, ● – B, ▲ – C

Conclusions

The paper serves the selected example of problems solving by thermal analysis. Moreover, the application of the simple statistic methods leads to a broader understanding of the relationship between processing history and morphology in the resultant engineering products. It was concluded that a reaction between rubber (e.g. disulfide bridges or double bonds) and isocyanate free groups, present in polyurethane prepolymers, took place in the tested cases. From the statistical point of view, the calculation errors were significantly high, however, it must be emphasised, that such a situation could be the results of the specific characteristics of the systems and the complexity of a production process. Mechanical parameters also revealed the properties of components for a certain degree of prepolymer concentration. Such a concentration indicated that the reaction required the right ratio of component content in the composites. In other words, two kinds of urethane networks were obtained, hence two kinds of supermolecular structure were formed. The first one consisted of the urethane network and the rubber grains as a filler (plasticizer) whereas the second one additionally included a urethane-rubber interregion. It must be emphasised that DMTA is a sensitive method for determination of the phase separation in the composite. It was shown that some portion of polyurethane reacted with the rubber grain (interregion) whereas the some excess amount of polyurethane formed separated domains. The mechanical properties of polyurethane determined the properties of the composites when the amount of prepolymer was sufficient for the domain structure formation. DMTA is a sensitive test for structural homogeneity of complex systems. The temperature of the maximum of the relaxation peak shifted on the temperature scale when the reaction occurred and new bounds were created. If the reaction did not occur, the position of the peak was stable, only its intensity varied.

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