

UV-curable polyester-acrylate coating with antimony doped tin oxide nanoparticles

Sihyun Sung, Dae Su Kim^{*}

Department of Chemical Engineering, Chungbuk National University

410 Sungbongro, Cheongju, Chungbuk 361-763, Korea

(e-mail: dskim@cbnu.ac.kr)

한국산학기술학회 발표논문(한글)

성시현, 김대수^{*}

충북대학교 화학공학과

요약

Antimony doped tin oxide (ATO) nanoparticles were added as nanofillers to UV-curable polyester-acrylate (PEA) resin for coating to improve thermal, mechanical, and electrical properties. In this study, ATO nanoparticles were grafted by 3-glycidyloxypropyltrimethoxysilane and 3-methacryloxypropyltrimethoxysilane respectively to improve dispersion and interfacial adhesion. The physical properties and surface scratch hardness of the UV-curable nanocomposite coating were improved considerably by introducing the modified ATO nanoparticles.

1. Introduction

UV curing of coatings, inks, and adhesives has found a broad range of commercial applications because it meets several industrial demands, such as high-speed process and room temperature operations and environmentally compatible aspects such as no volatile organic content (VOC) emission and low energy consumption.¹⁻⁴

The electrical conductivity of insulating materials can be increased by the addition of electrically conductive fillers. Particularly interesting conductive filler is antimony doped tin oxide (ATO) as it combines a good electrical conductivity with optical transparency.⁵⁻⁷

In this study, different silane and various amounts of silane-grafted ATO nanoparticles were prepared with PEA resin. The UV-curing behavior and physical properties of PEA/ATO nanocomposite systems were investigated and analyzed as a function of ATO nanoparticle

content and silane coupling agent type and content. Adding silane graft-ATO nanoparticles were compared with adding neat ATO nanoparticles and silane coupling agent separately to the PEA system.

2. Experimental

2.1 Materials

The UV curable polyester-acrylate resin (PEA, EB 81) having 2.5 functional acrylate groups per molecule was supplied by SK-Cytec Co., Korea. The molecular weight of the resin was 600g/mol and viscosity was 100 cP at room temperature.

Urethane monoacrylate (EB1039, SK-Cytec Co., mol. wt. = 215 g/mol, viscosity = 25 cP at RT) was used as a reactive monomer to improve flexibility and adhesion properties of the PEA resin. The concentration of EB1039 was 30phr.

1-Hydroxycyclohexyl phenylketone (Irgacure 184 from Ciba Specialty Chem., mol. wt. = 204.3

g/mol) was used as a photoinitiator. The concentration of the I184 was fixed to 2 phr.

Antimony doped tin oxide (ATO) nanoparticles (ISHIHARA, Japan) with a mean particle size of 10-30 nm, were used in this study. To organically modify the pristine ATO nanoparticles, 3-methacryloxypropyltrimethoxysilane (MPS from Dow Corning, USA, mol. wt. = 248.35g/mol, density = 1.045 g/cm³) and 3-glycidyloxypropyltrimethoxysilane (GPTS from Sigma-Aldrich, Germany, mol. wt. = 236.3 g/mol, density = 1.07 g/cm³) were used as a coupling agent.

2.2 Grafting procedure of ATO nanoparticles

To make ATO-dispersion in water, ATO particles were vigorously stirred (2000rpm) in water at room temperature for 72h (ATO particles: water = 2.5g: 25g).⁷

※ 27.5g of ATO-dispersion was mixed with GPTS (2wt% of ATO). This mixture was heated to reflux (0-5°C, 500rpm) for 12h. At the end of the reaction, the mixture was four or five times filtered (2μm) with methanol to remove homo-condensates and unreacted GPTS.^{7, 8}

※ 27.5g of ATO-dispersion was mixed with MPS (2wt% of ATO). This mixture was heated to reflux (72°C, 500rpm) for 24h. At the end of the reaction, the mixture was four or five times filtered (2μm) with methanol.^{7, 8}

Both types of samples were dried in a vacuum oven at 50°C for 24h.

2.3 Preparation of PEA/ATO nanocomposites

PEA coatings with neat ATO nanoparticles with different coupling agent or silane-grafted ATO nanoparticles were prepared respectively at the ATO contents of 1, 2, 3 phr.

To see the effects of organic modifications, the composition of every resin mixture was fixed, with the exception of ATO particles, as follows; PEA(100 phr), HDDA (30 phr), and photoinitiator (2 phr). Each nanocomposite resin system was stirred for 2 h using a mechanical stirrer to

obtain a homogeneous mixture. To obtain a nanocomposite film about 100 micron thick, mixed resin was coated on a glass plate using a bar applicator. And then, UV curing of the acrylate resin was performed using a conveyor type UV curing system.

3. Results and discussion

3.1 silane grafted ATO nanoparticles

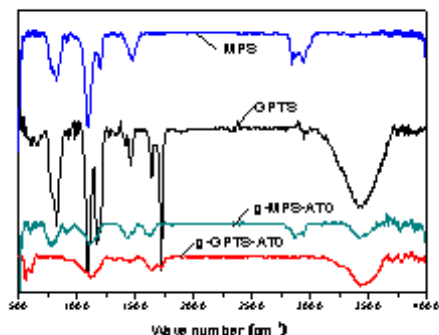
Organic modifications of the neat ATO nanoparticles were carried out in this study to improve the interfacial properties between the organic and inorganic phases of the nanocomposites.

Silane-grafted ATO nanoparticles were verified by FTIR. [Fig. 1] shows the FTIR spectra of pristine GPTS and GPTS-grafted ATO nanoparticles. The FTIR spectrum of grafted ATO showed characteristic peaks, at 1089 cm⁻¹ for the glycidyl groups. These peaks verified the formation of covalent bond produced between ATO and GPTS.

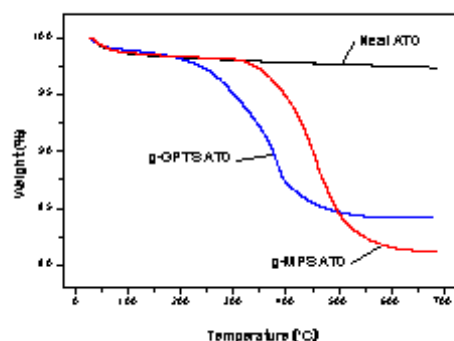
[Fig.1] shows also the FTIR spectra of pristine MPS and MPS-grafted ATO. The FTIR spectrum of grafted ATO showed two characteristic peaks, one at 1718 cm⁻¹ for the C=O band and the other at 1639cm⁻¹ for the C=C band of the methacryl groups. These peaks verified the formation of covalent bond produced between ATO and GPTS. These peaks confirmed that the organic modification of the pristine ATO nanoparticles was successful.

The TGA thermograms of the pristine ATO and the grafted ATO were obtained as shown in [Fig.2] to determine grafted silane contents. The weight loss below 100°C can be attributed to the vaporization of water present in the ATO nanoparticles. In the case of neat ATO nanoparticles, the weight loss below 700°C was approximately 3 wt% and there was no further considerable weight loss. In contrast, each silane-grafted ATO nanoparticles exhibited 13wt% and 16wt% weight losses in the range of 100~70

0°C, indicating thermal decomposition of grafted silane molecules.



[Fig.1] FTIR spectra of the silanes and silane-grafted ATO nanoparticles.



[Fig.2] TGA curves of neat and grafted ATO nanoparticles

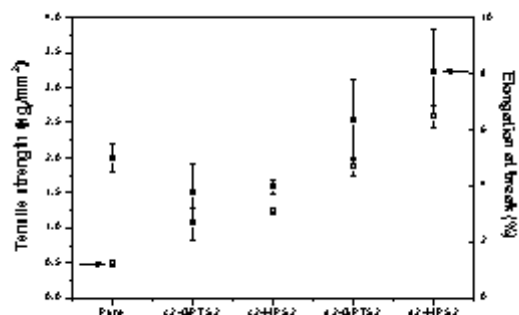
3.2 Physical properties

The tensile strength and elongation at break of the nanocomposites were shown in [Fig. 3]. In the case of the nanocomposites with silane grafted ATO nanoparticles, the mechanical properties were higher than those of the neat polymer and the nanocomposites with neat ATO and silane coupling agent. This result shows that the grafted ATO nanoparticles are more compatible and have stronger interactions with polymer matrix than neat ATO nanoparticles because functional group of the silane coupling agent could react with the polymer matrix to form covalent bonds.

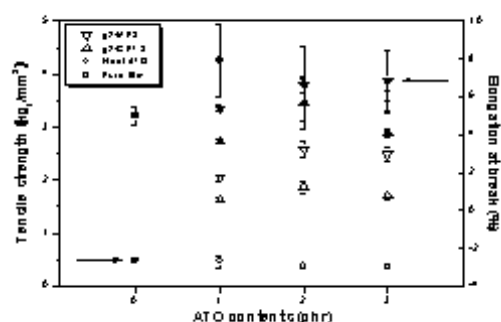
Physical properties of the neat polymer and the nanocomposites with different amounts of ATO nanoparticles are shown in [Fig. 4]. The nanocomposites with MPS grafted ATO nanoparticles at 2phr showed the best tensile properties. This result can be attributed to the

ATO nanoparticles dispersed well in the resin.

Moreover, the functional group of the silane grafted ATO nanoparticles can be covalently bonded to the polymer matrix and create the strong interactions between the ATO nanoparticles and the polymer matrix.



[Fig. 3] Tensile strength and elongation at break of neat polymer and nanocomposites according to modification



[Fig. 4] Tensile strength and elongation at break of neat polymer and nanocomposites with different amount of ATO nanoparticles

4. Conclusion

The characteristics of UV-curable nanocomposites with neat and silane-grafted ATO nanoparticles were investigated. The grafting of trialkoxysilane on to the surface of ATO nanoparticles was successfully carried out. The grafted ATO nanoparticles made the thermal properties of the nanocomposites improved. The nanocomposite with ATO nanoparticles showed improved mechanical properties. The nanocomposite with 2phr of the MPS grafted ATO nanoparticles showed the best

properties.

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