

Morphology Changes and Fillers Migration in Urethane Composites during Thermal Degradation

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Abstract. *Polyurethane composite coatings are frequently applied to strengthen the barrier properties of various construction materials such as wood, metal and concrete. The changes of color and glossiness of the composite coatings for building materials proceeds more slowly than that of polyurethane because of containing fillers and several types of additives. However, the most critical barrier properties have not been studied directly based on the difference from the degradation mechanism of polyurethane coatings. Additionally, the difference in thermal and UV degradation mechanisms of coatings is not clear in the existing studies dealing with conventional accelerated weathering tests and outdoor exposure tests. Therefore, the behavior of the filler contained in the coatings was observed using an oven to accelerate thermal degradation. The chemical analysis of the coating surface by XPS and the analysis of the images and elemental mappings by SEM-EDS were carried out, and the mechanism of degradation progress was investigated. In addition, the temperature dependency of the degradation was studied in changing the heating temperature. It was suggested that polymer and fillers interact in promoting mass transfer at the same time as the thermal degradation reaction consequently.*

Keywords: *Building Material, Coating, Filler, Polymer, Thermal Degradation.*

1 Introduction

Building material products used for topcoat contain so many chemical materials and consist of chemically complex systems. The products contain polyurethane, polyacrylic, modified silicone, and hybrid polymers. Furthermore, their products contain plasticizers, additives, and inorganic fillers in order to ensure performance and durability (Annamalai Pratheep Kumar *et al.* (2009), D.K. Chattopadhyay (2006), Ivan S. Stefanović *et al.* (2019), Jun Liu *et al.* (2017), Li Bin (2014), M.Sabzi *et al.* (2008) and S.M. Mirabedini (2013)).

In the present circumstances, the degradation process of coating materials containing polymers and inorganic substances has not been discussed. Even manufacturing companies have difficulty in elucidating their degradation mechanism, because such companies purchase raw materials from other companies and mix them to make products in many cases. In addition, there are few studies that separate thermal degradation from UV degradation through accelerated weathering tests and outdoor exposure tests. Therefore, this paper examines thermal degradation mechanism of coatings based on the result of the chemical analysis of the coating surface by XPS and the analysis of the images and elemental mappings by SEM-EDS.

2 Methods

2.1 Samples

In this study, both thermally-degraded and non thermally-degraded samples were prepared. The Conventional two-component type urethane coating including TiO_2 , CaCO_3 , and BaSO_4 as fillers was coated on a slide glass with a spin coater to control film thickness. After the surfaces of the samples were sufficiently dried, they were cured for 120 days at 20°C and 60% relative humidity, and cut to $7\text{mm}\times 7\text{mm}$ for fitting measuring instruments.

Subsequently, the samples after cutting were heat-degraded at 30°C , 50°C , and 70°C . The periods of the degradation are 0, 1, 3, and 7 days, and XPS measurement and SEM-EDS measurement were conducted respectively. The features of the measurements are briefly shown in Table 1.

2.2 XPS Measurement

X-ray photoelectron spectroscopy (XPS) was used to evaluate the chemical properties of urethane resin coatings. This technique is applied to analyze the type, concentration, and chemical state of elements on sample surfaces. Each sample is irradiated with an X-ray source using $\text{Mg-K}\alpha$ rays, and wide spectrums with a binding energy in the range of 10 to 1000 eV and narrow spectrums around the peak of each detected element was obtained at a measurement area of $1.0\text{mm}\times 1.0\text{mm}$. The shift of the peak due to charging is corrected by setting the C1s spectrum to 284.0 eV, and correction using a neutralizing electron gun is not performed.

2.3 SEM-EDS Observation

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDS) was applied due to analyze the elemental information of the cross section of the samples. The samples were preliminary processed with a cross section polisher (CP) using argon ion beam for cross sectional observation.

In addition, the surfaces of the samples were coated with Au by ion sputtering to avoid thermal degradation of the samples.

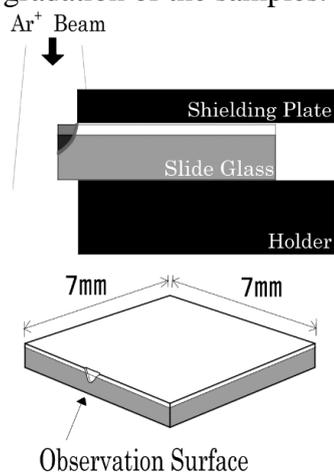


Figure 1. Processing before sample observation.

Table 1. Survey contents in each method.

XPS	<ul style="list-style-type: none"> History of elemental type and chemical bonding state of coating surface layer 	
SEM-EDS	SEM image	<ul style="list-style-type: none"> Cross section thickness of coating Filler particle size
	Elemental mapping	<ul style="list-style-type: none"> Distribution of elements in the cross section of coating film and its history

3 Results

3.1 XPS Scans

Figure 2 shows XPS narrow scan spectra of the urethane resin coatings that were thermally degraded at 70°C for 0, 1, 3, and 7 days. The peak of O 1s, N 1s, and Si-O increased as thermal degradation treatment continued. This result could be explained that the polymer such as urethane and siloxane was decomposed and appeared on the surface layer of the coatings due to low molecular weight and low density. On the other hand, the Ca peak was hardly detected on the surface layer. This result indicates that the substance in the coating may move up and down dramatically before the surface of the coating is cracked while the coating is thermally degraded. The fillers such as CaCO₃ originally floating on the surface of the coating film could be sunk as the polymers were scattered and float by heat.

Figure 3 shows O spectra of the samples that were thermally degraded at 30°C and 50°C for the same period. The graph shows that the peak increase on the 1st to 7th days at 30°C, however at 50°C, it increases on the 1st and 3rd days and decreases on the 7th day. These tendencies suggest the possibility of different thermal oxidation reactions on the coating surface, such as increases in C—O and C=O bonds and a decrease in O due to the progress of C crosslinking. Furthermore, each thermal oxidation reaction takes place at different times during the process of thermal degradation.

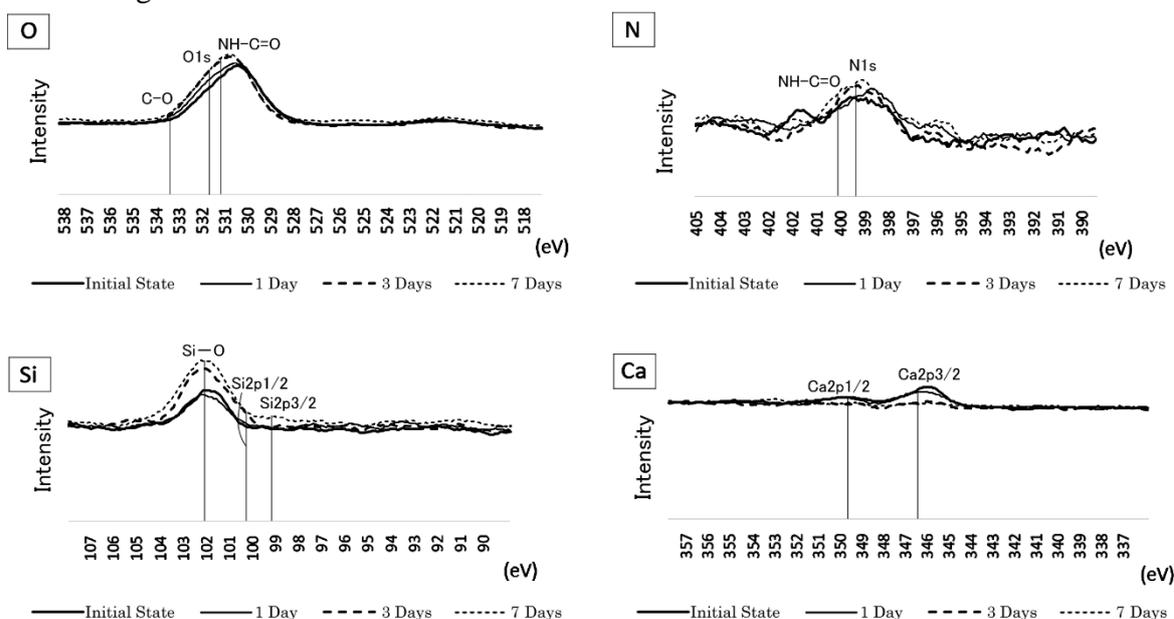


Figure 2. Narrow scan spectra of the urethane resin coatings that were thermally degraded at 70°C.

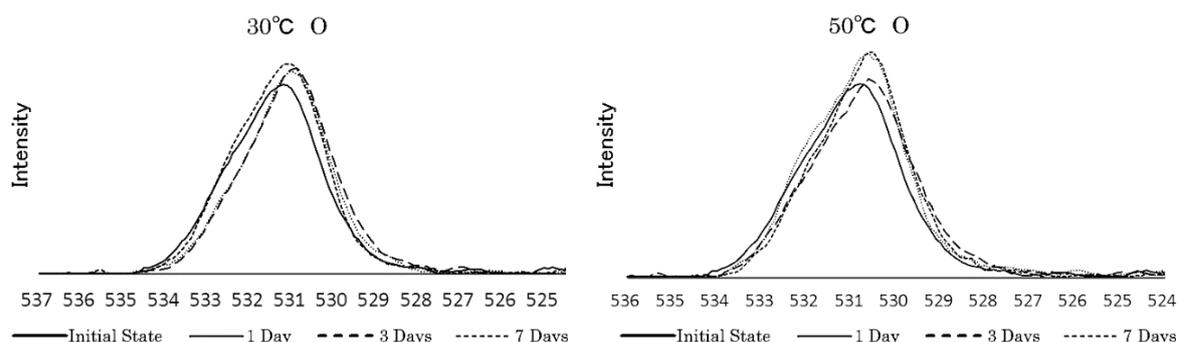


Figure 3. O spectra of the urethane resin coatings that were thermally degraded at 30°C and 50°C.

3.2 SEM Images

Figure 4 shows the film thickness history of each sample obtained from SEM image of the sample thermally degraded for 0, 1, 3, and 7 days, respectively, at 30°C, 50°C, and 70°C. However, it should also be noted that samples exposed at 70°C and samples at 30°C or 50°C are different in initial states. In the non thermally-degraded sample, the thickness of the coating was approximately 60 μm . The thickness of coating gradually decreased due to heat degradation at 70°C, and was 38 μm on 1st day, 18 μm on 3rd day, and 10 μm on 7th day. The coating thickness decreased due to thermal decomposition and volatilization of components such as plasticizers in the coating (Wei, X. (2019)). In contrast, at 30°C, the film thickness increased slightly, and at 50°C, it appeared to decrease on the 7th day. The dimensional change of the coating could be caused not only due to reduction of components in coating but also due to changes of gel structure in cross-linking and scission (Petrović *et al.* (2000) and Y. Nawab, *et al.* (2017)).

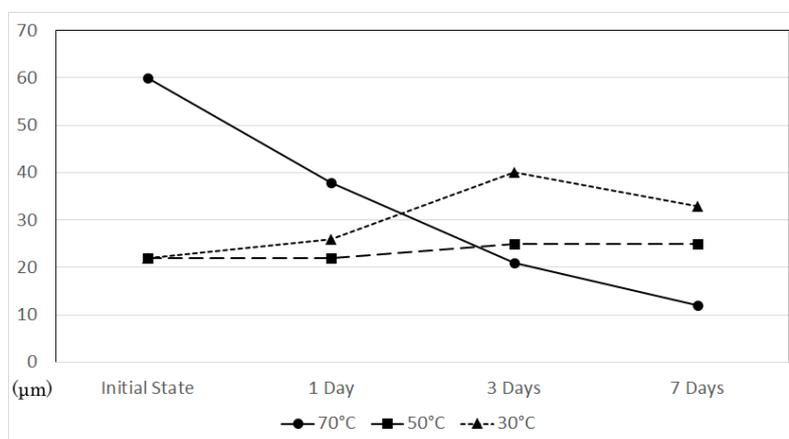


Figure 4. Changes in film thickness of each sample.

3.3 Elemental Mappings

Figure 5 shows the history of element mapping of Ti. Ti was homogeneous in the initial state, increased at the bottom on the first day, and gradually increased on the surface over time by heating at 50°C. On the first day, fillers move to the bottom of the coating as polymers become

smaller and less dense due to thermal decomposition. From the third day, filler have been pushed up from the bottom due to polymer cross-linking and polymerization reaction (Wei, X., *et. al.* (2019)).

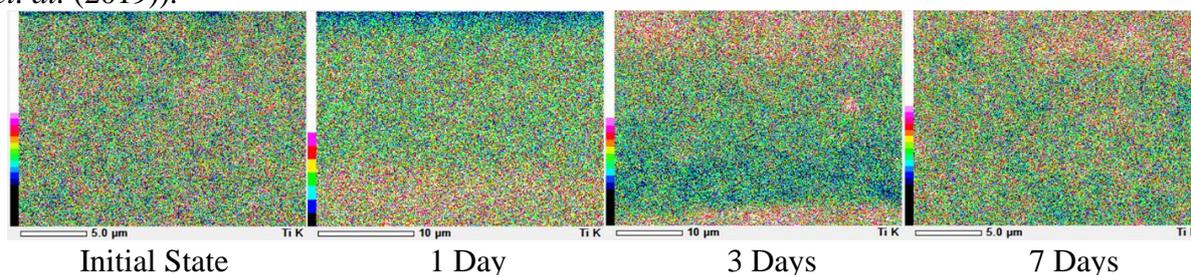


Figure 5. Sectional elemental mapping of Ti in urethane composite coatings at 50°C.

4 Discussion

4.1 Temperature Dependence of Coating Durability

The coating thickness increased initially at lower temperatures and decreased at higher temperatures, accompanied by the movement of the filler. Since fillers such as titanium dioxide have a role to protect the coating from UV degradation, the durability of the construction coating could vary greatly due to differences in temperature history.

4.2 Movement of the Filler

Why does the position of the inorganic filler in the coating fluctuate greatly due to thermal degradation? The movements of each filler of CaCO_3 , TiO_2 , and BaSO_4 were analyzed as follows.

4.2.1 CaCO_3

In elemental mapping, Ca is always homogeneous, whereas in XPS, the Ca peak increases and decreases depending on the temperature. There was no significant movement of CaCO_3 contained in the coating as a filler, and the XPS Ca peak changed due to a change in the state of the surface layer of the coating. The decrease in the Ca peak at 70 °C could indicate that the surface layer became smoother and covered with polymer as the temperature of the coating approached the glass transition temperature (L.S De Bernarde, *et. al.* (1984)).

4.2.2 TiO_2 and BaSO_4

XPS peaks of titanium and barium were not detected, however in elemental mapping by SEM-EDS, there were dramatic movements in the coating as shown in Figure 5. Moreover, the movement tendency of the position of the two elements is very similar and corresponds to the movement of TiO_2 and BaSO_4 in the coating as fillers. These fillers could move shrinkage stress due to polymerization, expansion stress due to heating, and stress due to movement of the polymer having a low molecular weight. The positions of these fillers are inhomogeneous unlike CaSO_4 , because the stress from the polymer may differ depending on the particle size of the filler (Nabil Hayeemasae *et. al.* (2018)). However, understanding these mechanisms require further studies.

5 Conclusions

- The position of the fillers contained in the organic composite coating are inhomogeneous due to thermal degradation.
- Polymerization, scission and cross-linking of the polymers can be accelerated by the action of heat, which can affect the thickness of the coating.
- The cross-sectional morphology of the coating changes depending on the temperature of thermal degradation.
- Changes in thickness and inhomogeneous distribution of materials due to thermal degradation of architectural composite coatings could affect their barrier performance because of the movements of the fillers and changes of the thickness.

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References

- Annamalai Pratheep Kumar, Dilip Depan, Namrata Singh Tomer and Raj Pal Singh (2009). Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives, *Progress in Polymer Science, Volume 34, Issue 6, June 2009, Pages 479-515*
- D.K. Chattopadhyay and K.V.S.N. Raju (2006). Structural engineering of polyurethane coatings for high performance applications, *Progress in Polymer Science, Volume 32, Issue 3, March 2007, Pages 352-418*
- Ivan S. Stefanović, Jasmina Dostanić, Davor Lončarević, Dana Vasiljević-Radović, Sanja Ostojić, Smilja Marković and Marija V. Pergal (2019). Preparation and characterization of poly(urethane-siloxane)/titanium-dioxide nanocomposites, *SCIENTIFIC PAPER UDC: 620.3: 549.514.6: 62-97 Hem. Ind. 73 (1) 13-24*
- Jun Liu, Youyuan Wang, Kun Xiao and Zhanxi Zhang (2017). Research on the Thermal Aging Behaviors of LDPE/TiO₂ Nanocomposites, *Journal of Nanomaterials, Volume 2017, Article ID 5048382, 11 pages*
- Li Bin, Li Song-Mei, Liu Jian-Hua and Yu Mei (2014). The heat resistance of a polyurethane coating filled with modified nano-CaCO₃, *Applied Surface Science, Volume 315, 1 October 2014, Pages 241-246*
- L.S De Bernarde, J. Ferrón, E.C. Goldberg and R.H. Buitrago (1984). The effect of surface roughness on XPS and AES, *Volume 139, Issues 2–3, 2 April 1984, Pages 541-548*
- M.Sabzi, S.M.Mirabedini, J.Zohuriaan-Mehr and M.Atai (2008). Surface modification of TiO₂ nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating, *Progress in Organic Coatings, Volume 65, Issue 2, June 2009, Pages 222-228*
- Nabil Hayeemasae, Hanafi Ismail, Suradet Matchawet and Abdulhakim Masa (2018). Kinetic of thermal degradation and thermal stability of natural rubber filled with titanium dioxide nanoparticles, *Polymer Composites, Volume 40, Issue 8, August 2019, Pages 3149-3155*
- S.M. Mirabedini and A. Kiamanesh (2013). The effect of micro and nano-sized particles on mechanical and adhesion properties of a clear polyester powder coating, *Progress in Organic Coatings, Volume 76, Issue 11, November 2013, Pages 1625-1632*
- Wei, X., Linde, E. and Hedenqvist and M.S. (2019). Plasticiser loss from plastic or rubber products through diffusion and evaporation, *npj Mater Degradation, 3, Article number: 18*
- Yasir Nawab, Pascal Casari, Nicolas Boyard and Frédéric Jacquemin (2017). Determination and modelling of the cure shrinkage of epoxy vinyl ester resin and associated composites by considering thermal gradients, *Composites Science and Technology, Volume 73, 23 November 2012, Pages 81-87*
- Zoran S. Petrović, Ivan Javni, Alan Waddon and György Bánhegyi (2000). Structure and properties of polyurethane–silica nanocomposites, *Journal of Applied Polymer Science, Volume 76, Issue 2, 11 April 2000, Pages 133-151*