UV-Curing and Mechanical Properties of Polyester–Acrylate Nanocomposites Films with Silane-Modified Antimony Doped Tin Oxide Nanoparticles

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ABSTRACT: Antimony doped tin oxide (ATO) nanoparticles were used as nanofillers to improve mechanical properties of UV-cured polyester–acrylate films. To improve the dispersion of ATO nanoparticles in the polyester–acrylate resin matrix and to strengthen interfacial interactions between ATO nanoparticles and the resin matrix ATO nanoparticles were first organically modified with 3-methacryloxypropyltrimethoxysilane (MPS). The modification of ATO nanoparticles with MPS was confirmed by FTIR spectroscopy and thermogravimetric analysis (TGA). UV-curing behaviors of the nanocomposites films were investigated by FTIR spectroscopy. Compared with the film with neat ATO nanoparticles, the film with the same amount of MPS-modified ATO nanoparticles showed slightly higher UV-curing rate and final conversion. The mechanical properties of the nanocomposites films were measured by universal testing machine. The MPS-modified ATO nanoparticles could improve considerably the mechanical properties of the UV-cured polyester–acrylate nanocomposites films. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1340–1344, 2013

INTRODUCTION

UV-curing of coatings, films, inks, and adhesives has been used widely because it meets several industrial demands such as high-speed, room temperature operations, environmental compatibility due to no volatile organic compounds emission, and low energy consumption.[1,2] All the components in a UV-curable resin formulation, i.e. oligomers, reactive diluents and photoinitiators, are completely reactive so that, unlike conventional solvent-based formulations, there is a negligible weight loss after curing. However, the insufficient hardness of the UV-cured resin products often results in scratch damages on their surfaces.[3–8] Though the final properties of UV-cured products strongly depend on the chemical conversion of the acrylate double bonds they can be improved or modified by optimizing the resin formulations or adding reinforcing fillers. Therefore, UV-curable polymer nanocomposites, typically composed of a UV-curable acrylate resin formulation and inorganic nanoparticles, have been studied to improve the physical properties of the UV-cured products.[9–13]

Nanoparticles are increasingly used as fillers in polymers to improve properties like abrasion resistance, stiffness, barrier properties, thermal and electrical conductivity, and refractive index.[14,15] They are generally inorganic materials, which differ from the organic polymer matrix in terms of their composition and structure. They occupy certain volume, and interact with the functional groups of polymers to confine possible mobility of polymer chains.[16,17] However, inorganic nanoparticles are not easily dispersed in organic polymer matrices unless an effective dispersing agent is used. Silane coupling agents have been frequently used as effective dispersing agents because they can form stable strong interactions with both inorganic nanoparticles and organic polymers.[18,19]

ATO nanoparticles have been used as fillers to prepare electrically conductive materials with optical transparency, which can be applicable in solar cells, light emitting diodes, and permanent antistatic coatings.[3,4,19–21] To make electrically conductive polymer nanocomposites, ATO nanoparticles were added to polyvinyl acetate–acrylate copolymer coatings,[19] gelatin and acrylate films,[22] PMMA films,[23] and urethane as well as polyester coatings.[24] ATO nanoparticles were also used to improve the thermal properties of polyurethane[25] and poly(vinyl alcohol)[26] nanocomposites. However, it is not easy to find studies elucidating the effects of adding ATO nanoparticles on the UV-curing and mechanical properties of UV-cured coatings or films.

Therefore, in this study, the effects of neat and silane-modified ATO nanoparticles on the mechanical properties as well as UV-
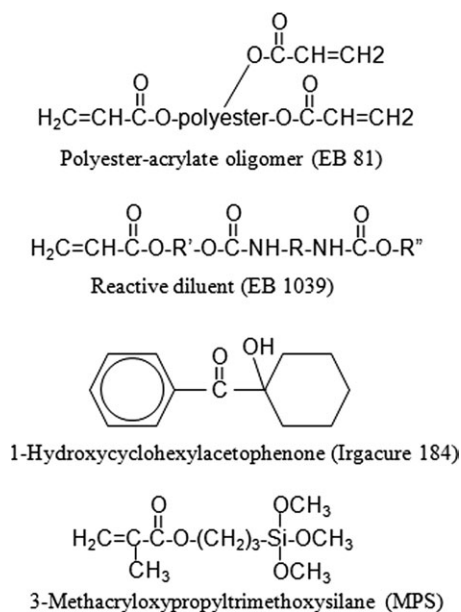
Figure 1. The chemical structures of the materials used in this work.

curing behavior of UV-cured polyester–acrylate films were investigated. 3-Methacryloxypropyltrimethoxysilane (MPS) was used to prepare silane-modified ATO nanoparticles and the silane modification was confirmed by FTIR and TGA.

EXPERIMENTAL

Materials

The UV curable polyester–acrylate oligomer (EB 81 from SK-Cytec, Korea) composed of di- and tri-functional acrylate oligomers was used. The oligomer has an average acrylate group functionality of 2.5, the number average molecular weight of 600 g/mol and the viscosity of 100 cP at room temperature. A low viscous (25 cP at room temperature), low molecular weight (215 g/mol) mono-functional acrylate resin (EB 1039 from SK-Cytec, Korea) was used as a reactive diluent. The concentration of EB 1039 was fixed to 30 phr (parts per hundreds of EB 81 resin) through preliminary coating tests to make films. 1-Hydroxycyclohexylphenylketone (Irgacure 184 from Ciba Specialty Chem.) was used as a photoinitiator. Antimony doped tin oxide (ATO) nanoparticles (Ishihara, Japan) with a mean particle size of 10–30 nm were used as inorganic nanofillers. To organically modify the ATO nanoparticles, 3-methacryloxypropyltrimethoxysilane (MPS from Dow Corning, USA) with one methacrylate functional group, which can react with the oligomers or diluents during UV-curing, was used. The chemical structures of the materials used in this work are shown in Figure 1.

Preparation of MPS-Modified ATO Nanoparticles

To prepare MPS-modified ATO nanoparticles, the methods used to modify ATO nanoparticles by silane molecules were referred to[18,19] 2.5 g of ATO nanoparticles and 25 g of distillated water were poured into a flask and vigorously mixed at room temperature for 72 h at 2000 rpm. Then, 0.5 g of MPS was added and refluxed at 72°C for 24 h at 500 rpm to modify ATO nanoparticles by MPS. The mixture was filtered and washed five times with methanol to remove free MPS molecules that did not

participate in the modification of ATO nanoparticles. The mixture was dried in a vacuum oven at 50°C for 24 h to finally obtain MPS-modified ATO nanoparticles.

Preparation of Polyester–Acrylate/ATO Nanocomposites Films
To see the effects of the silane modification of ATO nanoparticles, the composition of each resin formulation was fixed as follows; the oligomer (100 parts), the diluent (30 phr) and the photoinitiator (2 phr). Neat or MPS-modified ATO nanoparticles (1–3 phr) were poured into a beaker together with the oligomer, the diluent and the photoinitiator, and the mixture was stirred for 2 h at room temperature to obtain a homogeneous mixture. To obtain a nanocomposite film of about 100 μm thick, the homogeneous mixture was coated on a glass plate using a bar coater. And then, UV-curing of the film was performed using a conveyor-type UV-curing instrument (JU-101, JeilUV, Korea) equipped with a high pressure mercury lamp (80 W/cm, length = 15 cm, diameter = 2.54 cm). The high pressure mercury lamp released UV in the wavelength range of 250–450 nm with the maximum intensity at 365 nm. To measure UV intensity and UV dosage irradiated by the UV-curing instruments, an UV intensity tester (UVICURE Plus, EIT) was employed. The UV intensity at the position where UV-curing occurred was changed by changing the distance between the lamp and the film surface. UV dosage was changed up to 4.2 J/cm^2 by changing the conveyor speed. After UV-curing, the film was peeled off from the glass plate and tailored to desired sizes to perform the following measurements.

Characterization

Fourier Transform Infrared Spectroscopy. To investigate the functional groups of the materials and the chemical conversion change of each resin system during UV-curing, Fourier transform infrared spectroscopy (FTIR, Bomem MB100, Bomem, Quebec, Canada) was used. Each IR spectrum was obtained in the wavenumber range of 4000–500 cm^{-1}. To monitor the conversion change during UV-curing, each resin system was coated on a NaCl disk and UV-cured at different UV dosages, then the FTIR spectra of each partially UV-cured resin system were obtained. The conversion change of the acrylate double bonds could be obtained by monitoring the change of the characteristic IR absorption peak for the acrylate double bonds at 810 cm^{-1}.

Thermogravimetric Analysis. The thermal degradation behavior of the MPS-modified ATO nanoparticles was investigated using a thermogravimetric analyzer (SDT 2960, TA Instruments, New Castle, DE). Each scan was carried out from room temperature to 700°C at a heating rate of 10°C/min under nitrogen gas flow through the sample cell at 110 mL/min.

Mechanical Tests. The tensile properties of the UV-cured nanocomposites films were measured by universal testing machine (LR-30K, LLOYD, Hampshire, UK) according to ASTM D-2370. The average value of at least eight measurements was taken to report reliable tensile properties. Each tensile test was performed with a load cell of 50 N at a crosshead speed of 20 mm/min. The dimensions of tensile specimens were 15 mm × 5 mm × 0.100 mm.

The scratch resistance of the UV-cured nanocomposites films was measured using a pencil hardness tester (Pencil Hardness Tester CT-PC2, Core Tech, Korea). The test was carried out according to
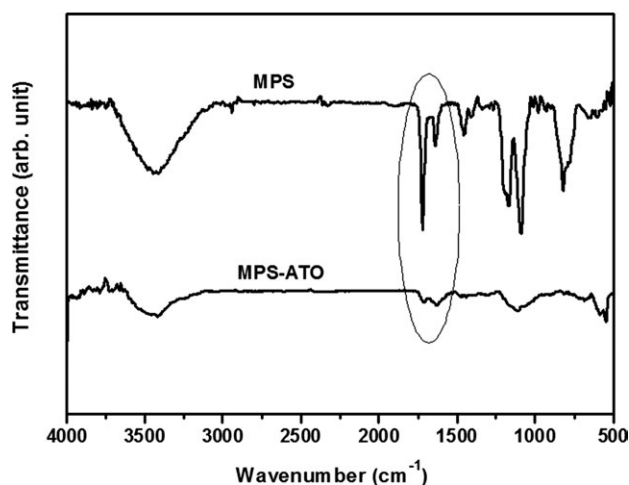
Figure 2. FTIR spectra of MPS and MPS-modified ATO nanoparticles.

KS M ISO 15184. The load at the pencil tip was fixed to 750 ± 10 g and the angle between the pencil and the film surface was maintained 45°. The pencil grades were from 6B (softest) to 9H (hardest).

RESULTS AND DISSCUSION

Characterization of MPS-Modified ATO Nanoparticles

Figure 2 shows the FTIR spectra of MPS and MPS-modified ATO nanoparticles. FTIR spectrum of neat ATO nanoparticles was not included in the figure because it did not show any particular IR absorption peak. The FTIR spectrum of MPS-modified ATO nanoparticles showed two distinct characteristic peaks, one at 1718 cm^{-1} for C=O groups and the other at 1639 cm^{-1} for C=C groups, which are originated from the methacrylate groups in MPS molecules. These IR peaks confirmed that the MPS-modification of the ATO nanoparticles was successful.

The TGA thermograms of neat and MPS-modified ATO nanoparticles and neat MPS are shown in Figure 3. It shows quantitatively how much the organic silane molecules are combined with ATO
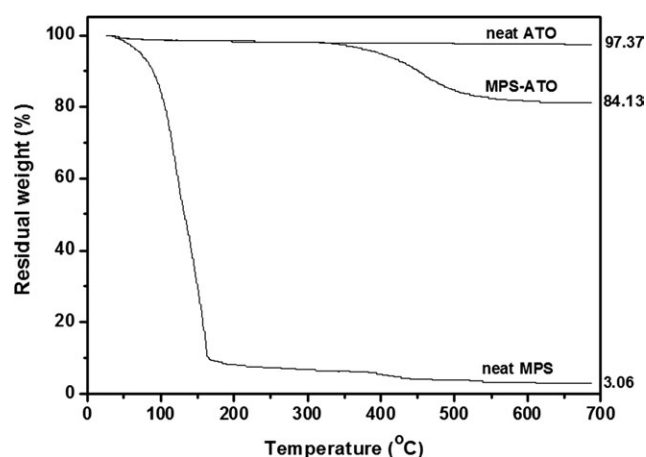
nanoparticles. The weight loss below 100°C can be attributed to the vaporization of moisture present in the ATO nanoparticles. Neat ATO nanoparticles were thermally very stable and exhibited negligible weight loss of 2.63 wt % up to 700°C. However, MPS-modified ATO nanoparticles started to degrade drastically at 320°C and exhibited considerable weight loss of 15.87 wt % up to 700°C. Neat MPS started to evaporate drastically at about 90°C (flash point of MPS is 92°C) and exhibited very little residual weight of 3.06 wt % at 700°C. From these data, it could be estimated that 14.04 wt % of the MPS-modified ATO nanoparticles would be MPS molecules. It was noteworthy that the MPS-modified ATO nanoparticles were thermally very stable up to 320°C. This thermal stability would be due to strong interactions between ATO nanoparticles and MPS molecules.

UV-Curing Behavior of Polyester–Acrylate/ATO Nanocomposites Films

UV-curing behavior of an acrylate resin system can be investigated by FTIR spectroscopy because all the characteristic IR absorption peaks for the acrylate double bonds occurring at 810, 984, 1409, and 1635 cm^{-1} continually decrease with UV-curing.[27–29] The conversion of the acrylate double bonds can be obtained by observing the decay of one of the characteristic absorption peaks. Since the peak at 810 cm^{-1} was free of any disturbance by other vibrators of the oligomer or reactive diluent of the resin system, it was used to analyze the UV-curing behavior of the resin system.[30,31]

As an example, the partial FTIR spectra of the pure (unfilled) polyester–acrylate film are shown in Figure 4. A continual decrease of the peak at 810 cm^{-1} was observed with increasing UV dosage from 0 to 3.15 J/cm^2. Assuming that the chemical reaction proceeds homogeneously in the sample, the conversion, α, as a function of UV dosage, D, can be obtained from the peak change at 810 cm^{-1} using the following equation.

$$\alpha = 1 - \frac{[\text{acrylate}]_D}{[\text{acrylate}]_{D=0}} = 1 - \frac{A_D^{810}/A_D^{870}}{A_{D=0}^{810}/A_{D=0}^{870}}$$
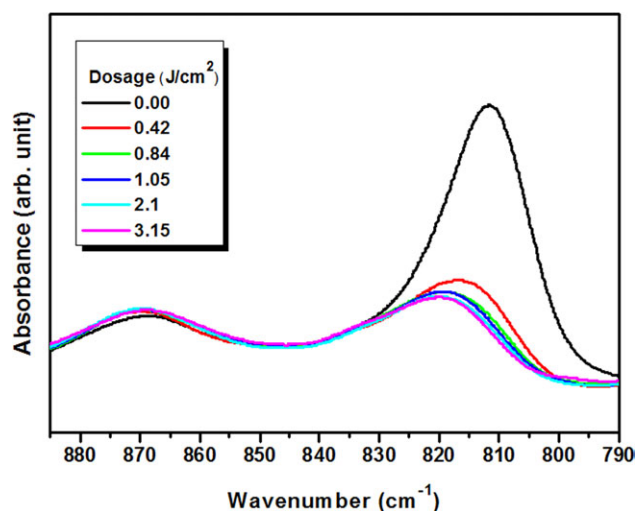

Figure 3. TGA thermograms of neat and MPS-modified ATO nanoparticles and neat MPS.

Figure 4. Partial FTIR spectra of the pure polyester–acrylate film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
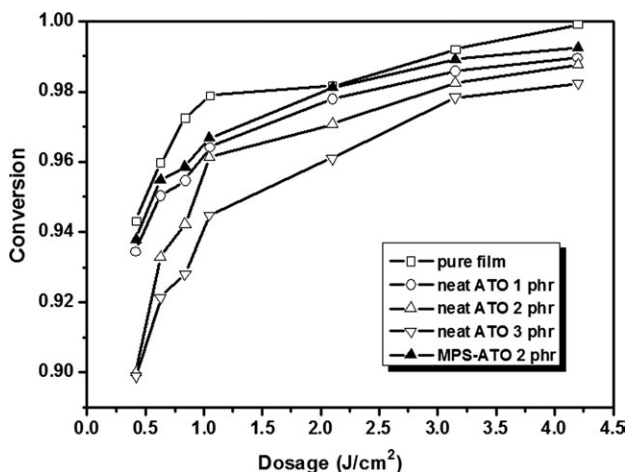
Figure 5. Conversion changes with UV dosage for the pure and ATO nanoparticles-filled films.

The peak at 810 cm^{-1} at each UV dosage was normalized by the peak at 870 cm^{-1} for the kinetic analysis because the peak did not change.

Figure 5 shows conversion changes with UV dosage for the pure and ATO nanoparticles-filled films. Effect of adding ATO nanoparticles on the UV-curing behavior of the nanocomposites films is well shown. A slight decrease in the UV-curing rate and final conversion was observed with increasing the amount of neat ATO nanoparticles. This result was considered due to a UV-shielding or UV-reflecting effect of ATO nanoparticles. However, compared to the film with 2 phr of neat ATO nanoparticles, the film with 2 phr of MPS-modified ATO nanoparticles showed slightly higher UV-curing rate and final conversion. This result was considered due to the methacrylate groups of MPS molecules because these groups could react with the acrylate groups of the binder resin to accelerate the consumption of the acrylate groups, resulting in UV-curing rate increase.
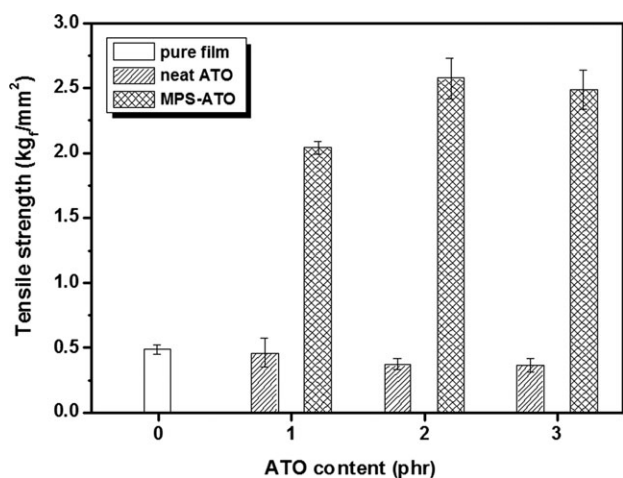
Mechanical Properties

The tensile strength of the pure and ATO nanoparticles-filled films is shown in Figure 6. This figure shows how much the MPS-modification of ATO nanoparticles affects the tensile strength of the films. The tensile strength of the films with MPS-modified ATO nanoparticles was four to five folds higher than that of the films with neat ATO nanoparticles. This result was considered due to improved interfacial adhesion between ATO nanoparticles and the resin matrix because the methacrylate groups of MPS molecules could react with the acrylate groups of the binder resin to form covalent bonds. In the case of the films with neat ATO nanoparticles, the tensile strength of the films decreased slightly with increasing the amount of ATO nanoparticles. This was considered due to insufficient interfacial interactions. However, in the case of the films with MPS-modified ATO nanoparticles, the tensile strength of the films increased slightly with increasing the amount of ATO nanoparticles up to 2 phr and almost leveled off over 2 phr.

The elongation at break of the pure and ATO nanoparticles-filled films are shown in Figure 7. In the case of the films with neat ATO nanoparticles, the elongation at break of the films was all larger than that of the pure film and decreased slightly with increasing the amount of ATO nanoparticles. One possible reason for this would be the decreased final conversion with increasing neat ATO nanoparticles as shown in Figure 5. However, in the case of the films with MPS-modified ATO nanoparticles, like tensile strength, the elongation at break of the films increased slightly with increasing the amount of ATO nanoparticles up to 2 phr and almost leveled off over 2 phr. This result was considered due to the strong interfacial interactions.

Surface scratch resistance of the pure and nanocomposites films was tested using the pencil hardness tester. The pencil hardness of the pure film was H. However, the pencil hardness of the nanocomposites films with MPS-modified ATO nanoparticles was 4H at ATO content of 1 phr and 5H at 2–3 phr. The pencil scratch hardness of the pure film considerably increased from H to 5H by adding just 2 phr of MPS-modified ATO
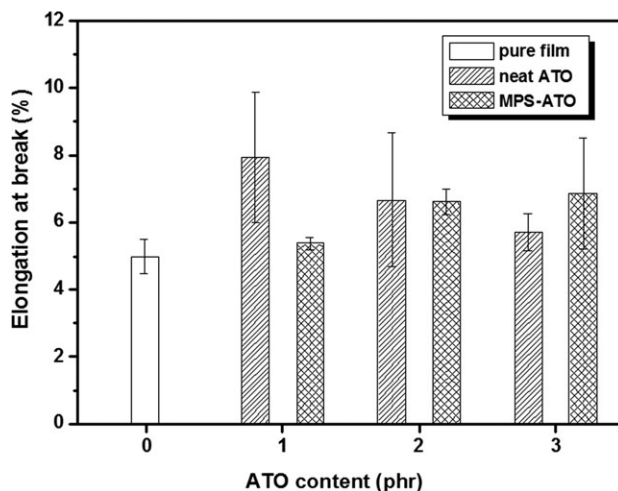

Figure 6. Tensile strength of the pure and ATO nanoparticles-filled films.

Figure 7. Elongation at break of the pure and ATO nanoparticles-filled films.

nanoparticles. This was considered due to the inherent hardness of the ATO nanoparticles and the strong interfacial interactions. Comparing the mechanical properties values of this work with those of other similar polymer composites with ATO was tried, but it was not easy because the composite systems were different each other.[32]

CONCLUSIONS

The antimony doped tin oxide (ATO) nanoparticles, which were used as nanofillers to improve mechanical properties of UV-cured polyester–acrylate films, were organically modified with 3-methacryloxypropyltrimethoxysilane (MPS) successfully. The modification of ATO nanoparticles with MPS was confirmed by FTIR spectroscopy and TGA. MPS-modified ATO nanoparticles were thermally very stable up to 320°C. A slight decrease in the UV-curing rate and final conversion was observed with increasing the amount of neat ATO nanoparticles. Compared to the film with neat ATO nanoparticles, the film with the same amount of MPS-modified ATO nanoparticles showed slightly higher UV-curing rate and final conversion. The tensile strength of the films with MPS-modified ATO nanoparticles was four to five folds higher than that of the films with neat ATO nanoparticles. The MPS-modified ATO nanoparticles could improve considerably the mechanical properties of the UV-cured polyester–acrylate nanocomposites films.

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