Weathering Effect on PE Coated with Thin Layer of PU/Nanosilica Composite

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Abstract. Polyethylene (PE) film coated with polyurethane/nanosilica composite with varying composition were prepared and then exposed to ultraviolet radiation for accelerated weathering studies. The chemical and physical changes on nanocomposite coated PE film induced by UV exposure were studied by monitoring the changes in tensile strength, tensile modulus, elongation, carbonyl index, and visible light transmission. The effect of polyurethane/nanosilica composite coating on the durability and optical properties of polyethylene substrate was determined after 200 hrs and 500 hrs of ultraviolet exposure. There is no significant change was observed on visible light transmission for nanocomposite coated PE film after 500 hrs UV weathering. The mechanical properties of coated and uncoated PE were tremendously affected by UV exposure. PE coated with 4 µm of nanocomposite containing 6 wt% nanosilica showed less tensile properties deterioration compared to uncoated PE film after UV weathering. The surface protective coating of polyurethane/nanosilica composite with 6 wt% nanosilica content reduced the photodegradation rate of PE due to its excellent thermal stability compared to PE.

Introduction

Polymeric materials are generally susceptible to oxidative degradation when exposed to ultraviolet (UV) irradiation or heat in the presence of oxygen due to the formation of free radicals and other reactive intermediates [1]. During outdoor exposure, PE degrades chemically due to the action of short wavelength UV rays present in the solar spectrum. The service life of PE in outdoor applications becomes limited due to weathering [2] which leads to a rapid loss of physical properties in PE. The loss is caused by scission of bonds randomly in the PE chain resulting in the formation of free-radicals, which migrate along the chain. Acrylic base polyurethane nanocomposites are highly promising materials as flame retardant coating since they have a unique resistance to oxidation and high temperature [3]. The concept of improvement of coatings through nano-technology is of great interests. Organic base coating composite modified with nanomaterial are becoming increasingly important due to the fact that the resultant material shows superior performance in terms of mechanical, permeability, selectivity, and photoconductivity for various applications [4].

In this work, PE film coated with polyurethane/nanosilica composite with varying composition are exposed to ultraviolet radiation for accelerated weathering studies. The chemical and physical changes on nanocomposite coated PE film induced by UV exposure are studied by monitoring the changes in mechanical properties, carbonyl index and visible light transmission. The effect of polyurethane/nanosilica composite coating on the durability and optical properties of polyethylene substrate was determined after 200 hrs and 500 hrs of ultraviolet exposure.
Experimental

160 µm thickness LLDPE/LDPE blended film produced by blown extrusion in a ratio of 75/25 wt% was used from as received. Silica Aerosil R972 (supplied by Degussa Chemicals) was used for the preparation of the nanocomposites. Aerosil R972 was a hydrophobic fumed silica treated with DDS (dimethydichlorosilane) based on a hydrophilic fumed silica, with a specific surface area of 130 m²/g. The average primary particle size is 16 nm. The primer used was 2K polyurethane refinish clear coat (SM 510n/60LG, 60% solid content) from Cytec. The hardener used was Desmodure N75 (a solution of 75% in xylene/MPA mixture) and was purchased from Bayer.

Solutions of nano-SiO₂/PU at various compositions were prepared by dispersing different amount of nano-SiO₂ powder in solvent borne polyurethane under rigorous stirring. Once proper dispersion was achieved, a stochiometric amount of curing agent, N75, with molar ratio of NCO/OH =1.1/1, was added to the mixture. The mixture was further stirred for a few minutes. The nanocomposite materials were then deposited on the surface of PE film using Rod Mayer technique. Composition of nanosilica/PU system with 0-14 wt% nanosilica was prepared. Two coating thicknesses were studied which were 4 µm and 8 µm. The weathering resistance was evaluated by exposing the samples in a QUV chamber equipped with UVB-313 fluorescent lamps. The structural changes occurring in PE films were investigated using a Nicolet 560 FTIR spectrophotometer. Carbonyl index (Cl) was used as a parameter to monitor the degree of photooxidation of PE. Tensile tests were performed on PE films according to ASTM 882-85 using a universal testing machine. The effect of weathering to thermal stability of the sample was studied by TGA while the visible light transmission of nanocomposite coated film was measured using a Cary 50 UV-vis spectrophotometer.

Results and Discussion

Fig. 1(a) -1(d) represented the effect of UV exposure to mechanical properties of PU/nanosilica composite coated and uncoated PE film. The tensile strength results as showed in Fig. 1(a) - 1(b) clearly indicated that the tensile strength for all the weathered samples decreased with increases of UV weathering time. Neat PE film showed a decrease of ≈ 15.6% in tensile strength after 200 hrs of UV exposure. The reduction in tensile strength is due to the photolytic degradation of PE film when exposed to UV radiation. PE film coated with 4 µm and 8 µm of nanocomposite containing 6 wt% nanosilica showed a significant drop of 27 % & 32 % in tensile strength respectively for the initial 200 hrs of UV exposure (Fig. 1(a)-1(b)). The PE coated with 4 µm nanocomposite containing 6 wt% nanosilica retained 62 % of the tensile strength compared to 50 % for uncoated PE film after 500 hrs of UV exposure. However, the PE film coated with 8 µm nanocomposite containing 14 wt% nanosilica showed a tremendous drop of tensile strength with increasing weathering time as shown in Fig. 1(b).
Fig. 1. Effect of UV exposure to mechanical properties of PE and nanosilica/PU coated PE film.

Fig. 1 (c) - (d) showed that the uncoated PE experienced a higher elongation loss compared to PE coated with pure PU and 6 wt% nano-SiO$_2$ modified PU after 200 hrs of UV exposure. This may be due to the excellent thermal stability of PU after UV weathering of 500 hrs as evaluated with TGA study (Fig. 2). Fig. 2 showed that there was no significant change occurs on PU composite after subjected to 500 hrs of UV exposure time. The elongation result also showed that the present of 14 wt% nano-SiO$_2$ on coating thickness of 8 µm accelerated the photodegradation of PE film. Great drop of mechanical properties after 500 hrs weathering for PE coated with 8 µm of PU/nanosilica-14% composite could be due to tremendous hardening which was caused by synergistic stiffening effect from high content of nano-SiO$_2$ and increase of crosslink network in PU after weathering [5].

Fig. 2. Effect of 500hrs QUV weathering to thermal stability of polyurethane binder

Fig. 3(a) and 3(b) show the effect of UV weathering to tensile modulus of PE and nanocomposite coated PE film. The UV weathering increase tensile modulus of PE but the increase was more marked for PE coated with PU/nanosilica composite coating. The tensile modulus of weathered nanocomposite coated PE film increased with increasing of nanosilica content and coating thickness as shown in Fig. 3(a) - 3(b). Both the increasing of nanosilica content and UV exposure time has resulted synergistic effect of stiffening for the increasing of tensile modulus values of the coated PE film. And it is well known that the tensile modulus is directly related to initial crystallinity of the polymer [6]. Nicole and Laurent [7] also reported that an increase in crystallinity and crosslinking will result an increase of tensile modulus.
Fig. 3. Effect of UV weathering to tensile modulus properties of PE and PE coated with a) 4 µm and b) 8 µm of PU/nanosilica composite coating.

Fig. 4 presented the effect of UV weathering on visible light transmission of PE coated with 4 µm thick nanocomposite coating. PE coated with PU containing nanosilica up to 14 wt% retained higher visible light transmission than PE film after UV exposure test. Fig. 4 also clearly indicated that the PE film coated with PU/nano-SiO$_2$ composite coating retained higher visible light transmission compared to uncoated PE after as much as 500 hrs of UV ageing. Similar results are obtained for 8 µm coating thickness. It also showed no significant transparency loss after extended weathering. This result indicated that PU/nanosilica composite coating is effective in improving visible light transmission of PE film and maintaining high light transmission of PE film even after UV weathering.

Fig. 4. Effect of weathering to visible light transmission of PE coated with 4 µm nanocomposite.

Fig. 5 showed FTIR spectra of PE and PE coated with 4 µm thick of nanocomposite containing 14 wt% nano-SiO$_2$ content as a function of weathering time. The most significant change in IR absorption spectra is in the carbonyl region (1680-1780 cm$^{-1}$) [8]. The absorption band around 1716 cm$^{-1}$, which can be assigned to the C=O stretch of ketonic groups, increased in intensity for PE coated with PU/nanosilica containing 14 wt% nanosilica. Carbonyl index is calculated by taking the ratio of the intensity of signals at 1716 cm$^{-1}$ and 2917 cm$^{-1}$ and the results were tabulated in Fig. 6.
The increase in carbonyl group formation for PE after weathering is known to be proportional to the number of chain scission that occurred in the PE [7]. Our results indicated that chain scission may have occurred on PE and nanocomposite coated PE immediately upon exposure and that the number of chain scissions increased with increasing of exposure time (Fig. 6). However, there was only slight increase of carbonyl for PE coated with 4 µm thicknesses of PU and nanocomposite with 6 wt% nanosilica content after 200 hrs UV exposure. This indicated that PU or PU/nanosilica composite with 6 wt% nanosilica content reduced the generation of carbonyl derivatives of the underlying PE film. The growth of carbonyl for PE coated with PU/nanosilica-14% increased with the UV exposure time.

![Figure 5. Carbonyl region as a function of exposure time for PE and PU/nano-SiO$_2$ coated PE.](image)

**Conclusions**

A factorial experimental design was used to examine the effects of PU/nanosilica composite coating on PE film. There was only minimal effect on the visible light transmission of both coated and uncoated polyethylene film after 500 hrs UV weathering. The delay of carbonyl growth though the FTIR study indicated that 4 µm PU coating layer with 6 wt% nanosilica has delayed the photodegradation rate of underneath PE substrate. PU containing 0 - 6 wt% nanosilica successfully reduced the strength loss rate of the samples due to its excellent thermal stability compared to uncoated PE after 200 hrs of UV weathering. 4 µm nanocomposite coating thickness with 6 wt% nanosilica was found to be an effective UV blocker for delaying the photodegradation of PE film after 200 hrs UV weathering test.

**References**
