



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia



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Contents

Volume II

Biophysical Chemistry, Photochemistry, Radiation Chemistry	443
Radiochemistry, Nuclear Chemistry	551
Material Science	589
Solid State Physical Chemistry	719
Macromolecular Physical Chemistry	757

PHYSICAL CHEMISTRY 2014

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Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with_*

Institute of Catalysis Bulgarian Academy of Sciences

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NOVEL SILOXANE BASED POLYURETHANE NANOCOMPOSITES

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ABSTRACT

A series of novel thermoplastic polyurethanes (TPUs) nanocomposites based on α,ω -dihydroxy ethoxy propyl poly(dimethylsiloxane) (EO-PDMS), 1,4-butanediol (BD) and 4,4'-diphenylmethane diisocyanate (MDI) was synthesized by *in situ* two-step polyaddition reaction in solution using modified clay (Cloisite 30B). The clay percentage in the nanocomposites was 1, 3, 5, 8 and 10 wt% in relation to the polymers. The aim of this study was to improve some properties of TPUs by the addition of clay nanoparticles. The prepared nanocomposites were characterized using FTIR, AFM and DSC analyses. The influence of nanoparticles dispersion on the morphology and thermal properties of TPUs was investigated.

INTRODUCTION

Segmented polyurethanes (TPUs) are an important class of thermoplastic elastomers, which have potential use as a biomaterial [1]. TPUs are linear block copolymers typically constructed with hard and soft segments (HS and SS), which cause the formation of microphase separated morphology [2]. They have very desirable properties, such as high abrasion resistance, flexibility and elasticity [3]. However, polyurethanes have some disadvantages, such as poor thermal stability and poor gas-barrier properties. These disadvantages are overcome by introducing inorganic fillers, especially nanoclay particles based on Montmorillonite [4]. Also, the incorporation of poly(dimethylsiloxane) into the polymer chain can enhance some properties of TPUs such as: low surface energy, thermal stability and flexibility. The objective of this work was to synthesize nanocomposites based on organoclay (Cloisite 30B) and polyurethane as matrix. The way, in which the dispersion of the clay nanoparticles may affect the structure,

thermal and morphological properties of TPUs was analyzed by different experimental techniques.

EXPERIMENTAL

α,ω -Dihydroxy ethoxy propyl poly(dimethylsiloxane) (EO-PDMS) (from ABCR, $M_n = 1000$ g/mol) was dried over molecular sieves before use. 4,4'-Diphenylmethane diisocyanate (MDI) (Aldrich, purity > 98 %), was used as received. 1,4-Butanediol (BD) (Aldrich) was purified by vacuum distillation. Cloisite 30B (Rockwood) was dried in vacuum oven at 30 °C for 24h. Tetrahydrofuran (THF) (Moss Hemoss) and *N,N*-dimethylacetamide (DMAc) (Merck) were distilled and purified before use. The catalyst in this reaction was stannous octanoate ($\text{Sn}(\text{Oct})_2$) (Aldrich). TPU nanocomposites (PUNC) with 20 wt% of HS were prepared with addition of organically modified montmorillonite clay (Cloisite 30B) by *in situ* two-step polyaddition reaction in solution of THF/DMAc (1:1 v/v). Hard segment of TPUs, which were prepared in the form of films, consist of MDI and BD, while EO-PDMS was used as the SS. Different content of organoclay (1, 3, 5, 8 and 10 wt%) was incorporated into TPU matrix. FTIR spectra were recorded using attenuated total reflection (ATR) mode on Nicolet 6700 FTIR spectrometer. AFM analysis was carried out on atomic force microscope (DimensionIcon, Bruker), equipped with the SSS-NLC probe, Super Sharp SiliconTM-SPM-Sensor (NanoSensorsTM Switzerland; spring constant 35 N/m, resonant frequency ≈ 170 kHz). Measurements were performed under ambient conditions using the tapping mode AFM technique. Differential scanning calorimetry (DSC) was carried out on a DSC Q1000V9.0 Build 275 thermal analyzer. The DSC scans were recorded under nitrogen atmosphere, in the temperature range from -90 to 230 °C, at a heating and cooling rate of 10 and 5 °C/min, respectively.

RESULTS AND DISCUSSION

The molecular structures of the TPU and polyurethane nanocomposites were confirmed by FTIR spectroscopy (Figure 1). Characteristic bands of samples appeared at 3310 cm^{-1} ($\nu_{\text{N-H}}$), 2960 and 2880 cm^{-1} (ν_{sym} and ν_{asym} of C-H), 1710 cm^{-1} ($\nu_{\text{C=O}}$), 1545 and 1260 cm^{-1} ($\nu_{\text{C-N}} + \delta_{\text{N-H}}$ i.e., amide II and amide III), 1030 and 1080 cm^{-1} ($\nu_{\text{Si-O-Si}}$ and $\nu_{\text{C-O-C}}$), 1600 cm^{-1} ($\nu_{\text{(C=C)arom}}$) and 800 cm^{-1} ($\rho_{\text{C-H}}$ in SiCH_3). However, the bands of the organoclay at 520 cm^{-1} ($\nu_{\text{Si-O-Al}}$) and 460 cm^{-1} ($\delta_{\text{Si-O-Si}}$) are also observed in the spectra of the nanocomposites. These bands indicate that the polyurethane chains are incorporated into the galleries of layered silicates from organoclay.

AFM analysis was used to investigate topography of the samples (Figure 2). The addition of clays significantly affected the topography of TPU nanocomposites in comparison with neat TPU. Based on AFM results it can be assumed that organoclay particles are homogeneously dispersed in the TPU matrix with 3 wt% of organoclay. Similar situation was observed for other TPU nanocomposites with 1, 5, 8 and 10 wt% of clay. RMS surface roughness, R_q values, ranged from 30.5 to 93.6 nm for TPU nanocomposites, while for the neat TPU sample, R_q value was 9.23 nm (Table 1). The samples with higher R_q values have rougher surface.

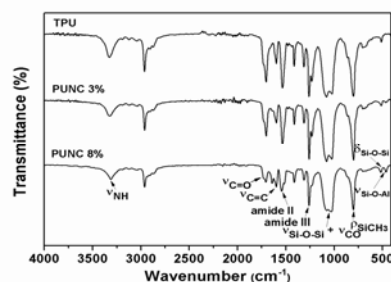


Figure 1. ATR-FTIR spectra of neat TPU and TPU nanocomposites with 3 and 8 wt% of organoclay

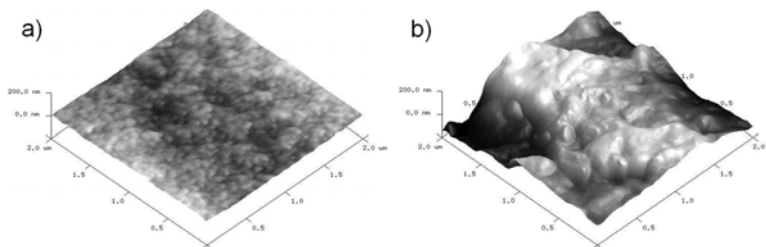


Figure 2. 3D AFM images of the cross-section of films of the neat TPU **a)** and TPU nanocomposites with 3 wt% of organoclay **b)** (scan area $2 \times 2 \mu\text{m}$)

Table 1. R_q values and DSC results of the neat TPU and TPU nanocomposites

DSC results showed that melting (T_m) and glass transition temperatures (T_g) of HS shift toward higher temperatures upon increasing	Sample	R_q (nm)	$T_{g\text{HS}}$ ($^{\circ}\text{C}$)	$T_{m\text{HS}}$ ($^{\circ}\text{C}$)	ΔH_m (J/g)	X_c %	$X_{c\text{HS}}$ %
		TPU	9.23	32	157	3.9	4.3
	PUNC 1%	92.1	15	169	3.6	3.9	17.9
	PUNC 3%	62.0	21	166	3.4	3.7	17.0
	PUNC 5%	53.9	29	185	2.8	3.1	14.2
	PUNC 8%	93.6	29	182	3.0	3.3	15.1
	PUNC 10%	30.5	28	186	3.3	3.6	16.5

the organoclay content to 5 wt%, but then there are no significant changes when the organoclay content increased up to 10 wt%. The total degree of

crystallinity (X_c) and degree of crystallinity of HS ($X_{c\text{ HS}}$) as well as enthalpy of melting (ΔH_m) of nanocomposites is lower in comparison with the neat TPU. The presence of layered silicates from organoclay in the TPUs can result in the more ordered HS, having higher T_m values, but on the other hand show losses in the degree of crystallinity of HS.

CONCLUSION

In this study, the TPU nanocomposites were successfully prepared by *in situ* two-step polyaddition reaction in solution. FTIR spectra of TPU nanocomposites showed characteristic peaks of urethane carbonyl group, stretching band of urethane –NH group, amide II and III stretching vibrations and characteristic bands of clay particles associated with the stretching Si-O-Al and bending of Si-O-Si. The band positions of distinctive functional groups of the TPUs are identical to those of the TPU nanocomposites, confirming that the chemical structure of TPUs is not significantly altered in the presence of silicate layers. AFM analysis confirmed well dispersion of organoclay nanoparticles in the TPU matrix. DSC results showed that T_m and T_g values of HS shift toward higher temperatures from 166 to 185 and from 15 to 29 °C, respectively upon increasing the organoclay content to 5 wt%, after which measured values do not change significantly. The degree of crystallinity of nanocomposites is lower in comparison with the neat TPU. The obtained results showed that low clay loading (≤ 5 wt%) have affected thermal properties of TPUs, which is significant for preparation of this kind of polyurethane materials.

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REFERENCES

- [1] D.J. Martin, L.A.P. Warren, P.A. Gunatillake, S.J. McCarthy, G.F. Meijs, K. Schindhelm, *Biomaterials*, 2000, 21, 1021 – 1029.
- [2] T. Choi, J. Weksler, A. Padsalgikar, J. Runt, *Polymer*, 2009, 50, 2320 – 2327.
- [3] R. Vermette, H.J. Griesser, G. Laroche, R. Guidoin, *Biomedical Applications of Polyurethanes*. Texas: Landes Bioscience; 2001.
- [4] O.I.H. Dimitry, Z.I. Abdeen, E.A Ismail, A.L.G. Saad, *J. Polym. Res.*, 2010, 17, 801 – 813.