Preparation and Application of an Ultraviolet Curable Coating Containing Nanoscale α-Aluminum Oxide

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Received 9 May 2006; accepted 29 June 2006
DOI 10.1002/app.25146
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study focuses on the preparation of an organic–inorganic ultraviolet (UV) curable coating containing the nanoscale α-aluminum oxide (α-Al_2O_3) powder and UV curable resin. This developed coating can form a protection film on the poly(vinyl chloride) (PVC) plastic tile surface. Thus, the abrasion resistance of the PVC plastic tile surface is improved. Besides, the adhesion between this UV cured film and the PVC plastic tile surface is well. After treatment with the UV curable coating that contains 6 wt % α-Al_2O_3, the abrasion resistance of the PVC plastic tile surface can be improved up to 57%. From the result of a scanning electron microscopy (SEM) mapping photograph, it shows that the nanoscale α-Al_2O_3 powder is well dispersed in the cured coating film. Under the wavelength of the visible light in the range of 400–800 nm, the degree of transparency for the coated film on poly(ethylene terephthalate) (PET) sheet is about 82–90%.
 J Appl Polym Sci 102: 5747–5752, 2006

Key words: α-Al_2O_3; poly(vinyl chloride); UV coating resin; abrasion resistance

INTRODUCTION

Curing by ultraviolet (UV) radiation is an internationally brand-new technique that was developed after 1970s. Coating produced by this technique is called as an UV curable coating. The major composition of the UV curable coating compound is organic oligomer, monomer, and various additives. By different formulations, various functions of UV curable coatings can be prepared. With proper UV radiation treatment, the UV curable coating can be coated to form a film and then hardened on the product surface. UV curing coatings can be used in numerous applications such as printing inks, wood finishing, protective coating for plastic tile, optical fibers and cables, silicone release coatings, adhesives, automotive plastic coating, etc.

Advantages from this technology versus thermal drying technology are significant, such as fast curing times resulting in high productivity, space saving, low energy consumption, and improved properties of the treated surfaces, environmental friendly. In addition, mechanical property of the products is well and this material can be easy to apply on the automatic production line, because the traditional thermal coatings are easily volatile, slowly curable, and not environment friendly. Thus, UV curable coating has begun to substitute the traditional thermal coatings in the coating industry.[1–6]

Poly(vinyl chloride) (PVC) is a widely used thermoplastic polymer. Suspension polymerization is the major route to manufacture PVC resins in the industry. Due to the inherent disadvantages, such as poor thermal stability and brittleness, PVC is generally compounded with various additives. After compounding with various additives, the characteristics of PVC compounds are improved, e.g., light weight, strong strength, chemical resistance, and cheap. Thus, the compounded PVC products are widely applied in the fields of automobile, houses, buildings, and packaging from food to electronic parts.[7–9] One of its important applications is the PVC plastic tile. The tile uses the PVC resin as the main component, and utilizes various additives to reach the different demands. The appearance of PVC plastic tile is diversity. It can be looked like wood, marble, etc. Since the life time of a PVC plastic tile is totally dependent on the abrasion resistance of its surface, how to improve the abrasion resistance is always an important topic for the researchers and producers.

The α-Al_2O_3 is a very commonly metal oxide ceramic. It has good physical properties, for example, abrasion resistance, corrosion resistance, thermal stability at high temperature, electrical insulation, high mechanical strength, etc. Up to today, α-Al_2O_3 ceramic is still very important on the areas of polishing tools, electronic products, composites, and medical materials, etc.[10,11]

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Contract grant sponsor: The Ministry of Economics Affairs, Republic of China.

Journal of Applied Polymer Science, Vol. 102, 5747–5752 (2006)

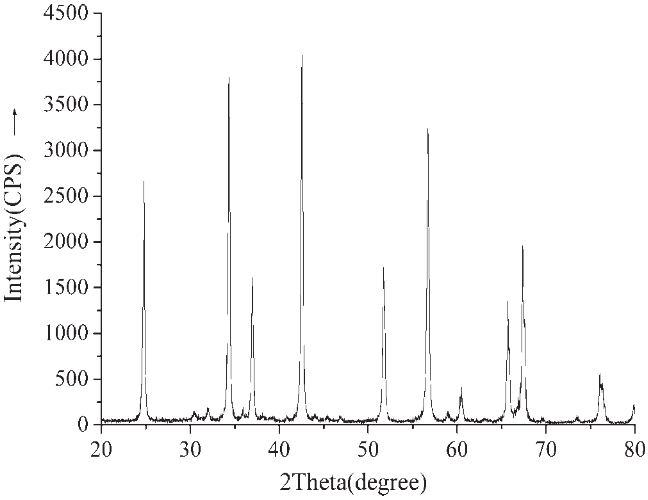

Figure 1 XRD pattern of α-Al_2O_3 powder.

Since its abrasion resistance ability is outstanding, α-Al_2O_3 ceramic is an ideal additive for UV curable coating to improve the abrasion resistance of the PVC plastic tile surface. Meanwhile, to have a good transparency for the UV curable coating film on the PVC plastic tile surface, a nanoscale α-Al_2O_3 is used as an abrasion resistance additive. Since there is very few papers, which study the nanoscale α-Al_2O_3 applied in UV curable coating system, the effect of the UV curable coating film containing various contents of nanoscale α-Al_2O_3 on the abrasion resistance of PVC plastic tile surface is examined and discussed. In addition, the surface morphology and the degree of transparency of the UV curable coating film coated on the PVC plastic tile surface are also examined.

EXPERIMENTAL

Materials

The nanoscale α-Al_2O_3 powder was kindly supplied by the Particulate Materials Research Center at the National Cheng-Kung University, Tainan, Taiwan. The primary crystalline phase of α-Al_2O_3 was ≥99.0 wt %. Its specific surface area was about 200 m^2/g. The UV curable coating (product name: AROCOAT UR-85213) was kindly supplied by the AGI, Taipei, Taiwan. Its viscosity at 25°C and 60 rpm was 2000–2500 cps measured by a Brookfield programmable rheometer (Model: DV-III). Its color was pale gray. The PVC plastic tile was kindly supplied by Win Ton Plastics Industry, Taiwan.

TEM examination

The nanoscale α-Al_2O_3 powder was homogeneously dispersed into alcohol and dropped on a copper grid. The particle size and shape of the nanoscale α-Al_2O_3 powder was examined by a field emission gun transmission electron microscopy (FEG-TEM) (FEI, USA, model Philips Tecnai G2 F20 FEG-TEM). The accelerating voltage was set at 200 kV.

XRD examination

The crystal structure of the nanoscale α-Al_2O_3 powder was examined by an X-ray diffractometer (XRD) (Rigaku, Japan, model Rigaku multiflex ZD3609N). Cu Kα ($\lambda = 0.154$ nm) radiation was adopted at ambient temperature. The scanning rate was set as 2°/min at the range from 20° to 80°.

Preparation and characterization of UV curable coating film

A UV exposure system with a UV lamp of 2.0 kW and a transport speed of 2 m/min (CSUN MFG, Taiwan, model UVC-201A) was used to cure the UV curable coating. The UV curable coatings containing various contents of the nanoscale α-Al_2O_3 powder were prepared by a magnetic stirrer at 600 rpm. The UV curable coating was evenly spread by using a No. 6 coating rod to form a film on the surface of the PVC plastic tile or poly(ethylene terephthalate) (PET) sheet. Furthermore, the UV curable coating on the surface of PVC plastic tile or PET sheet was curable by UV light. The final product was tested for abrasion resistance and degree of transparence. A TABER type abrasion tester (GOTECH, Taiwan, model GT-7012-T) was used. The test method for the abrasion resistance was according to the ASTM D4060. The weight loss (W_1) of the PVC plastic tile coated UV curable coating without nanoscale α-Al_2O_3 powder was measured by a TABER type abrasion tester after 2000 cycles. The weight loss (W_2) of the PVC plastic tile coated UV curable coating

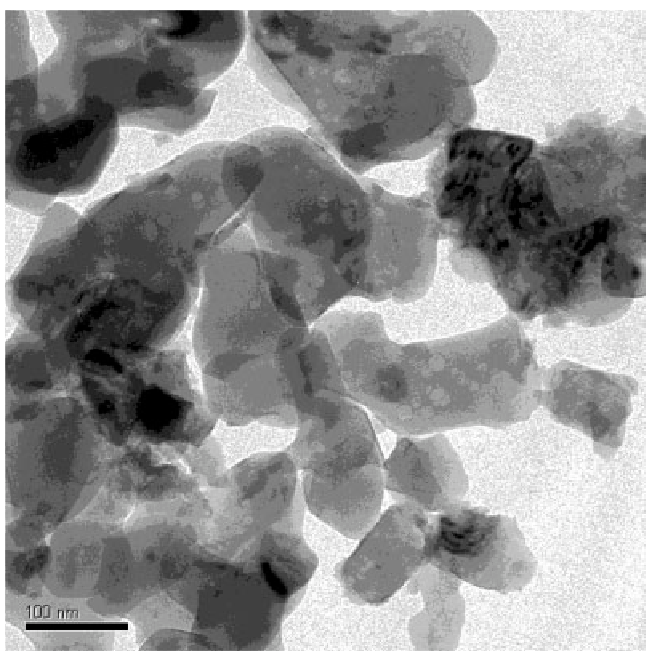

Figure 2 TEM photograph of α-Al_2O_3 powder.

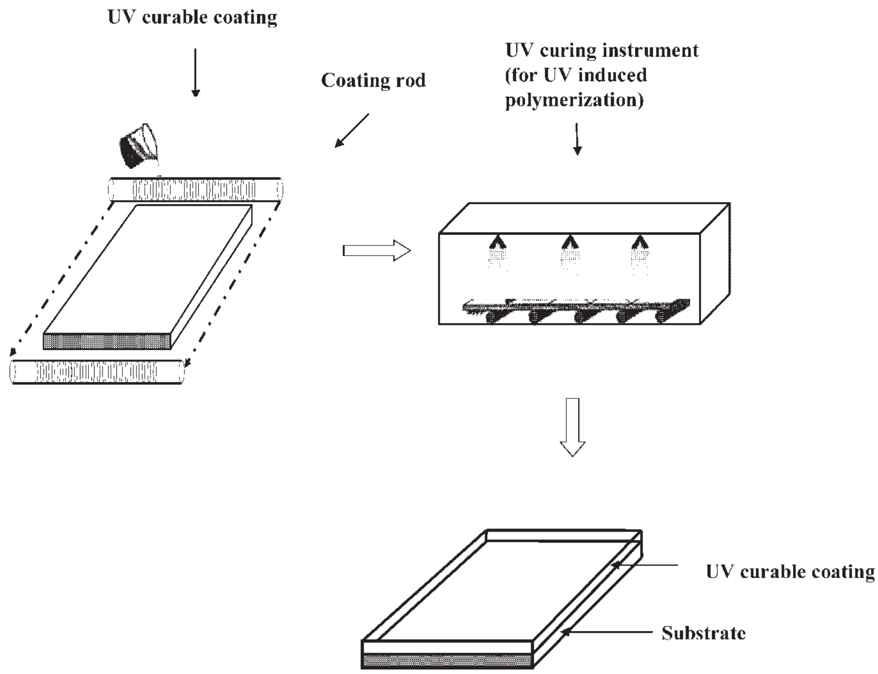

Figure 3 A UV induced polymerization process.

with various amounts of nanoscale α-Al_2O_3 powder was also measured by a TABER type abrasion tester after 2000 cycles. The abrasion resistance was defined as the following equation:

$$\text{Abrasion Resistance (\%)} = [(W_1 - W_2)/(W_1)] \times 100\%.$$

To study the degree of transparence of the UV curable coating with nanoscale α-Al_2O_3 powder, the UV curable coating with 10 wt % nanoscale α-Al_2O_3 powder was coated and curable on the surface of PET sheet. The degree of transparence was examined by an UV–vis spectrophotometer (Shimadzu, Japan, model UV-2401 PC).

SEM examination

The surface morphology of the UV curable coating film on the surface of PVC plastic tile or PET sheet was examined. These samples were coated with the gold palladium film and examined by a field emission scanning electron microscope (FE-SEM). The crosssection samples were prepared by immersing PVC plas-

Figure 4 A photograph of PVC plastic tile coated with the UV curable coating containing 10 wt % nanoscale α-Al_2O_3 powder. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

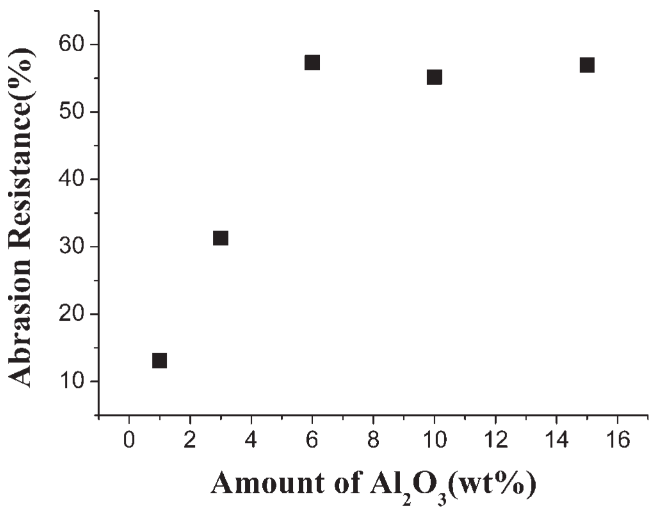

Figure 5 Effect of amount of nanoscale α-Al_2O_3 in the UV curable coating on the abrasion resistance of PVC plastic tile surface. Tested by the ASTM D4060 after 2000 cycles.

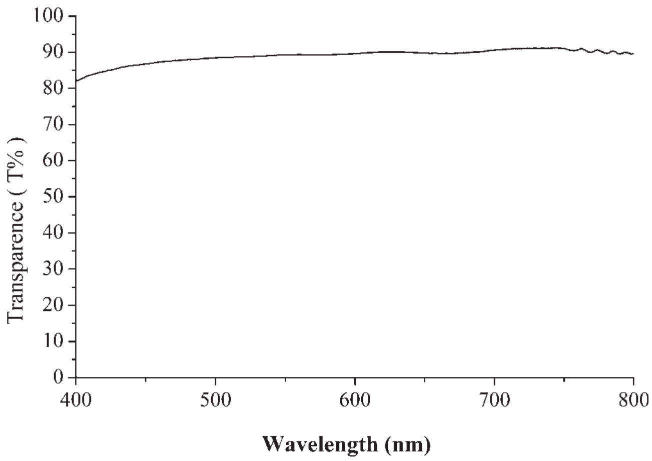

Figure 6 Degree of transparence (UV spectrum analysis) of a PET sheet coated with UV curable coating containing 10 wt % nanoscale α-Al_2O_3.

tic tile or PET sheet, coated by the UV curable coating, into liquid nitrogen for 45 s. Then, samples were fractured and coated with the gold palladium film. A FE-SEM (Jeol, Japan, model JSM 6700F) was used to examine the fractured surfaces. To realize the distribution of nanoscale α-Al_2O_3 particle in the UV curable coating film, a mapping analysis was also examined.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of nanoscale α-Al_2O_3 powder. The diffraction peaks were significantly observed at $2\theta = 25°, 35°, 43°, 57°, 66°, 68°$, and $77°$. These are the characteristic peaks of α-Al_2O_3. Figure 2 shows the TEM photograph of α-Al_2O_3. The particle size is ranged from 50–200 nm. These α-Al_2O_3 particles look like irregular shape.

Figure 3 shows a UV induced polymerization process. The UV curable coating contains reactive monomers, oligomers, photoinitiators, light stabilizers, and nanoscale α-Al_2O_3 powder. When this UV curable coating is coated by a coating rod and cured on the PVC plastic tile surface, a good transparence is shown in Figure 4. The appearance of the PVC plastic tile looks like wood. In addition to, an obvious improvement on the abrasion resistance property is also obtained. In Figure 5, when the amount of nanoscale α-Al_2O_3 powder in the UV curable coating is increased from 1 to 6 wt %, the abrasion resistance of the PVC plastic tile surface can be improved from 13 to 57%. When the amount of nanoscale α-Al_2O_3 powder is increased to 10 or 15 wt %, the abrasion resistance of the PVC plastic tile surface is almost kept as constant.

To investigate the degree of transparence of the UV cured coating film, the UV curable coating containing 10 wt % nanoscale α-Al_2O_3 powder is coated by a coating rod and cured on a PET sheet surface. The UV spectrum analysis, shown in Figure 6, indicates that the degree of transparence of the UV cured coating film containing 10 wt % nanoscale α-Al_2O_3 powder is as high as 82–90% in the wavelength range of 400–800 nm.

Figure 7(a–c) show SEM photographs of the surface of PVC plastic tile coated with UV curable coating film containing 0, 3, and 10 wt % nanoscale α-Al_2O_3, respectively. Figure 7(a) shows that the surface of PVC plastic tile coated with UV curable coating without nanoscale α-Al_2O_3. The surface appears to be smooth. However, there are some α-Al_2O_3 particles observed in Figure 7(b). This is because of the UV curable coating containing 3 wt % α-Al_2O_3 particle.

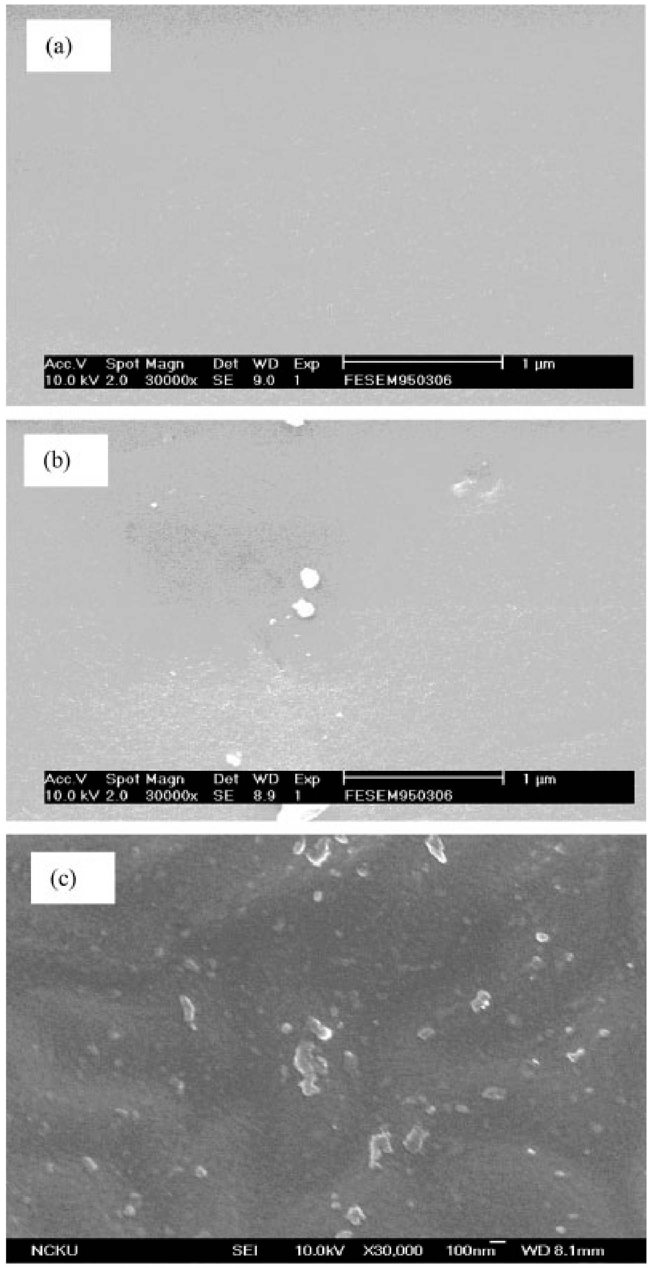

Figure 7 SEM photographs of the surface of PVC plastic tile coated with UV curable coating containing (a) 0 wt %, (b) 3 wt %, and (c) 10 wt % nanoscale α-Al_2O_3 (the particle size for α-Al_2O_3 ranging from 50–200 nm).

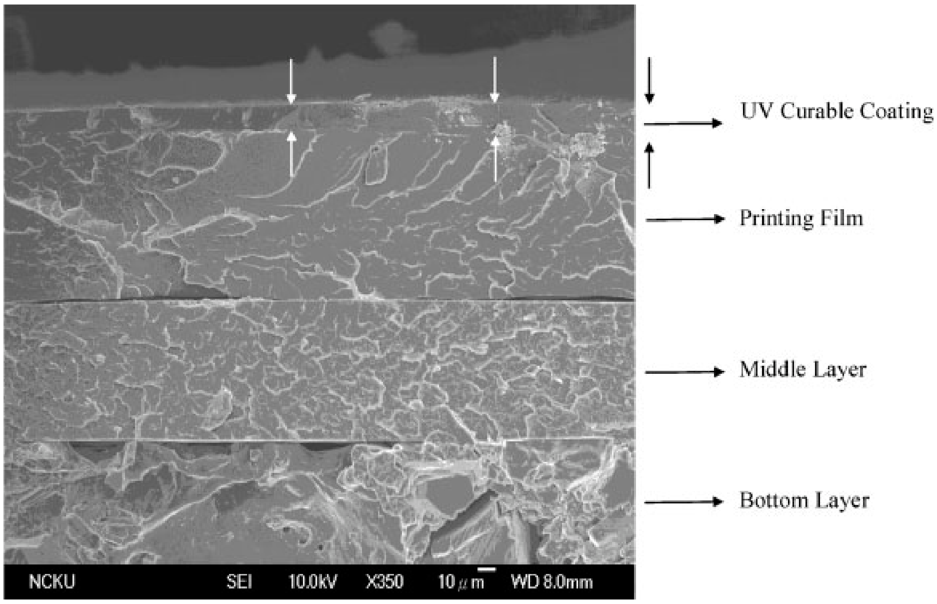

Figure 8 A SEM photograph of the crosssection of PVC plastic tile coated by UV curable coating containing 10 wt % nanoscale α-Al_2O_3.

There are more α-Al_2O_3 particles observed on Figure 7(c) due to the amount of α-Al_2O_3 increased to 10 wt %. These α-Al_2O_3 particles have the ability to increase the abrasion resistance of the surface of PVC plastic tile. From Figures 7(b,c), it can be found that the particle size of α-Al_2O_3 is between 50–200 nm.

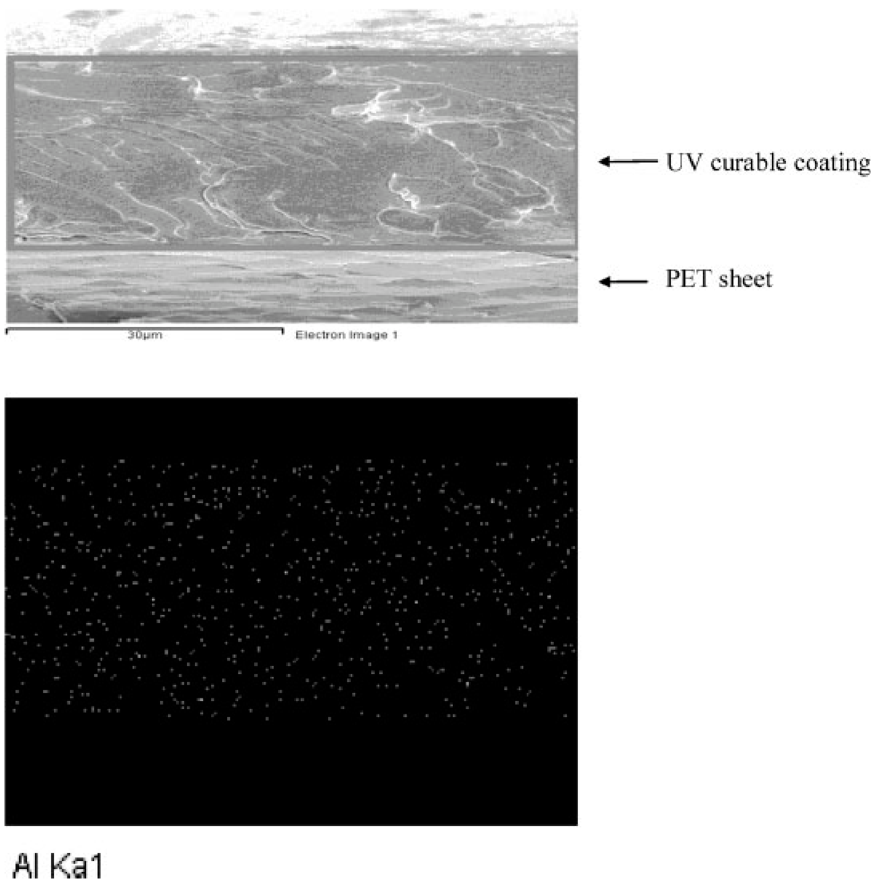

Figure 9 A SEM photograph of the crosssection of a PET sheet coated by UV curable coating containing 10 wt % nanoscale α-Al_2O_3 (top) and a mapping photograph for Al atoms (bottom).

Figure 8 shows a SEM photograph of the crosssection of PVC plastic tile coated by UV curable coating film containing 10 wt % α-Al_2O_3 particle. It can be found that there are four layers in the crosssection of the PVC plastic tile. The first layer is UV cured coating film that can provide proper abrasion resistance for the PVC plastic tile surface. From Figure 8, it can be observed that the thickness of the UV curable coating film is in the range of 15–30 μm. The lifetime of a PVC plastic tile is almost dependent on the abrasion resistance of the UV curable coating film. The second layer is a printing film that can provide various pictures on the PVC plastic tile. The third layer is called as middle layer that can provide suitable printing surface. The forth layer is called as bottom layer that can provide suitable thickness, hardness, and flexibility for the PVC plastic tile.

Figure 9 shows a SEM photograph of the crosssection of a PET sheet coated by UV curable coating containing 10 wt % nanoscale α-Al_2O_3 (top) and a mapping photograph for Al atoms (bottom). The mapping result shows that the α-Al_2O_3 particles were homogeneously dispersed in the UV curable coating film. This can provide an excellent abrasion resistance from top to bottom of the UV curable coating film coated on the PVC plastic tile surface.

CONCLUSIONS

A UV curable coating containing the nanoscale α-aluminum oxide (α-Al_2O_3) powder has been successfully prepared. This developed coating can form an effective abrasion resistance film on the PVC plastic tile surface. The adhesion between the UV cured film and the PVC plastic tile surface is well. The abrasion resistance of the PVC plastic tile surface can be improved up to 57% by the UV cured coating film that contains 6 wt % nanoscale α-Al_2O_3. The SEM mapping photograph shows that the nanoscale α-Al_2O_3 powder is well dispersed in the cured coating film. This result in the degree of transparency for the UV cured coating film is still kept as high as 82–90%.

References

1. Schrof, W.; Beck, E.; Etzrodt, G.; Hintze-Br̈uning, H.; Meisenburg, U.; Schwalm, R.; Warming, J. Prog Org Coat 2001, 43, 1.
2. Asif, A.; Huang, C. Y.; Shi, W. F. Polym Adv Technol 2003, 14, 609.
3. Wouters, M. E. L.; Wolfs, D. P.; van der Linde, M. C.; Hovens, J. H. P.; Tinnemans, A. H. A. Prog Org Coat 2004, 51, 312.
4. Chattopadhyay, D. K.; Panda, S. S.; Raju, K. V. S. N. Prog Org Coat 2005, 54, 10.
5. Cho, J. D.; Kim, H. K.; Kim, Y. S.; Hong, J. W. Polym Test 2003, 22, 633.
6. Kim, H. K.; Kim, J. G.; Hong, J. W. Polym Test 2002, 21, 417.
7. Chen, C. H.; Teng, C. C.; Yang, C. H. J Polym Sci Part B: Polym Phys 2005, 43, 1465.
8. Chen, C. H.; Teng, C. C.; Su, S. F.; Wu, W. C.; Yang, C. H. J Polym Sci Part B: Polym Phys 2006, 44, 451.
9. Chen, C. H.; Li, H. C.; Teng, C. C.; Yang, C. H. J Appl Polym Sci 2006, 99, 2167.
10. Yen, F. S.; Lo, H. S.; Wen, H. L.; Yang, R. J. J Cryst Growth 2003, 249, 283.
11. Yu, P. C.; Yen, F. S.; Lin, T. C. J Cryst Growth 2004, 265, 137.