



## Composites prepared from polyurethanes modified with silicone-acrylic nanopowders

Piotr Król<sup>a,\*</sup>, Bożena Król<sup>a</sup>, Janusz Kozakiewicz<sup>b</sup>, Szczepan Zapotoczny<sup>c</sup>,  
Barbara Pilch-Pitera<sup>a</sup>, Sylwia Kozdra<sup>a</sup>

<sup>a</sup> Department of Polymer Science, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

<sup>b</sup> Industrial Chemistry Research Institute, Warsaw, Poland

<sup>c</sup> Department of Chemistry, Jagiellonian University, Krakow, Poland

### ARTICLE INFO

#### Article history:

Received 7 May 2014

Received in revised form

16 December 2014

Accepted 22 December 2014

Available online 13 January 2015

#### Keywords:

Polyurethane films

Polysiloxane

Core-shell nanopowder

Surface structure

AFM microscopy

Surface free energy parameters

### ABSTRACT

Linear polyurethanes were obtained the reaction of 1,6-hexamethylene diisocyanate with poly( $\epsilon$ -caprolactone)diol and butane-1,4-diol. Synthesis was carried out in the presence of 1, 3 and 5 wt.% of polydimethylsiloxane-poly(methyl methacrylate) core-shell nanopowder. Solutions of resulting polyurethanes were cast on PTFE plates and dried at 140 °C to form films. The presence of structures originating from modifier was confirmed by IR and XPS spectroscopy. DSC analysis revealed the presence of crystalline phase in all samples. Contact angles were determined using standard fluids and surface free energy parameters were calculated. The results of these investigations proved that modification with silicone-acrylic nanopowder resulted in significant increase in hydrophobicity of polyurethane surfaces. Changes in surface characteristics were also reflected in surface images obtained in AFM studies. It is suggested that the polyurethane composites obtained in this study can be tested as coatings for biomedical applications.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Polyurethane elastomers constitute very important and universal group of polymers showing certain advantages, e.g. excellent mechanical strength, sound and vibration damping ability or elasticity combined with high abrasion resistance, i.e. features essential in their application, specifically in automotive industry. On the other hand, polyurethanes have highly polar surfaces what results in diminished thermal and hydrolytic stability. Thus, enzymatic hydrolysis at elevated temperatures is facilitated [1,2] that negatively affects application of polyurethanes as biomaterials. The polar character of polyurethanes can be decreased through appropriate selection of starting materials, e.g. the use of 2,2,3,3-terafluoro-butane-1,4-diol as chain extender for NCO-terminated prepolymers that was shown in one of our earlier works [3]. However, if polyurethanes are applied as biomaterials which remain in constant contact with body fluids the presence of fluorine is not acceptable because of its cancerogenic properties [4]. One of alternative ways leading to diminished polarity of polyurethanes is their chemical modification with polysiloxanes introduced as

fragments of soft segments [5–7]. However, problems may occur in segment compatibility if reactants are not carefully selected [8] and modification with polysiloxanes may not be effective if hydroxyl groups of polysiloxane diols are not equally reactive [9]. It was shown that the polarity of polyurethanes can also be diminished by physical modification during synthesis through the introduction of nanosilica [10]. In such processes of physical modification of polymers it is important that the nanofillers are equally distributed in the polymer matrix, so the film formation will not be disturbed. Those requirements can be met by the application of polymer nanopowders characterized by specific morphology and chemical composition. The concept of the synthesis of such modifiers was developed in the nineties by researchers from Wacker Chemie. They proposed to synthesize core-shell structured polymer nanoparticles where the core is made of polymer with low glass transition temperature ( $T_g$ ), e.g. of partly crosslinked silicone, and the shell is made of thermoplastic polymer with high  $T_g$ . Studies in that direction have been carried out for last few years in the Industrial Chemistry Research Institute in Warsaw [11].

It was found that core-shell nanoparticles can be formed in a process of emulsion polymerization of suitable monomers, usually methacrylate esters, in aqueous dispersion of polysiloxane with low crosslinking density, followed by spray-drying of the resulting hybrid dispersion [12,13]. Polysiloxane which constitutes the

\* Corresponding author. Tel.: +48 178651579; fax: +48 17 8543655.  
E-mail address: [pkrol@prz.edu.pl](mailto:pkrol@prz.edu.pl) (P. Król).

core of the dispersion particles has a very low  $T_{g1}$  ( $<-100^{\circ}\text{C}$ ) while poly(methyl methacrylate) or copolymer of methyl methacrylate with another methacrylate monomer, e.g. difunctional methacrylate, which constitutes the shell has high  $T_{g2}$  ( $>+120^{\circ}\text{C}$ ). At temperatures above  $T_{g2}$  applied e.g. during processing of thermoplastic polymer modified with such nanoparticles or during removal of solvent from coating modified with such nanoparticles, polysiloxane is released and can be distributed in the whole polymer or coating mass.

The study described in his paper is focused on exploring the possibility of using a selected nanopowder as a modifier that would increase the hydrophobicity of solvent-based polyurethane coatings. It was expected that such nanopowders would fill any local surface unevenness due to good affinity to both the hard and flexible polyurethane segments resulting in an increase in surface smoothness. On such smooth surface blood clotting does not occur providing an advantage in the context of surface interaction with blood cells in tissue engineering [6,14].

## 2. Experimental

### 2.1. Raw materials and reagents

1,6-Hexamethylene diisocyanate (HDI) from Aldrich, was used as purchased; poly( $\epsilon$ -caprolactone)diol,  $M_n = 2000$  (PCL) (from Aldrich), the polyester reagent was dried under vacuum in nitrogen, at  $120^{\circ}\text{C}$ , during 2–4 h; butane-1,4-diol (from Aldrich), the reagent was dried in the vacuum dryer, at  $105^{\circ}\text{C}$ , during 8 h; dibutyl tin dilaurate (DBTDL) (from Huntsman Performance Chemicals); polysiloxane–poly(methyl methacrylate) as the core–shell nanopowder from the Industrial Chemistry Research Institute, Warsaw, (Poland),  $T_{g1} = -119.5^{\circ}\text{C}$ ,  $T_{g2} = 123.3^{\circ}\text{C}$  (Fig. 1a and b; [15]). 1,4-Dioxane, analytical grade (99,8%) (from POCh Gliwice, Poland), the solvent was subjected to distillation before use and the fraction with B.P. =  $101^{\circ}\text{C}$  was collected, molecular sieves 4 Å (POCH Gliwice) freshly heated to  $300^{\circ}\text{C}$  were added to the distilled reagent in order to remove any traces of water; the analytical grade reagents: dibutylamine, diiodomethane and formamide (from Aldrich), the reagents were used as received; redistilled water.

### 2.2. Synthesis of polyurethane elastomers

Before polyurethane synthesis nanopowder dispersion in dioxane was prepared. For that purpose, the prescribed amount of silicone–acrylic nanopowder was introduced and distributed in dioxane in an ultrasound emitting device (ELMASONIC P)

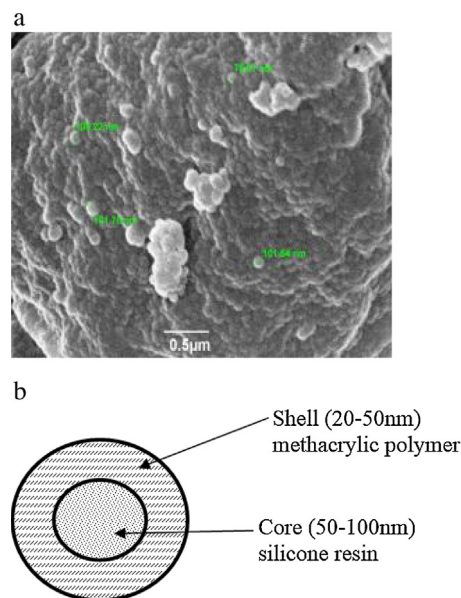


Fig. 1. (a) SEM micrograph of the nanopowder agglomerated core shell particles. (b) Scheme of the core–shell particle.

at frequency of 80 kHz during 30 min at  $50^{\circ}\text{C}$ . In the same time hydroxyl-functional reagent was prepared by incorporating DBTL catalyst in PCL–polyester (0.1 wt.% in respect of polyester amount).

A two-stage process of polyurethane synthesis was carried out in a three-necked glass flask equipped with heating mantle, mechanical agitator, dropping funnel, thermometer, reflux condenser and nitrogen supply nozzle. Nitrogen was purged through the reaction mixture to protect the reagents against contact with moisture. At stage 1, the NCO-terminated prepolymer was synthesized. PLC polyester was added dropwise at  $60^{\circ}\text{C}$  to HDI solution in dioxane which contained the dispersed silicone–acrylic nanopowder. The NCO:OH molar ratio was 2:1. The reaction mixture was maintained at  $60^{\circ}\text{C}$  during 2–3 h. The reaction was terminated when the concentration of free –NCO groups (as established analytically) was equal to that resulting from stoichiometric calculations. The content of unreacted –NCO groups was determined through well known acidimetric method. Excess of dibutylamine was titrated using HCl solution in the presence of bromophenol blue indicator [16].

Table 1

Chemical compositions of synthesized polyurethane elastomers.

Sample labeling	Reagents Stage	HDI ( $M = 168$ )		1,4-Dioxane + nanopowder Mass (g)	PCL ( $M = 2000$ )		BD ( $M = 90$ )	
		Mass (g)	Moles		Mass (g)	Moles	Mass (g)	Moles
		PU-0	1 2 Product	6.72 Prepolymer in dioxane containing ~5 wt.% NCO groups 97.04 g Of linear PU solution containing ~50% polymer	0.04	48.52 + 0.00	40.00	0.020
PU-1	1 2 Product	6.72 As in sample no. 1 97.53 g Of linear PU solution containing ~50 wt.% polymer with 1 wt.% nanopowder	0.04	48.52 + 0.4852	40	0.02	– 1.800	– 0.02
PU-3	1 2 Product	6.72 As in sample no. 1 98.50 g Of linear PU solution containing ~50 wt.% polymer with 3 wt.% nanopowder	0.04	48.52 + 1.460	40	0.02	– 1.800	– 0.02
PU-5	1 2 Product	6.72 As in sample no. 1 99.47 g Of linear PU solution containing ~50 wt.% polymer with 5 wt.% nanopowder	0.04	48.52 + 2.426	40	0.02	– 1.800	– 0.02

Download English Version:

<https://daneshyari.com/en/article/692226>

Download Persian Version:

<https://daneshyari.com/article/692226>

[Daneshyari.com](https://daneshyari.com)