Surface Modification of Nano-Al_2O_3 with Titanate Coupling Agent TC-114

Minhong Xu
Department of Materials Chemistry
Huzhou University
Huzhou, China
e-mail: xumh123@163.com

Yunfeng Wu
Department of Materials Chemistry
Huzhou University
Huzhou, China
e-mail: 1772256889@qq.com

Jvxiang Wang
Department of Materials Chemistry
Huzhou University
Huzhou, China
e-mail: 1004309354@qq.com

Ye Yang
Department of Materials Chemistry
Huzhou University
Huzhou, China
e-mail: 116306178@qq.com

Abstract—In order to improve the dispersive and lipophilic properties of Nano-Al_2O_3 in composite coatings, surface modification of Nano-Al_2O_3 by titanate coupling agent TC-114 was researched. The modification effect on Nano-Al_2O_3 was measured with the activation index and the lipophilic degree. The influences of modification dosage, time and temperature were also discussed. The results showed that Nano-Al_2O_3 was successfully modified with TC-114 which analyzed by FT-IR, and its hydrophobicity increased. The optimal conditions of modification were as follows: the TC-114 was 2 wt%, based on the quality of Nano-Al_2O_3, modification time was 50 min and temperature was 60 °C. The activation index of modified Nano-Al_2O_3 was 94 % and the lipophilic degree was 35 % under the best modified conditions. The hydrophily and lipophilicity experiments indicated that modified Nano-Al_2O_3 possessed well lipophilicity and could dissolve in xylene.

Keywords-Nano-Al_2O_3; titanate coupling agent TC-114; surface modification; activation index; lipophilic degree

I. INTRODUCTION

The Nano-Al_2O_3 powder as a special enhanced and filling material, not only can reduce the cost of the composite, but also can improve and adjust the properties of the materials. When the Nano-Al_2O_3 powder, which is a polar molecule and has high hydrophilic property, was filled in polymer, the compatibility is poor, the strength of interfacial bonding is low, and the performance of the composite is influenced [1]. There are some researches and explorations on modification of Nano-Al_2O_3.The modifier just as inorganic salt [2, 3], alkylphosphonic acids and diethyl butylphosphonate [4], polyfunctional organic reagents [5, 6], silane coupling agent [7], acrylic acid [8], fatty acid [9]. But there is few report on Nano-Al_2O_3 modified with TC-114, even the modification is not satisfactory.

In this paper, in order to improve dispersive and hydrophobic performances of Nano-Al_2O_3 in composite coating, surface modification of Nano-Al_2O_3 with titanate coupling agent TC-114 was studied at the condition of isopropyl alcohol as a dispersion medium. The activation index and the lipophilic degree were measured to evaluate the modified effect; even FT-IR was carried out to study the surface modification of Nano-Al_2O_3. The influences of modification dosage, modification time and modification temperature were also discussed.

II. EXPERIMENTAL

A. Modification of Nano-Al_2O_3

Nano-Al_2O_3 (15 nm), which was purchased from Hangzhou Wanjing New Material Co., Ltd., was modified by wet chemical method. Dry Nano-Al_2O_3 powder (120 °C, 12 h), a certain quality of TC-114, and a certain volume of isopropanol were added to a three-necked flask to stirring for a certain time at the different conditions. After a certain period of reaction time, centrifuged and got the precipitate, and then drying for 6 h at 120 °C.

B. Determination of the Activation Index

A certain amount of modified Nano-Al_2O_3 powder was added in 100 mL distilled water, and stirred for 1 h, then standing. Afterwards, the materials that deposited in the bottom of the beaker were separated, dried and weighed. The mass of the floating part of modified Nano-Al_2O_3 was obtained through the original quality minus the subsidence. The activation index was got by calculating with the equation as follow:

$$R = (W_1 - W_2)/W_1 \times 100\% \quad (1)$$

where R is the activation index, W_1 is the original quality, W_2 is the mass of subsidence, and (W_1-W_2) means the mass of the floating part. The higher the activation index, the better the modification effect is.

C. Determination of the Lipophilic Degree

The modified Nano-Al_2O_3 was placed in 50 mL water, the powder was titrated to complete wetting with the methanol and got the volume of methanol. The lipophilic degree was calculated with the formula (2) [10], where a is

the volume of methanol. The higher the lipophilic degree, the better the modification effect is.

$$\text{The lipophilic degree} = a/(50+a)\times 100\% \quad (2)$$

D. *The Measurement of Hydrophily or Lipophilicity*

Nano-Al_2O_3 or modified Nano-Al_2O_3 1 g was added to sample tube, and added water as a solvent, then stirring for 1 min. After that, observing and comparing the precipitation and describing phenomenon in solvent. The lipophilic test method was similar to the hydrophilic test, while the solvent was replaced with xylene.

III. RESULTS AND DISCUSSION

A. *IR Analysis of Modified Nano-Al_2O_3*

The structure of Nano-Al_2O_3 particles was characterized with a Nicolet 5700 FT-IR instrument. IR spectras of unmodified Nano-Al_2O_3 particles and those modified with titanate coupling agent TC-114 were presented in Fig. 1.

There were absorption peaks at 2500 cm^{-1} and 3000 cm^{-1} in the IR spectra as curve a shows, which were ascribed to the vibrations of -OH groups in the TC-114. In addition, Nano-Al_2O_3 had no C-H structure so there was no obvious stretching vibration absorption peaks between 2500 and 3000 cm^{-1} just as curve c shows. However, in curve b, there was C-H stretching vibration absorption peaks between 2500 and 3000 cm^{-1} after Nano-Al_2O_3 was modified with TC-114. These results indicated that TC-114 had been incorporated on the surface of Nano-Al_2O_3.

B. *Effect of Modifier Dosage*

The dosage of coupling agent is one of important elements which can influence the modified effect. The influences of modifier TC-114 dosage on surface modification of Nano-Al_2O_3 were investigated at modified temperature 30 °C and modified time 50 min. The TC-114 were 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%, 2.5 wt%, and 3.0 wt%, respectively, based on the quality of Al_2O_3, the results shown in Fig. 2.

From the Fig. 2, when the dosage was 0 wt%, the activation index was 0 %. When the dosage was 1.0 wt%, the activation index was 63 %. The activation index of Nano-Al_2O_3 increases obviously with the increasing of TC-114 dosage, especially the TC-114 dosage reached 2.0 wt%, the activation index could reach its highest value 90 % and the modified effect was best. However, added the TC-114 dosage to 3.0 wt%, the activation index decreased to 60 %. The results from the lipophilic degree were similar to the results from the activation index. When the dosage of modifier was 2.0 wt%, based on the quality of Al_2O_3, the lipophilic degree could reach its highest value 50 %.

This may be due to the number of superficial hydroxyl on Nano-Al_2O_3 was limited, too high modifier density in the solution would impact the adsorption and reaction between modifier and Nano-Al_2O_3 surface. Moreover, the long chain structure of TC-114 would block the reaction between TC-114 and Al_2O_3. Thus activation index decreased. So the optimal dosage of modifier TC-114 was 2.0 wt%, based on the quality of Al_2O_3.

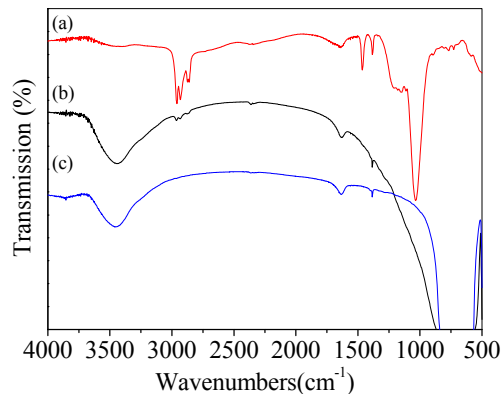

Figure 1. IR spectras of TC-114(a), modified Nano-Al_2O_3 (b) and Nano-Al_2O_3 (c)

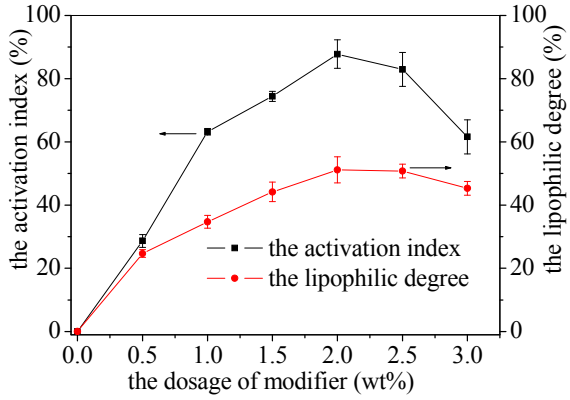

Figure 2. Effect of modifier dosage

C. *Effect of Modified Time*

The effects of modified time were researched at modified temperature was 30 °C and modifier dosage TC-114 was 2.0 wt%, the results shown in Fig. 3.

When the reaction time reached 10 min, the activation index of Nano-Al_2O_3 was 20 % and lipophilic index was 30 %. When reaction time increased to 30 min, the activation index of Nano-Al_2O_3 was 70 % and lipophilic index was 40 %. When reaction time increased to 50 min, the activation index reached its highest value 80 % and lipophilic index also reached its highest value 45 %. If we continued to extend the reaction time to 70 min, the activation index decreased to 75 % and lipophilic index also decreased to 40 %.

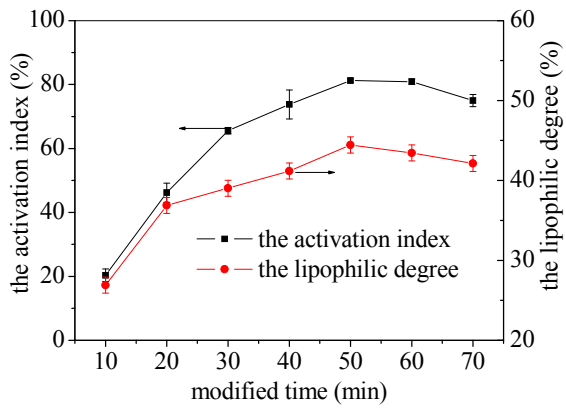

Figure 3. Effect of modified time

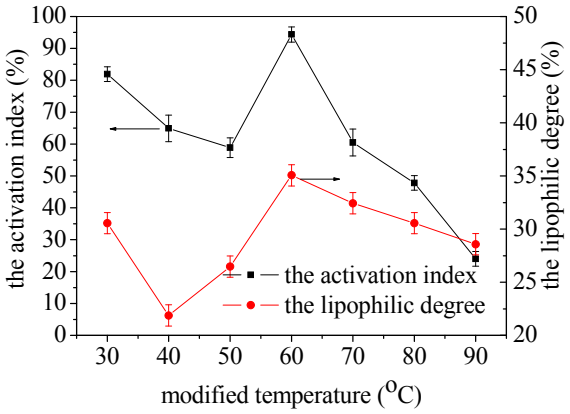

Figure 4. Effect of modified temperature

The possible reason was that the modifier had not reacted adequately with free hydroxy on Nano-Al_2O_3 superficial in short time. When the time increased to 50 min, the modified reaction was adequately. While continuing to extend the reaction time, the mechanical agitation could destruct the combination between TC-114 and Nano-Al_2O_3. From that the optimal reaction time for this experiment was 50 min.

D. *Influence of Modified Temperature*

The effect of modified temperature was researched in the condition of modifier dosage TC-114 was 2.0 wt% and modified time was 50 min, the results shown in Fig. 4. The modified temperature had important influence on Nano-Al_2O_3 seen in Fig. 4. When the temperature was 30 °C, the activation index was 80 % and the lipophilic index was 30 %. While the temperature reached 40 °C, the activation index was 65 % and lipophilic index was 20 %. The activation index of Nano-Al_2O_3 reached its highest value 90 % and lipophilic index also reached its highest value 35 % as temperature reached to 60 °C. The activation index decreased to 25 % and lipophilic index also decreased to 30 % while the temperature rose to 90 °C.

The plausible explanation was that the reaction between modifier and free hydroxy on the surface of Nano-Al_2O_3 was not adequately at low temperature, even the absorption was mainly physical absorption. When the temperature extended 60 °C, the movement of modifier and Nano-Al_2O_3 was so intensely that the reaction between of them decreased. This indicated that the activation index and lipophilic index of modified Nano-Al_2O_3 reached its highest value at 60 °C.

E. *The Measurement of Hydrophily or Lipophilicity*

In order to contrast the hydrophily of Nano-Al_2O_3 before and after modification, the measurement experiments of hydrophily and lipophilicity were carried. Nano-Al_2O_3 before and after modified was added into water respectively, and the hydrophily performances were observed, the result shown as Fig. 5. The experiment results indicated that Nano-Al_2O_3 could dissolve in water well and it also illustrated that Nano-Al_2O_3 had good hydrophilic performance. However, modified Nano-Al_2O_3 was suspended on water, and it meant that modified Nano-Al_2O_3 did not have hydrophily any more, so superficial property of Nano-Al_2O_3 had changed from hydrophily to hydrophobicity.

Figure 5. Nano-Al_2O_3 (A) and modified Nano-Al_2O_3 (B) in water

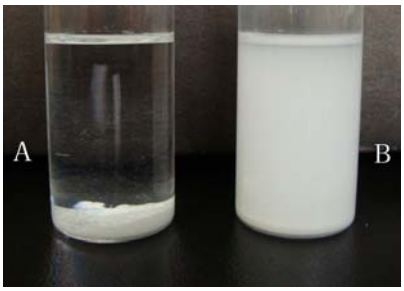

Figure 6. Nano-Al_2O_3 (A) and modified Nano-Al_2O_3 (B) in xylene

Xylene as a good non-polar inorganic solvent can dissolve most organic substance and a part of inorganic substance which have strong lipophilicity property. Nano-Al_2O_3 and modified Nano-Al_2O_3 were dissolved into xylene respectively, the result shown as Fig. 6. Comparison of picture A and B, Nano-Al_2O_3 did not dissolve in xylene and it just precipitated in the solvent, while modified Nano-Al_2O_3 dispersed in the xylene. Modified Nano-Al_2O_3 had TC-114, while TC-114 possessed lipophilicity which also let the property of Nano-Al_2O_3 changed to lipophilicity.

IV. Conclusions

Surface modification of Nano-Al_2O_3 by titanate coupling agent TC-114 was researched. The modified effect of Nano-Al_2O_3 was evaluated with the activation index and the lipophilic degree. The influences of modification dosage, time and temperature were also discussed. The result of activation index and lipophilic index measurement indicated that the best dosage of TC-114 was 2.0 wt% based on the quality of Al_2O_3. The best modified time was 50min and the best temperature was 60 °C. The hydrophily and lipophilicity experiments indicated that modified Nano-Al_2O_3 possessed well lipophilicity and could dissolve in xylene.

Acknowledgment

Authors wish to thank for the financial support of scientic research project of Huzhou University (2015XJKY30).

References

[1] S. A. Trifonov, A. A. Malygin, A. K. D'yakova, J. M. Lopez-Cuesta and N. Cinausero, "Thermal stability of polymer compositions with modified alumina," Russian Journal of General Chemistry, vol. 78, Dec. 2008, pp. 2214-2219, doi: 10.1134/S107036320811042X.

[2] A. Braithwaite and M. Cooper, "A study of the surface modification of alumina for GC," Chromatographia, vol. 42, Jan. 1996, pp. 77-82, doi: 10.1007/BF02271059.

[3] E. Yu. Yakovleva, "Effect of chemical modification on the adsorption and chromatographic properties of aluminas," Journal of Analytical Chemistry, vol. 67, Sep. 2012, pp. 754-760, doi: 10.1134/S1061934812090109.

[4] P. G. Mingalyov, M. V. Buchnev and G. V. Lisichkin, "Chemical modification of alumina and silica with alkylphosphonic acids and their esters," Russian Chemical Bulletin, vol. 50, Sep. 2001, pp. 1693-1695, doi: 10.1023/A:1013067409225.

[5] T. I. Tikhomirova, S. S. Kubyshev and A. V. Ivanov, "Modification of the alumina surface with polyfunctional organic reagents," Russian Journal of Physical Chemistry A, vol. 87, Aug. 2013, pp. 1357-1361, doi: 10.1134/S0036024413070327.

[6] B. Wang, W. Liu, Y. Zhu, J. Yu and Z. Guo, "A general procedure for surface modification of nano-alumina and its application to dendrimers," Journal of Wuhan University of Technology-Mater. Sci. Ed., vol. 22(3), Sep. 2007, pp. 453-456, doi: 10.1007/s11595-006-3453-z.

[7] L. Fernández, G. Arranz, L. Palacio, C. Soria, M. Sánchez, G. Pérez, A. E. Lozano, A. Hernández and P. Prádanos, "Functionalization of γ-alumina cores by polyvinylpirrolidone: properties of the resulting biocompatible nanoparticles in aqueous suspension," Journal of Nanoparticle Research, vol. 11, Feb. 2009, pp. 341-35, doi: 10.1007/s11051-008-9409-9.

[8] W. Li, S. Zheng, Q. Chen and B. Cao, "A new method for surface modification of TiO_2/Al_2O_3 nanocomposites with enhanced anti-friction properties", Materials Chemistry and Physics, vol. 134, May. 2012, pp. 38-42, doi: 10.1016/j.matchemphys.2012.02.009.

[9] Y. Wang, W. Li, L. Zhang, H. Gao, Y. Liu and P. Li, "A new method for surface modification of nano-$CaCO_3$ and nano-Al_2O_3 at room temperature," Advanced Powder Technology, vol. 21, Mar. 2010, pp. 203-205, doi: 10.1016/j.apt.2009.12.006.

[10] R. Y. Hong, T. T. Pan, J. Z. Qian and H. Z. Li, "Synthesis and Surface Modification of ZnO Nanoparticles," Chemical Engineering Journal, vol. 119, 2006, pp. 71-81, doi: 10.1016/j.cej.2006.03.003.