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Wiesław W. Sułkowski [a], Gabriela Bartecka [a], Anna Sułkowska [b], Jerzy Borek [a], Sławomir Maślanka [a], Adam Danch [c] & Marek Moczyński [a]

[a] Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna, Katowice, Poland

[b] Department of Physical Pharmacy, Medical University of Silesia, Jagiellońska, Sosnowiec, Poland

[c] Institute of Physics, University of Silesia, Uniwersytecka, Katowice, Poland

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Relaxation Properties of Composites Obtained from Polyurethane and Rubber Waste

WIESŁAW W. SUŁKOWSKI,[1] GABRIELA BARTECKA,[1] ANNA SUŁKOWSKA,[2] JERZY BOREK,[1] SŁAWOMIR MAŚLANKA,[1] ADAM DANCH,[3] AND MAREK MOCZYŃSKI[1]

[1]Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna, Katowice, Poland
[2]Department of Physical Pharmacy, Medical University of Silesia, Jagiellońska, Sosnowiec, Poland
[3]Institute of Physics, University of Silesia, Uniwersytecka, Katowice, Poland

The aim of the investigation was the dynamic thermo-mechanical analysis (DMTA) study of the polyurethane-rubber composites obtained from used polymer products. Polyols obtained in the glycolysis process from used semi-rigid polyurethane foams, hardened by diphenylmethane 4,4′-diisocyanate (MDI) and rubber granules obtained from mechanical granulation of used car tyres were used to receive polyurethane-rubber composites. On the basis of the DMTA spectra the glass transition temperature T_g was determined. The analysis of loss module E'' allowed us to observe two relaxation processes for polyurethane-waste rubber composites α – originating from the rubber and α′ – from the polyurethane glue. The dependence of the changes of activation energy of relaxation processes with the change of weight ratio of polyurethane glue in polyurethane-waste rubber composites was observed.

Keywords Dynamic thermo-mechanical analysis (DMTA); polyurethane-rubber composites

Introduction

Products obtained from polymers and rubber have gained worldwide popularity. One of the most often used products made of polymer materials is polyurethane foams, which can be found in almost every sphere of life. It is used as foam insulation in the construction or heating industry, as part of insulation in the automotive industry, as noise absorbents, elements of car fittings, in the footwear industry, in the furniture industry and in many others.

Rubber products are mainly used by the manufacturers of rubber tyres. Other articles made of rubber are also commonly used by the car industry e.g., car fittings.

Address correspondence to Wiesław W. Sułkowski, Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, Katowice 40-006, Poland. E-mail: wieslaw.sulkowski@us.edu.pl

Similarly as in case of all other functional products, polyurethanes and rubber products should be recycled after use [1–8].

One of the possible way to convert used products made of polyurethane foam is their chemical recycling in the process of glycolysis. As a result of this process different polyols are obtained which can be reused for the production of polyurethane products [9–11].

Due to the increasing number of waste car tyres and the limited capabilities to landfill them seems that the most prospective method to manage them is to cut them and to use the obtained rubber granules as a additive to receive composites [12–16].

Results of the research should contribute to the widening of the possible ways of utilizing these used products [1–5].

Until now polyurethane-waste rubber composites were received from granulates of car tyres and of polyurethane prepolymers (glues) [1–5].

In our research products from chemical recycling of semi-rigid integral polyurethane foam in the form of glue and car tyres granulate received from material recycling were used.

Materials and Methodology

Polyols obtained in the glycolysis process from used semi-rigid polyurethane foam obtained by the method developed by the German company RAMPF Ecosystems GmbH [9–11] and rubber granulate of 1.5 mm to 2 mm were used to receive polyurethane-rubber composites.

Recypol®201 and Recypol®601 which are polyetherpolyols received from semi-rigid integral polyurethane foam were used in our study. These polyols contain except for the remains of glycol, fragments of polymer chains ending with OH groups. Polyols Recypol®201 and Recypol®601 have different hydroxyl value (OHN). OHN of Recypol®201 is 45–55 mg KOH/g, and OHN of Recypol®601 is 360–390 mg KOH/g.

To obtain polyurethane glue various quantities of Recypol®201 and Recypol®601 and various quantities of isocyanates diphenylmethane 4,4′-diisocyanate (MDI) were used (Table 1).

Polyurethane-rubber composites were obtained from all prepared polyurethane glues using them in quantities of 5; 7.5 and 10 weight % respectively.

Obtained polyurethane glue was mixed at respective proportion with rubber granulates. Very well mixed components were put in forms under pressure 2 MPa.

Next the composites were heated up in temperature 363 K during 90 min. The composites were taken out of forms after 24 hours.

The obtained composite and polyurethane glues hardened under the same conditions were subjected to the tests with the use of a dynamic thermo-mechanical analysis in the DMA Q800 apparatus of TA Instruments. Measurements were carried out at the temperature range from 123 K – 323 K at a heating rate equal to 2 K/min with the bending frequency range from 1 to 150 Hz. The analysis of the DMTA spectra allowed us to determine the glass transition temperature T_g and the course of the relaxation processes in the composites.

The analysis of the changes in the storage module E' and loss module E'' as a function of temperature enabled the calculation of the activation energy for relaxation processes of various polyurethane glues and polyurethane-rubber composites.

Table 1. Composition of polyurethane glue used to make polyurethane-waste rubber composites

No. of glue	Quantity % of raw materials of composites			
	Mass fraction of polyols		Mass fraction of MDI on 10 g of polyol	Quantity % of rubber granulate of composite
	Recypol®201	Recypol®601		
	Quantity % of glue of composite			
No. 1	30	70	26.4	95
		5		
No. 2	50	50	19.4	92.5
		7.5		
No. 3	70	30	13.3	90
		10		

Results and Discussion

Stable polyurethane-rubber composites obtained from rubber granulate of car tyres of 1.5 mm to 2 mm and polyurethane glue from polyols, the product of recycling semi-rigid integral polyurethane foam, and hardener (MDI) were obtained.

The thermo-mechanical tests were used to study of the properties of the received composites. On the basis of spectra, the glass transition temperature T_g was determined by using two methods, i.e., from a maximum peak of E'' loss module (by Peak) [6,7] and from the front of the peak of E' storage module (by Onset) [6,7] (Table 2).

On the DMTA spectra analysis (Figs. 1–3) of the polyurethane-rubber composite two glass transition temperatures T_g are observed. The two glass transition temperatures T_g for composites show that the structure of the composites is non-homogeneous. The lower glass transition temperatures T_g determined from the front of the peak of storage modulus (by Onset) for the composites of different content fall within the range of 177.2 K do 181.5 K. The higher glass transition temperatures T_g, whose values differ from the value of T_g of pure and hardened polyurethane glues (215.3 K to 217.4 K), are within the range of 211.9 to 206.8 K and depend on the composition as well as the content of the glue in the composites. For the polyurethane-rubber composite obtained with the use of polyurethane glue No. 3, for mass fractions of polyurethane glue/rubber granules 10/90, a lower value of T_g of the DMTA analysis was not determined due to lack of clear peaks in the spectrum.

The results of previous studies of composites obtained from one-component polyurethane prepolymers for which the T_g shift towards higher temperatures was observed for a polyurethane which probably due to the chemical reaction of polyurethane prepolymer (free isocyanate groups) with disulfide bridges of rubber granulate [1–5]. In this case the T_g shift towards lower temperatures is observed which may indicate the lack of reaction between the used polyurethane glues and rubber granulate and/or that their rigidity is greater in the received composites.

The T_g values determined from a maximum peak of loss module E' (by Peak) are higher but the observed dependences are similar (Table 2). In this case both glass

Table 2. T_g values determined with DMTA method for polyurethane-waste rubber composites and polyurethane glues obtained under pressure of 2 MPa

Quantity %		Polyurethane glue No. 1			
Polyurethane glue No. 1	Rubber granulate	T_g by E' Onset [K]		T_g by E'' Peak [K]	
5	95	207.6	178.7	216.8	184.7
7.5	92.5	208.4	180.2	219.2	186.4
10	90	209.9	179.5	219.1	185.4
100	0	215.7	—	222.8	—
Quantity %		Polyurethane glue No. 2			
Polyurethane glue No. 2	Rubber granulate	T_g by E' Onset [K]		T_g by E'' Peak [K]	
5	95	206.8	180.7	219.8	184.6
7.5	92.5	211.9	181.1	219.0	186.0
10	90	209.5	177.2	219.3	186.6
100	0	215.3	—	225.8	—
Quantity %		Polyurethane glue No. 3			
Polyurethane glue No. 3	Rubber granulate	T_g by E' Onset [K]		T_g by E'' Peak [K]	
5	95	208.5	181.5	219.7	186.9
7.5	92.5	209.4	179.9	219.9	186.7
10	90	211.6	brak	220.9	183.6
100	0	217.4	—	222.7	—

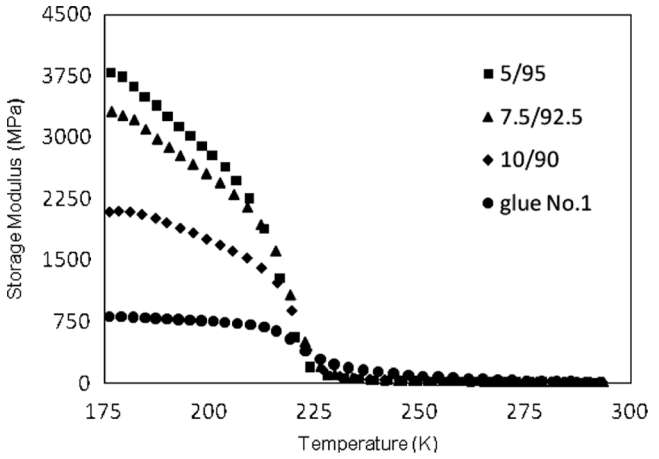

Figure 1. Temperature dependence of storage modulus for chosen frequency 1 Hz: ● the polyurethane glue No. 1, polyurethane-waste rubber composites of weight mass glue No. 1/rubber granules: ■ 5/95; ▲ 7.5/92.5; ◆ 10/90.

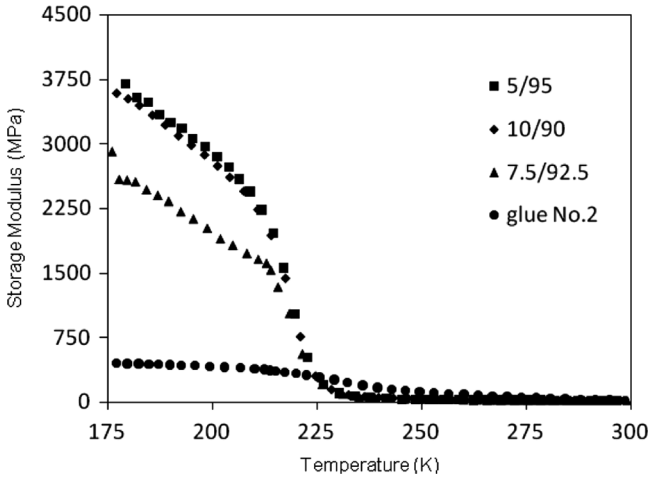

Figure 2. Temperature dependence of storage modulus for chosen frequency 1 Hz: ● the polyurethane glue No. 2, polyurethane-waste rubber composites of weight mass glue No. 2/rubber granules: ■ 5/95; ▲ 7.5/92.5; ◆ 10/90.

transition temperatures of the composite of glue No. 3/rubber granulates were determined.

The course of the curve of storage module E' as a function of temperature for the low temperatures is typical for polymers and illustrates the state of glass. The fall in the value of E' is related to the changes of the polymer properties and to the transition of material from the glass to the flexible state (viscoelasticity). In the studied temperature range (123 K to 323 K) it was observed that values of E' for the same frequency have different values for different hardened polyurethane glues as well as for polyurethane-waste rubber composites (Table 3). The values of E' for polyurethane-waste rubber composites are higher than those for hardened

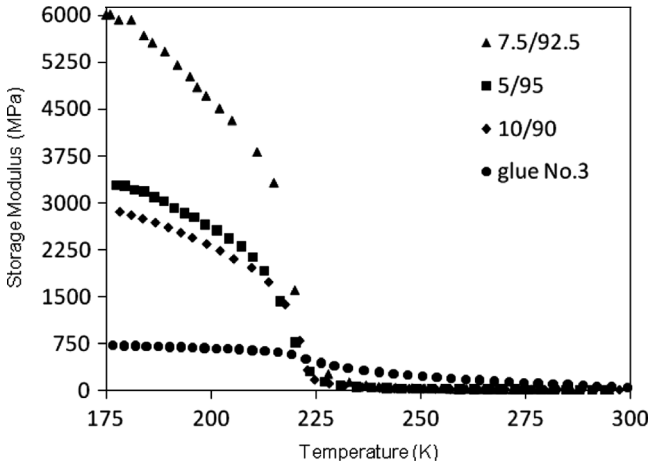

Figure 3. Temperature dependence of storage modulus for chosen frequency 1 Hz: ● the polyurethane glue No. 3, polyurethane-waste rubber composites of weight mass glue No. 3/rubber granules: ■ 5/95; ▲ 7.5/92.5; ◆ 10/90.

Table 3. Value of storage modulus E' for hardened polyurethane glues obtained with the use of these glues at the measurement frequency of 1 Hz

Quantity [%] for composites		Storage modulus E' [MPa]
Glue No. 1	Rubber granulate	Glue No. 1
5	95	3809.9
7.5	92.5	3327.6
10	90	2091.7
100	0	810.9
Glue No. 2		Glue No. 2
5	95	3655.1
7.5	92.5	2908.6
10	90	3584.2
100	0	444.7
Glue No. 3		Glue No. 3
5	95	3280.8
7.5	92.5	5930.2
10	90	2901.1
100	0	721.8

polyurethane glues used to receive them. Low values of E' module for polyurethane glues in comparison to the value of E' module for polyurethane-rubber composites can be caused by the changes occurring at the phase boundary. The lack of dependence between the changes in the value of this module for the composites obtained using different polyurethane glue and their amounts and composition makes it impossible to explain the reasons for those changes. We can only conclude that they are probably related to the different weight ratio of polyurethane glue to the rubber granules in the composition and the weight ratio of MDI in the polyurethane glue. This could affect the preparation of composites and the layer thickness of glue between rubber granulates as well as the sum of E' for the polyurethane glue and rubber in composites.

On analysis of the loss module E'' the distinct maxima characterizing relaxation processes for rubber and polyurethane glue were observed.

The activation energy E_A of the observed processes can be determined on the basis of the modified Arrhenius equation proposed by Vogel-Foulcher (for the processes which are not Arrhenius the $T = (T_{max} - T_g)$) [8]:

$$log f_{max} = A - \frac{E_A}{2,303\, R\left(T_{\max} - T_g\right)}$$

where

$f_{\max}$ – frequency of measurement
A – pre-exponential factor [min^{-1}]
E_A – activation energy [kJ/mol]
T_{max} – temperature at which the max of E' occur [K]
T_g – glass transition temperature [K]
R – gas constant 8,31 [J/(molK)]

The value of the activation energy of the relaxing process can be determined by applying the dependence $\log f_{max}$ versus $1000/(T_{max} - T_g)$.

The relaxation α processes for rubber and for the polyurethane component in polyurethane-waste rubber composites were observed at lower temperatures α and at higher temperatures α′ respectively.

The values of activation energy α′ of relaxation of polyurethane glues used to obtain polyurethane–waste rubber composites differed. This fact may be related to the differences in the composition of these glues (Table 4).

The values of activation energy of relaxation processes determined for rubber and polyurethane in the polyurethane-waste rubber composites are in accordance with the values of the activation energy of α relaxation processes observed for rubber and polyurethanes. The lowest value of activation energy for α′ relaxation process was determined for glue No. 2 of weight ratio of polyols Recypol®201 to Recypol®601: 50/50 and ratio of diisocyanate (MDI) in polyurethane glue 19.4 g for a 10 g mixture of polyols. It was equal to 199.6 [kJ/mol]. The highest value of activation energy for α′ relaxation was determined for glue No. 1 of weight ratio of polyols Recypol®201 to Recypol®601: 30/70 and ratio of diisocyanate (MDI) in polyurethane glue 26,4 g for a 10 g mixture of polyols and was equal to 341.3 [kJ/mol].

On analyzing the values of the activation energy for polyurethane glues and polyurethane-waste rubber composites no dependence between change of E_A and the change of weight ratio of glue to the rubber granules in composites can be observed. This can be related to the different participation of diisocyanate (MDI) in the glue used for the obtained composites.

Table 4. Value of activation energy E_A calculated on the basis of DMTA analysis of relaxation processes for polyurethane glues and polyurethane-waste rubber composites obtained by using these glues

		Activation energy E_A [kJ/mol]	
Quantity [%]		α′ relaxation	α relaxation
Glue No. 1	Rubber granulate		
5	95	267.0 ± 18.4	93.1 ± 16.7
7.5	92.5	181.9 ± 17.7	170.0 ± 10.5
10	90	226.2 ± 17.6	109.8 ± 18.3
100	0	341.3 ± 18.7	—
Glue No. 2			
5	95	253.1 ± 19.0	122.2 ± 17.5
7.5	92.5	258.3 ± 18.6	102.9 ± 17.6
10	90	292.4 ± 17.8	223.7 ± 16.8
100	0	199.6 ± 18.5	—
Glue No. 3			
5	95	252.0 ± 18.4	126.0 ± 18.2
7.5	92.5	246.9 ± 18.6	150.5 ± 17.6
10	90	313.9 ± 18.4	116.8 ± 18.8
100	0	275.6 ± 17.9	—

Therefore a more detailed research on the influence of quantity of MDI on the properties of the received polyurethane glues and the effect of glues used for polyurethane-waste rubber composites should be carried out.

Conclusion

Stable and flexible composites from rubber granulate of car tyres and polyurethane glues were obtained from polyols prepared from recycled semi-rigid integral polyurethane foams and isocyanate (MDI). Two glass temperatures T_g show that the products were non-homogenous.

The T_g shift towards lower temperatures connected with the content of polyurethane used for polyurethane-waste rubber composites which contradicts the results of previous studies on composites [1–5] and may point to a lack of reaction between used polyurethane glues and rubber granulate. However the most probably it is related to a greater rigidity of polyurethane in the thin layer between rubber granulates in composites and/or to big amounts of MDI in polyurethane glues. That makes the correct interpretation of the results difficult.

For the same reasons the interpretation of the difference of modulus E'' and E' as well as the activation energy values of the relaxation process on the DMTA investigations are also difficult. The analysis of loss module E' allowed us to observe two relaxation processes for polyurethane-waste rubber composites α – originating from the rubber and α' – from the polyurethane glue.

The dependences of the changes of the activation energy of relaxation processes with the change of weight ratio of polyurethane glue in polyurethane-waste rubber composites were observed.

The results of the performed examination showed that application of Recypol®201 and Recypol®601, received in the processes of glycolysis of used polyurethane foams, as an ingredient of polyurethane glue for polyurethane-waste rubber composites allows us to obtain stable composites with good mechanical properties.

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