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Short communication

Thermo(oxidative) stability of novel polyurethane/POSS nanohybrid elastomers

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ABSTRACT

In this work, thermo(oxidative) stability of novel PU/POSS nanohybrids was investigated by thermogravimetry (TG). PU/POSS nanohybrids were synthesized from diphenylmethane-4,4′-diisocyanate (MDI), polytetramethylene glycol (Terathane 1000, 1400 and 2000), 1,4-butanediol and 1-(1-(2,3-dihydroxypropoxy)butyl)-3,5,7,9,11,15-isobutyl-pentacyclo[9.5.1.1.(3,9).1(5,5).1(7,13)] octasiloxane (PHIPOSS). TG showed that the highest thermal stability, both of inert and oxidative atmosphere, have the samples containing 4 and 6 wt.% of PHIPOSS. Maximum rate degradation temperatures are shifted toward higher temperatures. These results are discussed in terms of restricted molecular mobility of PU macrochains in the presence of POSS and by reduction of rate of volatile products' emission.

1. Introduction

Recent years have seen an increased demand in organic–inorganic (nano)hybrid polymer materials in a wide range of applications [1,2]. These needs have been met with accelerated advances in polymer science and technology taking the benefit of nanophase technology that offers a number of enhancements to the polymeric materials [3,4]. Thermal properties of nanostructured hybrid materials play an important role for a number of e.g. engineering applications and are to be carefully examined.

POSS are unique nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required [5,6]. POSS nanohybrid polymers are materials that contain nanoscale, silicate cagelike segments directly bound to the polymer chains [7,8]. These segments have sizes of 1–3 nm and can be thought of as the smallest particles of silica possible. Reactive oligosilsesquioxanes can be incorporated into traditional polymers *via* copolymerization, grafting and blending processes [9]. Various POSS/polymer covalent systems for different applications have been described in the literature, such as polyurethanes [10–12], poly(alkyl methacrylates) [13], epoxies [14], polynorbornene [15], polyimides [16]. Segmented polyurethane (PU)-based elastomers have a set of promising properties, including mechanical and thermal properties, due to the formation of microphase separation from the thermodynamic immiscibility of solid-like hard segments and rubbery soft segment sequences. The hard segment is formed as a result of the interaction of the isocyanates with either diol or diamine molecules, used as a chain extender, while the soft segment may consist of ether, ester or carbonate groups, with the latter being the most resistant to degradation.

In this work, we report on the thermo(oxidative) properties of PU/POSS nanomaterials based on polytetramethylene glycol with different molecular weights.

2. Experimental

2.1. Materials

For synthesis of polyurethane/POSS nanohybrid elastomers 4,4′-diphenylmethane diisocyanate (MDI) (Aldrich), polytetramethylene glycol (PTMG, $M = 1000$, $M = 1400$, $M = 2000$) (Terathane® 1000, 1400, 2000 Invista) (T 1000, T 1400, T 2000), 1,4-butanediol (BD) (Aldrich), and 1-(1-(2,3-dihydroxypropoxy) butyl)-3,5,7,9,11,15-isobutylpentacyclo [9.5.1.1.(3,9).1(5,5).1(7,13)] octasiloxane (PHIPOSS) (Hybrid Plastics) were used.

2.2. *Preparation of polyurethane/POSS nanohybrid elastomers*

MDI was charged into a 100 ml three-necked round-bottomed flask, equipped with a mechanical stirrer and nitrogen inlet. It was melted at 70 °C and PHIPOSS solution in suitable type of PTMG was then added in one portion. Previously the PHIPOSS mixture in PTMG was heated to 120 °C to dissolve the POSS cages in the polyol and

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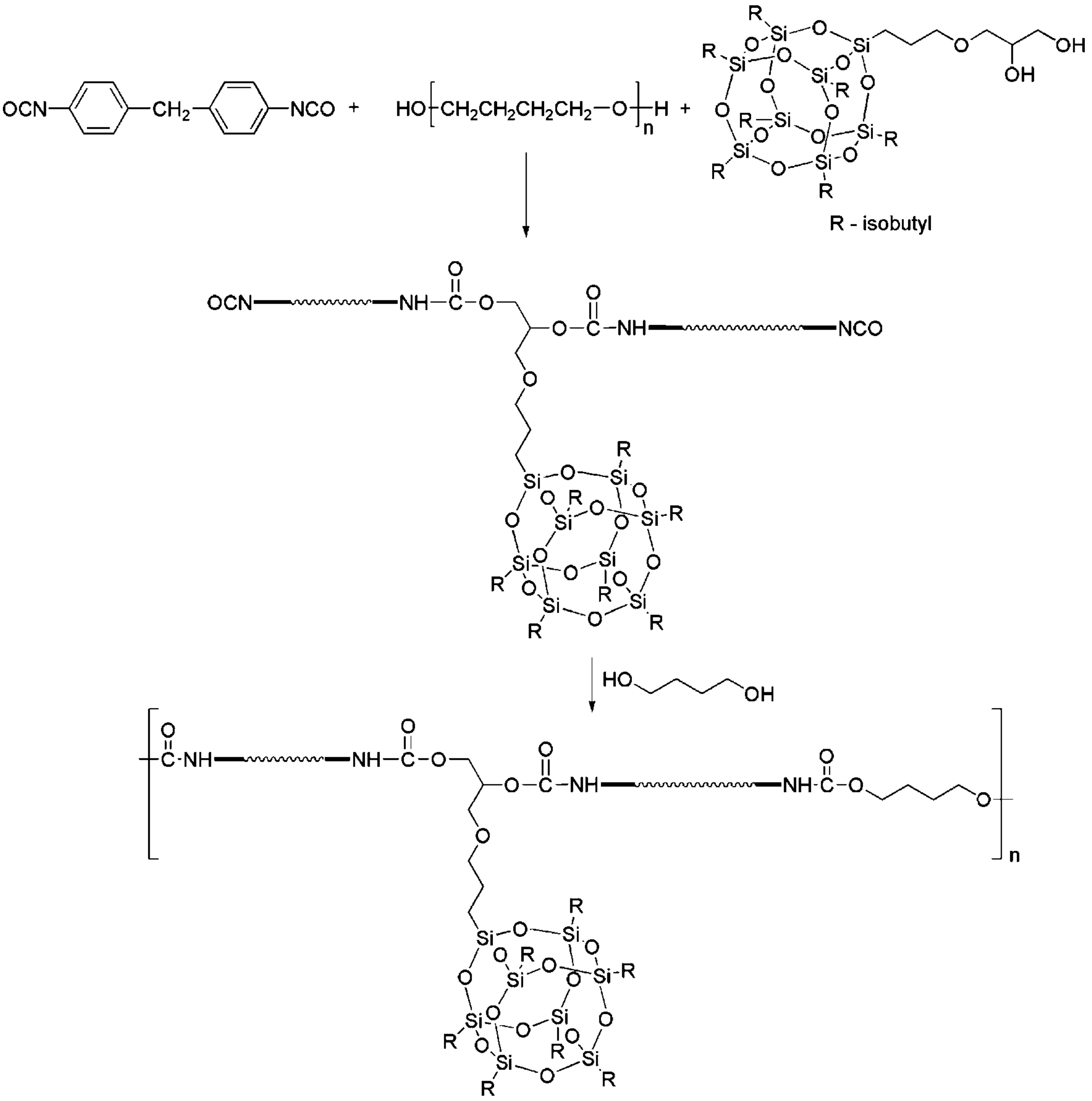

Scheme 1. Schematic diagram of the synthesis route for PU/POSS nanomaterials.

then cooled to 60 °C (Scheme 1). The reaction was performed under a nitrogen atmosphere at 80 °C for 2 h to form a polyurethane prepolymer. The NCO groups content was then determined and the prepolymer was mixed with suitable amount of 1,4-butanediol. Mixture was poured out on Petri dish and cured at 110 °C for 2 h and post-cured at 80 °C in 16 h. The obtained polyurethane elastomers contained 40 wt.% of soft segments and 2, 4, 6, 8 and 10 wt.% of PHIPOSS [17].

3. Results and discussion

A Netzsch thermogravimetric analyzer TG 209 was used to investigate the thermal stability of the obtained elastomers. The samples (about 4 mg) were heated in an open α-Al_2O_3 pan, from 25 °C up to 600 °C at a heating rate of 10 °C/min under argon or air atmosphere.

3.1. Thermal degradation studies

The decomposition process of the nanohybrids in inert atmosphere ran in three steps. The major weight loss started at *ca.* 290 °C and it can be connected with the degradation of the hard segments of polyurethane. A minor weight loss that began above 350 °C was attributed to the degradation of the PU elastic segments. In inert atmosphere PU/PHIPOSS nanohybrids show three overlapping peaks in the DTG profiles. Within the experimental temperature range, all the polymers displayed similar degradation profiles in argon atmosphere, suggesting that the incorporation of the PHIPOSS did not significantly alter the degradation mechanism of the matrix polyurethanes—TG results are summarized in Table 1. It was found that the thermal stability of the PU/POSS nanohybrids increase as the PHIPOSS contents increase from 0 to 6 wt.%. It was noted that the highest growth of the T_{onset} takes place for the samples containing 4 wt.% (T 1400 and T 2000) and 6 wt.% of PHIPOSS (T 1000). Maximum rate degradation temperature defined as a first maximum in DTG curve T_{DTGmax} is shifted toward higher temperatures for samples containing 6 wt.% PHIPOSS (T 1000) and for all nanohybrids based on Terathane 1400. In case of Terathane 2000 slighter decrase of T_{DTGmax} was observed.

The decomposition process of the nanohybrids in air atmosphere ran also in three steps. In oxidative atmosphere PU/PHIPOSS nanohybrids exhibit three good separate peaks in the DTG. In

Table 1
Thermal degradation parameters of the PU/POSS nanohybrids

Type of oligodiol	PHIPOSS content	Inert atmosphere		Oxidative atmosphere	
		T_{onset}	T_{DTGmax}	T_{onset}	T_{DTGmax}
T 1000	0	301.1	324.0	302.9	328.2
	2	303.6	323.4	305.3	327.0
	4	303.5	323.8	305.7	327.0
	6	306.1	330.2	306.8	327.2
	8	302.4	326.0	304.4	326.6
	10	301.7	322.6	303.8	326.2
T 1400	0	295.1	321.0	298.4	320.7
	2	302.8	325.1	304.7	328.3
	4	306.6	331.2	307.2	326.7
	6	304.0	327.5	304.8	328.3
	8	300.9	328.7	303.2	323.1
	10	303.5	327.9	302.6	326.4
T 2000	0	297.7	323.7	302.4	327.0
	2	302.2	321.3	304.5	322.8
	4	303.5	319.5	306.5	326.9
	6	300.4	323.3	307.1	327.8
	8	300.5	322.3	305.0	323.0
	10	301.7	321.7	302.1	321.6

comparison with degradation in inert atmosphere the initial decomposition temperature of nanohybrids is shifted toward higher temperatures. The same tendency is observed in case of maximum rate degradation temperature.

This effect can be explained in two ways. On the one hand, according to Vyazovkin model [18], the enhancement of the thermal stability of PU/POSS polymers is caused by suppression of the molecular mobility of polymer chains by bulky oligosilsesquioxane pendant groups or crystals formed. Because the molecular mobility is the major factor that contributes to the transport of reactive species within the polymer, the nanohybrid elastomers are likely to have lower reactivity and, therefore, greater chemical and thermal stability than pristine polyurethanes. On the other hand, chemically incorporated POSS groups (or POSS agglomerates) can reduce the rate of volatiles' release from the material, which results in an improvement of the thermal stability as well [19–21]. Further structural and morphological studies to fully understand this effect are underway and the results will be reported in a full-length paper.

4. Conclusions

TGA showed that the highest growth of the T_{onset} takes place for the samples containing 4 and 6 wt.% of PHIPOSS both of inert and oxidation atmosphere. Maximum rate degradation temperatures defined as a first maximum in DTG curve T_{DTGmax} are shifted toward higher temperatures for samples containing 6 wt.% PHIPOSS (T 1000) and for all nanohybrids based on Terathane 1400. In case of Terathane 2000 slighter decrase of T_{DTGmax} was observed. These results can be discussed in terms of restricted molecular mobility of PU macrochains in the presence of POSS and by reduction of rate of volatile products' emission. From the results obtained it can be concluded that for PU/POSS nanocomposites the largest enhancement in the thermal stability can be achieved at a low POSS load up to 6 wt.%, which is an unexpected but promising effect. It may be utilized for further special applications of these novel reactive nanostructured materials.

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