PHYSICAL CHEMISTRY 2018

14th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

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Volume II

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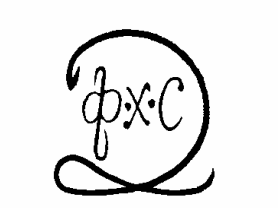

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SURFACE CHARACTERISTICS OF POLYURETHANE NETWORKS BASED ON POLYCAPROLACTONE

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ABSTRACT

A series of polyurethane networks (PUN) having different soft segment content (SSC) was synthesized by the prepolymer method in solution, using polycaprolactone diol as soft segment, and hyperbranched polyester and isophorone diisocyanate (IPDI) as components of hard segments. FTIR spectroscopy confirmed the structure of the prepared PUN. Furthermore, it has been shown that swelling degree of PUN in tetrahydrofuran (THF) and molecular weight of polymer chains between crosslinks (M_c) increase with increasing SSC, while the opposite was observed for the crosslinking density (v) and percent of the water absorption.

INTRODUCTION

Polyurethanes (PU) have been utilized as engineering materials in a broad range of applications, due to the possibility to easily tailor their properties by altering PU components [1,2]. However, in order to prepare novel PU with desired end-use properties, the structure-property relationship must be well understood. In segmented polyurethanes, which represent multiblock copolymers composed of alternating soft and hard segments, extent of the phase separation and, consequently, properties of PU, strongly depend on the chemical structure and molecular weights of the soft and hard segments, their content and interactions between them. Polycaprolactone (PCL) is synthetic, aliphatic, semicrystalline biodegradable polyester with very low glass transition and melting temperature, which has been progressively used for drug delivery and tissue engineering, in manufacturing biomedical devices, as a soft segment in the synthesis of environmentally-friendly PU coatings, etc. [3,4]. Aliphatic hydroxy-functional Boltorn® hyperbranched polyesters are due to the presence of numerous end functional groups and their three-dimensional and compact structure, often applied as crosslinkers in the synthesis of PUN [5]. In this work, Boltorn® hyperbranched polyester of the

second pseudo generation (BH-20) was, together with PCL diol and IPDI applied for the synthesis of novel PUN. The morphology, swelling behavior and water absorption of the prepared PUN was examined in order to investigate surface properties of these networks for their possible application in coatings.

EXPERIMENTAL

Five PUN with different SSC (presented in wt.% as last two numbers in the name of PUN) were synthesized by catalyzed two-step polymerization in solution (DMAc/THF), from PCL (Sigma-Aldrich, M_n = 2000 g/mol), BH-20 (Perstorp Specialty Chemicals AB, M_n = 1340 g/mol, 12 end –OH groups) and IPDI (Sigma-Aldrich), keeping the molar NCO/OH ratio at 1.05. In the first step of the synthesis, prepolymer was prepared by reacting PCL and excess of IPDI for 3h, at 80 ^oC in argon atmosphere, while in the second step, BH-20 was added. After short stirring, the reaction mixture was transferred into the Teflon® dishes and the crosslinking reaction was continued in the air oven first at 60 ^oC for 24 h and then at 80 ^oC for 3 h, and finally at 50 ^oC for 24 h in a vacuum oven.

FTIR spectra of PUN were obtained using ATR NICOLET 6700 FTIR spectrometer. Scanning electron microscopy (SEM) images of samples were recorded on a JEOL JSM-6460LV scanning electron microscope. Prior to scanning, samples were prepared by gold sputtering and cryo-fracturing. Swelling behavior of square PUN samples was examined in THF at room temperature. Water absorption of PUN was investigated by their immersion in distilled water for 48 h at room temperature.

RESULTS AND DISCUSSION

FTIR spectra of PCL, BH-20 and synthesized PUN_{IPDI}-30 are given in Figure 1a. In the FTIR spectrum of PCL the following absorption bands characteristic for different groups can be observed: hydroxyl groups (around 3500 cm^{-1}), stretching of symmetric and asymmetric CH_2 groups (2868 and 2950 cm^{-1}, respectively), stretching vibrations of ester carbonyl groups (1726 cm^{-1}) and stretching of asymmetric and symmetric C-O-C (1242 and 1186 cm^{-1}, respectively). FTIR spectrum of BH-20 shows bands characteristic for the hydroxyl groups (3300 cm^{-1}), $–CH_2–$ and $–CH_3$ groups (2900-3000 cm^{-1}), carbonyl ester groups (1723 cm^{-1}), C-O linkage of ester groups (1040-1210 cm^{-1}) and ether groups (1010-1120 cm^{-1}). The absence of peak at 2260 cm^{-1} in the FTIR spectrum of PUN_{IPDI}-30 indicates complete reaction of NCO groups and formation of urethane bonds. Furthermore, bands characteristic for the N-H stretching of urethane group (3365 cm^{-1}), amide II vibrations (1538 cm^{-1}), symmetric and asymmetric CH_2 groups (2867 and 2952 cm^{-1},

respectively), free carbonyl groups (1733 cm^{-1}) and hydrogen bonded carbonyl groups from ester bonds (1646 cm^{-1}) can also be observed in the FTIR spectrum of PUN_{IPDI}-30 [4].

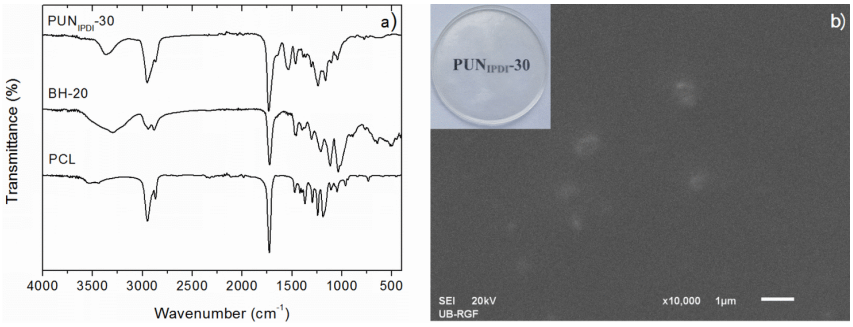

Figure 1. a) FTIR spectra of PUN_{IPDI}-30, BH-20 and PCL and b) SEM image of PUN_{IPDI}-30 (photo of PUN_{IPDI}-30 sample is given as inset).

The surface morphology of the prepared PUN was examined using SEM analysis (Figure 1b). It can be seen that PUN_{IPDI}-30 has certain surface homogeneity and smoothness with small surface roughness, indicating possible application in coatings. Similar was obtained for other PUN, showing lack of influence of SSC on the surface morphology of these PUN.

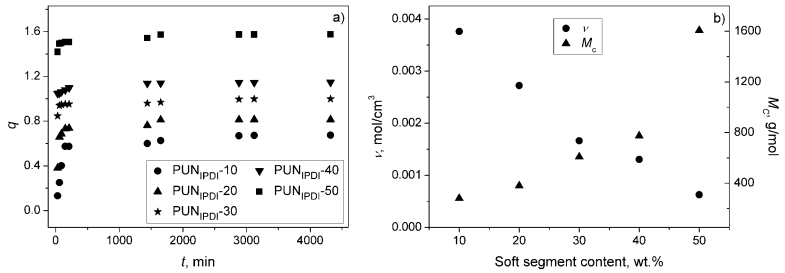

Figure 2. a) Change of the swelling degree (q) with time and b) dependence of the crosslinking density (ν) and molecular weight of polymer chains between crosslinks (M_c) on the SSC.

The change of swelling degree of PUN in THF, calculated using conventional gravimetric method, with time is shown in Figure 2a. It has been found that equilibrium swelling degree of PUN was reached after 48 h of networks immersion in THF, and that it increases from 0.6 to 1.6 with SSC increasing, indicating higher crosslinking density of samples with lower SSC. This was confirmed from the values of crosslinking density, calculated using Flory-Rehner equation, and M_c presented as a function of SSC in Figure 2b [5]. As expected, the presence of higher amount of crosslinker BH-20 during

the PUN synthesis led to the formation of networks with higher v and smaller M_c.

The dependence of the water absorption of PUN on SSC is given in Figure 3. The weight percent of the absorbed water decreased with increasing SSC, due to the increased amount of the hydrophobic PCL in the structure of prepared PUN.

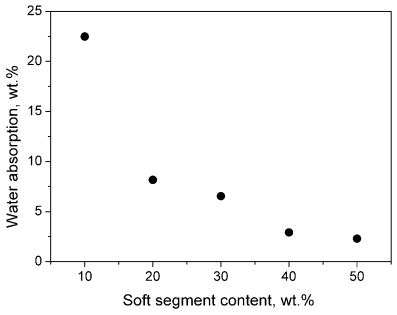

Figure 3. Dependence of the water absorption of PUN on the SSC.

CONCLUSION

Five PUN with different SSC was synthesized from PCL, BH-20 and IPDI. FTIR spectroscopy confirmed the structure of the prepared networks. The swelling ability of PUN in THF increased with increasing SSC, due to the decrease of the crosslinking density. PUN with higher content of hydrophobic PCL showed better water resistance.

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