Effect of Functionalized SiO₂ Nanoparticles on the Performance of Polyurethane Coatings†

MINGHUA LI^{1,*}, ZIQUANG ZOU², DIFANG ZHAO¹, CHANGAN TIAN¹, KANG ZHOU¹ and YUNRAN ZHANG¹

¹Department of Chemistry and Materials Engineering, Hefei University, Hefei 230601, P.R. China

²Department of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China

*Corresponding author: Tel: +86 551 62158393; E-mail: minghualiahu@hfu.edu.cn

Published online: 10 March 2014;

AJC-14901

In this paper, based on the pristine polyurethane coatings, four groups of coatings composite which had different mass ratio of functionalized SiO₂ nanoparticles suspending liquid were tested. The result was that polyurethane coatings composite modified with (1.2 wt %) functionalized SiO₂ nanoparticles suspending liquid could significantly increase their resistance to chemical corrosion. More interestingly, it has little influence on the transparency of polyurethane coatings film and thermal stability.

Keywords: Polyurethane coatings, Functionalized SiO₂, Chemical corrosion.

INTRODUCTION

Polymer nanocomposites are a progressively large category of hybrid composites^{1,2}. Since the introduction of SiO₂ nanoparticles, their nanocomposites have attracted a major interest from both scientific and technological viewpoints. It is well-known that SiO₂ nanoparticles have unusual structural, mechanical and optical properties, which provide great potential in a wide range of applications as reinforcing fillers in nanocomposites³⁻⁶.

One of the major challenges is actually to easily and individually disperse these SiO₂ nanoparticles in polymer matrix to obtain materials with improved properties for different applications. Thus, many research groups have focused on the functionalization of SiO₂ nanoparticles with various inorganic and organic structures using covalent approaches to improve the compatibility with polymer matrix⁷⁻⁹. When SiO₂ nanoparticles are applied in preparing nanocomposites such as polymer nanocomposites, they must be available in large volumes at low cost and dispersible in polymer matrix, also the strong interactions between SiO₂ nanoparticles and the surrounding matrix should be formed.

In this study, we have prepared functionalized SiO₂ nanoparticles *via* a novel crosslinking reaction to study its dispersion stability and effect for polyurethane coatings. The whole research process is divided into two parts containing the preparation of polyurethane coatings nanocomposites and

effect of functionalized SiO₂ nanoparticles on the performance of polyurethane coatings. The first part, in accordance with established programme and steps (**Scheme-I**), we have prepared industrial polyurethane coatings nanocomposites with different concentration of SiO₂ nanoparticles suspending liquid. The second part is to study its effect for polyurethane coatings and develop a simple preparation procedure for preparing polymer nanocomposites.

Scheme-I: Preparation route of polyurethane coatings nanocomposites

EXPERIMENTAL

Functionalized SiO₂ nanoparticles suspending liquid was prepared in our Lab. All solvents employed and pristine polyurethane coatings were commercially available and used without further purification.

Preparation of industrial polyurethane coatings nanocomposites: Scheme-I shows the progress of industrial polyurethane coatings nanocomposites. Table-1 shows the

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

TABLE-1
PRESCRIPTION OF INDUSTRIAL POLYURETHANE COATINGS NANOCOMPOSITES WITH
DIFFERENT CONCENTRATION OF SiO₂ NANOPARTICLES SUSPENDING LIQUID

Sample (%)	Main coatings	Curing agent	Diluent	Functionalized SiO ₂ nanoparticles suspending liquid
0.0	20	10	12	0.000
0.3	20	10	12	0.126
0.6	20	10	12	0.252
0.9	20	10	12	0.378
1.2	20	10	12	0.504

formulation of industrial polyurethane coatings nanocomposites with different concentration of SiO₂ nanoparticles suspending liquid.

RESULTS AND DISCUSSION

Thermogravimetric analysis: In Fig.1(1a), the thermal decomposition temperature range of original SiO₂ nanoparticles is 60–450 °C. Surface functionalized SiO₂ nanoparticles was washed by butyl acetate and dried. When compared decomposition curves of functionalized SiO₂ nanoparticles (Fig. 1c) with original nanoparticles, it is easy to find that there is a little decomposition when temperature is below 200 °C due to small molecule. From 300 to 600 °C, SiO₂ nanoparticles decompose quickly, mainly because of the decomposition of grafted polymer. Therefore, the comprehensive comparison between original SiO₂ nanoparticles and functionalized SiO₂ nanoparticles in heat stability approves that we succeeded in grafting polyurethane onto the surface of SiO₂ nanoparticles.

Fig. 1. Comprehensive comparison between original SiO₂ nanoparticles and functionalized SiO₂ nanoparticles (a and c. TGA curves, b and d. DTG differential curve); (4) the thermal decomposition of polyurethane coatings nanocomposites with different concentration of SiO₂ nanoparticles (a1) 0 % (a2) 0.3 % (a3) 0.6 % (a4) 0.9 % (a5) 1.2 %

As shown in Fig. 1(2), there are TG curves of polyurethane coatings nanocomposites with different content of functionalized SiO₂ nanoparticles suspending liquid in thermal decomposition performance. As can be seen from the Fig. 1, the decomposition temperature of original polyurethane coatings and polyurethane coatings nanocomposites ranges from 290 to 500 °C. After adding nanoparticles, the impact on the thermal decomposition of the coatings become less and the weight loss is around 80 %, possibly due to smaller proportion of nanoparticles (0.3–1.2 %).

Analysis of corrosion resistance: Anticorrosion coatings not only has common properties of the regular coatings, but also has good stability against aggressive media, good permeability, excellent electrical insulation¹⁰. Results shown in Fig. 2, original polyurethane coatings film picture (a₀), that is, don't add functional additives and are not receiving strong alkali corrosion. a₁ is the sample that didn't add functional additives and received an alkali corrosion. It can be seen from the figure that polyurethane coatings surface presents flower-shaped morphology and has suffered serious corrosion. It can be seen from the comparison between Fig. a₂₋₅, a₃ and a₄ present small flower-shaped morphology showing suffered minor corrosion. In addition, a₅ (1.2 wt %) presents little flower-shape, showing a high level of corrosion resistance.

Fig. 2. Anticorrosion photos of the original polyurethane coatings film (a₀) and polyurethane coatings film doped with functionalized SiO₂ nanoparticles (a₁: 0.0 %, a₂: 0.3 %, a₃: 0.6 %, a₄: 0.9 %, a₅: 1.2 %)

Conclusion

In summary, this work studies on thermal stability of polyurethane chains functionalized SiO₂ nanoparticles suspending liquid and the anticorrosion effect in the industrial polyurethane coatings. Processed SiO₂ nanoparticles dispersed in butyl acetate clearly prevent the reunion of nanoparticles and have less impact on the transparency on polymer films. In addition, TGA and alkali resistance test show that when industrial polyurethane coatings nanocomposites compared with the original product can significantly increase their resistance to chemical corrosion and has less impact on its thermal stability.

ACKNOWLEDGEMENTS

The authors thank the "Talents Programme" from Hefei University (No. 13RC07), Natural Science Research Project of Anhui Provincial Education Department (No. KJ2013B228), National Science Foundation of China (No. 51102073), Research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201361) and the College Students' Innovation and Entrepreneurship Training

Program of China (No. 201311059022, 201311059024, 201311059017, 201311059018).

REFERENCES

1. Y.Y. Huang, S.V. Ahir and E.M. Terentjev, *Phys. Rev. B*, **73**, 125422 (2006).
2. D.W. Schaefer and R.S. Justice, *Macromolecules*, **40**, 8501 (2007).
3. H. Zou, S. Wu and J. Shen, *Chem. Rev.*, **108**, 3893 (2008).
4. R.Y. Hong, H.P. Fu, Y.J. Zhang, L. Liu, J. Wang, H.Z. Li and Y. Zheng, *J. Appl. Polym. Sci.*, **105**, 2176 (2007).
5. J. Suffner, G. Schechner, H. Sieger and H. Hahn, *Chem. Vap. Depos.*, **13**, 459 (2007).
6. R.P. Bagwe, L.R. Hilliard and W.H. Tan, *Langmuir*, **22**, 4357 (2006).
7. D. Knopp, D. Tang and R. Niessner, *Anal. Chim. Acta*, **647**, 14 (2009).
8. S.R. Corrie, G.A. Lawrie and M. Trau, *Langmuir*, **22**, 2731 (2006).
9. V.A. Bakaev and C.G. Pantano, *J. Phys. Chem. C*, **113**, 13894 (2009).
10. M. Tamboura, A.M. Mikhailova and M.Q. Jia, *J. Coat. Technol. Res.*, **10**, 381 (2013).