IMPROVEMENTS OF MECHANICAL PROPERTIES AND SPECULAR GLOSS OF POLYURETHANE BY MODIFIED NANOCRYSTALLINE CELLULOSE

Hao Zhang, Ying She, Shuping Song, Heyu Chen, and Junwen Pu *

In this study, the optical and mechanical properties of polyurethane were improved by modified nanocrystalline cellulose (NCC). The surface of NCC was modified by 3-glycidoxypropyltrimethoxysilane (GPTMS) and 3-methacryloxy-propyltrimethoxysilane (MPS) to overcome the lack of compatibility with polyurethane. Polyurethane with modified NCC was characterized by wetting property, X-ray powder diffraction, and thermogravimetric analysis. The pencil hardness, specular gloss, and abrasion resistance of modified polyurethane were determined using the methods of Chinese National Standards GB/T 6739-2006, GB/T 9754-2007, and GB/T 1768-2006. The wetting property of NCC modified by GPTMS increased by 25.9%, and modification from MPS resulted in a 22.5% decrease of the contact angle. MPS-modified NCC affected the crystal structure and thermal stability of polyurethane more significantly than NCC modified by GPTMS. The pencil hardness of polyurethane was enhanced with 1.5% modified NCC. The specular gloss and abrasion resistance of modified polyurethane increased by 253.1% (1.0% NCC modified by GPTMS) and 59.4% (1.5% NCC modified by GPTMS), respectively. MPS-modified NCC led to the inconspicuous improvements.

Keywords: Polyurethane; Nanocrystalline cellulose; Wetting property; Specular gloss; Abrasion resistance

*Contact information: College of Materials Science and Technology, Beijing Forestry University, Haidian District, Beijing 100083, PR China; * Corresponding author: pujunwen@126.com*

INTRODUCTION

Different kinds of molecular architectures designed for each application has made polyurethane one of the most popular polymers used in a variety of products. Low cost and relatively low pollution are some of the major advantages of polyurethane, while some limitations include the hardness, specular gloss, and abrasion resistance. Using environmentally friendly fillers, such as modified NCC, is the most promising approach in improving the optical and mechanical properties of polyurethane.

Inorganic fillers have shown significant effects on the physical properties of polyurethane. Nanosilica modified by poly (propylene glycol) phosphate ester has been used to improve the hardness of polyurethane (Blagojevic *et al.* 2012; Gao *et al.* 2011; Rostami *et al.* 2010; Chen *et al.* 2010). The thermal stability and water resistance of polyurethane were influenced by silane coupling agent functionalized nanosilica (Sun *et al.* 2011). Nanosilica modified by vinyl isocyanate was used to synthesize nanocomposite with polyurethane, and the mechanical properties of the coating were enhanced (Nikje and Tehrani 2010; Turunc *et al.* 2008; Jang *et al.* 2008). Particles of granulated alundum were used as the additive agent to improve the corrosion performance of polyurethane coating (Kotnarowska *et al.* 2011; Dhoke *et al.* 2009). The permeability of water vapor and gas of modified polyurethane were enhanced with the addition of nano-TiO_2 (Chen *et al.* 2009). Amino propyltrimethoxy silane was used to modify nano-TiO_2 for the improvement of compatibility with polyurethane, and the mechanical properties and UV protection of polyurethane coating were improved by the modified TiO_2 (Sabzi *et al.* 2009). The tensile strength and elongation of polyurethane were enhanced by surface modified nanocarbon particles (Liu *et al.* 2008). Modified multiwall carbon nanotubes were used to improve the mechanical properties and melt viscosity of polyurethane (Kuan *et al.* 2005). The modification of polyurethane foams based on bifunctional soybean oil-based polyol by nano-clay was observed to make a rigid foam system (Banik and Sain 2010).

Organic fillers have many advantages over inorganic fillers, such as biocompatibility, low toxicity, and their promising potential applications in solid fuels, fiber, and biomedical fields (Luo *et al.* 2009; Sun *et al.* 2005; Zeng *et al.* 2002). Nano-scale surface modification of segmented polyurethane was operated for the improvement of tensile strength with a phospholipid polymer (Morimoto *et al.* 2004). Strong hydrogen bonding networks from NCC and cellulose whiskers were used to reinforce the tensile strength of polyurethane (Wang *et al.* 2010).

As a kind of natural and environmentally friendly polymer, NCC is emerging as an organic material for the specific crystal structure and superior property. Nanocomposites synthesized by NCC have attracted much attention for its renewable and environmentally benign nature during recent years (Hubbe *et al.* 2008; Pielichowska and Blazewicz 2010). Besides this, the excellent optical and mechanical properties of NCC led to the significant improvements of the hardness, specular gloss, and abrasion resistance of polyurethane with modified NCC.

EXPERIMENTAL

Materials

The original NCC was prepared by acid hydrolysis in a laboratory, which showed a length of 200 to 300 nm and a diameter of 30 to 50 nm. The solids content of polyurethane was 61.6%, and the polyurethane was purchased from LEYI Co. Ltd. (China). The modifiers for changing the surface structure of NCC, GPTMS, and MPS were analytical grade and were used as received without any further purification. All experiments were conducted under air atmosphere.

Methods

Modification of NCC

GPTMS and MPS were used to modify the original NCC for improving the compatibility with polyurethane. Ethanol was treated as a solvent for the modifiers. Four kinds of solutions for each modifier were prepared, and the concentrations of each kind of modifier were 2, 4, 6, and 8% (v/v). The pH of the solutions was decreased to the range of 3 to 4 using hydrochloric acid for the hydrolysis of modifiers. GPTMS and MPS were hydrolyzed for 5 to 10 min until the solutions turned pellucid. One gram of NCC was modified by 100 mL of the ethanol and modifier solution. The modifications were operated at 60 °C for 3 h.

Accession of modified NCC to polyurethane

The modified NCC was added into polyurethane at concentrations of 0.5, 1.0, 1.5, and 2.0% (w/w). An ultrasonic probe was used for the dispersion of modified NCC in polyurethane and the ultrasonic power was 1200 watts. The ultrasonic was turned on for 10 seconds and was turned off for 10 seconds in one period; the total time of the intermittent ultrasonic was 15 min.

Test of polyurethane with modified NCC

Wetting property of modified NCC was tested by the optical contact angle-measuring instrument from DATAPHYSICS (Germany). An X-ray diffractometer (XRD) from SHIMADZU (Japan) was used for examining the crystal structure of polyurethane with modified NCC. The thermal behavior of the modified polyurethane was detected by thermogravimetric analysis (TG) from SHIMADZU (Japan) at a constant heating rate (10 °C/min) in flowing air from 30 °C to 600 °C.

The pencil hardness, specular gloss, and abrasion resistance were tested by the methods of Chinese National Standards GB/T 6739-2006, GB/T 9754-2007, and GB/T 1768-2006. The pencil hardness test was operated with oven-dried polyurethane. The angle between the pencil and polyurethane films was 45° and the load of pencil was 750 g. Specular gloss of modified polyurethane was tested with 75 μm thick films. A kind of glass, the refractive index of which was 1.567, was treated as a control group. The abrasion resistance of polyurethane with modified NCC was determined using a rubber wheel.

RESULTS AND DISCUSSION

Wetting Property of Modified NCC

The wetting properties of NCC were indicated by contact angle (CA); CA determination is a kind of simple technique for examining the surface structure of solids. The chemical treatments of NCC surface affected the CA significantly in this study.

The lipophilic groups from GPTMS and MPS affected the wetting properties of modified NCC. GPTMS showed an obvious role in reducing the contact angles of NCC, which are indicated in Fig. 1a and b. The CA left and CA right of modified NCC decreased from 85.8° and 85.2° to 66.8° and 66.4° when the concentration of GPTMS was 4%, respectively. The increase in wetting property of modified NCC was 25.9% with 8% GPTMS. The CA left and CA right of NCC modified by MPS decreased from 85.8° and 85.2° to 70.6° and 71.0° with 4% MPS (shown in Fig. 1c and d). The wetting property, improved by MPS, increased 22.5% when the content of MPS was 8%. Compared with the control group, the lipophilic groups from GPTMS led to more obvious effects than that from MPS on the compatibility of NCC.

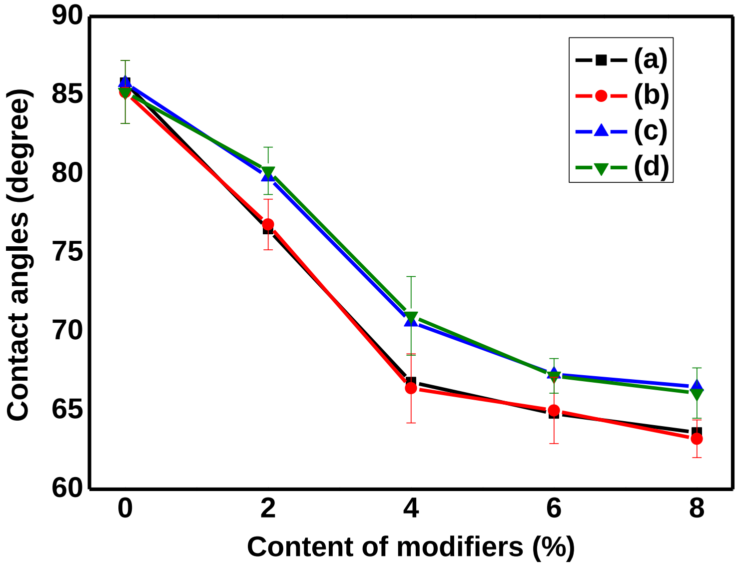

Fig. 1. CA between modified NCC and polyurethane: (a) CA left of GPTMS-modified NCC; (b) CA right of GPTMS-modified NCC; (c) CA left of MPS-modified NCC; (d) CA right of MPS-modified NCC

XRD Patterns of Polyurethane with Modified NCC

Modified NCC affected the crystal structure of polyurethane and the XRD patterns of modified polyurethane are indicated in Fig. 2. NCC modified by different modifiers led to different effects on the characteristic diffraction peaks of polyurethane.

The addition of modified NCC resulted in the enhancements of diffraction intensity. The diffraction peaks of polyurethane at 2θ = 27.8° and 29.2° increased obviously with the NCC modified by MPS (shown in Fig. 2B), while the diffraction peaks of polyurethane with GPTMS-modified NCC were stable which were shown in Fig. 2A. The diffraction peaks of polyurethane at 2θ = 35.9° were affected by the modified NCC inconspicuously and the diffraction intensity was steady.

The NCC modified by GPTMS and MPS affected the amorphous regions and crystal regions of polyurethane. The increases of crystallinity of modified polyurethane are shown in Table 1.

Table 1. Crystallinity of Polyurethane with Modified NCC

		Control Group	Content of Modified NCC (%)			
			0.5	1.0	1.5	2.0
Crystallinity (%)	GPTMS-modified NCC	49.05	49.25	50.84	51.54	52.72
	MPS-modified NCC	49.05	49.79	50.13	51.39	53.42

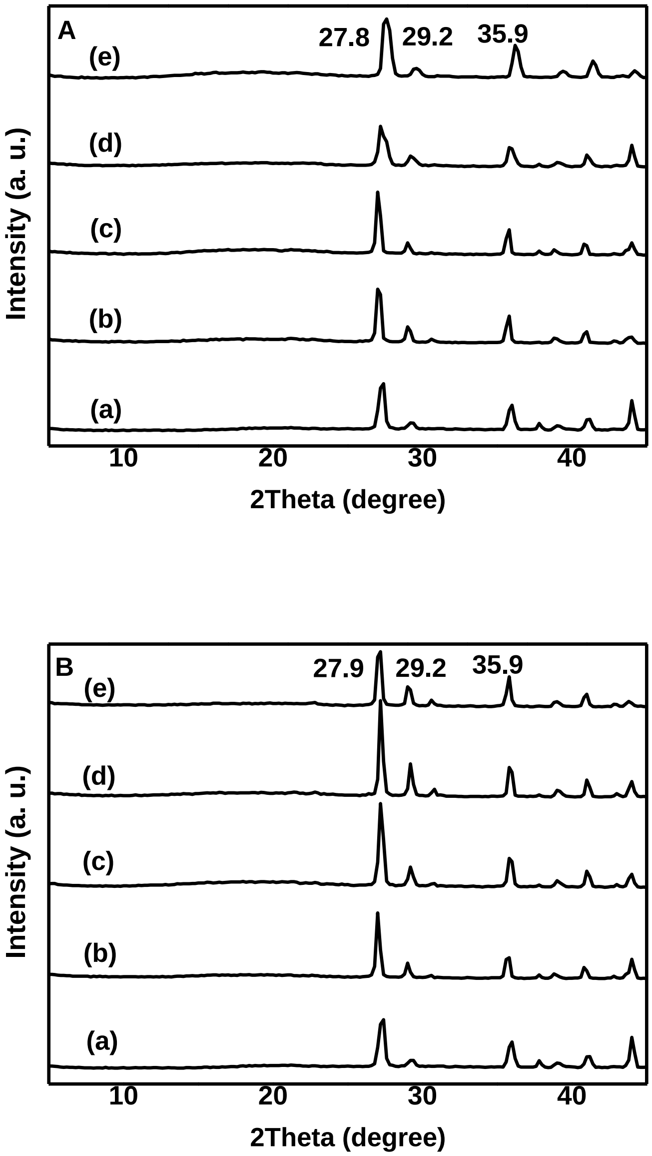

Fig. 2. XRD patterns of polyurethane with modified NCC: A: polyurethane with GPTMS-modified NCC: (a) original polyurethane; (b) 0.5% modified NCC; (c) 1.0% modified NCC; (d) 1.5% modified NCC; (e) 2.0% modified NCC; B: polyurethane with MPS-modified NCC: (a) original polyurethane; (b) 0.5% modified NCC; (c) 1.0% modified NCC; (d) 1.5% modified NCC; (e) 2.0% modified NCC

Thermal Stability of Modified Polyurethane

Different kinds of modified NCC had different effects on the thermal stability of polyurethane. TG was used to further investigate the thermal behavior of modified polyurethane, and the TG curves of modified polyurethane are shown in Fig. 3. The weight loss of the control group occurred at 381.3°C, and the weight loss was attributed to the thermal degradation of polyurethane. The diversification of thermal stability of polyurethane with GPTMS-modified NCC is shown in Fig. 3b, and the weight loss temperature increased by 3.7% (from 381.3°C to 393.6°C). NCC modified by MPS led to an increase of the weight loss temperature of polyurethane from 381.3°C to 397.5°C (shown in Fig. 3c).

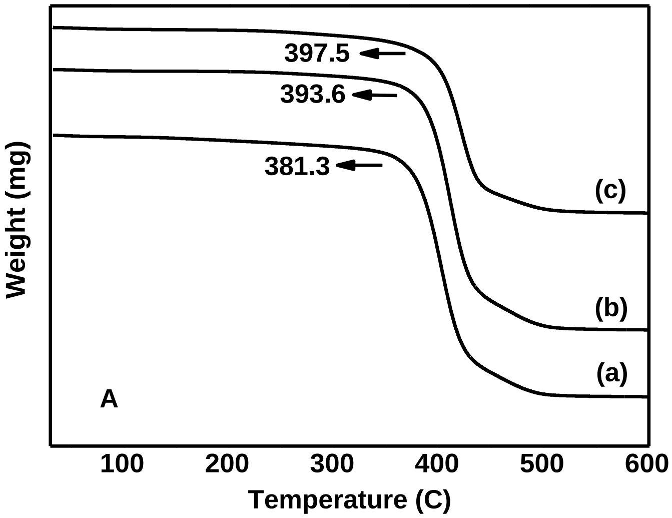

Fig. 3. Thermal stability of modified NCC: (a) original polyurethane; (b) polyurethane with GPTMS-modified NCC; (c) polyurethane with MPS-modified NCC

The Pencil Hardness of Modified Polyurethane

The pencil hardness values of modified polyurethane are indicated in Table 2, and the improvements were affected by the addition of modified NCC. The pencil hardness of polyurethane with 1.5% modified NCC increased from 2H to 4H. The reunion of modified NCC resulted from hydrogen bonds and destroyed the increase of pencil hardness of polyurethane (when the content of modified NCC was 2.0%). Different kinds of modifiers for NCC showed little effect on the pencil hardness of modified polyurethane.

Table 2. The Pencil Hardness of Polyurethane with Modified NCC

		Control Group	Content of Modified NCC (%)			
			0.5	1.0	1.5	2.0
Pencil Hardness	GPTMS-modified NCC	2H	3H	3H	4H	3H
	MPS-modified NCC	2H	3H	3H	4H	3H

The Specular Gloss of Polyurethane with Modified NCC

Distinguishing lipophilic groups of modifiers affected the structure of NCC, and different kinds of modified NCC resulted in different improvements in the specular gloss of polyurethane.

Enhancements of specular gloss (60°) of modified polyurethane are shown in Fig. 4. Compared with the original group, the specular gloss of polyurethane with 1.0% GPTMS-modified NCC increased by 253.1% (shown in Fig. 4a). The NCC modified by MPS resulted in the increase of specular gloss from 9.8 to 28.7 when the content was 1.0%. The reunion of modified NCC led to an obvious decrease of specular gloss when the concentration was more than 1.5%.

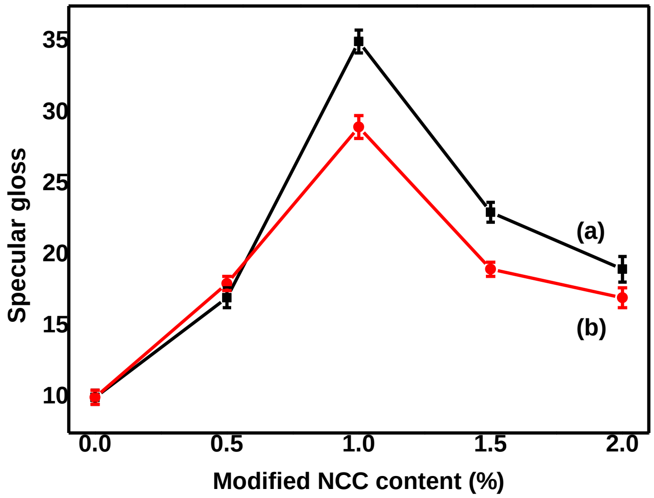

Fig. 4. The specular gloss of polyurethane with modified NCC: (a) polyurethane with GPTMS-modified NCC; (b) polyurethane with MPS-modified NCC

The Abrasion Resistance of Polyurethane with Modified NCC

The crystalline region of NCC influenced abrasion resistance of polyurethane. NCC modified by GPTMS and MPS led to different effects on the abrasion resistance of polyurethane and the improvements are shown in Fig. 5.

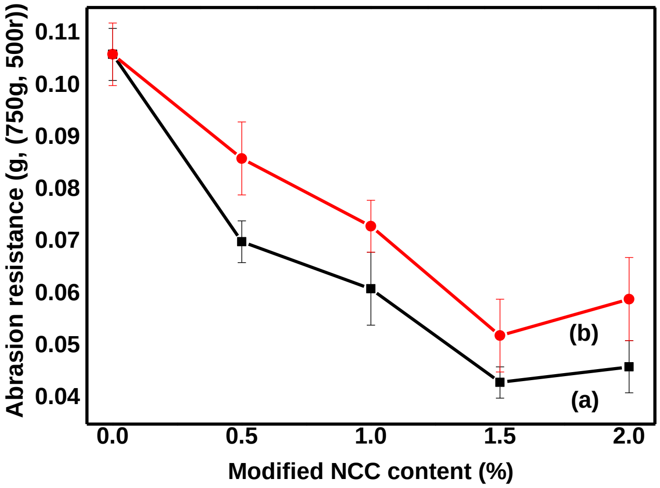

Fig. 5. The abrasion resistance of polyurethane with modified NCC: (a) polyurethane with GPTMS-modified NCC; (b) polyurethane with MPS-modified NCC

The improvements of the abrasion resistance slowed down as the concentrations of modified NCC increased. With the NCC modified by GPTMS, the abrasion resistance of polyurethane increased by 59.4% (from 0.106 g of the virgin polyurethane to 0.043 g when the content of modified NCC was 1.5%). The abrasion resistance of polyurethane increased by 49.0% with 1.5% MPS-modified NCC. It was obvious that the contribution to the abrasion resistance from modified NCC was reduced by the self-agglomeration (occurring when the content of modified NCC was more than 2.0%).

CONCLUSIONS

1. Surface modifications of NCC with GPTMS and MPS were operated to improve the compatibility with polyurethane. The contact angle between GPTMS-modified NCC and polyurethane decreased by 25.9%, and the modification from MPS resulted in a 22.5% decrease of the contact angle. MPS-modified NCC affected the XRD diffraction peaks of polyurethane at $2\theta = 27.8°$ and 29.2° more obviously than that modified by GPTMS. The thermal stability of polyurethane with GPTMS-modified NCC increased by 3.7%, while the degradation temperature of polyurethane with MPS-modified NCC increased from 381.3 °C to 397.5 °C.
2. Modified NCC affected the optical and mechanical properties of polyurethane significantly. The pencil hardness of polyurethane increased from 2H to 4H with 1.5% modified NCC and modifiers of NCC did not affect the improvements. Compared with the 192.9% increase of polyurethane with 1.0% MPS-modified NCC, the specular gloss of polyurethane with 1.0% NCC modified by GPTMS increased by 253.1%. The abrasion resistance of polyurethane with 1.5% GPTMS-modified NCC increased by 59.4%, while the MPS-modified NCC led to an inconspicuous increase of the abrasion resistance.

ACKNOWLEDGEMENTS

The authors are grateful for the support of the Forestry Industry Research Special Funds for Public Welfare Projects: Research and Demonstration of Fast-growing Wood Modification and Application (201204702-B2) and Beijing Natural Science Foundation (Effects and Crosslinking Mechanism of Amino-Methyl-Urea on wood modified) (2112032).

REFERENCES CITED

Banik, I., and Sain, M. M. (2010). “Nanoclay modified water-blown polyurethane foams derived from bifunctional soybean oil-based polyol,” *Polym-Plast. Technol.* 49, 701-706.

Blagojevic, S. L., Buhin, Z., Pustak, A., and Kovaic, R. L. (2012). "Influence of nanosilica on the morphology, thermal and mechanical properties of polyurethane elastomer," *J. Appl. Polym. Sci.* 125, 181-190.

Chen, Y., Fan, H. J., Liu, R. W., and Yuan, J. X. (2010). "Nano-SiO_2 in-situ hybrid polyurethane leather coating with enhanced breathability," *Fiber. Polym.* 11, 241-248.

Chen, Y., Zhang, X. L., Fan, H. J., and Shi, B. J. (2009). "Nano-TiO_2 in-situ hybrid polyurethane with enhanced permeability for PU leather manufacture," *Am. Leather Chem. As.* 104, 210-217.

Dhoke, S. K., Sinha, T. J. M., and Khanna, A. S. (2009). "Effect of nano-Al_2O_3 particles on the corrosion behavior of alkyd based waterborne coatings," *J. Coat. Technol. Res.* 6, 353-368.

Gao, X. Y., Zhu, Y. C., Zhao, X., Wang, Z. C., An, D. M., Ma, Y. J., Guan, S. A., Du, Y. Y., and Zhou, B. (2011). "Synthesis and characterization of polyurethane/SiO_2 nanocomposites," *Appl. Surf. Sci.* 257, 4719-4724.

Hubbe, M. A., Rojas, O. J., Lucia, L. A., and Sain, M. (2008). "Cellulosic nanocomposites: A review," *BioResources* 3, 929-980.

Jang, M. K., Lee, S. K., and Kim, B. K. (2008). "Polyurethane nano-composite with functionalized silica particle," *Compos. Interface.* 15, 549-559.

Kotnarowska, D., Przerwa, M., and Wojtyniak, M. (2011). "Effect of epoxy and polyurethane coating modification with nanofillers on their resistance to erosive wear," *J. Vibroeng.* 13, 870-875.

Kuan, H. C., Ma, C. C. M., Chang, W. P., Yuen, S. M., Wu, H. H., and Lee, T. M. (2005). "Synthesis, thermal, mechanical and rheological properties of multiwall carbon nano tube/waterborne polyurethane nanocomposite," *Compos. Sci. Technol.* 65, 1703-1710.

Liu, X. H., Zhao, Y., Liu, Z., Wang, D. J., Wu, J. G., and Xu, D. F. (2008). "Preparation and characterization of modified nanocarbon black/polyurethane composites," *Chem. J. Chinese U.* 29, 2096-2100.

Luo, X. G., Liu, S. L., Zhou, J. P., and Zhang, L. N. (2009). "In situ synthesis of Fe_3O_4/cellulose microspheres with magnetic-induced protein delivery," *J. Mater. Chem.* 19, 3538-3545.

Morimoto, N., Watanabe, A., Iwasaki, Y., Akiyoshi, K., and Ishihara, K. (2004). "Nano-scale surface modification of a segmented polyurethane with a phospholipids polymer," *Biomaterials* 25, 5353-5361.

Nikje, M. M. A., and Tehrani, Z. M. (2010). "Novel modified nanosilica-based on synthesized dipodal silane and its effects on the physical properties of rigid polyurethane foams," *Des. Monomers Polym.* 13, 249-260.

Pielichowska, K., and Blazewicz, S. (2010). "Bioactive polymer/hydroxyapatite (nano) composites for bone tissue regeneration," *Adv. Polym. Sci.* 232, 97-207.

Rostami, M., Ranjbar, Z., and Mohseni, M. (2010). "Investigating the interfacial interaction of different aminosilane treated nano silicas with a polyurethane coating," *Appl. Surf. Sci.* 257, 899-904.

Sabzi, M., Mirabedini, S. M., Zohuriaan-Mehr, J., and Atai, M. (2009). "Surface modification of TiO_2 nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating," *Prog. Org. Coat.* 65, 222-228.

Sun, D. X., Miao, X., Zhang, K. J., Kim, H., and Yuan, Y. G. (2011). "Triazole-forming waterborne polyurethane composites fabricated with silane coupling agent functionalized nano-silica," *J. Colloid Interf. Sci.* 361, 483-490.

Sun, Z. Y., Liu, Z. M., Han, B. X., Wang, Y., Du, J. M., and Xie, Z. L. (2005). "Fabrication of ruthenium-carbon nanotube nanocomposites in supercritical water," *Adv. Mater.* 17, 928-932.

Turunc, O., Kayaman-apohan, N., Kahraman, M. V., Menceloglu, Y., and Gungor, A. (2008). "Nonisocyanate based polyurethane/silica nanocomposites and their coating performance," *J. Sol-gel Sci. Techn.* 47, 290-299.

Wang, Y. X., Tian, H. F., and Zhang, L. N. (2010). "Role of starch nanocrystals and cellulose whiskers in synergistic reinforcement of waterborne polyurethane," *Carbohyd. Polym.* 80, 665-671.

Zeng, H., Li, J., Liu, J. P., Wang, Z. L., and Sun, S. H. (2002). "Exchange-coupled nanocomposite magnets by nanoparticle self-assembly," *Nature* 420, 395-398.

Article submitted: June 16, 2012; Peer review completed: August 2, 2012; Revised version received: August 27, 2012; Accepted: September 3, 2012; Published: September 6, 2012.