Structural Relaxation and Morphology of the Rubber–Urethane Composites

Adam Danch,[1] Wieslaw W. Sułkowski,[2] Marek Moczyński,[2] Agnieszka Radon,[2] Franz Stelzer,[3] Stefan Jurga[4]

[1]Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland
[2]Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland
[3]Institut für Chemische Technologie Organischer Stoffe, TU Graz, Stremayrgasse 16, A-8010 Graz, Austria
[4]Department of Macromolecular Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

Abstract: The supermolecular structures and structural relaxation of the waste rubber–urethane composites are discussed on the basis of results of calorimetric measurements and mechanical spectroscopy. The results give a broader understanding of the relationship between processing history and morphology in the resultant engineering products. The effect of different kinds of urethane prepolymer on the thermomechanical properties of commercial composite products is presented. The idea of reaction between rubber granulate and urethane prepolymer is under consideration. The shear and tensile modes were applied to better explore relaxations that occur in rubber grains and in an interphase area created by the urethane agents. The rubber waste management problem was taken into account also. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1186–1193, 2004

Key words: rubber–urethane composites; tyre waste; mechanical spectroscopy; DSC–structural relaxation
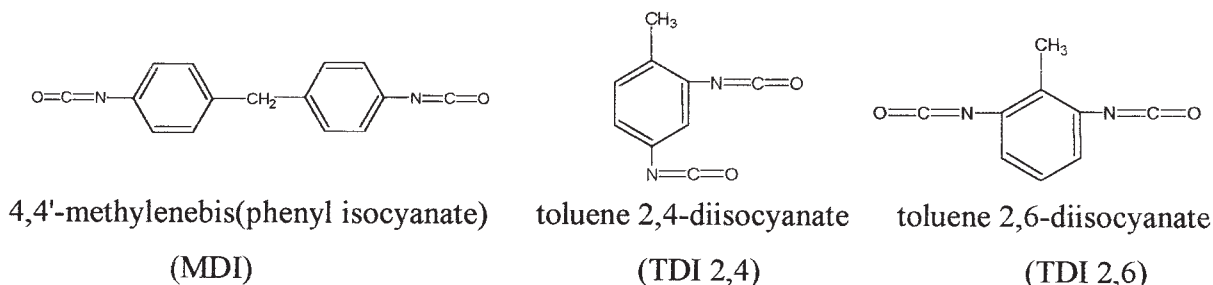
INTRODUCTION

The solution of the rubber waste utilization depends on an advance towards the development of utilization methods and management, application of recycling rules, and on law regulations connected with waste. The processing and waste rubber management is a global problem and is not resolved in any country until now. One possibility of rubber waste management is to break it up and use the obtained granulate, fine rubber, or rubber dust as valuable raw materials. Applications stemming from products obtained from the waste rubber granulate or fine rubber mixed with a small amount of elastomer are observed.[1–3] These products do not need additional vulcanization. A thin prepolymer layer covering rubber grains polymerizes under suitable conditions, giving a stable composite. However, the possibility of using this kind of material depends on its properties and stability. The waste rubber–polyolefine composites are used for porous elements extrusion.[1,4] Products from these composites are pipes, which can be used for field fertilization and watering, and porous tapes for thermal insulation and vibration damping. Rubber granulates and cast polyurethane elastomers are used for production of synthetic running tracks (such as sport surfaces) and carpets, which are widely used in foot therapy and correction and also foot massage. Another possibility for used rubber is to produce waste rubber–urethane composites. It must be emphasized that a large variety of the urethane prepolymer would give a wide range of composite material properties. It is commonly accepted that the properties of the material result from different possible morphologies, which can be created and partially controlled by physical and chemical treatments. Both treatments strongly influence the composite's supermolecular structure; hence, they influence the temperature of the glass transition (T_g). According to the literature data, the polyurethane T_g value depends on the kind of isocyanate component and polyol component used to synthesize them (e.g., T_g 203–210 K).[5,6] It was found that the T_g value depends on isocyanate free groups content in polyurethane prepolymers as well (e.g., T_g 237 K, 2% free, NCO groups, and 257 K, 8% free, NCO groups).[7–9]

Studies of dynamic mechanical and dielectric behaviors of polymeric material demonstrate that many polymers exhibit complex structural relaxations and in some cases low-temperature relaxation.[10,11] However, it is commonly accepted that the highest temperature relaxation (main transition) corresponds to the glass transition, although there are different processes. These phenomena are characterized by an enthalpy of

4,4'-methylenebis(phenyl isocyanate)
(MDI)

toluene 2,4-diisocyanate
(TDI 2,4)

toluene 2,6-diisocyanate
(TDI 2,6)

Scheme 1

process activation (in the case of Arrhenius relationship) and temperature at which the material changes its properties.

The results of our previous investigation point to the nonhomogenous structure of composites.[1,12] According to T_g data for the obtained composites, the waste rubber, polyurethane, and the reaction product of rubber with polyurethane existed separately.[1,12] Another T_g value observed at temperatures different than T_g's of polyurethane and rubber would be a proof occurrence of reaction between polyurethane and rubber. Studies of dynamic mechanical behaviors of polymeric material may give a more precise answer.

In this article, we present dynamic mechanical and calorimetric studies of the structural relaxations of the rubber–urethane composites. The shear and tensile modes were applied to better explore relaxations occurring in rubber grains and in an interphase area created by the urethane agents. The rubber waste management problem was taken into account. The properties and influence of isocyanate structure on the urethane–rubber waste composites, obtained from waste car tires' fine rubber, and the postulate reaction between waste rubber granulate and polyurethane, were investigated.

MATERIALS AND METHODS

Sample preparation

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

Rubber granulate (fine rubber, the specimen labeled FR) of granularity below 1.5 mm received from the car tire waste; from Stilon Rubber Factory, Bełchatów, Poland. According to results of our investigations and literature data, the granulate contained natural rubber, styrene–butadiene rubber, and/or butadiene rubber and low-weight molecular additives.[12–14]

Urethane prepolymers [i.e., Chemolan M, 5.6–5.9% free, NCO groups (obtained from the mixture of toluene-2,4-diisocyanate, 80%, and toluene 2,6-diisocyanate, 20%, and polyoxypropylene 2000), Chemolan M-50, 8.0% free, NCO groups (obtained from mixture of 4,4'-methylenebis(phenyl

isocyanate), 60%, and a mixture of toluene 2,4-diisocyanate, 80%, and toluene 2,6-diisocyanate, 20%–40% and polyoxypropylene 2000) and Chemolan B-3, 10.0%, free NCO groups (obtained from 4,4'-methylenebis(phenyl isocyanate) and polyoxypropylene 2000; from Interchemol sp. z o.o., Oborniki Śląskie, Poland)].

The rubber–urethane composites contained 10% suitable urethane prepolymers Chemolan M (the composite labeled K-M), Chemolan M-50 (K-M50), or Chemolan B-3 (K-B3) and fine rubber. To obtain proper compositions, the urethane prepolymers were mixed in the proportion mentioned above, with fine rubber, and transferred into molds. The prepared profiles of compositions were held at 363 K under load of 2.5 $\times 10^6$ N/m^2 for 1.5 h for all compositions. After this time, they were held at a dryer under load until total cooling.

Methods

Calorimetric measurements were performed by using a Perkin–Elmer DSC7-type and the first heating run was recorded. The T_g was defined from the infection point of the change in a heat flow versus temperature curve. The first derivative of the DSC curve was analyzed. The measurements were performed under the following conditions: environment, nitrogen atmosphere; flow rate, 20 ml/min; sample pan, aluminum; reference, empty aluminum pan; sample size, ~ 5 mg; heating rate, 20 deg/min; calibration procedure, done with indium and mercury standards.

Mechanical thermal analysis was carried out in a tensile and a shear mode with a PL DMTA Mk III system and a Rheometric Scientific ARES system, respectively. E'', E', G'', and G' curves were recorded within a temperature range from 190 to 560 K and in a frequency range of 0.03–300 Hz after temperature stabilization. The samples were cut down from the composites as bars nearly the same size.

RESULTS AND DISCUSSION

Glass transition and thermal degradation

The analysis of the raw DSC curves for the studied waste rubber–urethane composites (K-B3, K-M,
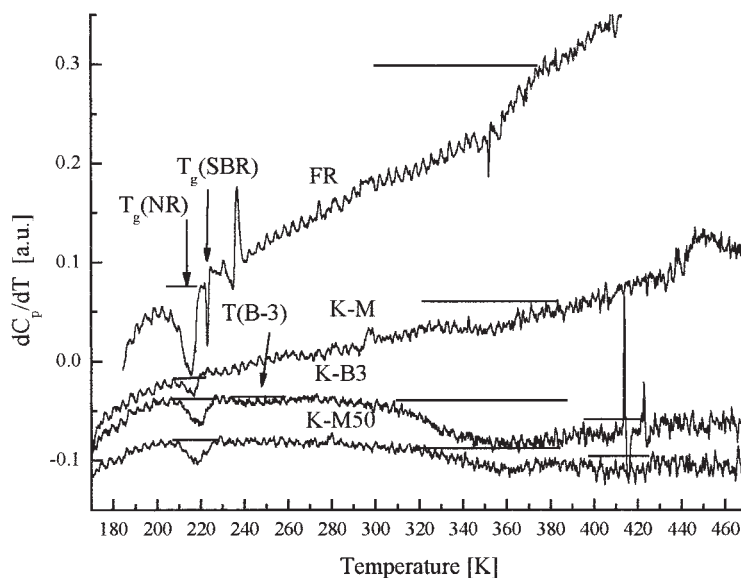
Figure 1 The first derivatives of the DSC traces for studied samples: FR, rubber granulate; K-M-, composite including Chemolan M; K-M50 composite including mixture of Chemolan M and B-3; K-B3-, composite including Chemolan B-3.

K-M50) and the fine rubber (FR) hardly proved the glass transition's existence. It was very difficult to find the proper experimental conditions to obtain a correct base line. Therefore, the first derivative of the DSC signals, presented in Figure 1, were analyzed in each case. The detailed description of such a method was presented in previous articles.[15,16] It must be emphasized that the T_g was defined as an inflection point of the DSC trace in such a case. Therefore, the minimum of the derivative was taken as a T_g value. One can find that the raw DSC signal for the rubber waste (the FR curve), the sample taken directly from the rubber granulate, must exhibit three stepwise transitions and one endothermal peak in the studied temperature range, 180–470 K. The lowest temperature transition would reflect the glass transition of natural rubber, T_g(NR). It was mentioned in Experimental that the rubber waste consisted of natural rubber (NR), styrene–butadiene rubber (SBR), and/or butadiene rubber (BR) and some low-weight molecular additives.[12,13] The next stepwise transition, at higher temperature, would reveal the structural changes occurring for the SBR and/or BR supermolecular structure [i.e., the glass transition, T_g(SBR) or T_g(BR)]. The endothermal peak that disappeared in the second heating run would suggest an irreversible process. Because the composites were prepared at 363 K, most likely, the annealing at such a temperature would be a reason for the peak vanishing from the DSC traces for the composites. The T_g for all studied samples are presented in Table I. It is easy to find that the glass transition of NR is well pronounced in the derivatives of the DSC signals recorded for the composites. However, more detailed analysis of the curves shows that the glass transition of SBR could be detected as a

shoulder in the curve. Moreover, the third glass transition, with temperature between T_g(NR) and T_g(SBR), could be found in the case of the composite samples. Owing to the fact that the reaction between sulfate groups from waste rubber granulate and free isocyanate groups from polyurethane prepolymer (as it took place during waste rubber vulcanization with DeLink agent[4]) is possible, it is supposed that new local supermolecular structure could be created by the polymeric system. That would be revealed by the another glass transition T_g(NR/SBR). Because all of the transitions overlap in a very narrow temperature range, it is impossible to find some quantity relationship for them. It is worth noting that the idea of the reaction between the sulfate and isocyanate groups was postulated and roughly proved in our previous article concerning the decomposition process.[12]

One can find that the T_g (NR) values for the composites are almost the same but are shifted slightly

TABLE I
The Glass Transition Temperatures of the Studied Samples

Sample	T_g(NR) [K]	T_g(SBR) [K]	T_g(PU) [K]
FR	215.7	223.7	—
K M	216.7	—	229.6
K M-50	216.2 (218.8)	223.5	231.0
K B-3	216.7 (220.1)	224.1	234.0

Note. The value of the glass transition of the structure created due to reaction between the rubber and urethane agent is given in parentheses, T_g (NR/SBR). The glass transition temperatures of the adequate urethane agent in the composite is presented in the last column (data are taken from ref. [12]).
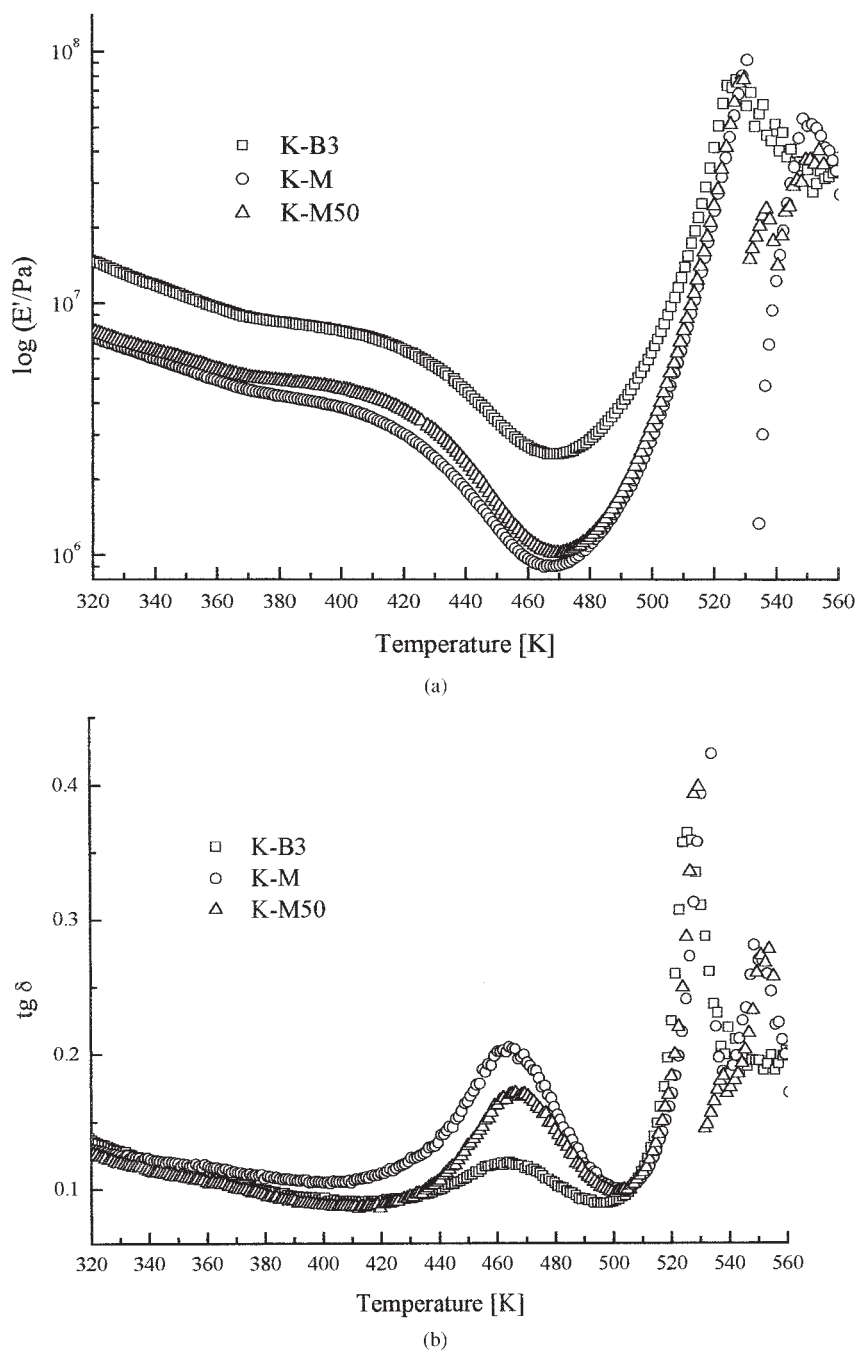
Figure 2 (a) Elastic modulus as a function of temperature for the studied composites, the examples for 1 Hz. (b) Loss tangent as a function of temperature for the studied composites, the examples for 1 Hz.

towards high temperature, as compared with the *R* sample. Likely, low content of the urethane agents in the composites (10%) made it impossible to find their glass transition, although it was possible in the case of the composites prepared from the granulated rubber waste when the grains size was 2.0 mm.[1] Only a very wide transition could be detected for the K-B3 composite, T(B-3) = 248 K. The absence of the glass transitions of the urethane agents in the DSC curves would additionally confirm very good dispersion of the agents (i.e., lack of the urethane domains in the super-

molecular structure of the composites). The T_g of pure polyurethanes Chemolan M, Chemolan M-50, and Chemolan B-3 were 229.6, 231.0, and 234.0 K, respectively.[1] It was found from the DSC data that the T_g value of the polyurethane, obtained from MDI (Chemolan B-3), was higher. It means that this polymer exhibits higher molecular weight or is less flexible than those obtained from TDIs and their mixture with MDI. The latter suggestion seems to be less probable, considering elasticity data.[12]

The urethane agents changed little the decomposition temperatures of the studied composites. Three

(a)

(b)
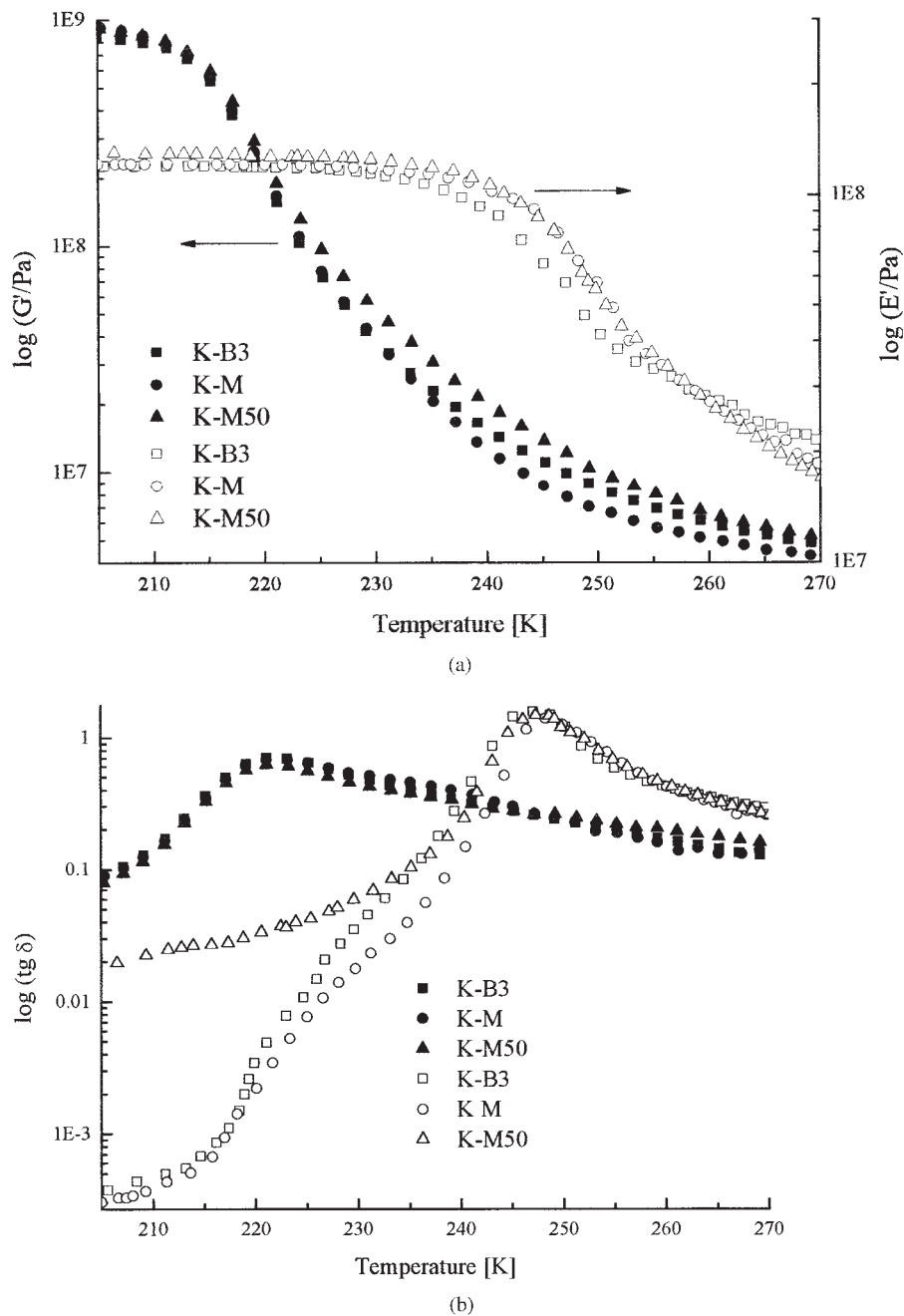
Figure 3 (a) The real part of $G*$ and $E*$ moduli, measured in the shear and tensile experiments, obtained for the studied composites at 1 Hz: open symbols, E'; solid symbols, G'. (b) Loss tangents of the shear (solid symbols) and tensile (open symbols) experiments obtained for the studied composites at 1 Hz.

decompositions processes were found. The temperature of 434 K was pointed out as the beginning of the process.[12] The first process was attributed to the removal of occluded plasticizer molecules (434–690 K). The second process revealed the destruction of the NR and SBR and/or BR fragments. The third weight loss was connected with SBR and/or BR. To remove the low-weight molecules of the occluded plasticizer from the tangled and cross-linked supermolecular structure, we needed adequate free volume, which means the fluidity of fragments of the macromolecules must

be more global than local. This motion was found in a temperature range of 420–500 K as a high temperature relaxation, see Figure 2(a, b), for every composite. Unfortunately, because of the rubber waste consistency (fine granulate), we were not able to perform the mechanical investigation for this material. It can be supposed that this relaxation is a feature of the NR/SBR and/or BR structure of the pure rubber. However, the structure would be modified little by the urethane agents that are reflected in the position and the value of the maximum in the tg δ curves versus
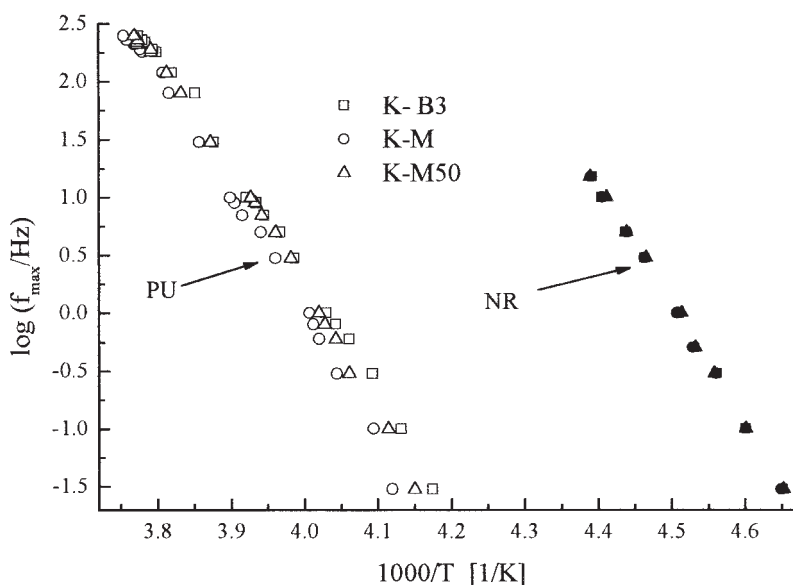
Figure 4 Arrhenius plots for the structural relaxations of the urethane and the rubber supermolecular structure created in the composite materials.

temperature. A drastic increase of Young's moduli at temperatures higher than 480 K would additionally confirm the plasticizer evaporation. The mechanical destruction of the composites started at 530 K and the sample cracking took place then.
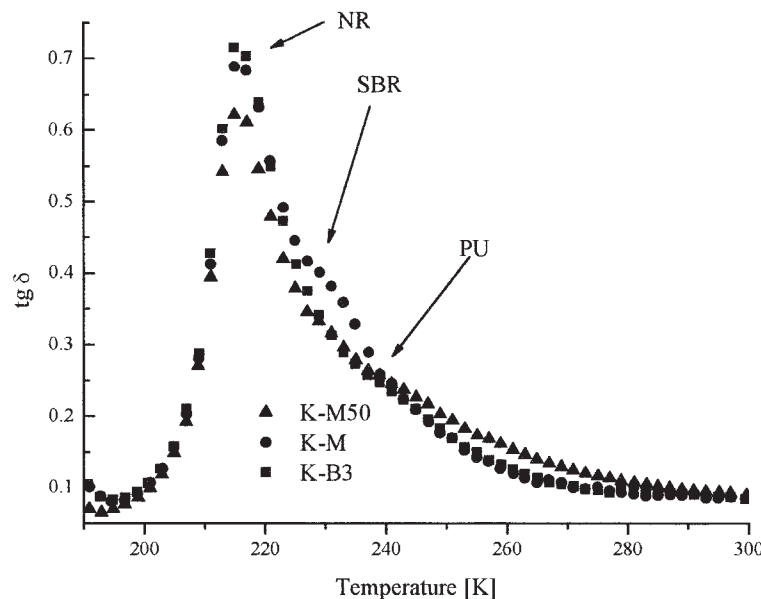
Structural relaxation

Mechanical spectra of the studied composites are presented in Figure 3(a, b). Both mechanical experiments exhibited the same relaxations in the low temperature range, 190–270 K. However, different intensities of the processes, observed by either the tensile mode or the shear mode, were recorded. It is understandable because different experimental conditions were applied in both cases. The stronger static force, which had to be used in the former experiment, pronounced more relaxation connected with motion of the polyurethane. The maximum temperature of the tg δ curves for that experiment (open symbols) were nearly the same: 246.2 K (K-B3); 247.6 K (K-M50); 247.6 K (K-M), and the intensities varied in the following manner: 1.57 (K-B3); 1.47 (K-M50); 1.39 (K-M). One can find more

differences in the curves, in the temperature range related to the relaxation of the rubber. Most likely, additional relaxation occurred at low temperature for the composites K-M50 (213 K). The shear experiment exhibits a small difference (solid symbols), too. The temperature of the maximum of the tg δ curves (obtained for 1 Hz, see Fig. 3b) for the structural relaxation related to the rubber is nearly the same in all studied composites, 221.8 K for K-B3 and K-M, and 221.4 K for K-M50. It would confirm our DSC investigation, where T_g's were 216.7 and 216.2 K, respectively. The amplitude changes a little in a different manner as compared with the tensile mode. Likely, the reason is the mode used, as it was mentioned above. It was shown earlier for other polymeric systems[17–19] that the tensile mode is more sensitive to the relaxation of an interphase region. It would mean that the urethane agent, adequate for the studied composite, creates some kind of structure that links rubber grains. The question of whether some chemical bonds between rubber and polyurethane exist is still open. It requires further mechanical investigation for the samples with a different polyurethane agent content that

TABLE II
Mechanical Parameters for Studied Composites

Sample	ΔH_α(NR) (kJ/mol)	ΔH_α(PU) (kJ/mol)	$G' \times 10^6$ (Pa)	$G'' \times 10^5$ (Pa)	$E' \times 10^7$ (Pa)	$E'' \times 10^6$ (Pa)
K M	199 ± 3	198 ± 4	3.11	2.79	1.24	2.13
K M-50	199 ± 3	191 ± 3	3.73	3.97	1.08	1.79
K B-3	197 ± 3	184 ± 3	3.41	3.29	1.41	1.45

Note. Real and imaginary parts of E^* and G^* moduli were obtained in tensile and shear experiments at 1 Hz, respectively. The mechanical parameters were pointed out for room temperature from the curves. The activation enthalpies of structural relaxations for the rubber, ΔH_α(NR), and the urethane, ΔH_α(PU), segments are presented for all composite samples.

Figure 5 The curve interpretation concerning the possible relaxations based on data obtained in the shear experiments.

will reveal other structural relaxations, most likely, existing at a higher temperature.

The Arrhenius plot obtained for the composites shows only the structural relaxation, shown in Figure 4 as open symbols for the relaxation connected with the urethane agents and solid symbols for NR. In both cases, the straight line was fitted to obtain the enthalpy of activation; the results are presented in Table II. However, it must be emphasized that, although the procedure gave low fitting errors for both relaxations, the curve would seem to be more adequate in the case of the PU relaxation. One can see that the urethane agents did not influence the structural relaxation of NR and the same values of the activation enthalpy were obtained for all composites. The highest activation enthalpy of the urethane agents was calculated for the K-M sample, whereas the lowest one was obtained for K-B3. These values are well correlated with the position of the peak maximum in the temperature scale for the studied composites. It means that the activation of motion of the B3 urethane agent is the easiest.

Low-frequency shear experiments additionally revealed another relaxation. Unfortunately, due to overlapping of the peaks at frequencies higher then 0.1 Hz, it was impossible to obtained the Arrhenius plot for this relaxation. The possible interpretation of all relaxation peaks is presented in Figure 5. The measurement, performed at 0.03 Hz, exhibited that the relaxation of the SBR fragments were the most intensive in the case of the K-B3 composites. It would mean that the miscellaneous intermolecular structures were created when the urethane agents were different.

The mechanical properties, measured at ambient temperature (293 K), are presented in Table II. One can

easily find that the mechanical properties changed as compared with the properties exhibited at temperatures below the temperature at which the structural relaxation of the rubber component occured (i.e., below 210 K). The tendencies for the G' and the E' values at low temperatures, observed for the composites with the different polyurethane agents, are the following: K-B3 < K-M50 < K-M and K-B3 < K-M < K-M50, respectively. The change of both tendencies begin in the temperature range of the structural relaxation of polyurethanes. It would mean that the polyurethane agent strongly influences the mechanical properties of the composites. Also, one can conclude that the polyurethane creates some kind of network that is filled by the rubber granulate. Therefore, the size granulate and the kind of urethane prepolymer (the reactivity of isocyanate and polyol components) seem to strongly affect the mechanical properties (dumping effects).

CONCLUSION

The mechanical spectrum is complex and includes the structural relaxation of both the rubber and the urethane agent. The same is true of the DSC analysis. It means that the situation is quite similar to the semicrystalline polymers, where the features of two amorphous structures are pronounced well. The domains composed of the rubber granulate are linked by the interphase areas created by polyurethane. One can conclude that the polyurethane creates some kind of network that is filled by the rubber granulate. Most likely, the size of rubber grain and the kind of the urethane agent are significant. The additional glass transition revealed the supermolecular structure changes. Most likely, the changes took place because of the reaction between the rubber and urethane

agent. Because the additional glass transitions were observed only in the composites including Chemolan B-3, it would mean stronger reactivity with the rubber grains.

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