

THE EFFECT OF NANOCLAY ON PHOTO-OXIDATION OF POLYETHYLENE

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Introduction

Polyethylene (PE) is one of the commercial thermoplastic materials that are in high demand due to its excellent properties. The continued use of PE in packaging and agricultural applications produce large quantity of plastic waste every year. Recent increase in environmental concerns about plastic waste has led to the development of biodegradable polymeric materials. PE can be made biodegradable by blending it with bio polymers such as starch and/or pro-oxidants. Recent studies on PE degradation have found that nanoclay, which is used as filler in polymer composites to enhance the mechanical properties, increases also the photo-oxidative degradation of PE.



Figure 1. Environmental pollution by PE waste

The present work describes a study in which the effect of montmorillonite nanoclay (MMT) on the photodegradation of polyethylene was investigated. Results from this work will help in the design of environmentally-friendly degradable polymeric materials.

Methods

Brabender twin screw extruder was used for the preparation of PE/MMT nanocomposites. Initially LDPE was mixed with 5% maleic anhydride grafted PE (PMMA) to facilitate compatibility with clay. Modified PE and clay (cloisite 15A) were then mixed thoroughly and extruded again. PE and PE nanocomposite films (65 -75 mm thickness) were prepared using an advanced co-extrusion blown film assembly unit. Wide angle X-ray diffraction was used to evaluate the morphology of nanocomposites films.

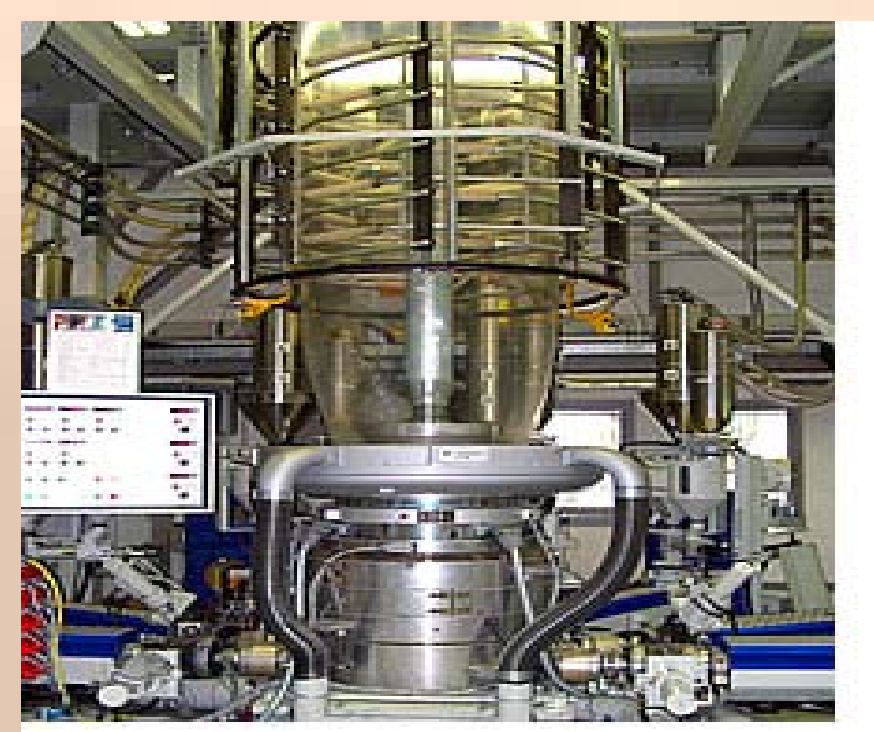


Figure 1. Preparation of PE films by blown film process

Photo-oxidative degradation of PE and its nanocomposites was carried out in an accelerated QUV weathering tester (Figure 2) according to ASTM G-154. The tester reproduces the damage that can occur in outdoor environment by several environmental factors such as sunlight, temperature and rain. Films were cut into strips (150 x 75 mm) and subjected to 0.89 W/m²/nm intense UVA irradiation at 60°C black panel temperature for 8 hours followed by 4 hour condensation of de-mineralized water on the surface of the film at 50°C. Samples were allowed to dry for 1 hour after each testing cycle.

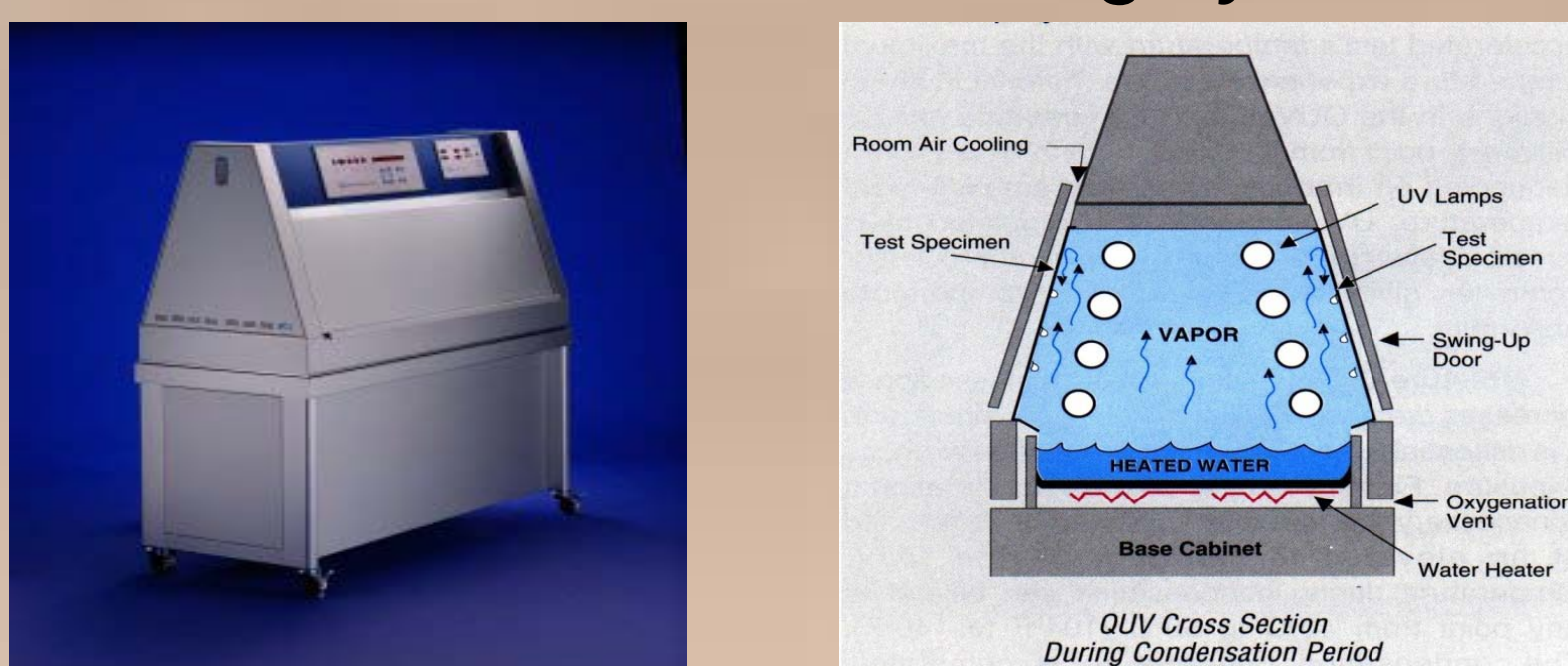


Figure 2. Accelerated QUV weathering tester

The progress of degradation was followed by monitoring the physical and chemical changes of the samples using Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

Results and Discussion

Morphological characterization

The d-spacing of cloisite 15A and nanocomposites was determined using Bragg's law $n = 2d\sin\theta$. All nanocomposites display their characteristic peak with intensities that are lower than that of clay towards lower angles or higher d-spacing indicating the formation of intercalated structures except for the sample with 2 wt% clay in which the clay has nearly exfoliated in the polymeric matrix (Figure 3).

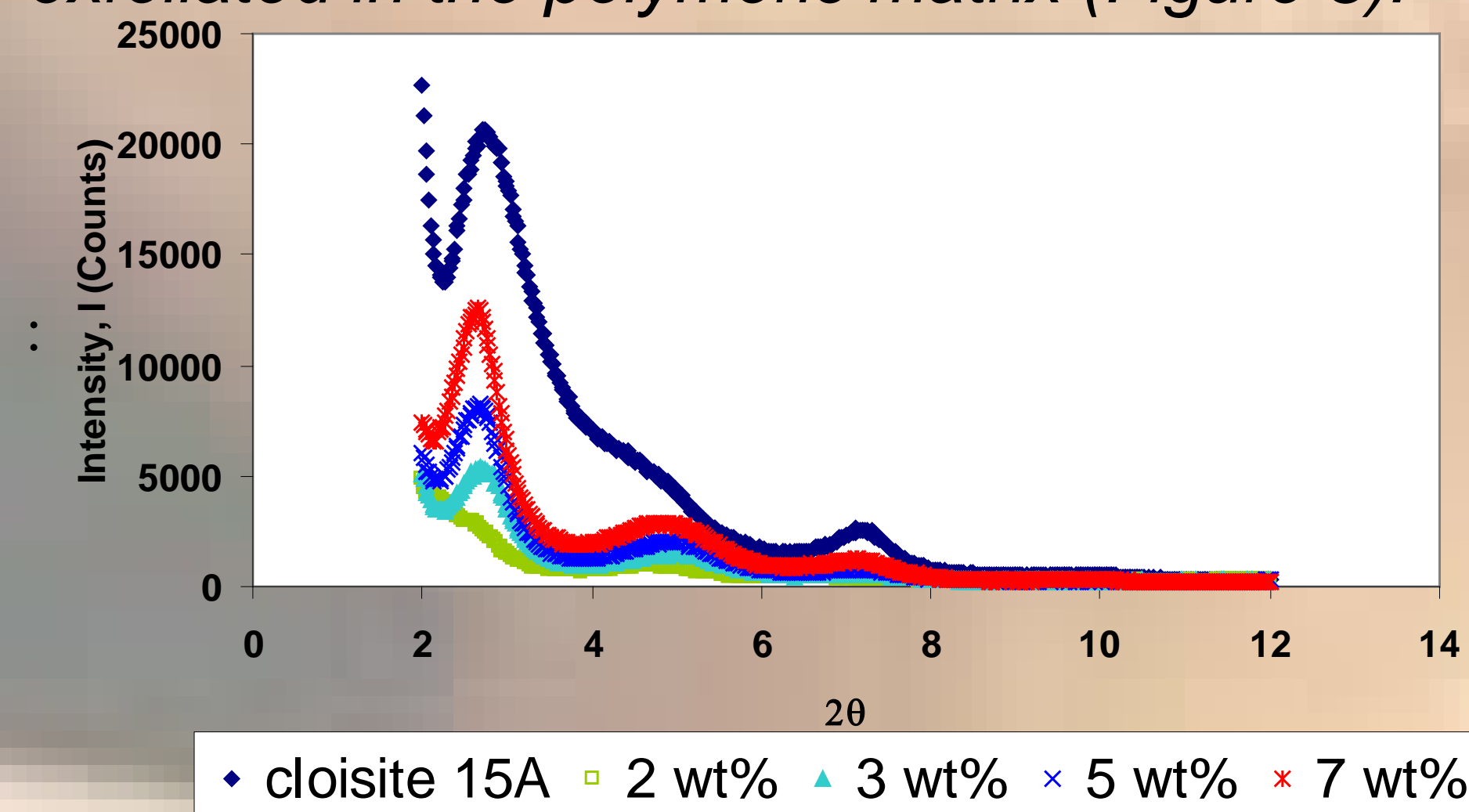


Figure 3. XRD patterns of cloisite 15A and PE/MMT nanocomposites with different clay concentrations

Infrared Analysis

During photo-oxidation, polymer macromolecules degrade leading to the formation of alkyl radicals. These unstable alkyl radicals in the polymer matrix are degraded further due to propagation leading to the formation of a mixture of carbonyl and hydroxyl species.

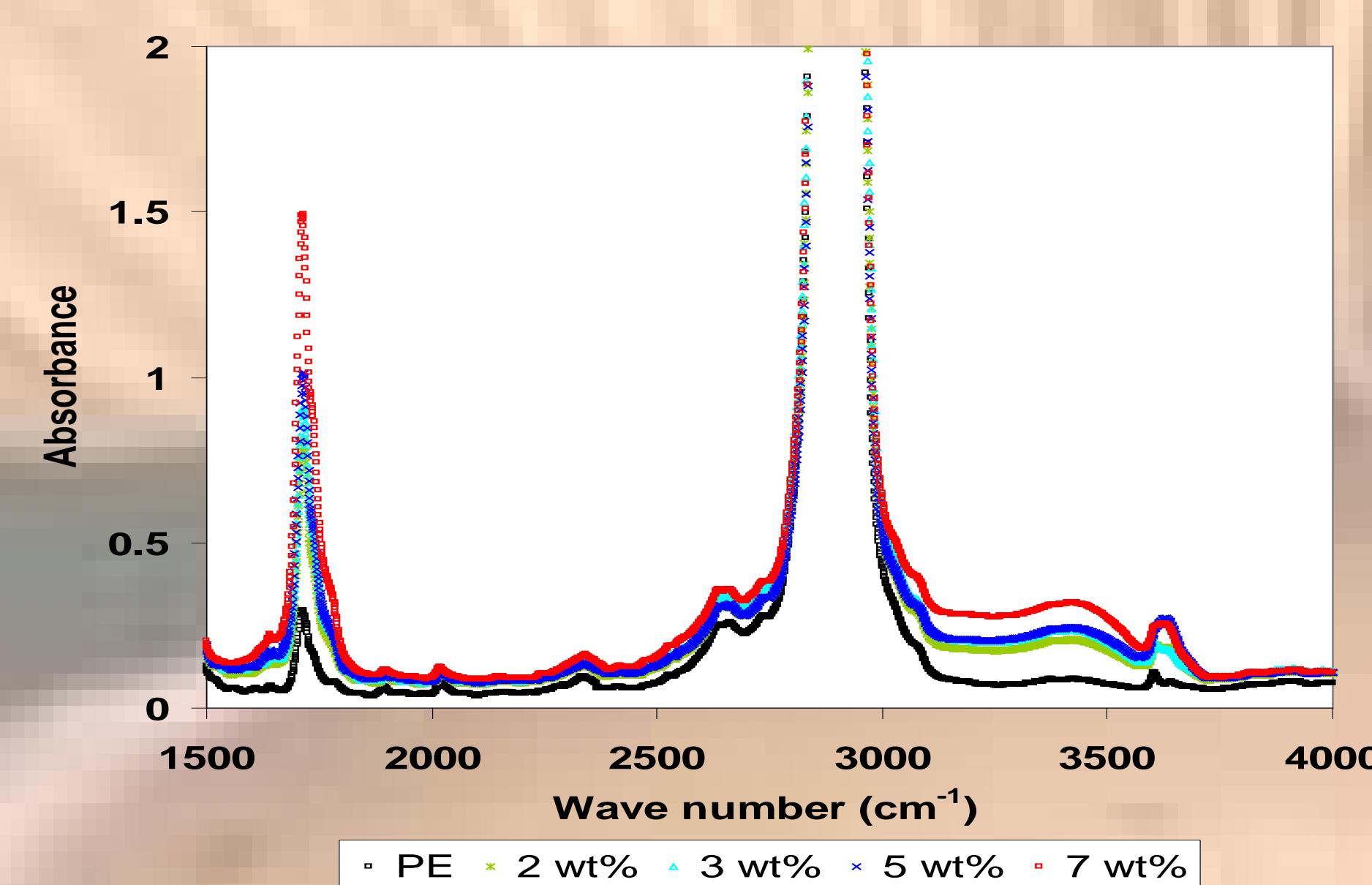


Figure 4. FTIR spectra (1500 - 4000 cm⁻¹) of PE and its nanocomposites after 14 days irradiation

The FTIR spectra peak observed at 1713 cm⁻¹ in Figure 4 are due to the formation of carbonyl groups (C=O) and the broad peak at 3000-3600 cm⁻¹ could be assigned to free OH groups, OH groups in MMT, and the carboxylic acids formed during the oxidation of the polymeric matrix. The effect of photo oxidation is significant on all nanocomposite samples whereas it is negligible on PE. Also the level of absorbance increases with the increase in clay concentration.

Carbonyl index (CI) is often used as a measure of the rate of photo-oxidation. It is defined as the ratio of carbonyl and methylene absorbance as shown in the following equation.

$$CI = \frac{\text{Absorbance@1713cm}^{-1}}{\text{Absorbance@1464cm}^{-1}} \dots\dots\dots (1)$$

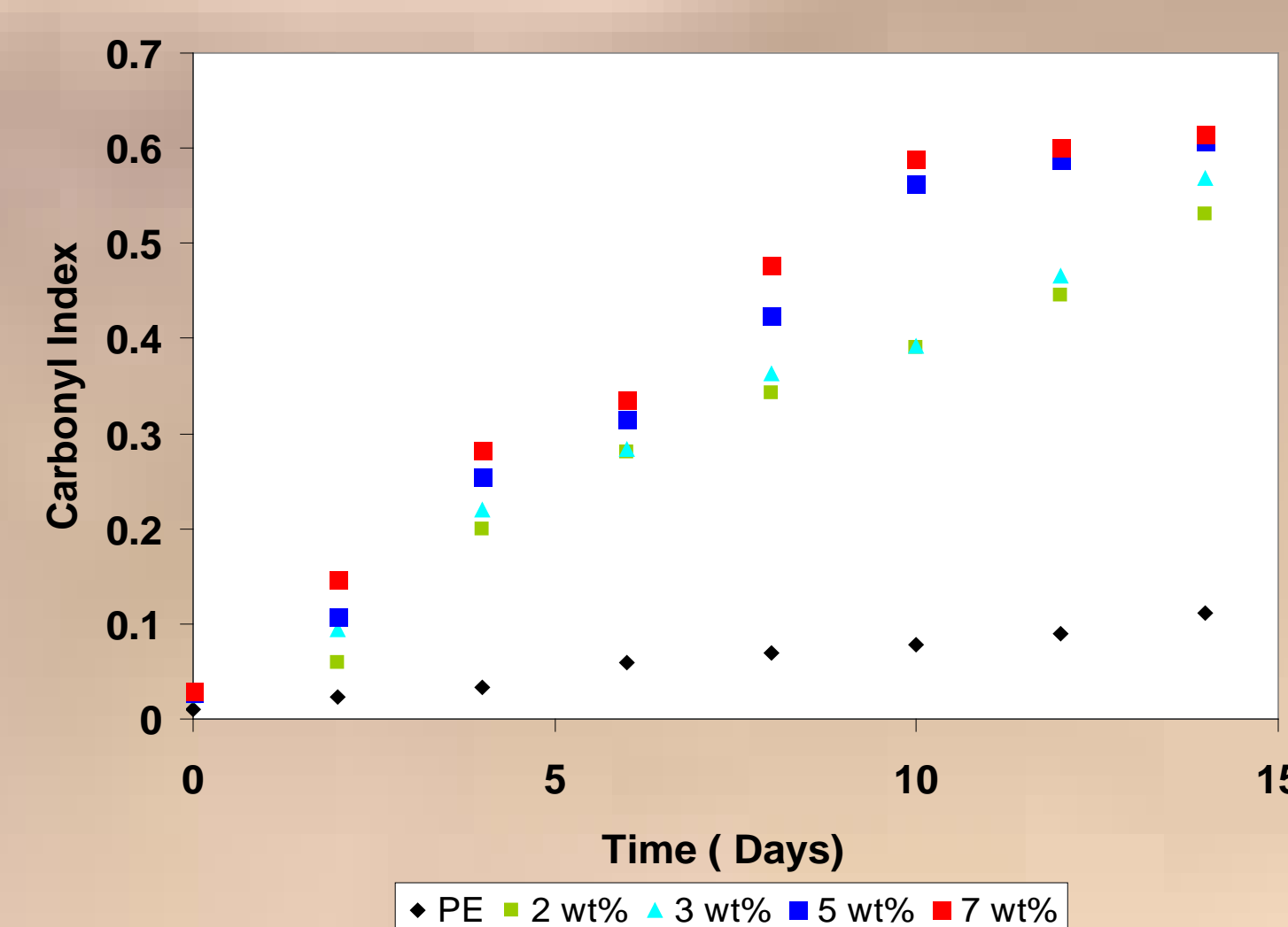


Figure 5. Carbonyl index of PE and its nanocomposites irradiated for 14 days at 0.68 W/m²/nm.

CI values for PE and its nanocomposites are shown in Figure 5 as a function of irradiation time. The rate of increase in CI values for nanocomposites is substantially greater than that for PE.

Changes in molecular weight distribution

The changes in molecular weight distribution (MWD) obtained by GPC for irradiated samples of pure PE and its nanocomposites are shown in Figure 6.

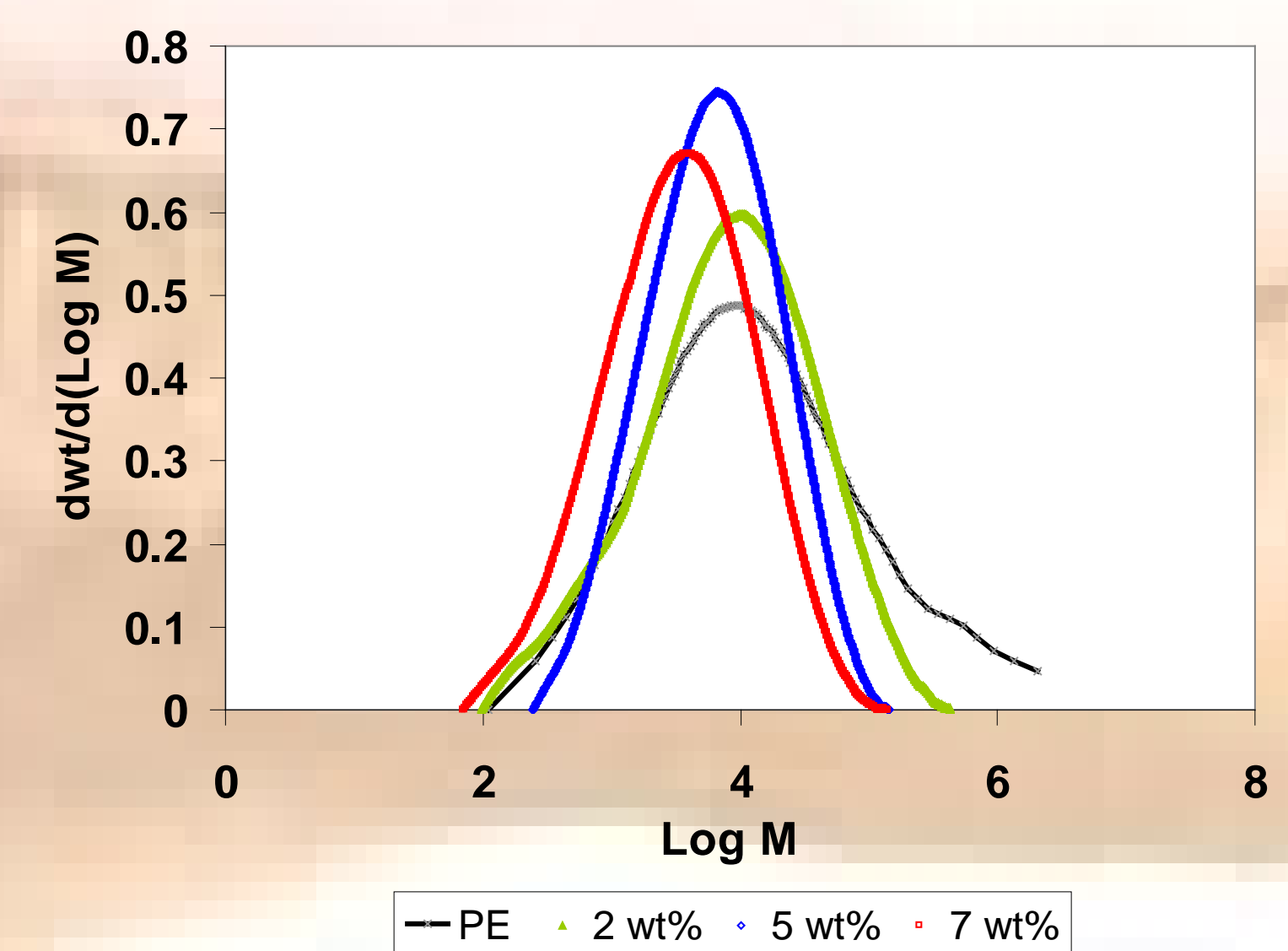


Figure 6. Molecular weight distribution of irradiated PE and its nanocomposites, Irradiation period = 14 days.

With irradiation, the MWD curves for the nanocomposites have shifted towards the low molecular weight scale indicating the formation of low molecular weight compounds. At the end of 14 days, the decrease in the molecular weight due to irradiation is 65% for PE whereas it is 94% for nanocomposite with 7 wt% clay (Figure 7). It is also clear that the average molecular weight of the polymer decreases rapidly with increasing clay concentration.

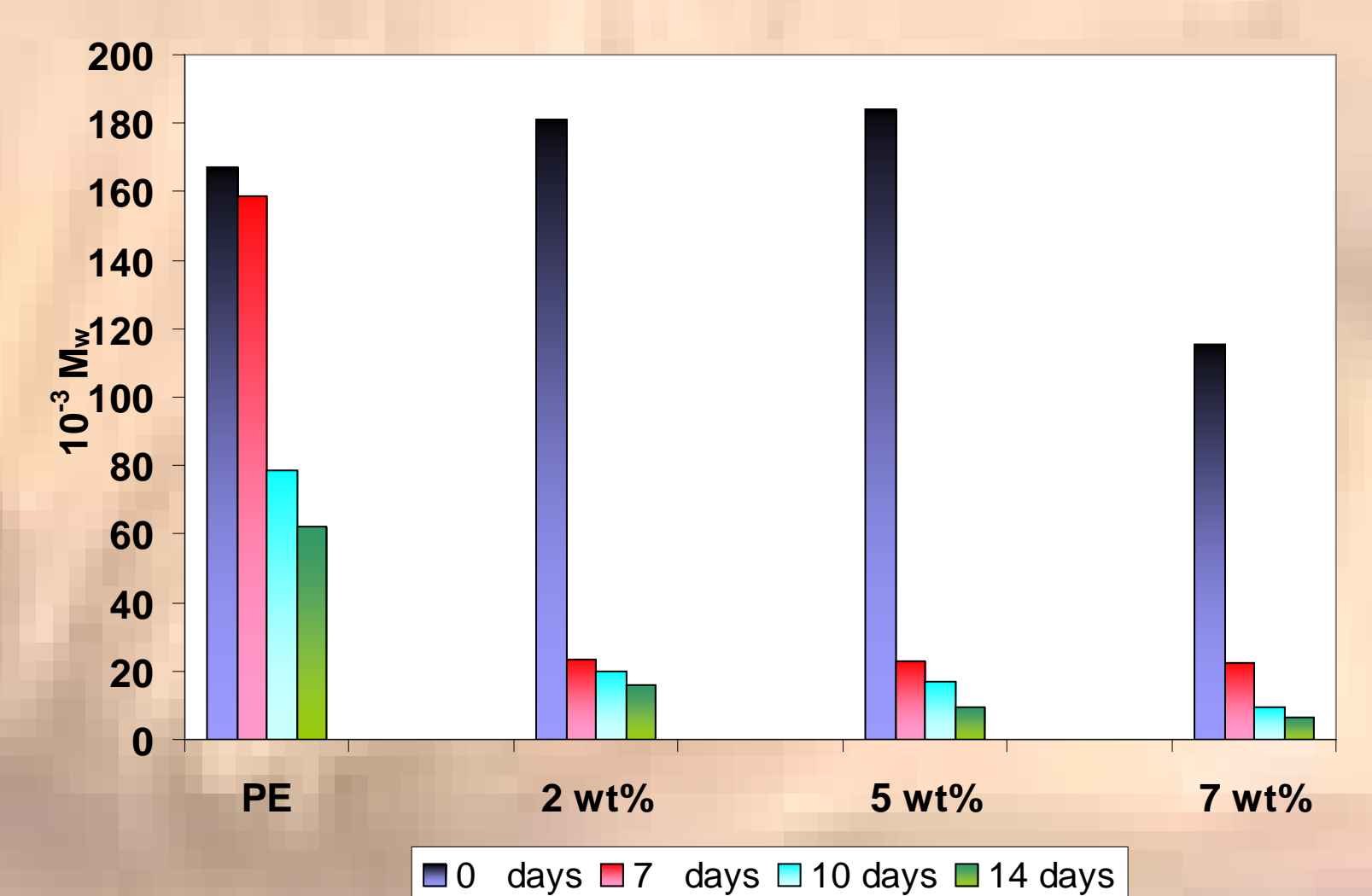


Figure 7. Changes in molecular weights of PE and its nanocomposites irradiated at 0.89 W/m²/nm.

GPC results confirm that nanoclay plays an important role in the degradation of the polymer by enhancing the breakdown of high molecular weight species into low molecular weight molecules. Since it is easy for the micro-organisms to utilise the low molecular weight species, it can be expected that the molecular mass conversion occurred during the photo-oxidation will facilitate easier biodegradation.

Conclusions

This research demonstrates the potential use of nano clay in enhancing the degradation of polyethylene which is otherwise not easily degradable due to its high molecular weight and hydrophobic nature. The rate photo-oxidation of PE nanocomposites is found to be significantly greater than that of pure PE. Results obtained from FTIR and GPC analyses show that, upon exposure to UV radiation, the polymer matrix undergoes chain scissions leading to the production of low molecular weight species. The formation of radicals in the polymer matrix is possibly accelerated by the decomposition of alkyl ammonium ions in MMT which creates acidic sites on the clay surface as well as on olefins.



Figure 8. Photo-degraded samples of PE and its nanocomposites