



Mechanisms of Photo Degradation for Layered Silicate-Polycarbonate Nanocomposites

by James M. Sloan and Philip Patterson

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14. ABSTRACT The use of advanced lightweight materials to improve combat survivability has been of crucial interest to the U.S. Army for a number of years. Specifically, hybrid organic/inorganic polymer matrix nanocomposites show promise in providing many of the physical properties required (i.e., lightweight structure, rugged abrasion resistance, and high ballistic impact strength). However, as with any polymer system, these materials are susceptible to degradation over time when exposed to various environmental (i.e., sunlight, moisture, temperature, etc.) conditions. This structural degradation will eventually comprise the original integrity of the materials' desired properties. Polycarbonate (PC) has outstanding ballistic impact strength, good optical clarity, and high heat-distortion resistance. The Army has a continuous interest in research on PC for better chemical resistance and enhanced resistance to abrasion. The focus of our research is to exploit nanotechnology through incorporation of layered silicates for property enhancement. Typical mica-like clays consist of stacked platelets with the thickness of each individual platelet on the order of 1 nm. In this study, the effect of accelerated weathering upon newly developed PC-layered silicate nanocomposite materials was investigated. The silicate loading varied from 0–3.5% by weight. A fluorescent ultraviolet (UV)/condensation weatherometer was selected for the exposure study. The materials were characterized by UV/VIS spectroscopy and Fourier transform infrared spectroscopy. The results reveal that the carbonate linkages undergo a scission reaction upon UV exposure, thereby compromising the original properties of the material. Furthermore, these scissions produce a yellowing of the polymer matrix which can inhibit its use where optical clarity is important.					
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1. Introduction

The use of advanced lightweight materials to improve combat survivability has been of crucial interest to the U.S. Army for a number of years. Specifically, hybrid organic/inorganic polymer matrix nanocomposites show promise in providing many of the physical properties required (i.e., lightweight structure, rugged abrasion resistance, and high ballistic impact strength). However, as with any polymer system, these materials are susceptible to degradation over time when exposed to various environmental (i.e., sunlight, moisture, temperature, etc.) conditions. This structural degradation (1–4) will eventually comprise the original integrity of the materials' desired properties.

Polycarbonate (PC) has outstanding ballistic impact strength, good optical clarity, and high heat-distortion resistance. The Army has a continuous interest in research on PC for better chemical resistance and enhanced resistance to abrasion. The focus of our research is to exploit nanotechnology through incorporation of layered silicates for property enhancement. Typical mica-like clays consist of stacked platelets with the thickness of each individual platelet on the order of 1 nm (5).

In this study, the effect of accelerated weathering upon newly developed PC-layered silicate nanocomposite materials was investigated. The silicate loading varied from 0–3.5% by weight. A fluorescent ultraviolet (UV)/condensation weatherometer was selected for the exposure study. The materials were characterized by UV/Visible (VIS) spectroscopy and FTIR spectroscopy.

2. Technical Background

Polymer layered-silicate (PLS) nanocomposites are an emerging class of polymer-ceramic hybrids with an engineered nanostructure controlled through the manipulation of interactions between the silicate and the organic species. Due to synergism between the polymer and ceramic phases, these materials exhibit an astounding combination of properties, which include enhanced mechanical performance, flame resistance, barrier properties, solvent resistance, and thermal stability in comparison to conventional filled polymers (5–8). By virtue of their primarily polymeric nature, these materials also exhibit ultra-lightweight, processability, and low cost. Furthermore, due to the unique physical characteristics of the dispersed silicate reinforcement particles, it is possible to achieve property enhancements while retaining transparency in the polymer-ceramic hybrids. Preliminary studies have indicated that PLS nanocomposites have potential in applications such as ablative materials (9) and transparent coatings, but exploitation in military systems is still in its infancy.

PLS nanocomposites are characterized by a molecular dispersion of polymeric molecules and high aspect ratio silicate platelets. The key to achieving synergistic property enhancements is in the proper design and tailoring of the nanostructure. If the organic species fully penetrates the galleries, swelling the structure without causing loss of registry between the layers, the system is referred to as an intercalated PLS nanocomposite. If the penetration of the organic results in a disruption of the registry between the silicate layers and dispersion of the silicate platelets within the polymer matrix, the system is referred to as an exfoliated PLS nanocomposite. The potential morphologies are illustrated in figure 1. The formation of intercalated and exfoliated structures may be achieved by control of thermodynamic interactions between the organic modifiers used to control silicate surface chemistry within the galleries and the matrix.

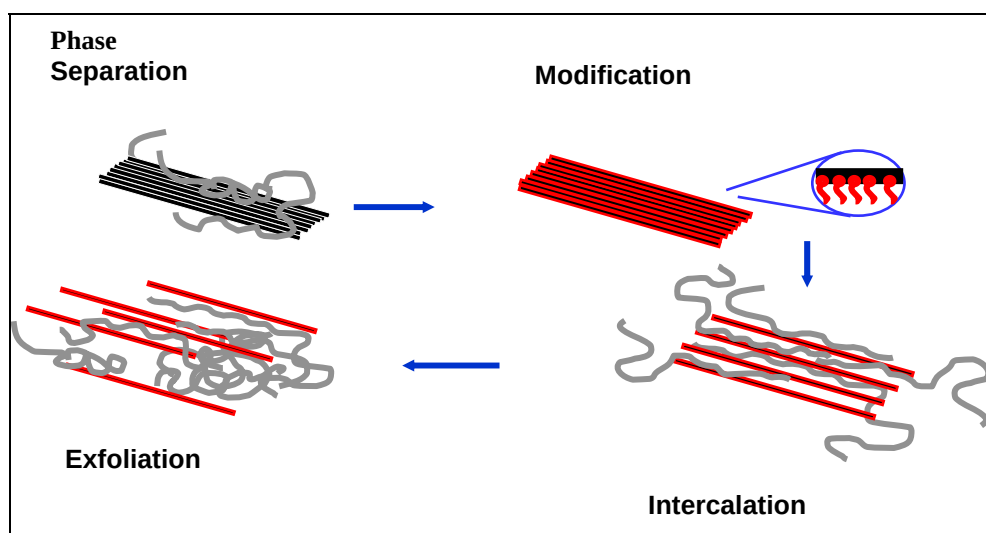


Figure 1. Schematic of polycarbonate/clay nanocomposite structure.

3. Experimental

3.1 Materials

PC nanocomposites used in this study were prepared through a small business innovative research program funded to Triton Systems, Inc., by the Army. The clays were incorporated into the polymer by using a twin-screw extruder at about 290 °C. Then, these nanocomposite compounds were compression molded into sheet at 290 °C. The PC structure can be found in figure 2.

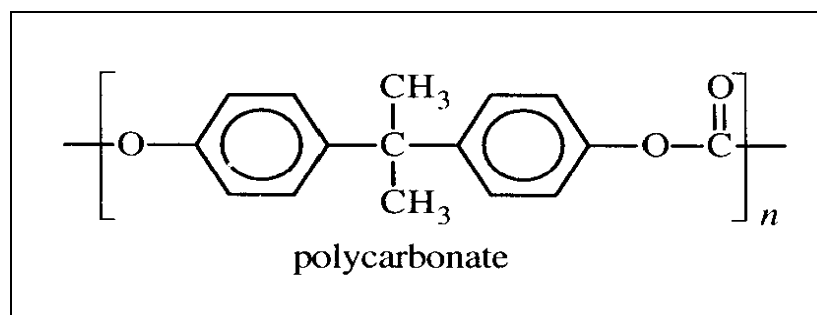


Figure 2. Polycarbonate structure.

3.2 Weathering

The specimens were weathered using accelerated weathering Q-UV testers (Q-Panel Laboratory Products, Cleveland, OH) conforming to the requirements as set forth in ASTM G 53 (10). The exposure cycle was established at 8 hr of UV radiation at 60 °C followed by 4 hr of dark condensation at 40 °C. The testers were equipped UV lamps emitting a spectral irradiance of 0.77 W/m² at 340 nm. The lamp output was checked and calibrated after every 40 hr of operation. The study was conducted following an interval time schedule, with the exposure durations set for ~500, 750, and 1000 hr. After each exposure interval, the samples were wiped clean before spectroscopic analysis.

3.3 Spectroscopic Measurements

Infrared measurements were recorded on a Nicolet model 560 Magna FTIR. Spectra consisted of 64 coadded scans with a resolution of 4 cm⁻¹. An Analect attenuated total reflectance accessory equipped with a 45° KRS-5 crystal was used as the sampling accessory. The UV/VIS spectra were recorded using a Cary 5G UV/VIS/near-infrared (NIR) spectrometer set to scan in the 190–2500 nm range. A holmium oxide-glass filter was used to calibrate the instrument.

4. Results and Discussion

Figure 3 shows the 380–500 nm portion of the UV/VIS spectrum for the exposed PC plastic. The unexposed or “control” sample is shown in the bottom spectra for comparison. As displayed, it is quite apparent that as the material is “aged,” there is a corresponding increase in the UV/VIS absorbance. Overall band broadening and intensity changes between 400 and 430 nm can clearly be observed. These spectral differences represent the changes in the appearance (yellowing) of the material, over time, as it photochemically degrades under the accelerated exposure conditions.

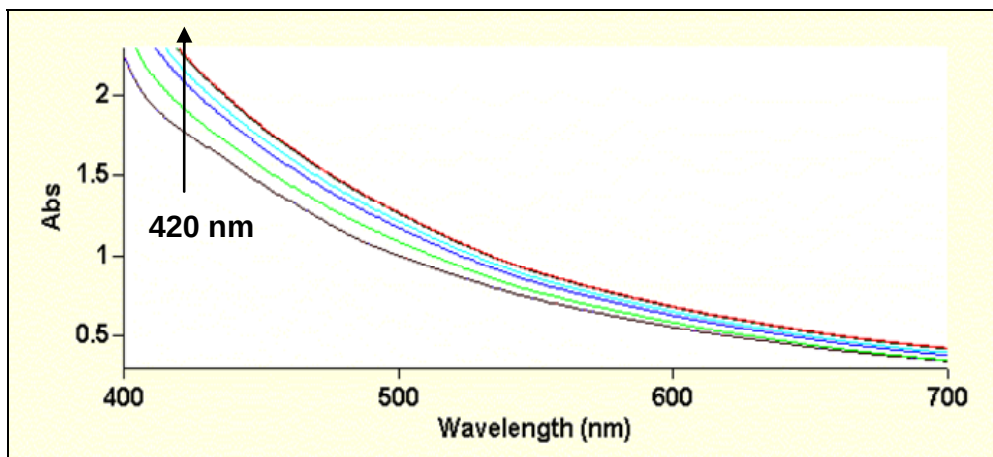


Figure 3. Polycarbonate UV/VIS absorption spectra for the various Q-UV exposure intervals. Control = 0 hr. Advanced exposure time is represented by the upper curves.

Figure 4 graphically represents the changes in the UV/VIS spectra at 420 nm over exposure time. These data are generated from figure 3. The 420-nm wavelength corresponds to the yellow part of the visible spectrum. A trend toward yellowing can be detected upon UV exposure of the PC. In the control specimen, no appreciable yellowing is observed until ~1000 hr have passed. Both silicate-filled specimens show identical behavior; in fact, the rate of yellowing can be superimposed upon one another. In each of the filled specimens, a much faster rate of degradation is observed when compared to the control specimen. In addition to the increased rate of weathering, the final absorbance values for the silicate filled samples are larger. The control shows a leveling off at ~0.64-abs units, while the control sample level off at 0.30-abs units. This would suggest that the filled specimens degrade to a much larger overall extent.

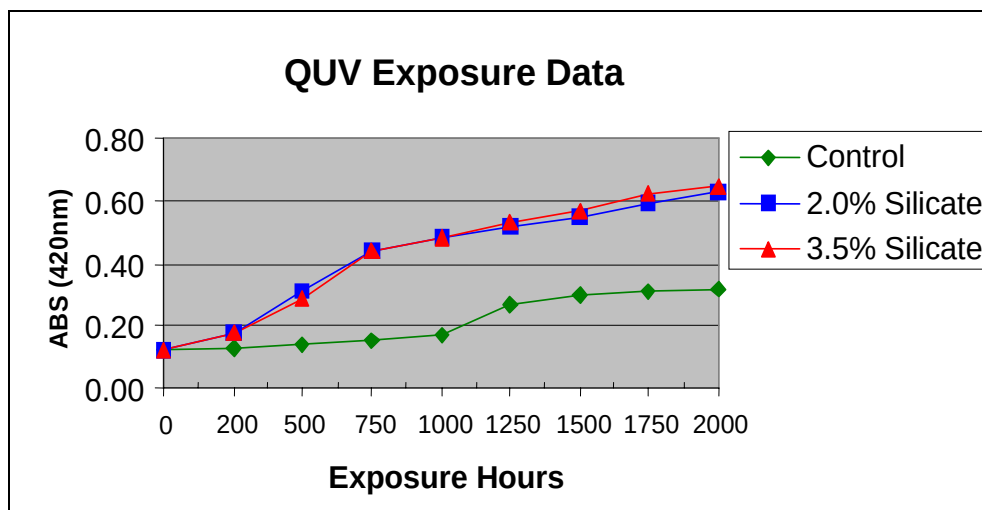


Figure 4. Absorbance of 420-nm band intensity with exposure time for silicate filled and unfilled polycarbonate.

The faster weathering rates of the filled PLS are most likely due to coloring effect of the clay particles. The darker clay particles have a tendency to absorb more UV radiation, likely producing an abundance of free radicals that apparently serve to initiate chain scission reactions. The net effect is that a more dramatic effect in the photolytic reaction rate.

In an attempt to determine if any changes to the chemical structure were occurring during the weathering cycles of these PCs, FTIR experiments were performed. FTIR allows one to follow changes occurring in the structure of the polymer.

The FTIR spectra for the unexposed PC PLS with 2.5% clay and after 750 hr of exposure are shown in figure 5. The bottom spectrum is the unexposed material and the upper curves represent the PC after 500, 1000, and 1500 hr of exposure. Changes in the infrared spectra can be seen at 1766 cm^{-1} and 1222 cm^{-1} . These absorbances relate to infrared bands in the **C=O** and a **C-O** regions of the spectra, respectfully. These losses are believed to be due to scission of the carbonate linkages. Additionally, several new, broad absorbance bands appear. The two most significant are at 1713 cm^{-1} , and at 1101 cm^{-1} that represents a new carbonyl **C=O** functional group and a new **C-O**. This corresponds to the formation of by-products as a result of the chain cleavage.

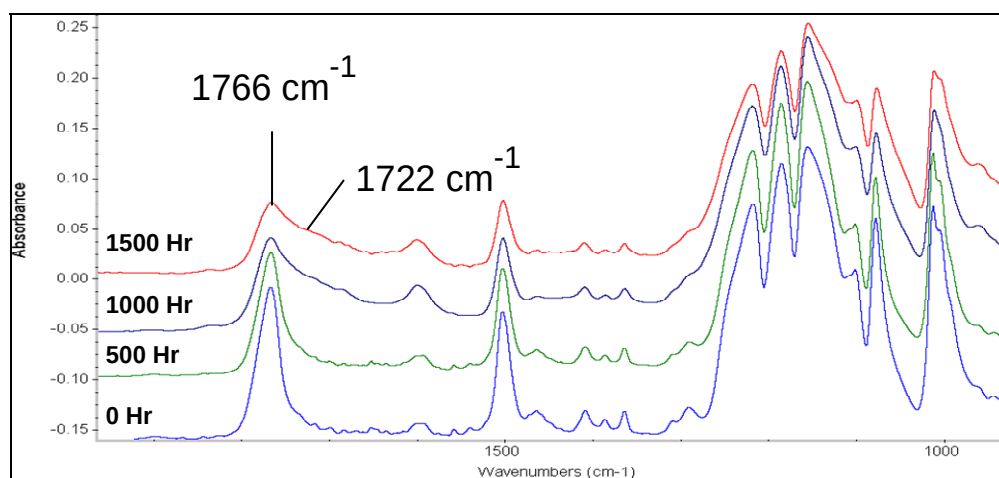


Figure 5. FTIR spectra for polycarbonate nanocomposite – Q-UV exposure times of 0, 500, 1000, and 1500 hr.

One suggested mechanism for the structural changes observed in the FTIR spectra is shown in figure 6. In this mechanism, the UV photon is preferentially absorbed by the “impurity.” This would be the silicate filler. A free radical is then formed to initiate a rearrangement followed by a chain cleavage reaction. This mechanism appears valid for the PC resin under investigation.

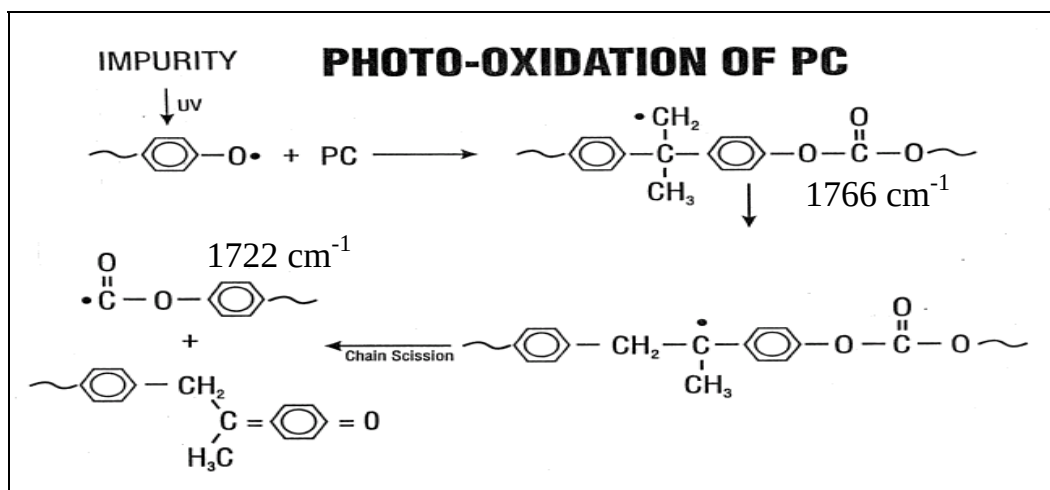


Figure 6. Proposed mechanism for photolytic degradation of polycarbonate resins.

Figure 7 demonstrates that a correlation exists between the monitored changes in the physical discoloration (i.e., increased yellowness) and the chemical structure (i.e., decreased carbonyl intensity) for these materials. It is important to remember that this correlation is valid for this specific polycarbonate aged under the accelerated weathering conditions previously outlined. Figure 7 shows that there is an excellent correlation between the monitored changes in the physical (i.e., increased yellowness) vs. the chemical (i.e., decreased carbonyl intensity) properties for this material.

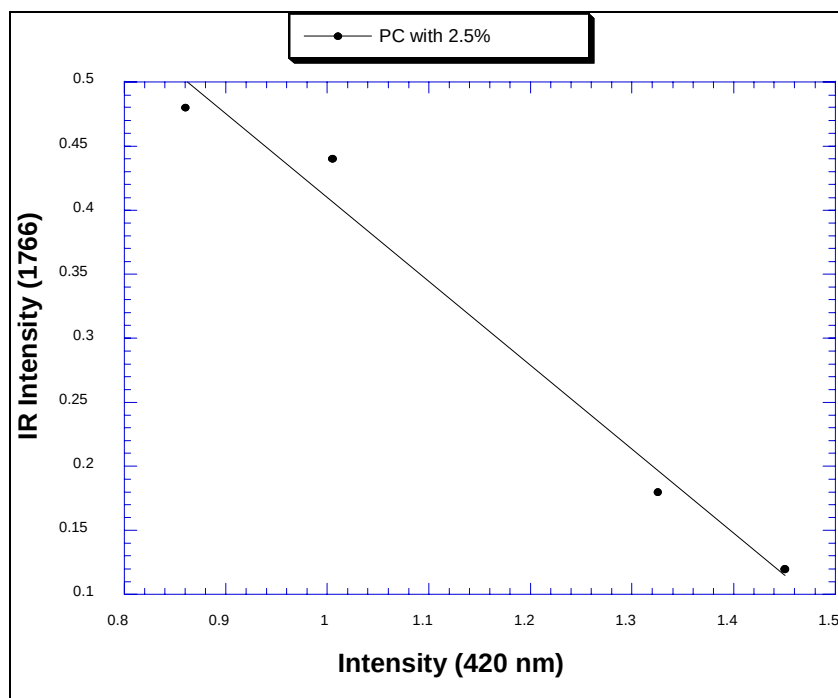


Figure 7. Relationship between UV yellowing and breakdown of carbonate linkages.

5. Conclusions

The effect of accelerated weathering upon an unmodified PC resin and PC nanocomposites developed for transparent armor applications was studied. The spectroscopic data show clear evidence that the both filled and unfilled polymer resins undergo a chain scission reaction where the carbonate structural linkages rupture when exposed to UV radiation. These UV radiation conditions are similar to that found in natural sunlight. A significant amount of yellowing was observed in both the standard PC as well as the PC nanocomposites during the exposure. In our experiments, it was determined that the PC nanocomposites demonstrated a much faster rate of yellowing than the PC control specimen. Furthermore, a reasonable correlation was established between the carbonate scissions and the increase in the material's yellowing. This correlation could be used as a predicative parameter in material selection for other transparent armor items (i.e., goggles, visors, windshields, etc.) where optical clarity is crucial.

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