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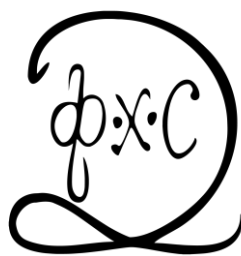
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PHYSICAL CHEMISTRY 2022

*16th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

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Serbia*

in co-operation with

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and

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and

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PREPARATION AND SWELLING PROPERTIES OF POLYURETHANE/TiO₂ NANOCOMPOSITES

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ABSTRACT

Polyurethane/TiO₂ nanocomposites (NCs) were fabricated from environmentally friendly polyurethane (PU) network, based on polycaprolactone (PCL) and Boltorn[®] aliphatic hyperbranched polyester of the second pseudo generation (BH-20) as crosslinking agent, and unmodified and surface modified TiO₂ nanoparticles (NPs). The surface modification of TiO₂ NPs was done with lauryl gallate. The chemical structure of the prepared PU/TiO₂ NCs was studied by Fourier transform infrared spectroscopy (FTIR), while their amorphous nature was confirmed by X-ray diffraction (XRD). The influence of type and content of the applied TiO₂ NPs on swelling properties in toluene and tetrahydrofuran (THF) and on water absorption of the prepared PU/TiO₂ NCs were investigated. The obtained results revealed that swelling behavior depends on the used solvent, while percentage of absorbed water decreases with increasing content of TiO₂ NPs and it is generally lower in NCs prepared with modified TiO₂ NPs.

INTRODUCTION

Polymer nanocomposites are materials in which inorganic nano-sized particles, having dimensions less than 100 nm, are dispersed using different procedures in a polymer matrix. In this manner, material with significantly improved physical and mechanical properties, compared to the pure polymer, can be obtained. The improvement of properties is achieved through the establishment of unique synergisms between the properties of polymer and NPs. Properties of polymers, which are often reported in the literature to be improved after incorporation of NPs, include mechanical properties (strength, modulus and dimensional stability), thermal stability and heat distortion temperature, electrical and thermal conductivity, chemical resistance, surface appearance, barrier properties, refractive index and optical clarity, flame resistance and reduced smoke emission, etc [1]. One of the main challenges in developing high performance polymer NC is uniform dispersion of NPs in polymer matrix. This will enable appearance of very large interfacial area per volume between the NPs and applied polymer, and consequently increase the possibility for the improvement of material performances.

In this study, polyurethane/TiO₂ NCs were prepared using environmentally friendly polyurethane network, based on PCL as soft segment and BH-20 as crosslinking agent, and unmodified and surface modified TiO₂ NPs. The surface modification of TiO₂ NPs was done with lauryl gallate. The chemical structure, crystallinity, swelling properties and water absorption of the pure PU and prepared NCs were investigated.

METHODS

Lauryl gallate (LG) and acetonitrile (AN) were obtained from Sigma-Aldrich, while commercial TiO₂ NPs (P25, size 25 nm) were purchased from Degussa. The surface modification of commercial

TiO₂ NPs with lauryl gallate was performed according to the following procedure. In 100 cm³ solution of LG in AN (concentration 0.01 mol dm⁻³), 2 g of TiO₂ was added. The mixture was kept in ultrasonic bath for 10 min, and then left overnight. After that, TiO₂ NPs surface modified with LG (TiO₂-LG) were precipitated using centrifuge, washed twice with AN, and dried in vacuum oven at 40 °C until constant weight was achieved. Pure polyurethane network (PU), based on PCL, BH-20 and isophorone diisocyanate (IPDI), with soft segment (PCL) content of 30 wt.%, was prepared by a two-step solution polymerization method, according to the procedure described elsewhere [2]. The stoichiometric ratio between –NCO and –OH groups was 1.1. Nanocomposites PU/TiO₂ and PU/TiO₂-LG were prepared using the same procedure, by addition of adequate amount of unmodified or modified TiO₂ NPs (0.5, 1.0 or 2.0 wt.% based on the total weight of PCL, BH-20 and IPDI) during the first step of the reaction. In order to achieve uniform dispersion of TiO₂ NPs in PU, adequate amount of TiO₂ NPs was first mixed in a small amount of THF for 20 min in ultrasonic bath. The number in the name of prepared NCs stands for NPs content.

FTIR spectra of prepared samples were recorded using ATR Nicolet spectrophotometer Magna System 560, in the scanning range from 400 to 4000 cm⁻¹, at spectral resolution of 4 cm⁻¹, using 64 scans.

X-ray diffraction (XRD) patterns of PCL and prepared samples were obtained with a Bruker AXS D8 ADVANCE Plus diffractometer in Bragg-Brentano geometry, using CuK α radiation (λ = 0.154 nm) ranging from 10° to 35° 2 θ , with a step width of 0.05° and a constant counting time of 0.5s per step.

Swelling properties of pure PU and prepared NCs were examined in THF and toluene at room temperature. Square test samples (10.0 mm \times 10.0 mm \times 1.0 mm \pm 0.2 mm) were immersed in selected medium, and their weight, w , was periodically measured until constant value (equilibrium swelling). The excess of medium was carefully removed using filter paper, before each weight measurement. The swelling degree, q , was calculated according to the following equation:

$$q = \frac{w - w_0}{w_0} \quad (1)$$

where w_0 is the weight of the sample before swelling. The average value obtained from three different specimens was used.

Water absorption of samples (10.0 mm \times 10.0 mm \times 1.0 mm \pm 0.2 mm) was examined after their immersion in distilled water for 48h, at room temperature. The weight percent of the water absorption, WA , was calculated as follows:

$$WA = \frac{w_w - w_{w0}}{w_{w0}} \times 100 \quad (2)$$

where w_w is the weight of the sample after 48h and w_{w0} is the weight of dry sample. Results from three different specimens were averaged.

RESULTS AND DISCUSSION

FTIR spectra of PU and NCs prepared with 0.5 wt.% of modified and unmodified TiO₂ NPs are given in Figure 1a. In the FTIR spectra of PU and NCs the band at 2260 cm⁻¹ was not observed, indicating completion of the reaction of –NCO groups and formation of urethane bonds. The band which appear around 3330 cm⁻¹ is ascribed to the stretching vibrations of hydrogen-bonded urethane N-H groups, while bands at around 2950 and 2870 cm⁻¹ correspond to asymmetric and symmetric stretching vibrations of CH₂ groups, respectively. Band characteristic for carbonyl groups appears between 1715 and 1721 cm⁻¹ and its position moves to the higher wavenumber for NCs, indicating presence of lower degree of hydrogen bonding after incorporation of modified and unmodified TiO₂ NPs in PU. Furthermore, band ascribed to the deformation vibrations of CH₂

groups appears at 1460 cm^{-1} , while bands characteristic for amide II and amide III vibrations can be observed at around 1540 and 1240 cm^{-1} , respectively. Bands which correspond to asymmetric and symmetric stretching vibrations of C-O-C groups appear at around 1090 and 1030 cm^{-1} , respectively.

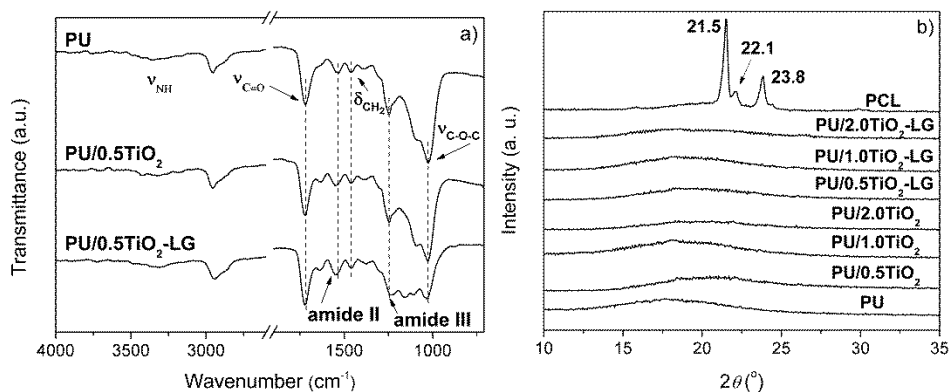


Figure 1. a) FTIR spectra of pure PU and nanocomposites PU/0.5TiO₂ and PU/0.5TiO₂-LG and b) XRD patterns of pure PU and prepared nanocomposites.

XRD patterns of PCL, PU and all prepared NCs are displayed in Figure 1b. The reflections observed in diffractogram of PCL at $2\theta = 21.5^\circ$, 22.1° and 23.8° correspond to the (110), (111) and (200) planes of PCL orthorhombic crystal lattice (space group $P2_12_12_1$), respectively. These reflections are characteristic for semicrystalline PCL [3]. On the other hand, a broad weak reflection at $2\theta \sim 20.1^\circ$ appeared as a consequence of amorphous contribution in PCL. In XRD pattern of PU and prepared NCs only amorphous halos are present, indicating amorphous character of synthesized samples, due to the presence of crosslinked structure.

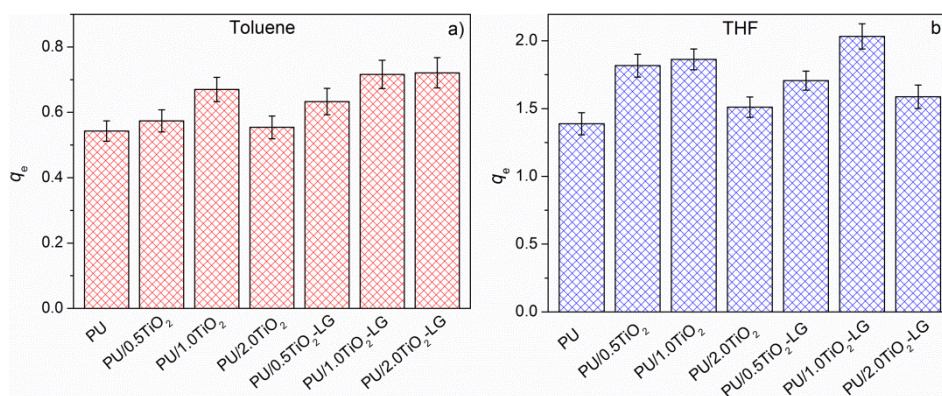


Figure 2. Equilibrium swelling degree (q_e) of pure PU and prepared nanocomposites.

The swelling behavior of PU and prepared NCs was investigated in toluene and THF and obtained results are given in Figure 2. It can be observed that equilibrium swelling degree (q_e) in both solvents depends on type and content of the applied TiO₂ NPs. Since q_e of NCs is in both solvents higher than q_e of pure PU, it can be concluded that the presence of unmodified and surface modified TiO₂ NPs in PU network decreases the crosslinking density of PU. Generally, q_e values are only slightly higher for PU/TiO₂-LG NCs than q_e values of PU/TiO₂ NCs. The increase of the content of TiO₂ and TiO₂-LG NPs up to 1.0 wt.% led to greater swelling of NCs in both solvents, while further increase up to 2 wt.% induced additional slight increase of q_e value only for

PU/2.0TiO₂-LG NC in toluene. The presence of 2 wt.% of the applied NPs probably reduced the diffusion of solvents in prepared NCs and therefore led to the q_e lowering.

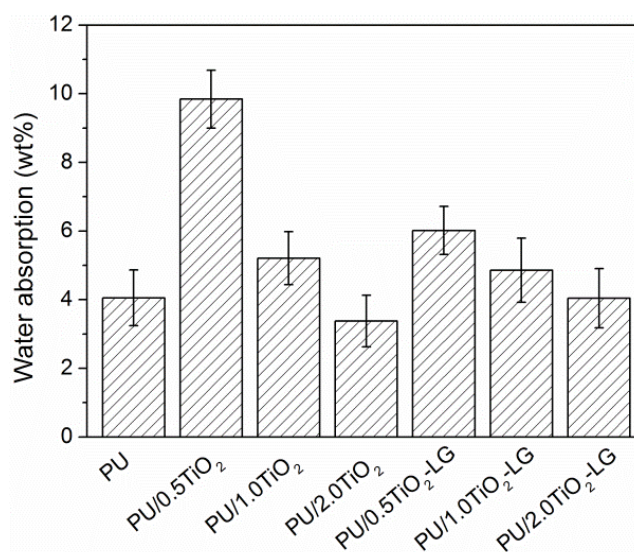


Figure 3. Water absorption of pure PU and prepared nanocomposites.

The water absorption of the pure PU and prepared NCs was examined at room temperature by their immersion in distilled water for 48h, and the obtained results are presented in Figure 3. Polyurethane network itself has hydrophobic character due to the presence of hydrophobic PCL as soft segment [2]. The incorporation of 0.5 wt.% of TiO₂ NPs in PU network reduces its crosslinking density, leading to greater water absorption ability than pure PU. Due to the presence of long hydrophobic aliphatic groups (C12) on the surface of TiO₂ NPs modified with LG, the percentage of absorbed water of PU/0.5TiO₂-LG is lower than for PU/0.5TiO₂. The increase of the content of incorporated unmodified and modified TiO₂ NPs in PU, led to further decrease of water absorption, as a consequence of the hydrophobic character of the applied TiO₂ NPs.

CONCLUSION

Polyurethane/TiO₂ NCs were prepared using different content of unmodified TiO₂ NPs and TiO₂ NPs surface modified with lauryl gallate. The chemical structure of the prepared NCs was examined by FTIR spectra. XRD results revealed amorphous character of pure PU and prepared NCs. Swelling behavior of prepared NCs depends on the used solvent, while percentage of absorbed water decreases with increasing content of TiO₂ NPs and it is generally lower in NCs prepared with modified TiO₂ NPs.

Acknowledgment

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