Preparation of polyurethane-acrylate and silica nanoparticle hybrid composites by a free radical network formation method

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Abstract. In this study, hybrid composites of polyurethane-acrylate (PUA) and silica nanoparticle were prepared by a radical method. For this aim, silica nanoparticles were chemically functionalized with 3-methacryloxypropyltrimethoxysilane. Polyurethane was synthesized and then modified with 2-hydroxyethyl methacrylate to yield PUA. Then, different amounts of modified-silica were used to prepare PUA composites by the addition of an ethylene glycol dimethacrylate crosslinker. Fourier-transform infrared spectroscopy confirmed the successful functionalization of silica nanoparticles and the preparation of PUA. Structural investigation of the functionalized-nanoparticles and also nanocomposites was carried out using X-ray diffraction and electron microscopy. According to the thermal gravimetric analysis results, char residue of HSiO_2 is 86.6%, which decreases to 81.3% in the case of MSiO_2 as a result of its modifier degradation content of 5.3%. PUAS5 shows main decomposition temperatures of 396.5 and 454.9°C and also char content of 5.7% at 700°C. The high amount of MSiO_2 can also be resulted in higher degree of crosslinking and therefore higher thermal stabilities and char residue.

Keywords. Polyurethane acrylate; nanocomposite; silica nanoparticle; radical method; thermal properties.

1. Introduction

Polymer nanocomposites are one of the important categories of advanced materials with improved mechanical and thermal properties. In comparison with the ordinary composites, nanocomposites were extensively considered because of strong interactions between their structural components of the polymeric matrix and nanodimensional filler. Polyurethane (PU) is an applicable polymer which can be used in wide variety of applications, such as composites, coatings, flexible and rigid foams, adhesives and sealants [1–3]. Polyurethane-acrylate (PUA) is a PU which is end-capped with acrylic functionality by using hydroxyl group containing unsaturated acrylic monomers of hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA). The hard segments of PUA generally consist of isocyanate and acrylic functionality, and the soft segments are formed from polyols in most cases [4–7]. PUA exhibits excellent impact strength and also high adhesion. However, low-thermal stability limits its application in wide variety of engineering fields. Most of PUA characteristics can be improved by the incorporation of inorganic components and the formation of hybrid materials [8–10].

Organic/inorganic hybrid materials combine beneficial characteristics of organic polymers like processability with the useful properties of inorganic domains such as thermal stability. Silica nanoparticles have widely been used because

of their effects on lowering shrinkage during curing and decreasing thermal expansion coefficients [11–13]. Strong interactions between the silica nanoparticles and silanol groups with PU chains can result in their high degree of dispersion in the PU matrix [14]. However, simple blending of silica nanoparticles with polymers is often restricted as a result of the large amount of their hydroxyl groups and consequently, their aggregation because of weak interactions between the two phases [15]. To overcome this problem, silica nanoparticles can be functionalized with different chemicals for enhancing their dispersion and compatibility with the polymer matrix not only in PU composites, but also in various polymer composites [16–18].

In the case of PUA composites, Qiu and coworkers [19] prepared nanocomposites of silica/waterborne polyurethane acrylate (WPUA) using a sol–gel process, where T_g of the hybrid composites increased with the addition of inorganic domain content. WPUA was prepared from isophorone diisocyanate and polyether polyol as the main components of the PU oligomer and HEMA as the hydroxyl group containing unsaturated acrylic modifier. Finally, silica/WPUA nanocomposites were prepared by using coupling agents of tetraethoxysilane and 3-glycidioxypropyltrimethoxysilane and also application of the sol–gel reaction. Wang and coworkers [20] prepared nanocomposites *via* photopolymerization of WPUA in the presence of octavinyl polyhedral oligomeric silsesquioxane. They showed that the thermal

Table 1. Sample names with a brief description.

Sample	Description
HSiO ₂	Hydroxylated silica nanoparticles
MSiO ₂	MPS-modified HSiO ₂
PU	Polyurethane
PUA	Polyurethane-acrylate
CPUA	Cured PUA
PUAS1	PUA nanocomposite with 1 wt% of MSiO ₂
PUAS3	PUA nanocomposite with 3 wt% of MSiO ₂
PUAS5	PUA nanocomposite with 4 wt% of MSiO ₂

properties of these hybrid composites were higher than the neat WPUA. Lately, they used HEA-modified graphene oxide in the preparation of PUA composites with high-thermal stability using UV curing technology [21]. They showed that strong interfacial interactions were formed between the uniformly dispersed-modified layers and PUA as a result of UV cross-linking.

A free radical method can be used for network formation in PUA and its composites. Similar to the preparation of hybrid polymer gels that the network formation occurs by using crosslinkers, and PUA hybrid composites can also be prepared by using ethylene glycol dimethacrylate (EGDMA) as the free radical crosslinker. Therefore, double bonds of PUA, modified silica and EGDMA crosslinker form a network by thermal dissociation of azobisisobutyronitrile (AIBN). Here, hybrid composites of PUA and silica nanoparticles were prepared by using the radical method. To this end, silica nanoparticles were modified with 3-methacryloxy propyltrimethoxysilane (MPS) and incorporated into the PUA matrix in different contents by the free radical method. PUA was also prepared by a sequential reaction of hexamethylene diisocyanate (HMDI) and polyethylene glycol (PEG) and its end-capping with HEMA. This well-tuned process resulted in covalent bending between the PUA matrix and also modified silica nanoparticles. Finally, structural, morphological and thermal characteristics of the nanocomposites were investigated using different methods. Sample names with a brief description are given in table 1.

2. Experimental

2.1 Materials

PEG ($M_n = 600$ Da, Sigma-Aldrich), silica nanoparticles (SiO₂, Tecnan-Nanommat, Spain) and EGDMA (Sigma-Aldrich) were used as received. HMDI, AIBN, HEMA, MPS, triethylamine (TEA) acetone, tetrahydrofuran (THF), ethanol, methanol and acetic acid were received from Merck Company.

2.2 Preparation of hydrophilic SiO₂ (HSiO₂)

According to the literature [22,23], SiO₂ (2.5 g) was mixed in distilled water (100 ml) and sonicated for 30 min. After addition of NaOH (1.5 g) and stirring at 60°C for 24 h, acetic acid was gradually added for neutralization. Finally, HSiO₂ was obtained after centrifugation of the mixture for 10 min, washing the solid with methanol, and drying at 80°C for a day.

2.3 Functionalization of HSiO₂ by MPS to obtain MSiO₂

According to the literature [24,25], HSiO₂ (2 g) was mixed in a 100 ml ethanol and water mixture (volumetric ratio of 8:2) and sonicated for 30 min. Then, TEA (15 ml) was added and agitated at 50°C for 2 h. In another flask, MPS (1 ml) was added to the ethanol and water mixture (volumetric ratio of 9:1) and pH of the solution was adjusted to 3–4 by the addition of acetic acid solution (0.1 molar) for the progression of the hydrolysis process by stirring at 50°C for 2 h. Afterwards, the MPS solution was gradually added on HSiO₂ dispersion and stirred at 50°C for 8 h. Finally, MSiO₂ was obtained by centrifugation of the mixture at 8000 rpm for 15 min, washing with acetone, and drying at 60°C for a day.

2.4 Preparation of PUA resin

Isocyanate-terminated PU was synthesized in an isocyanate to hydroxyl molar ratio of 2:1. For this purpose, HDI (1 ml) was mixed with THF (10 ml) in a flask. PEG (1.66 ml) was gradually added into the flask and prepolymerization of PU was accomplished in a nitrogen atmosphere at 60°C for 3 h. Then, the flask content was cooled to 50°C and HEMA (0.75 ml) was gradually added into the flask. For dilution of the mixture, THF (10 ml) was added and the temperature was kept at 50°C for 3 h to yield PUA resin (figure 1).

2.5 Preparation of MSiO₂/PUA hybrid composites

After synthesis of PUA resin, it was sequentially used in the preparation of MSiO₂/PUA hybrid composites with different weight percents of MSiO₂ (table 2). To this end, temperature was increased from 50 to 65°C. EGDMA as the crosslinker (0.23 ml) was added in a molar ratio of 0.2:1 with respect to HEMA. Then, after dispersing MSiO₂ in THF and sonication for 10 min, it was added into the flask at 65°C. Then, AIBN in 2 wt% with respect to HEMA and EGDMA was dispersed in THF and added into the flask. Finally, the free radical reaction was maintained at 65°C for 2 h till the reaction medium changed to the gel state. The product was dried at 50°C for a day to yield MSiO₂/PUA hybrid composites (figure 2).

2.6 Characterization

Fourier-transform infrared (FTIR) spectroscopy was performed on a Bruker spectrometer (Germany) using KBr

Figure 1. Schematic illustration for the preparation of PUA resin.

Table 2. Recipes used in the preparation of MSiO_2 /PUA hybrid nanocomposites.

Sample	PUA (g)	EGDMA (g)	MSiO_2 (g)	AIBN (g)
CPUA	3.72	0.242	0	0.021
PUAS1	3.72	0.242	0.040	0.021
PUAS3	3.72	0.242	0.119	0.021
PUAS5	3.72	0.242	0.198	0.021

pellets method with an average of 24 scans, which collects the spectra at a 4 cm^{-1} resolution in the wavelength range of $500\text{--}4000\text{ cm}^{-1}$. The X-ray diffraction (XRD) curves were obtained by a reflection scan with monochromatic $\text{CuK}\alpha$ ($\lambda = 0.1540\text{ nm}$) radiation (Bruker-AXS, Germany). Thermogravimetric analysis (TGA) was performed using Polymer Laboratories thermal analyser (TGA 1000, UK) with a heating ramp of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere at a flow rate of 50 ml min^{-1} . The SEM image of MSiO_2 was obtained by scanning electron microscopy (Vega Tescan SEM instrument, Czech Republic). The specimen was prepared by the precipitation of a thin sample layer on a mica surface using a spin coater and its subsequent gold-coating using a sputtering coater. The morphological study of the MSiO_2 and composites was carried out by transmission electron microscopy (TEM, TECNAI-12, Philips Co.,

The Netherlands) with an acceleration voltage of 120 kV . For this purpose, MSiO_2 was mixed in ethanol using an ultrasonic bath for half an hour and then deposited on the lacy grids. In the case of hybrid composites, microtomy was used for cutting a thin layer of samples.

3. Results and discussion

FTIR spectra of SiO_2 , MSiO_2 , PUA, CPUA and PUAS5 are presented in figure 3. Accordingly, SiO_2 and MSiO_2 show a wide absorption peak at $1050\text{--}1150$ and 474 cm^{-1} , which originates from Si-O-Si units [26,27]. After modification of SiO_2 with MPS, some characteristic bands related to MPS can be observed in the spectrum of MSiO_2 , such as the C=C absorption peak at 1520 cm^{-1} and the C=O absorption peak at 1690 cm^{-1} [28,29]. In addition, the stretching vibration of C-H moieties is shown at $2855\text{--}2935\text{ cm}^{-1}$, which originates from the methylene groups of MPS. The peak at 1450 cm^{-1} is also assigned to the bending vibration of C-H units in MPS [30,31]. FTIR analysis can also be used for the investigation of the HEMA attachment reaction completion. The absence of the -N=C=O band at near 2270 cm^{-1} and also the presence of the N-H stretching vibration at 3310 cm^{-1} confirm the successful attachment of HEMA to PU in PUA [32]. There is also a strong peak at near 1715 cm^{-1} for PUA and

Figure 2. Schematic illustration for the preparation of MSiO₂/PUA hybrid nanocomposites.

Figure 3. FTIR spectra of SiO₂, MSiO₂, PUA, CPUA and PUAS5.

Figure 4. (A) TGA and (B) DTG thermograms of HSiO₂, MSiO₂, CPUA, PUAS1, PUAS3 and PUAS5.

CPUA, which correspond to the urethane carbonyl groups. Additionally, the peak at 1460 cm^{-1} can be assigned to the C=C bond of HEMA in PUA [19]. In the CPUA and PUAS5 samples, stretching vibrations of C–H groups are shown at $2875\text{--}2940\text{ cm}^{-1}$.

TGA and derivative weight loss (DTG) curves for the HSiO₂, MSiO₂, CPUA and also MSiO₂/PUA hybrid composites with different MSiO₂ content are displayed in figure 4A and B, respectively. The difference between HSiO₂ and MPS-modified nanoparticles is significant. For HSiO₂, a weight loss around 13.6% can be observed till 700°C. The weight loss below 200°C originates from the removal of the absorbed water on nanoparticles. The weight loss between 200 and 700°C can be attributed to the degradation of Si–OH moieties. MSiO₂ shows a lower weight loss up to 350°C which

originates from its lower capacity for water adsorption at the surface [33]. However, a considerable weight loss was observed at 350–550°C, which originates from decomposition of MPS at the surface of MSiO₂. Char residue HSiO₂ is 86.6% at 700°C which decreases to 81.3% in the case of MSiO₂ as a result of its modifier degradation at higher temperatures. Therefore, MPS content in MSiO₂ can be estimated to be 5.3%. In the case of hybrid composites (figure 4A), the slight weight loss at relatively low temperatures (lower than 250°C) is because of humidity evaporation. The weight loss at 320–500°C originates from the decomposition of PUA chains [5,21]. In these samples, hydrogen bonding is a physical crosslinker resulting in improved thermal stabilities. Additionally, three-dimensional network formation upon the radical crosslinking process is another reason for increased thermal stabilities [34]. All the hybrids show three major degradation steps, both of them in 320–430°C and another one in 420–500°C. This shows that decomposition of PUA chains starts at 320–420°C at the HDI hard segments with breakage of urethane units. The decomposition step at 420–500°C can be assigned to the decomposition of PEG soft segments and of PUA [35–38]. TGA curves and the extracted results in table 3 show that higher MSiO₂ content in the nanocomposites results in higher char residues and also thermal degradation temperatures in each step. For example, PUAS5 shows the main decomposition temperatures of 396.5 and 454.9°C and also

Table 3. Summarized TGA and DTG results.

Sample	DTG peak (°C)	Char residue (%)
HSiO ₂	52.7 and 493.9	86.6
MSiO ₂	162.8, 421.7 and 543.2	81.3
CPUA	343.8, 383.9 and 443.5	1.1
PUAS1	347.2, 388.4 and 445.1	1.5
PUAS3	347.2, 393.1 and 445.7	3.5
PUAS5	339.2, 396.5 and 454.9	5.7

Figure 5. XRD curves of MSiO₂, CPUA, PUAS1, PUAS3 and PUAS5.

Figure 6. (A) SEM, (B) TEM images of MSiO₂ and (C) TEM image of PUAS5.

char content of 5.7% at 700°C. The high amount of MSiO₂ can also be resulted in higher degree of crosslinking and therefore, higher thermal stabilities and char residue.

The XRD patterns for MSiO₂, CPUA and SiO₂/PUA nanocomposites with different amounts of MSiO₂ are displayed in figure 5. In the case of MSiO₂, a broad peak at around 23° is observed, which is attributed to the amorphous structure of silica domains. In the case of CPUA powder, a broad diffraction peak at near 20° is assigned to the amorphous phase of cured PUA. Additionally, all the nanocomposites with different amounts of MSiO₂ show a diffraction peak at about 20° as a result of the presence of small crystalline structures and partial ordered arrangement of PU chain segments. Flexible and linear polyether chains of PEG and the symmetric structure of HMDI can be resulted in crystalline structures [39–41]. The peak intensity of nanocomposites is lower in comparison with CPUA and it decreases with increasing MSiO₂ content, which confirms the existence of a strong interaction among PUA and MSiO₂ in the cured nanocomposites [42]. The partial ordered arrangement of PU chain segments decreases with increasing MSiO₂ content and therefore, the peak intensity is diminished.

MSiO₂ was dispersed in ethanol and gold-coated to record SEM images (figure 6A). Also, MSiO₂ dispersion in ethanol was deposited on lacy carbon grids for taking TEM images (figure 6B). Finally, by cutting a thin layer from PUAS5 with a thickness of about 70 nm, the sample was prepared for TEM imaging (figure 6C). According to the images, MPS-modified silica nanoparticles with a size in the range of several nanometres are in an aggregated form. In the case of PUAS5, MSiO₂ nanoparticles were pushed apart during the mixing and curing reactions. MSiO₂ can be observed as spherical nanoparticles within the dark matrix of PUAS5. This shows that MSiO₂ was homogenously distributed in the PUA matrix [26,27].

4. Conclusion

Hybrid composites of PUA and MSiO₂ were prepared by the radical method using different amounts of MSiO₂ and also the EGDMA crosslinker. After modification of SiO₂ with MPS, some characteristic bands related to MPS can be observed in the spectrum of MSiO₂. The absence of the –N=C=O band at near 2270 cm^{–1} and also the appearance of the N–H stretching vibration at 3310 cm^{–1} confirm the successful attachment of HEMA to PU in PUA. Three-dimensional network formation upon the radical crosslinking process is a reason for increased thermal stabilities. Decomposition of PUA chains starts at 320–420°C at the HDI hard segments. The decomposition step at 420–500°C is associated with the decomposition of PEG soft segments and PUA. With the addition of the MSiO₂ content in the nanocomposite matrix, char residue and thermal degradation temperature were increased. PUAS5 shows the

main decomposition temperatures of 396.5 and 454.9°C and also char content of 5.7% at 700°C. A broad XRD diffraction peak at near 20° for CUPA is related to the amorphous phase of cured PUA. Aggregated nanoparticles of MSiO₂ with a size in the range of several nanometres were pushed apart and homogeneously dispersed in the PUA matrix. The TEM image of PUAS5 showed that MSiO₂ was homogeneously distributed within the PUA matrix.

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References

- [1] Chattopadhyay D K and Raju K V S N 2007 *Prog. Polym. Sci.* **32** 352
- [2] Engels H W, Pirkel H G, Albers R, Albach R W, Krause J, Hoffmann A *et al* 2013 *Angew. Chem. Int. Ed.* **52** 9422
- [3] Cao X, Lee L J, Widy T and Macosko C 2005 *Polymer* **46** 775
- [4] Zhang T, Wu W, Wang X and Mu Y 2010 *Prog. Org. Coat.* **68** 201
- [5] Wang Z, Gao D, Yang J and Chen Y 1999 *J. Appl. Polym. Sci.* **73** 2869
- [6] Peruzzo P J, Anbinder P S, Pardini O R, Vega J, Costa C A, Galembeck F *et al* 2011 *Prog. Org. Coat.* **72** 429
- [7] Wang F, Hu J Q and Tu W P 2008 *Prog. Org. Coat.* **62** 245
- [8] Oh I S, Park N H and Suh K D 2000 *J. Appl. Polym. Sci.* **75** 968
- [9] Alishiri M, Shojaei A and Abdekhodaiea M J 2016 *RSC Adv.* **6** 8743
- [10] Ha H, Kim S C and Ha K 2010 *Macromol. Res.* **18** 674
- [11] Chen C, Justice R S, Schaefer D W and Baur J W 2008 *Polymer* **49** 3805
- [12] Azimi R, Roghani-Mamaqani H and Gholipour-Mahmoudalilou M 2017 *Polymer* **126** 152
- [13] Barus S, Zanetti M, Lazzari M and Costa L 2009 *Polymer* **50** 2595
- [14] Goda H and Frank C W 2001 *Chem. Mater.* **13** 2783
- [15] Zou H, Wu S and Shen J 2008 *Chem. Rev.* **108** 3893
- [16] Han Y, Dong W, Chen Z and Xin Z 2016 *Mater. Res. Innov.* **20** 247
- [17] Mousavi A, Roghani-Mamaqani H, Salami-Kalajahi M, Shahi S and Abdollahi A 2018 *Express Polym. Lett.* **12** 187
- [18] Abdollahi A, Roghani-Mamaqani H, Salami-Kalajahi M, Mousavi A, Razavi B and Shahi S 2018 *Prog. Org. Coat.* **117** 154
- [19] Qiu F, Xu H, Wang Y, Xu J and Yang D 2012 *J. Coat. Technol. Res.* **9** 503
- [20] Wang X, Hu Y, Song L, Xing W, Lu H, Lv P *et al* 2011 *J. Polym. Res.* **18** 721
- [21] Yu B, Wang X, Xing W, Yang H, Song L and Hu Y 2012 *Ind. Eng. Chem. Res.* **51** 14629
- [22] Mousavi A, Roghani-Mamaqani H, Salami-Kalajahi M, Shahi S and Abdollahi A 2018 *Mater. Chem. Phys.* **216** 468
- [23] Abdollahi A, Roghani-Mamaqani H, Salami-Kalajahi M, Razavi B, Mousavi A and Shahi S 2018 *Polym. Compos.* **39** E2316
- [24] Jiang J C J, Wang W, Shen H and Wang J 2016 *Appl. Surf. Sci.* **397** 104
- [25] Stöber W, Fink A and Bohn E 1968 *J. Colloid Interface Sci.* **26** 62
- [26] Mirshafiei-Langari S A, Haddadi-Asl V, Roghani-Mamaqani H, Sobani M and Khezri K 2013 *J. Polym. Res.* **20** 163
- [27] Mirshafiei-Langari S A, Haddadi-Asl V, Roghani-Mamaqani H, Sobani M and Khezri K 2013 *Polym. Compos.* **34** 1648
- [28] Roghani-Mamaqani H, Haddadi-Asl V, Khezri K, Zeinali E and Salami-Kalajahi M 2014 *J. Polym. Res.* **21** 333
- [29] Roghani-Mamaqani H, Haddadi-Asl V, Khezri K and Salami-Kalajahi M 2014 *Polym. Int.* **63** 1912
- [30] Roghani-Mamaqani H, Haddadi-Asl V, Ghaderi-Ghahfarrokhi M and Sobhkhiz M 2014 *Colloid Polym. Sci.* **292** 2971
- [31] Roghani-Mamaqani H and Haddadi-Asl V 2014 *Polym. Compos.* **35** 386
- [32] Lee S I, Hahn Y B, Nahm K S and Lee Y S 2005 *Polym. Adv. Technol.* **16** 328
- [33] Jiang J, Wang W, Shen H, Wang J and Cao J 2017 *Appl. Surf. Sci.* **397** 104
- [34] Hu T, Chen S, Tian Y, Pojman J A and Chen L 2006 *J. Polym. Sci. A: Polym. Chem.* **44** 3018
- [35] Patel A and Mequanint K 2011 *J. Bioactive Compat. Polym.* **26** 114
- [36] Zhang Q, Huang C, Wang H, Hu M, Li H and Liu X 2016 *RSC Adv.* **6** 107942
- [37] Petrovic Z S, Zavargo Z, Flynn J H and Macknight W J 1994 *J. Appl. Polym. Sci.* **51** 1087
- [38] Gaikwad M S, Gite V V, Mahulikar P P, Hundiware D G and Yemul O S 2015 *Prog. Org. Coat.* **86** 164
- [39] Mo M, Zhao W, Chen Z, Yu Q, Zeng Z and Wu X 2015 *RSC Adv.* **5** 56486
- [40] Liu H, Gao J, Huang W, Dai K, Zheng G and Liu C 2016 *Nanoscale* **8** 12977
- [41] Wang C, Ma C, Mu C and Lin W 2017 *RSC Adv.* **7** 27522
- [42] Zhang S, Jiang J, Yang C, Chen M and Liu X 2011 *Prog. Org. Coat.* **70** 1