

THERMAL STABILITY AND DAMPING PROPERTIES OF POLYURETHANE HYBRID MATERIAL BASED ON CASTOR OIL

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Abstract: This study reports the fabrication of environmentally friendly polyurethane materials using either 2,4-toluene diisocyanate or isophorone diisocyanate, castor oil as a polyol component, and TiO₂ nanoparticles. Samples were prepared with stoichiometric balance of reactive groups. Dynamic viscoelastic properties of prepared samples were studied. The ratio of the loss component to the storage component ($\tan\delta$) was used as a measure of the material damping properties. The glass transition temperature was determined as a position of the $\tan\delta$ curve maximum. The temperature range with $\tan\delta > 0.3$ was used to evaluate damping capacity of elastomers. Thermal stability of prepared samples was estimated by TGA method. It was assessed that PU based on aliphatic diisocyanate have higher thermal stability. Obtained values of the glass transition temperature and the starting degradation temperature are important for the application window of novel materials.

Keywords: Castor oil, polyurethanes, DMA, nanocomposites.

1. INTRODUCTION

Polyurethanes (PU) are polymers composed of a chain of organic units joined by carbamate (urethane) links and have enormous diversity of chemical composition, tissue biocompatibility, biodegradability and mechanical properties. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups. These materials are produced in the form of microcellular foam seals and gaskets, fibers, durable elastomeric wheels and tires, electrical potting compounds, coatings, adhesives and auxiliary agents, for wind turbine blades, memory shape materials, acoustic foams, hard-plastic parts for electronic instruments [1–5]. The formation of polyurethanes based on vegetable oils is very complex and thus for industrial production it is important to determine the optimal temperature for synthesis and finally to obtain materials with the proper mechanical and

thermal properties. Some PU types are very prominent damping materials for reduction of noise and prevention of fatigue failure of materials because they can be easily tailored either as thermoplastic elastomers or as permanent polymer networks [6–11]. In the case of polyurethane hybrid materials the damping behavior is affected by intramolecular friction and molecular relaxation, friction between polymer chains and filler, and friction between two filler particles [12]. PU with dangling chains in network structure have good energy absorbing properties [13]. The materials based on aliphatic 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (isophorone diisocyanate, IPDI) due to its stable aliphatic structure makes them ideal for producing durable, non-yellowing materials. Isocyanate groups of different reactivity allow selective chemical reactions and application for wood coatings, leather adhesives, network precursors, and powder coatings. The aromatic isocyanates are more

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reactive than aliphatic isocyanates. The 2,4-diisocyanato-1-methyl-benzene (2,4-TDI) have two groups with different reactivity. The goal of this work was to synthesized eco-friendly polyurethane materials using either aromatic 2,4-toluene diisocyanate or aliphatic isophorone diisocyanate and castor oil and to prepare its hybrid materials with TiO₂ nanoparticles.

2. EXPERIMENTAL SECTION

2.1. Raw Materials

The vegetable triglyceride castor oil with hydroxyl number (OH) 170 mg KOH/g; 2,4-diisocyanato-1-methyl-benzene (2,4-toluene diisocyanate, 2,4-TDI), 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane (isophorone diisocyanate, IPDI) and titanium(IV) oxide nanoparticles TiO₂ (average particles size 60 nm), were supplied from Sigma-Aldrich Company.

2.2. Sample preparation

Synthesis was carried out in bulk without catalyst by a one-step reactive process with stoichiometric balance of reactive groups. The samples were prepared with stoichiometric balance of reactive groups in the absence of catalyst. The castor oil was dried in vacuum for 10 hours at 70 °C before the use. The reaction was carried out by the addition of diisocyanate to castor oil under stirring for 15 minutes in dry nitrogen atmosphere. Then the mass was cast into preheated mold and kept in an oven at 110 °C for 12 h. Hybrid materials based on 2,4 TDI were prepared with TiO₂ particles (0.5; 1.0; 2.0 mass%). In the first step crude castor oil was dried in vacuum at 70 °C. During this period acetone suspension was treated in ultrasonic bath. In the second step the suspension and the castor oil were mixed under stirring for 15 minutes. In the next step the appropriate amount of diisocyanate was added to the reaction mixture which was stirred further 15 minutes and cast into preheated mold and kept in the heated chamber at 110 °C during 12 h.

2.3. Characterization of materials

Viscoelastic properties of materials were evaluated by dynamic mechanical analyser DMA Tritec 2000 (Triton Technology) in dual cantilever bending mode. Temperature dependence of the complex Young's modulus was measured at heating rate 2 °C/min in temperature range from -50 °C to 100 °C. Storage modulus (E') and tan δ (the ratio

of the loss component to the storage component) against temperature were registered. The temperature range where tan δ > 0.3 was used to evaluate damping capacity of synthesized materials. Simultaneous TGA-DSC measurements were performed in air and nitrogen atmospheres at a heating rate of 20 °C min⁻¹ in temperature interval from 50 to 450 °C.

3. RESULTS AND DISCUSSION

Polyurethanes based on vegetable oils have a very heterogeneous composition and it is difficult to find correlation between the structure and properties. For the case of materials based on triglyceride castor oil (Figure 1) and diisocyanate (prepared with stoichiometric balance of NCO and OH groups) the structure of polymer network is shown in the Figure 2.

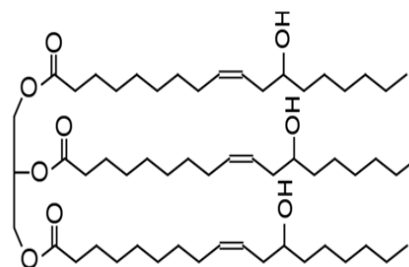


Figure 1. The structure of triglyceride castor oil.

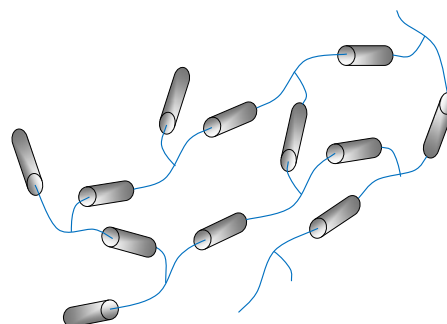


Figure 2. The structure of polyurethane network based on vegetable triglyceride castor oil as triol component (lines) and diisocyanate (cylindres).

In general polyurethanes are relatively thermally unstable. During heating of polyurethanes several decomposition processes take place. The urethane bond decomposition and polyol component depolycondensation are the most important. Thus degradation usually has different steps breaking of the urethane bond, dissociation to isocyanate and alcohol, formation of primary amine and olefin and secondary amine formation. Summarized data for

some properties determined by TGA are given in Table 1. (T_{ons} , $T_{10\%}$, T_{deg}). It was assessed that the decomposition temperature (T_{ons}) is higher than 270 °C. The nanopaticles have substantial effects on the thermal properties of prepared hybrid materials, even at the relatively small content. When compared with the decomposition temperature of the corresponding unfilled material an increase in thermal stability is more than 10 °C for samples based on 2,4-TDI. It was determined that samples based on aliphatic diisocyanate (isophorone diisocyanate) have higher thermal stability. The viscoelastic property of a prepared materials was studied by dynamic mechanical analysis where a sinusoidal force is applied to a material and the resulting dis-

placement is measured. For dynamic data, the glass transition temperature (T_g) is defined as the temperature at which $\tan \delta$ has a peak. A broader T_g region is desirable for covering wider-vibration-frequency damping to sustain a large temperature variation. Temperature dependencies of the storage modulus and $\tan \delta$ is also given in Figure 1. From the temperature dependence of $\tan \delta$ the glass transition T_g was set as a maximum at the frequency of 1 Hz. The changes of storage modulus and $\tan \delta$ against temperature are given in the figure 3. It is obvious that the addition of filler nanoparticles decreased the T_g values.

Table 1. Some properties of polyurethane materials based on castor oil and its hybrid materials with different content of TiO_2 nanoparticles assessed by TGA and DMA methods.

Sample	TiO_2 [wt %]	$T_{ons, TGA}$ [°C]	$T_{10\%, TGA}$ [°C]	$T_{deg, TGA}$ [°C]	T_g [°C]	Damping capacity [°C]
PU/IPDI/0	0	298	316.40	386.17	/	/
PU/2,4-TDI/0	0	272	307.48	373.62	10.09	from -2,5 to 24,6
PU/2,4 TDI/0.5	0.5	281	307.65	373.69	7.34	from -4,1 to 21,7
PU/2,4-TDI/1.0	1.0	280	313.33	392.54	4.27	from -7,5 to 19,2
PU/2,4-TDI/2.0	2.0	291	301.25	372.81	0.11	from -11,2 to 15,8

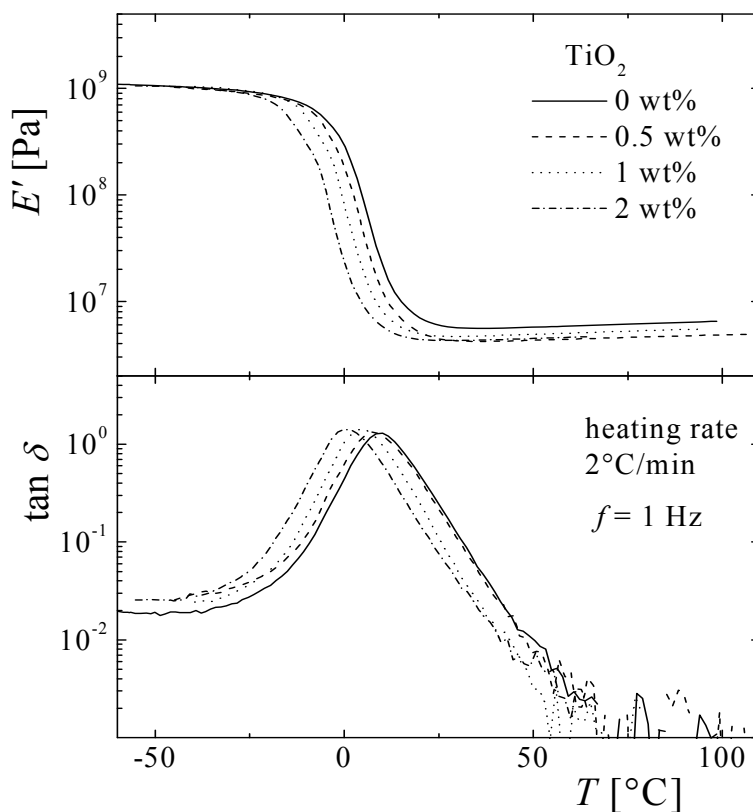


Figure 3. Storage modulus (E') and $\tan \delta$ against temperature for samples based on 2,4-toluene diisocyanate, vegetable triglyceride castor oil, and different content of TiO_2 nanoparticles at the frequency of 1 Hz

5. CONCLUSION

This study was an attempt to fabricate environmentally friendly polyurethane materials based on castor oil as a renewable resource. Thermal and damping properties of PUs differing in isocyanate type were studied. Samples were prepared using stoichiometric balance of reactive groups. It was estimated that the T_g of the samples decreased as the TiO_2 nanoparticle content increased due to the changes in the segmental mobility. The loss tangent, $\tan\delta$, was used as a measure of the materials damping properties. From TGA measurements it was assessed that the starting decomposition temperature is about 260 °C. As it was expected it has been assessed that PU based on aliphatic diisocyanate have higher thermal stability.

6. ACKNOWLEDGEMENTS

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ТОПЛОТНА ПОСТОЈАНОСТ И КАРАКТЕРИСТИКЕ ПРИГУШЕЊА
ПОЛИУРЕТАНСКИХ ХИБРИДНИХ МАТЕРИЈАЛА
НА ОСНОВУ РИЦИНУСОВОГ УЉА

Сажетак: Овај рад се бави развојем поступака добијања полиуретанских материјала на основу различитих диизоцијаната, ричинусовог уља као полиолне компоненте и TiO_2 наночестица. Синтетисани су узорци са стехиометријским балансом реактивних група. Динамичка високоеластична својства узорака су одређивана. Однос модула губитака и модула акумулације ($\tan\delta$) коришћен је као карактеристика пригушења материјала. Температуре преласка у стакласто стање су одређене као положаји максимума на кривама $\tan\delta$. Капацитет пригушења материјала је одређиван као температурни опсег у коме је $\tan\delta > 0.3$. Топлотна стабилност синтетисаних узорака је одређена термогравиметријском методом. Установљено је да су полиуретански материјали на основу алифатских диизоцијаната топлотно стабилнији. Добијене вриједности за температуру преласка у стакласто стање и почетне температуре деградације у пракси дефинишу прозор примјенљивости добијених нових материјала.

Кључне ријечи: ричинусово уље, полиуретани, ДМА, нанокмозити.

