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The Influence of Polyurethane Component on the Properties of Polyurethane-Rubber Composites Obtained from Waste Materials

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Properties of the polyurethane-rubber composites obtained from used products were studied. The influence of the amount of polyurethane glue and amount of isocyanate diphenylmethane 4,4′-diisocyanate (MDI) on composites selected properties was observed.

The dynamic thermo-mechanical analysis allowed us to determine the glass transition temperature Tg 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.

Keywords Polyurethane-rubber composites; DMTA studies; recycling

Introduction

Polymeric materials due to their properties are used in various industries. Depending on the raw materials used in their preparation, and various conditions of their processing, a wide range of products with the desired properties is obtained. The universality of their application is the cause of a significant amount of polymer waste generated after the period of their useful application.

Utilization of such wastes in an appropriate way so that the products obtained from them could be used for the production of subsequent polymeric articles with properties like or similar to the starting product or with other beneficial functional properties is being studied. One of the possible methods of utilization of post-use condensation polymers in the process of their chemical recycling can be their glycolysis.

The process of glycolysis can also be applied to post-use products made of polyurethanes.

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Depending on the used type of post- use polyurethane products such as polyurethane foams and other substances involved in the process, and also depending on the conditions of the process of glycolysis, the products of the process that can be obtained are polyols with different chemical properties. The obtained polyols may have different applications [1–3].

Rampf Ecosystems Company, in accordance with the method invented, subjects various types of polyurethane foams to the glycolysis process to obtain the products, which then can be used as a raw material to produce new polymer products (e.g. polyurethane plastics) in various industries (e.g. footwear industry–footwear soles, automotive industry–automobile steering wheels, armrests, etc., furniture industry–furniture foam ...) [4–8].

Another commonly occurring waste, post-use polymer material (rubber), are scrap car tires. These wastes may be used in material recycling, chemical recycling and energy recycling used as a fuel (recovery of material chemical energy) [9, 10].

Material recycling of waste tires mostly consists in their fragmentation and using the fragmentation products to obtain different praducts. Waste tires are fragmented at ambient or by cryogenic method [11–14].

As a result of this process the following products can be obtained:

- Cut tires (halves and smaller pieces) size $>$ 300 mm
- Shreds with a size of 300–50 mm
- Chips with a size of 50–10 mm
- Granules rubber with a size of 10–1 mm
- Crumb rubber with a size of 1–0.1 mm
- Pulp (by-product of tire retreading).

The way of utilization of fragmented waste from scrap automobile tires depends on the degree of fragmentation [15–18].

Most shreds and chips are used as a lightweight fill in the construction of tunnels, underpasses, embankments, as road base courses, vibration–absorbing materials, etc. [19–22].

The granulate is used for the preparation of artificial turf for football fields, surfaces for playgrounds, sports fields, jogging paths, noise absorbing barriers, sleepers cushioning shocks and vibration, etc. It is also used when modifying asphalt surfaces by a dry method, [23–26].

The crumb rubber can be used to produce such products as car mats, rugs, mats for cattle, soles, flooring, roofing, compositions with polypropylene of thermoplastic properties, which are used in the manufacture of lining and seals [27, 28].

The crumb rubber is also used to modify the asphalt binder used in road construction. It is used to modify asphalt surfaces by the so-called "wet method" and gives the so-called asphalt rubber [29, 30]. The crumb rubber introduced to the asphalt mixture causes the increase of its hardness and surface abrasion resistance; it reduces slip at precipitation conditions and at low temperature. The added crumb rubber also affects the reduction of road noise and provides good adhesion and cohesion.

Fragmented post-use rubber waste may also be used for the preparation of polyurethane- rubber composites with specific, required properties.

Utilization of polyurethane post-use products and scrap tires and development of a method that would allow the products of their recycling to be used as raw materials for the production of polyurethane- rubber composites with fixed properties are the subject of our studies [31–35].

Previously conducted studies on the use of rubber granulate obtained from car tires using polyurethane prepolymers as an glue for the preparation of polyurethane- rubber

Table 1. The polyurethane glues

Quantity of polyol [%]		
Recypol®201	Recypol®601	MDI isocyanate index NCO
30	70	150
50	50	175
70	30	

composites provided an opportunity to obtain stable products with the required properties [36–40].

The application of post-use products for the preparation of raw materials (post-recycling polyols) used for the production of polyurethanes, which were subsequently used as glues for polyurethane-rubber composites, can help to extend the area of application of these polyols and receiving the composites with the expected beneficial properties.

Experimental

Materials and Methods

The following raw materials were used to the tests:

- Recypol®201 and Recypol®601 polyols, are the polyether polyols obtained by the process of glycolysis developed by the German company Rampf Ecosystems GmbH.
- 4,4′diphenylmethane diisocyanate (MDI) manufactured by Elastogran.
- Rubber granulate with a grain size from 1.5 to 2.0 mm, obtained from car tires. The excess of isocyanate was used according to the calculated NCO index (Table 1).

The amount of isocyanate (m_{iso}) required to obtain a polyurethane adhesive was calculated using the formula:

$$m_{iso} = \frac{m_{polyol} \cdot LOH}{M_{KOH} \cdot 1000} \cdot \frac{100 \cdot 42,02}{c_{iso}}$$

where:

m_{polyol} – weight of the polyol [g]
LOH – hydroxyl number of the polyol [mg KOH/g]
M_{KOH} – molar mass KOH [56.1 g/mol]
c_{iso} – % isocyanate group content

The calculated quantity of isocyanate corresponds to the stoichiometric quantity of the substance needed to obtain the polyurethane foam [41].

The measurements were performed on samples with the adopted isocyanate index of 150 and 175.

Polyurethane-rubber composites were obtained with the following % shares of polyurethane glue/rubber granules: 5/95, 7.5/92.5 and 10/90 (Table 2).

The resulting composites were placed in the matrix under a load of 2 MPa, and then heated at 320 K for 90 min.

Table 2. The polyurethane-rubber composites

Quantity [%]	
Glue	Rubber granulate
5	95
7.5	92.5
10	90

A dynamic mechanical thermal analysis was carried out on the DMA Q800 apparatus of TA Instruments in the temperature range from 123 K to 323 K at a heating rate of 2 K/min, at a bending frequency from 1 Hz to 150 Hz, which permitted to determine a glass transition temperature *Tg*, and a course of relaxation processes in composites.

The hardness of polyurethane glues and polyurethane rubber composites was determined on the Shore apparatus, according to the Polish standard PN–ISO 868 with a penetrator according to PN-93/C-04206.

Polyurethane-rubber composites were also subjected to aging for 7 days at 343 K according to the Polish standard PN–ISO 188:2000.

Results and Discussion

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA spectra analysis allowed to determine the glass transition temperature T_g from the peak maximum of the loss modulus E'' by Peak and from the face of the storage modulus E′ by Onset (Tables 3, 4) as well as the course of relaxation processes in the resulting composites.

The analysis of changes in storage modulus E' and loss modulus E'', as a function of temperature, allowed the calculation of the activation energy E_A for relaxation processes of polyurethane glues and polyurethane-rubber composites.

The activation energies of the observed processes have been calculated on the basis of a modified Arrhenius equation proposed by Vogel-Foulcher for non-Arrhenius processes, where $T = (T_{max}–T_g)$.

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

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 activation energy of relaxation processes may be determined using the relationship $log\ f_{max}\ 1000/(T_{max}\text{-}T_g)$.

Table 3. T_g values determined with DMTA method for polyurethane-waste rubber composites and polyurethane glues obtained under pressure of 2 MPa for NCO 150

Quantity [%]		Glass transition (T_g) K			
Glue Recypol® 201/601 30/70	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
5	95	181.7	208.4	179.8	221.0
7.5	92.5	180.5	208.1	179.5	219.9
10	90	179.8	207.6	180.0	220.7
100	0	213.6	—	223.2	—
Glue Recypol® 201/601 50/50	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
5	95	180.2	209.7	181.5	219.7
7.5	92.5	183	208.5	180.4	221.2
10	90	182.8	209.5	179.9	219.9
100	0	214.0	—	222.6	—
Glue Recypol® 201/601 70/30	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
5	95	181.6	209.2	181	221.2
7.5	92.5	181.5	209.1	182	221.7
10	90	180.6	208.9	181.4	219.6
100	0	213.8	—	222	—

The DMTA spectra analysis showed that for the polyurethane-rubber composites the two glass transition temperatures were observed, which may be related with their heterogeneous supermolecular structure.

It was observed that the T_g values for the composites obtained from the polyurethane glues with lower content of MDI (index NCO150) show lower glass transition temperatures than the composites obtained from polyurethane glues with a higher content of MDI (index NCO175) [31].

Analysis of the loss modulus E'' allowed to observe the presence of two relaxation processes in polyurethane-rubber composites. An α process likely associated with the relaxation processes in rubber and an α‘ process–with the relaxation processes occurring in the polyurethane glue. The α relaxation processes of rubber in polyurethane–rubber composites were observed at lower temperatures, and the α‘ of polyurethane glue at higher temperatures [31, 33].

The determined values of the activation energy of relaxation processes for polyurethane glues and polyurethane-rubber composites are given in Table 5.

Higher values of the activation energy of relaxation processes for the polyurethane glue with a lower content of MDI (NCO150) were observed for its fraction of 7.5% (Table 5). This may indicate that, for this glue, for that his fraction, the most durable polyurethane-rubber composites were obtained. The higher activation energy value may additionally indicate that for such a fraction of glue in the composite a greater number of bonds was formed between the polyurethane glue and the rubber granules. The ability to create such

Table 4. T_g values determined with DMTA method for polyurethane-waste rubber composites and polyurethane glues obtained under pressure of 2 MPa for NCO 175

Quantity [%]		Glass transition (T_g) K			
Glue Recypol® 201/601 30/70	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
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	—
Glue Recypol® 201/601 50/50	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
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	—
Glue Recypol® 201/601 70/30	Rubber granulate	DMTA E′ onset		DMTA E″ peak	
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	—

bonds has already been suggested in our other studies [37–40]. This may indicate a greater stability of the composite with such a fraction of polyurethane glue. Also we stated that there is no effect of the fraction of post-recycling polyols on the dependence previously described.

It is different when applying the polyurethane glue with a higher content of MDI (NCO175) to the preparation of polyurethane-rubber composites. It seems that in this case the effect on the value of the activation energy of relaxation processes in polyurethane rubber composites depends not only on the proportion of free isocyanate groups in the glue but also on the amount and type of post-recycling polyols Recypol 201 and Recypol 601 (Table 5) used to obtain a polyurethane glues. It can be assumed that the higher values of the activation energy of relaxation processes are associated with a higher content of polyurethane glue (with a higher content of Recypol 201 polyol) in the composite.

One could argue that the stability of polyurethane- rubber composites obtained from polyurethane glues prepared from polyols from the recycling processes of semi-rigid polyurethane foams and MDI isocyanate and rubber granules depends on the fraction of glue in the composites but also on the quantity of MDI glue and the fraction of individual polyols therein.

Mechanical Properties of Polyurethane-Rubber Composites

In order to determine the effect of aging on the polyurethane- rubber composites, obtained from polyurethane glues prepared from polyols from recycling of semi-rigid polyurethane

Table 5. Value of activation energy E_A calculated on the basis of DMTA analysis of relaxation processes for polyurethane glues and polyurethane-waste rubber composites

Quantity [%]		Activation energy E_A [kJ/mol]	
Glue Recypol®201/601 and MDI with isocyanate index	Rubber granulate	α' relaxation	α relaxation
	Recypol®201/601 = 30/70, and NCO 150		
5	95	230.5 ± 17.3	101.1 ± 18.4
7.5	92.5	272.7 ± 18.0	97.1 ± 17.8
10	90	245.7 ± 16.1	91.5 ± 17.6
100	0	202.3 ± 17.8	—
	Recypol®201/601 = 50/50, and NCO 150		
5	95	220.5 ± 17.1	143.5 ± 17.9
7.5	92.5	260.7 ± 17.6	101.8 ± 17.8
10	90	193.7 ± 17.2	158.7 ± 16.1
100	0	195.2 ± 17.2	—
	Recypol®201/601 = 70/30, and NCO 150		
5	95	232.5 ± 17.6	85.9 ± 18.6
7.5	92.5	234.5 ± 17.2	98.8 ± 16.3
10	90	228.3 ± 18.4	110.8 ± 18.2
100	0	239.8 ± 16.3	—
	Recypol®201/601 = 30/70, and NCO 175		
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	—
	Recypol®201/601 = 50/50, and NCO 175		
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	—
	Recypol®201/601 = 70/30, and NCO 175		
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	—

foams and MDI isocyanate and rubber granules, their hardness was determined, as well as the hardness of polyurethane glues with different% fractions of Recypol® 201 and Recypol® 601 polyols and MDI isocyanate, before and after aging for 7 days at a temperature of 233 K (Table 6). The hardness of post-use automobile tires from which the rubber granules was obtained amounted to 60 °Shore A.

On the basis of obtained test results it can be concluded that the hardness of polyurethane glues–for different fractions of polyols from recycled semi-rigid polyurethane foams Recypol® 201/Recypol® 601 in them–decreases with the increase of% fraction of Recypol® 201 polyol in the glues for NCO150 (Table 6). In contrast, the hardness for the

Table 6. Hardness of polyurethane glue and polyurethane–rubber composites before and after the process of their ageing

Quantity [%] Recypol® 201/Recypol® 601								
		30/70		50/50		70/30		
Quantity [%]		Hardness° Shore A–before and after the process of their aging						
Polyurethane glue	Rubber granulate	Before	After	Before	After	Before	After	Index NCO
100	0	78.6	77.8	68.4	70.8	47.6	46	150
5	95	65.2	63.9	65.9	63.7	60.9	61.7	
7.5	92.5	67.4	66.6	67.8	66.4	62.6	65.3	
10	90	68	67.3	68.2	67.3	65.7	67.7	
100	0	50.4	53.6	58.8	62	65.8	65.8	175
5	95	65.2	65	67.2	62.8	65	64.8	
7.5	92.5	67.5	67.4	68	66	67.2	68.4	
10	90	68.2	67.8	70.2	68.3	68	68.4	

glues with NCO175 increases with increasing content of Recypol® 201 polyol in the glues (Table 6). It can be concluded that the hardness of obtained polyurethane glues depends on the quantity of polyol used to produce it, as well as on the fraction of isocyanate in the glues. This result may confirm the suggested influence of both the quantity of MDI and the quantity and type of polyols from the recycling processes of semi-rigid polyurethane foams used in the preparation of polyurethane glues onto the values of activation energy of the relaxation processes in the glues and in the composites obtained with using them (Table 6).

Based on the obtained results it can be concluded that the hardness of polyurethane obtained from the glue of NCO 150 decreases with the increase of the fraction of Recypol®201 polyol in the said glue. This points to a decrease of the number of free isocyanate groups to react with the hydroxyl groups of polyols and obtain a product with a higher hardness value (Table 6).

The opposite situation can be observed in the case of the glue NCO 175. With an increase in Recypol® 201 polyol content the hardness of polymer obtained from it increases. Probably the number of free isocyanate groups exceeds the number of available hydroxyl groups. It also has a pronounced effect on the hardness values of polyurethane- rubber composites obtained with the use of this glue. The high hardness values of composites with the low harness values of corresponding polyurethanes may again indicate to the reaction of free isocyanate groups with the hydrogen sulphide groups of the rubber granule (Table 6), as suggested previously [33–35].

Based on the results of aging the samples of polyurethanes and polyurethane- rubber composites at 343 K for 7 days, one can find a slight change in their hardness located in the range from 0.1 to 4.1%, which may indicate the resistance of the obtained composites to elevated temperature. The increase in hardness after aging for the composites with % fraction of the Recypol® 201/Recypol® 601 polyol mixture amounting to 70/30 and the index NCO150 and index NCO175, which is particularly clear in the case of polyurethane-rubber composites obtained with the use of the glue of NCO 175, may also indicate

supplementary cross-linking of those composites involving the excess free isocyanate groups, or that the process of polyurethane glue bonding with granulate has not been completed prior to their annealing.

Conclusions

Based on the polyurethane glues manufactured from polyols from chemical recycling of semi-rigid polyurethane foams and MDI and rubber granules from recycling of scrap tires the stable polyurethane-rubber composites with heterogeneous supermolecular structure were obtained. The results of the studies showed that the use of Recypol® 201 and Recypol® 601 polyols, obtained in the process of glycolysis of post-use polyurethane foams, as an ingredient of the polyurethane glue used for the manufacture of polyurethane-rubber composites, allows to obtain of stable composite.

On the basis of the results of performed tests of selected properties of the resulting polyurethane-rubber composites, it can be concluded that the stability of these composites depends both on the quantity of glue in the composite but also on the quantity of MDI isocyanate as well as the fraction of individual polyols in it.

Based on the results of the aging test of the samples of polyurethanes and polyurethane-rubber composites it can be concluded that during their aging process the supplementary cross-linking of polyurethane glue may proceed or that the polyurethane glue bonding with granules has not been completed prior to their annealing.

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