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Urea–urethane nanocomposites obtained from modified methylalumoxane oligomers

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Urea–urethane elastomers were synthesized in a polyaddition reaction of ethylene oligoadipate (OAE) of an average molecular weight 2000 u with bis(4-isocyanatephenyl)methane (MDI). Dicyandiamide was used as a chain extender. In order to obtain hybrid nanocomposites, OAE was modified by the reaction with methylalumoxanes (MAO) prior to use. The excess of active methyl groups of MAO was deactivated by reactions with alcohols or alkylphosphates. This method allowed one to introduce nano-sized aluminum-oxide based moieties into the polyurethane. The amount of nanoparticles was equal to 3 wt. %. The aim of the study was a homogeneous molecular dispersion of aluminum-oxide units in order to obtain urea–urethane nanocomposites with a higher fire resistance and improved mechanical properties. Microstructure of the nanocomposites was studied with the high resolution scanning electron microscopy (HRSEM). Mechanical properties were examined by standard testing procedures. Flammability tests were also performed using a cone calorimeter under heat flux equal to 50 kW/m^2. The results of the microstructure studies show even distribution of the nano-sized aluminum-oxide units in the polyurethane bulk. We observed an increase of such properties as Young's modulus and hardness, accompanied by a significant decrease in the heat release rate.

Key words: *urea–urethane elastomer; nanocomposite; methylalumoxanes*

1. Introduction

Polymer matrix–ceramic composites are nowadays commonly researched and developed for variety of applications. For example, particles of SiO_2, SiC, TiC, Al_2O_3 are added to polymer matrices to increase their hardness, stiffness and wear resistance [1].

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Polymer nanocomposites are formed through the union of two very different materials with organic and mineral pedigrees. They are distinguished by high tensile strength, elastic modulus and heat distortion temperature without a loss in impact resistance. They also have a lower water sensitivity, permeability to gases and thermal coefficient of expansion. Due to those features, such nanocomposites found many industrial applications, especially in food packaging and automobile industries [2].

Segmented urea–urethane elastomers have their macromolecules built of soft (S) and hard segments (H). The soft segments are formed in an addition reaction of oligodiols with diisocyanate. The hard segments are obtained in a polyaddition reaction of the isocyanate groups (–NCO) with the chain extender such as low -molecular-weight compound terminating with hydroxyl (–OH) or amino groups ($–NH_2$) [3]. The molar ratio of hard and soft segments can be changed according to the molar ratio of substrates. Urea–urethane elastomers are characterized by such advantageous properties like high tear strength and tensile modulus. Therefore they have found many applications for a wide range of products like for instance sieves for mining industry.

We have developed a new method of fabrication of hybrid urea–urethane nanocomposites obtained from oligodiols modified with methylalumoxanes [4]. Oligodiols were reacted with methylalumoxanes (MAO) prior to their use. This method allowed to introduce nano-sized aluminium oxide based moieties into the polyurethane [5].

In this work, we present results of our studies on introduction of modified methylalumoxanes as fillers of urea–urethane elastomers. This allowed us to obtain hybrid urea–urethanes with nano-sized $(AlO)_n$ moieties evenly distributed in the elastomer. The aim of the study was to obtain urea–urethane nanocomposites with higher fire-resistance and improved mechanical properties.

2. Experimental

Urea–urethane elastomers were synthesized in a polyaddition reaction of ethylene oligoadipate (OAE) of an average molecular weight 2000 a.u. with bis(4-isocyanatephenyl)methane (MDI). Dicyandiamide (DCDA) was used as a chain extender. DCDA contains two amino groups and one highly polar cyanimine group bonded to the same carbon atom. The polar urea groups are formed as a result of the reaction of amino and isocyanate groups. The presence of a strong polar urea group and a strong polar nitrylimide side-group in every short hard segment influences the urea–urethane properties. Such polyurethanes are distinguished by low water absorption, high resistance to hydrolysis and high resistance for abrasive wear, especially at the moisture conditions. They are also characterized by such advantageous properties like high tear strength and tensile modulus.

The urea–urethane polymer and its composites were synthesized in a one-pot reaction of MDI with OAE and DCDA at a molar ratio of MDI/(OAE+DCDA) equal to 2.0. All reactions were carried out in a vacuum reaction vessel at 2–5 hPa with a me-

chanical stirring. In order to obtain hybrid nanocomposites, methylalumoxanes (MAO) were modified by the reaction with OAE, alcohols and/or alkylphosphates prior to use. The modification process is described in Sect. 3. The amount of MAO based fillers introduced into polyuretanes was equal to 3 % by weight. The mixture of substrates was cast into special moulds and then curing process was carried out at elevated temperature.

Microstructure of the nanocomposites was studied using the HRSEM LEO 1530 (Zeiss). Mechanical properties were examined by standard testing procedures developed for elastomers. The parameters measured were: tensile strength, elastic modulus, tear strength, elongation at break, hardness and abrasive wear.

Flammability tests were made using a cone calorimeter under the heat flux equal to 50 kW/m^2. The following parameters were measured: maximum heat release rate, average specific extinction area, average CO and CO_2 yields and time to sustained ignition.

3. Results and discussion

Alumoxanes are compounds containing Al–O–Al groups. Their properties have been intensively studied as they play a key role in the Ziegler-type polymerization [6]. Despite many detailed studies, the structure of methylalumoxane (MAO) still remains a "black box". It cannot be elucidated directly, because of multiple equilibria present in MAO solutions. The structure of MAO can be described as oligomers of $[CH_3AlO]$ moieties containing some associated $(CH_3)_3Al$ molecules. The formula of commercially available MAO is best represented as $[-(CH_3)_{1.4–1.5}AlO_{0.75–0.80}]_n$ [7, 8]. Molecular weights of MAO range from 1000 to 2700 [7, 9, 10]. In the present studies, we have used methylalumoxane purchased from Crompton GmbH as 10% solution in hexane (MAO2), and the only structurally characterised methylalumoxane, synthesised in our group [11] (MAO1). The structure of the latter alumoxane is presented in Fig. 1.

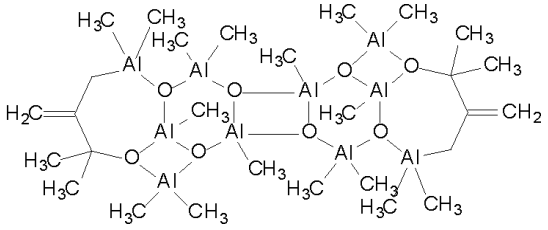
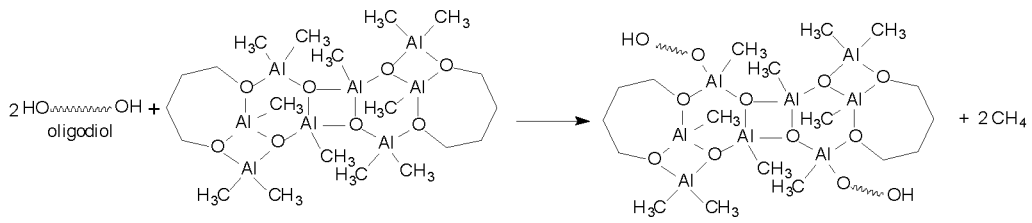


Fig. 1. The structurally characterised methylalumoxane (MAO1)

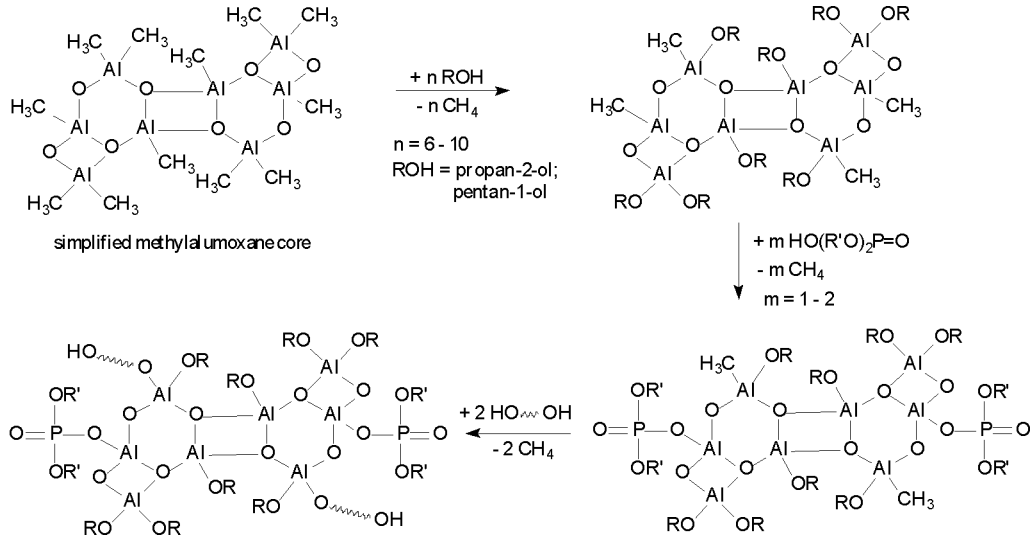
Methylalumoxane molecules have several methyl groups bonded to aluminum. These reactive groups have been used for a modification. The idea of the modification was to react a molecule of methylalumoxane with two molecules of ethylene oligo-

adipate (OAE) used in the synthesis of polyurethane. This should lead to the formation of the following compound (Scheme 1):



Scheme 1

The remaining methyl groups had to be blocked to prevent their further reactions. It was achieved by the reactions with alcohols (propan-2-ol or pentan-1-ol) and/or with alkylphosphates. The final products retained the character of a diol and were used for synthesis of polyurethanes with evenly distributed nano-sized $[–Al–O–]_n$ moieties. A simplified scheme of the synthetic procedure of modified methylalumoxanes is presented in Scheme 2.



Scheme 2

The diameter of the molecule of the structurally characterised methylalumoxane is about 1.5 nm, while the size of inorganic particles incorporated into polyurethane structure is within the range of 20–100 nm (Figs. 2 and 3). This indicates that further association of alumoxane molecules occurs during modification and the actual structure of alumoxane moieties remains unknown. Nevertheless, this schematic picture illustrates the idea of an incorporation of alumoxane moieties into the polyurethane chains.

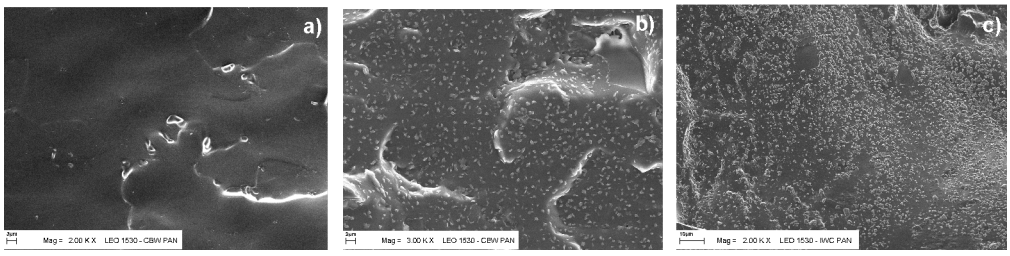


Fig. 2. SEM images of brittle fractures of PU without nanofillers (a) and with: b) PU + M1, c) PU + MP4

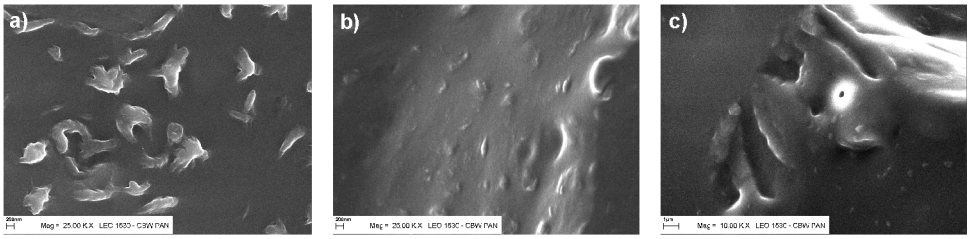


Fig. 3. SEM images of brittle fractures of PU nanocomposites obtained from:
a) MAO1 with propan-2-ol, b) MAO1 with pentan-1-ol, c) MAO2 with pentan-1-ol

The reagents used for the fabrication of the samples are listed in Table 1.

Table 1. Reagents used for the fabrication of samples

Sample	Metyloalumoxane	Alcohol	Ester[a]
PU + M1	MAO1	propan-2-ol	–
PU + M2	MAO1	pentan-1-ol	–
PU + M3	MAO2	pentan-1-ol	–
PU + MP7	MAO1	pentan-1-ol	ester 1
PU + MP1	MAO2	–	ester 2
PU + MP3	MAO2	pentan-1-ol	ester 2
PU + MP4	MAO2	pentan-1-ol	ester 1
PU + M4	MAO2	pentan-1-ol	-
PU + MP5	MAO2	pentan-1-ol	ester 2
PU + MP6	MAO2	pentan-1-ol	ester 2
PU + MP11	–	–	ester 1

[a]Ester 1 – $CH_3P(O)(OCH_3)_2$, ester 2 – $[CH_3(CH_2)_3CH(CH_2CH_3)$-$CH_2O]_2P(O)OH$

As is shown in Fig. 2, the use of oligoadipate chemically bonded to methylalumoxane leads to even distribution of the nano-sized aluminum-oxide units in the polyurethane matrix.

The aluminum-oxide units may differ in shape and size according to the kind of MAO (MAO1 or MAO2) and the way of its modification. The modification of both

MAO1 and MAO2 with pentan-1-ol leads to the formation of more elongated (needle-like) particles (Figs. 3b, c). Modification of MAO2 with ester 2 gives spherical nanoparticles (Figs. 4a, b) in comparison to modification with ester 1 (Fig. 4c). Such differences in nanocomposite structures can influence their mechanical properties.

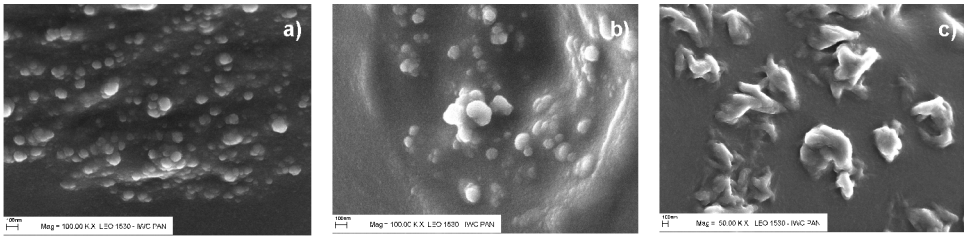


Fig. 4. SEM images of brittle fractures of nanocomposites obtained from:
a) MAO2 with ester 2, b) MAO2 with pentan-1-ol and ester 2, c) MAO2 with ester 1

It was found that the highest increase in Young's modulus is observed after modification of MAO2 with pentan-1-ol and additionally with ester 2 (Fig. 5). Modification of PU matrix with nanoparticles gives a significant increase of Young's modulus and slight increase of the hardness (Fig. 6).

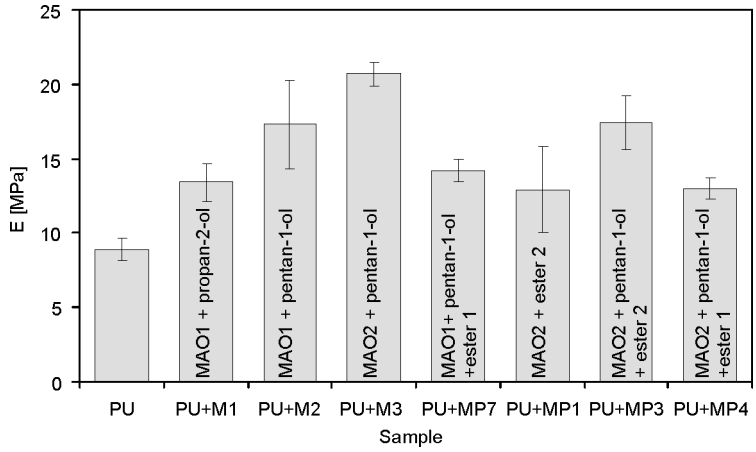


Fig. 5. Young's modulus of poly(urea–urethane) nanocomposites

One of the most important properties of polyurethanes studied was their abrasive wear. As is shown in Fig. 6, the incorporation of methylalumoxanes after the modification only with alcohol did not change the abrasive wear. A significant increase in the abrasive wear was observed in nanocomposites obtained from MAO modified with esters.

Flammability test results are shown in Table 2. The addition of MAO modified with phosphoric acid esters to PU matrix led to a significant reduction of HRR_{max}. Unfortunately, the reduction of SEA, which is responsible for smoke emission, was

not achieved. The benefit of usage of MAO modified with phosphoric acid ester was a visible shortening of the sustained ignition time. The sample PU + MP11 was modified only with phosphoric acid ester. It was found that such modification without application of MAO did not give satisfactory flammability results.

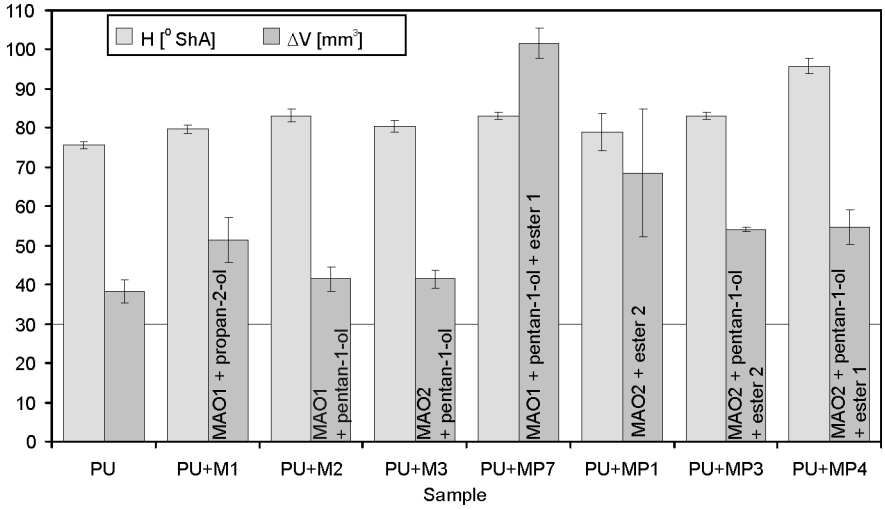


Fig. 6. Hardness and abrasive wear of poly(urea–urethane) nanocomposites

Table 2. Results of the flammability test

Symbol	Parameter	PU	PU + M4	PU + MP4	PU + MP5	PU + MP6	PU + MP11
HRR_{max}	maximum heat release rate [kW/m^2]	1178 ±92	1704 ±176	703 ±34	621 ±40	694 ±38	1166 ±91
SEA	specific extinction area [m^2/kg]	218 ±24	203 ±9	299 ±82	287 ±61	323 ±22	381 ±25
t_{ig}	time to sustained ignition [s]	26.39 ±0.13	22.78 ±0.73	25.20 ±0.35	20.08 ±0.02	23.34 ±0.35	22.81 ±0.37
CO	average CO yield [kg/kg]	0.07769 ±0.04815	0.06530 ±0.02492	0.01673 ±0.00091	0.01546 ±0.00113	0.01632 ±0.00197	0.14231 ±0.01425
CO_2	average CO_2 yield [kg/kg]	1.95632 ±0.03287	2.07708 ±0.09619	1.86797 ±0.00769	2.00365 ±0.05704	1.96577 ±1.01983	1.76922 ±0.05274

4. Conclusions

It was found that methylalumoxanes with methyl groups substituted by alcohols (propan-2-ol or pentan-1-ol) and/or alkylphosphates and ethylene oligoadipate can be successfully applied in synthesis of urea–urethane hybrid polymers. The results of the studies of microstructure show even distribution of the nano-sized aluminum-oxide units in the polyurethane bulk. Young's modulus, hardness and tensile strength at

100% elongation increased; on the other hand, a significant decrease was observed in the heat release rate.

Acknowledgements

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