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Photo-induced Structural Changes in Polyolefin-nanoclay Composite

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ABSTRACT

The morphology of films prepared by melt-blending polyethylene (PE) and polypropylene (PP) with and without nanoclay was investigated after exposure to outdoor solar radiations for 45 days utilising many techniques. The Raman spectra revealed decreased intensity for all the characteristic Raman bands for PP and PE. The Fourier transform infrared spectroscopy showed formation of hydroxyl/hydroperoxy and carbonyl groups in the exposed samples. The weathered films after 45 days of solar exposure became brittle as indicated by loss in physical properties and the stress-strain curves. The clay-containing films showed higher strength loss after solar exposure. The fractured ends of the exposed films showed flat, smooth, and sharp surfaces, indicative of brittle fracture, compared to the unexposed sample.

Keywords: Photodegradation, polyethylene, polypropylene, nanoclay, composite, structural changes, Raman spectroscopy, scanning electron microscopy

1. INTRODUCTION

It is known that a polymer structure can be modified to introduce higher stability as well as propensity to degrade as per the required end use[1-3]. Photodegradability of polyolefins has been studied for reducing the problem of waste disposal and to understand its mechanism[4-10]. In general, it is found that pure polyolefins, specially polyethylene, are transparent down to < 200 nm wavelength and therefore, can be called indefinitely stable to sunlight having wavelengths >290 nm[9-10]. However, for practical purposes, on exposure to solar radiation these polymers are found to degrade to varying extents. The degradation of polyolefins by solar radiation has been attributed to photolysis of either oxidative-impurities introduced inadvertently during the processing of polymer or residual impurities from the synthesis of the polymer. Thus, addition of impurities or additives having UV absorption capability beyond 290 nm, have been attempted to enhance the photodegradability of polyolefins[11-13].

It is a fact that polyethylene retains its functional properties (flexibility and strength) at subzero temperature, but is not sensitive to photodegradation. Polypropylene on the other hand becomes stiff at subzero temperature but is photodegradable. Blending of these two polyolefins has never been an easy option. The present work deals with the study of structural changes that occur after solar exposure in a polyethylene (PE)-polypropylene (PP) blend film. Nanoclay was incorporated in one of the films to observe its effect on photodegradability. Photodegradation is a desirable property in certain packaging films that are thrown in the environment as litter, particularly at high altitude, and subzero temperature areas like Siachin. No study appears to have been reported on the morphology of solar-exposed PE and PP blend film.

2. EXPERIMENTAL

2.1 Preparation of Nanoclay

Commercially available smectonic clay was modified by sequential grinding, sieving through 400 mesh and chemical treatments[11]. The clay was dispersed in water and sonicated for 15 min to further reduce the particle size. After sonication, the bigger clay particles were allowed to settle down and the supernatant was collected and dried. The size of the particles was evaluated using an electron microscope. The nanoclay having the size range from 10 nm to 0.5 μ, was incorporated during compounding. Even during compounding, the size of clay particles further get reduced due to the large shear forces generated during extrusion.

2.2 Sample Preparation

Films of 50 μ were prepared by melt-blending PE and PP (90:10 ratio) in the presence of a modified styrene-maleic anhydride-based copolymer compatibiliser (1 part by weight) having melting point of 180 ºC. Films with (one per cent by weight of nanoclay) and without clay were made on a Colline Blow Film machine after compounding these in a JSW Twin Screw Extruder. The composition consisted a commercially available linear low-density polyethylene, MFI-0.9/10 min, and polypropylene, MFI 0.7/10 min, and a compatibiliser based on a copolymer of styrene-maleic anhydride. Films were made by melt-extrusion in a tubular form having a radius of 7.6 cm(3 inch). A 5 kg batch size was taken to prepare the films of about 75 m length.

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2.3 Solar Exposure

The films were exposed to solar radiation by keeping the films on the roof top of a building (4 m high) at Gwalior, situated at a latitude of 26°13 N and longitude of 78.13 E, for 45 days during July-August, when the temperature varies between 23 °C to 43 °C. After 45 days, it was rather difficult to handle clay filled samples as they became fragile and brittle enough to get damaged.

2.4 Mechanical Properties

Tensile strengths of control films and solar-exposed films were recorded on an Instron tensile tester with a cross-head speed of 150 mm/min. Test specimens of 50 mm long and 10 mm in wide were prepared from the films and used. The loss in strength was computed from their respective unexposed samples.

2.5 Infrared Spectroscopy

IR spectrometer, Perkin Elmer, FTIR-1720X, was used to obtain IR spectra of composite films before and after the solar exposure. The spectra were taken in the spectral range of 4000 cm^{-1} to 400 cm^{-1} at 4 cm^{-1} resolution using DTGS detector.

2.6 Laser Raman Spectroscopy

Renishaw In via Raman Microscope was used to obtain Raman spectra of films before and after the solar exposure. A solid diode laser operating at λ=785 nm was used as the excitation source with a laser power of 25 mW. The Rayleigh lines were eliminated from the scattering by a holographic notch filter. The samples were mounted on an X-Y scanning stage controlled by a stepper motor. The laser beam was focused via a microscope onto the sample. The system has a variable aperture for confocal acquisition of images. Signals were detected using a charged couple device (CCD) camera at a spectral resolution of 4 cm^{-1}. The instrumental parameters like laser power, exposure time, and number of accumulations were kept constant for all the experiments. The instrument was used in the normal mode with a 50X objective for the Raman mapping.

2.7 Scanning Electron Microscopy

Electron microscopic studies were performed with a FEI Quanta-400, SEM. Samples were coated with a thin layer of gold produced by ion sputtering in Ion Sputter JFC-1100 before observing these in the electron microscope at 5 kV. The cross-sections of unexposed and exposed films were obtained by freeze-fracturing in liquid nitrogen.

3. RESULTS AND DISCUSSION

Table 1 and Fig. 1 show a comparative tensile strength data before and after the solar exposure for control blended films made from PE and PP and films made from the composition having PE, PP, and clay. Incorporation of clay enhanced the tensile strength of the polyethylene/polypropylene film from 22.5 MPa to 31.8 MPa [Fig1(c)]. The improvement in the mechanical properties has been attributed to the development of a large volume fraction of an interface crystalline zone around nanoclay particles and polymer molecules. Formation of hydrogen bonds between the polymer matrix and silicate layers may also contribute for higher tensile strength[9,14,15]. It can be seen that loss in strength of control films having ten percent polypropylene registered 39 per cent strength loss and about 10 per cent loss in elongation after the solar exposure [Fig. 1(b)]. However, after exposure to solar radiations for 45 days, the deterioration in clay-incorporated film was very high with about 68 per cent strength loss and 20 per cent loss in elongation [Fig 1(d)]. It has been reported that clay facilitates faster degradation in polymeric materials when exposed to external stimuli like UV components in solar radiations [9,16]. A polymer matrix, that has strong intermolecular forces, normally has a large constrained regions as compared to a polymer with weak intermolecular forces[15]. These highly constrained regions become more susceptible to imposed stresses in the form of solar energy, and day-night temperature fluctuations. The photosensitivity has also been attributed to higher proportion of radicals that are formed in the crystal boundaries (that are present in higher proportion in nucleated polymers) and can migrate to the amorphous regions where degradation is usually faster[16-18].

Coupled with solar radiations, the humidity, rains, and elevated temperatures during the day can influence the destructive effect of solar radiation, by accelerating the rate of secondary reactions. These, in turn, alter the reaction process that follows the primary photochemical step of bond breaking by increasing the rate of oxygen and water permeation into the material[7,9,10].

The deformation behaviour (stress-strain curve) of control samples indicated [Figs 1(a)and 1(c)] homogeneous deformation where the stress built up continued steadily as the sample remained drawn with increasing elongation, till failure. The solar-exposed samples on the other hand [Figs 1(b) and 1(d)], deformed with a neck-formation during the drawing of the specimen. The neck formation perhaps indicates fluctuation in material properties resulting in stress concentration at places and causes localised reduction of

Table 1. Mechanical properties of PE, PP and clay containing blends before and after solar exposure

	Control		Exposed	
	Strength (MPa)	Elongation (%)	Strength (MPa)	Elongation (%)
PE: PP	22..5 ± 2.94	870 ± 47	13.72 ±3.92	680 ± 59
PE: PP:NCl	31.8 ± 2.94	700 ± 32	9.8 ± 2.94	560 ±74

PE: Polyethylene, PP: Polypropylene, NCl: Nano clay

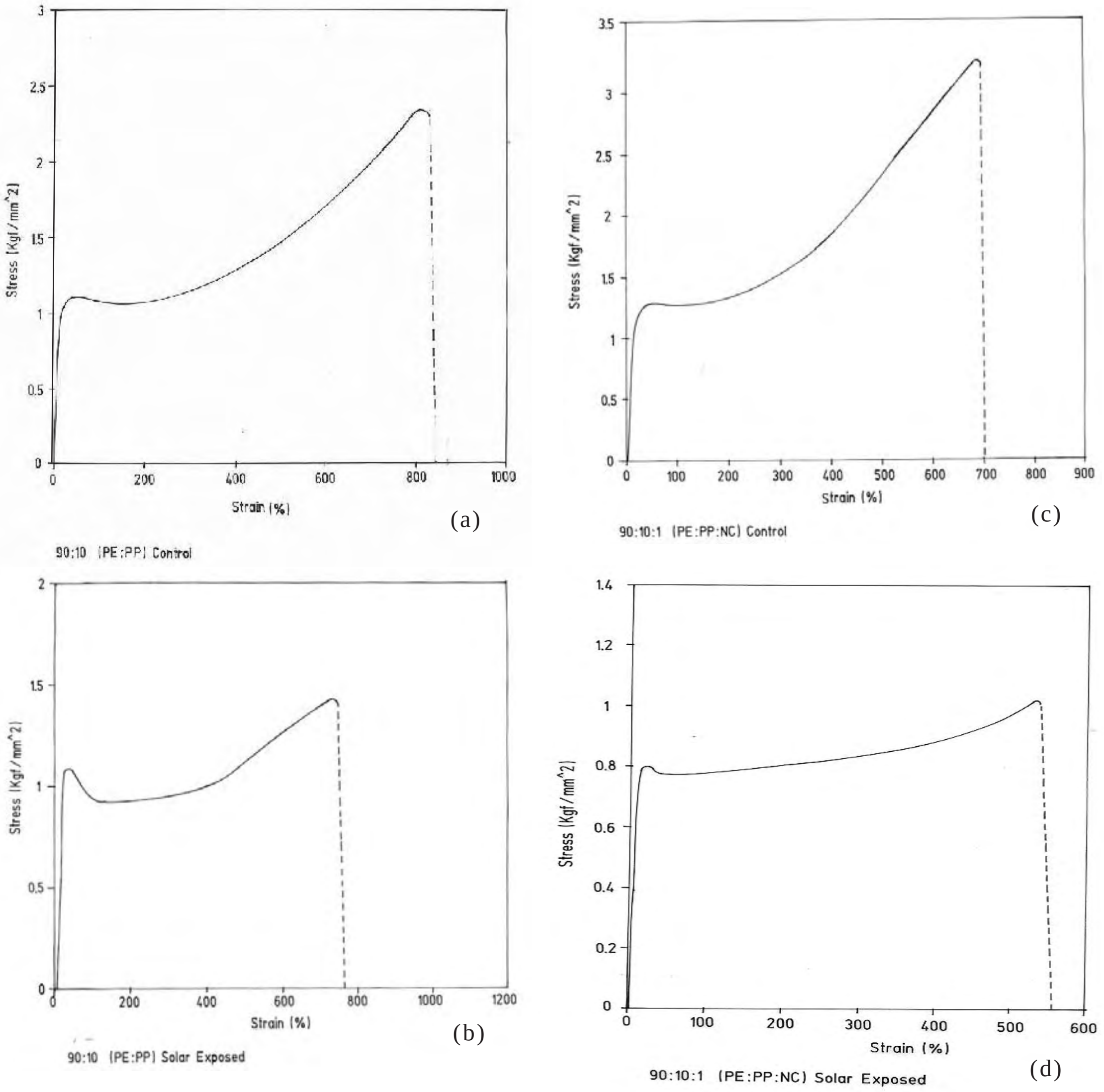


Figure 1. Stress-strain curve of films. (a) PE:PP, Control; (b) PE:PP, solar-exposed; (c) PE:PP:Clay, Control; (d) PE:PP:Clay, solar-exposed.

the yield stress during straining[19]. The steeper initial part of the curve indicates stiffness of the material that sets in after the solar exposure. Both stress, as well as strain, registered lower values than their respective control samples.

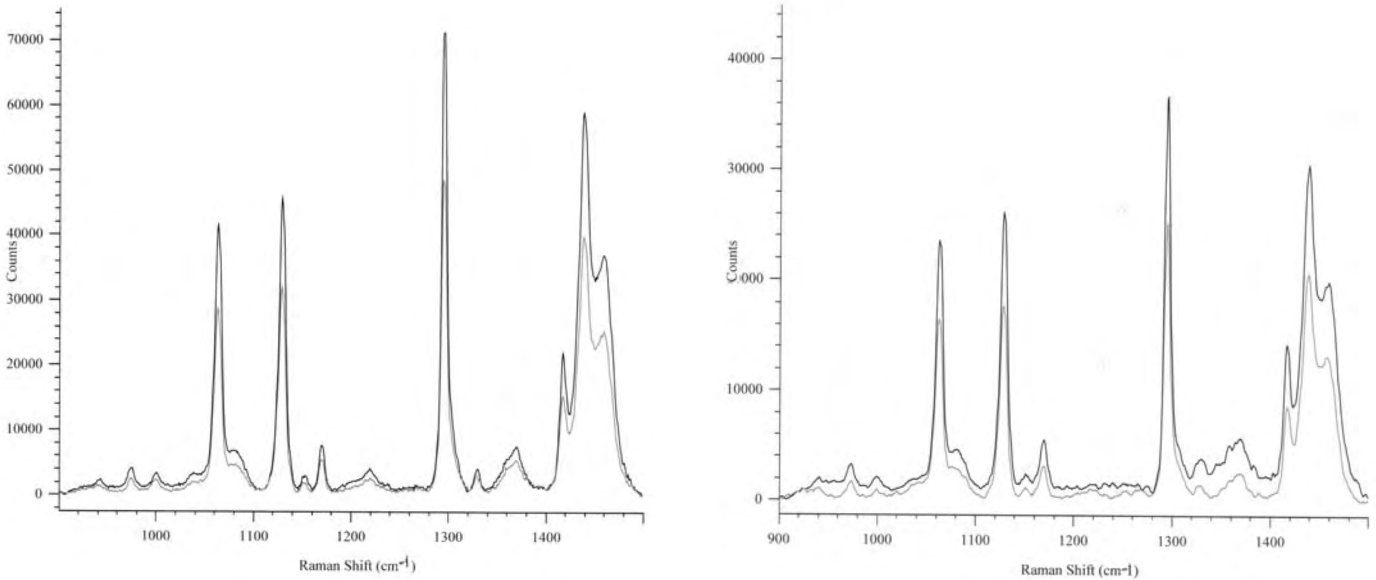
Figure 2(a) shows the Raman spectra of the control polyethylene and polypropylene films superimposed on a spectra of photo-exposed film between 900 cm^{-1} to 1500 cm^{-1}. The spectra shows the characteristic peaks of polyethylene[20] around 1062 cm^{-1}, 1080 cm^{-1}, 1129 cm^{-1}, 1169 cm^{-1}, 1295 cm^{-1}, 1360 cm^{-1}, 1415 cm^{-1}, 1440 cm^{-1} and 1470 cm^{-1}. The peaks at 940 cm^{-1}, 973 cm^{-1} and 998 cm^{-1} correspond to polypropylene and compatibiliser, whereas, peaks at 1152 cm^{-1}, 1218 cm^{-1}, 1328 cm^{-1} and 1460 cm^{-1}, correspond to polypropylene. Exposure to solar radiation resulted in a Raman spectra having decreased intensity for all the characteristic peaks of PE and PP. The peak at 1062 cm^{-1}, which is assigned to asymmetric *C-C* stretching mode in crystalline regions of PE registered lower intensity. The band at 1080 cm^{-1}, due to the *C-C* stretching mode in amorphous region, also show perceptible change in the intensity. The peak at 1129 cm^{-1} due to symmetric *C-C* stretching mode in the crystalline region of the polyethylene registered decreased intensity after solar exposure. The Raman intensity at 1170 cm^{-1} resulting from CH_2 rocking mode in crystalline region registered a decreased intensity compared to the control unexposed sample. The peaks at 1295 cm^{-1}, normally assigned to CH_2 twisting vibration mode in the crystalline region show lower intensity after exposure to solar radiations. The peak at 1370 cm^{-1} due to CH_2 bending in both the crystalline as well as amorphous region registered decreased intensity. However, there was very little change in the Raman intensity at 1415 cm^{-1} resulting due to CH_2 wagging in crystalline region after the exposure. The peak at 1440 cm^{-1} corresponding to CH_2 deformation in the region, where both crystalline and amorphous phases contribute for Raman scattering registered decrease in the intensity over the control unexposed sample. Small but sharp peak at 1470 cm^{-1} which was present in the control sample having contributions from CH_2 bending from crystalline and amorphous phase, disappeared after solar exposure.

Figure 2(b) shows the Raman spectra of the control PE and PP (90:10) and clay film, superimposed on a spectrum of photo-exposed film between 900 cm^{-1} and 1500 cm^{-1}. It was observed that the intensity of all the major peaks in the exposed film had reduced. The reduction in intensity was of the order of 30 per cent compared to their corresponding controls. Likewise, the characteristic bands representing PP had also registered reduction in intensities after exposure,which was higher in clay-containing film compared to the films without it.

Figure 3(a) shows IR spectra of unexposed and the solar exposed PE:PP blended films and [Fig 3(b)] shows IR spectra of unexposed and solar exposed clay-containing PE:PP films, for 45 days. The IR spectrum of film before the solar exposure was devoid of peaks corresponding to carbonyl and hydro peroxide absorptions. On the other hand, spectra of exposed films showed an increase in hydroperoxide (~ 3400 cm^{-1}) and carbonyl (~1715 cm^{-1}) absorptions. It has been reported that exposure to solar radiation induced yellowing and loss of strength in PE and generation of carbonyl group and loss in tensile strength in PP[7,14]. It is well known that both UV exposure and γ irradiation generate hydro peroxide and carbonyl product on PP films[2,15,16]. The present study reveals that the developed blended membrane shows high sensitivity towards photooxidation as shown by hydroperoxide and carbonyl absorption in spite of low percentage of incorporated PP. It has been reported that exposure to solar radiation induced yellowing, loss of strength and generation of carbonyl group in polyolefins[7,14]. Addition of PP in PE in the present case has resulted in a system, having propensity for faster photodegradation than PE.

It is known that photooxidation of polyolefins by exposure to solar radiations (weathering) is a complex process involving macromolecular mobility, diffusion-controlled reactions, reactions caused by free radicals resulting into chain scission as well as cross-linking and formation of hydroxyl/hydroperoxy and carbonyl groups[10,16]. These factors make the structure of the exposed sample highly strained. Effects of mechanical strain on the intensity reduction of Raman scattering for all the peaks in high-density polyethylene (HDPE) has already been reported[21]. The decrease in intensity has been attributed to the imposed strain in *C-C* bonds. The intensity of a Raman band is also governed by the change in polarisability, as atoms pass through their equilibrium positions as a result of incident energy. The solar exposed films indicate change in polarisability as indicated by the Raman spectra of the films. Oxidation of semicrystalline polymers such as polyolefins having high chain mobility at environmental conditions is generally considered to occur predominantly in the amorphous region, which can be treated as a boundary phase of the neighbouring crystalline regions[22, 23]. Thus one of the manifestations of photooxidation would be decrease in the Raman sensitive bands and increase in carbonyl groups.

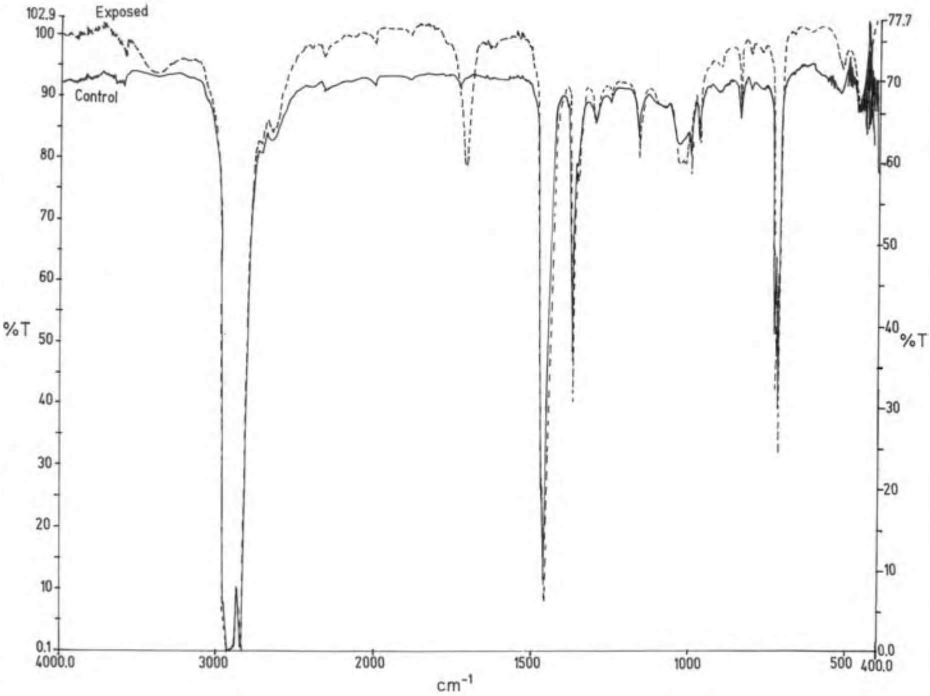
Figure 4(a) shows the liquid nitrogen fractured surface of unexposed polyethylene:polypropylene film. The fractured ends of the unexposed film show deformation in the form of ridges (bundles of fibrils) parallel across the width of the film. [Fig. 4(b)] shows the fractured end of solar- exposed film. The fracture surface was relatively smooth that consisted of small domains of fibrils and revealed discontinuities in the fracture. [Fig. 4(c)] shows the liquid nitrogen fractured end of control film (PE:PP:clay). Compared to [Fig. 3(a)], the fracture is devoid of long fibrils and appeared smooth. [Fig. 4(d)] shows the fractured end of the film after the



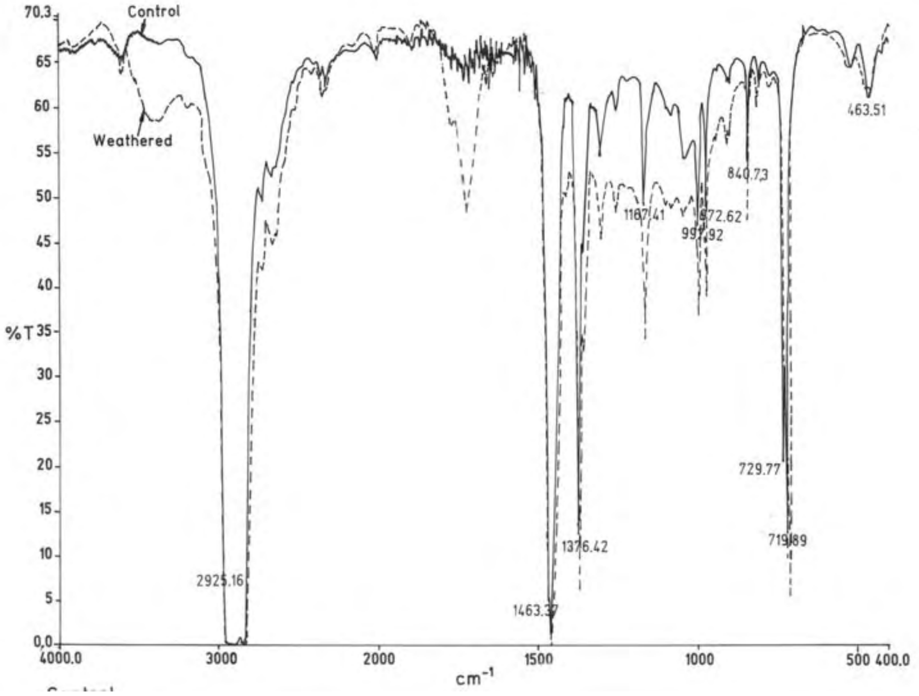
(a)

(b)

Figure 2. (a) Raman spectra of control film (black) and photo-exposed PE:PP film (gray); 900 cm^{-1} to 1500 cm^{-1}. (b) Raman spectra of control film (black) and photo-exposed PE:PP:Clay film (gray); 900 cm^{-1} to 1500 cm^{-1}.



(a)



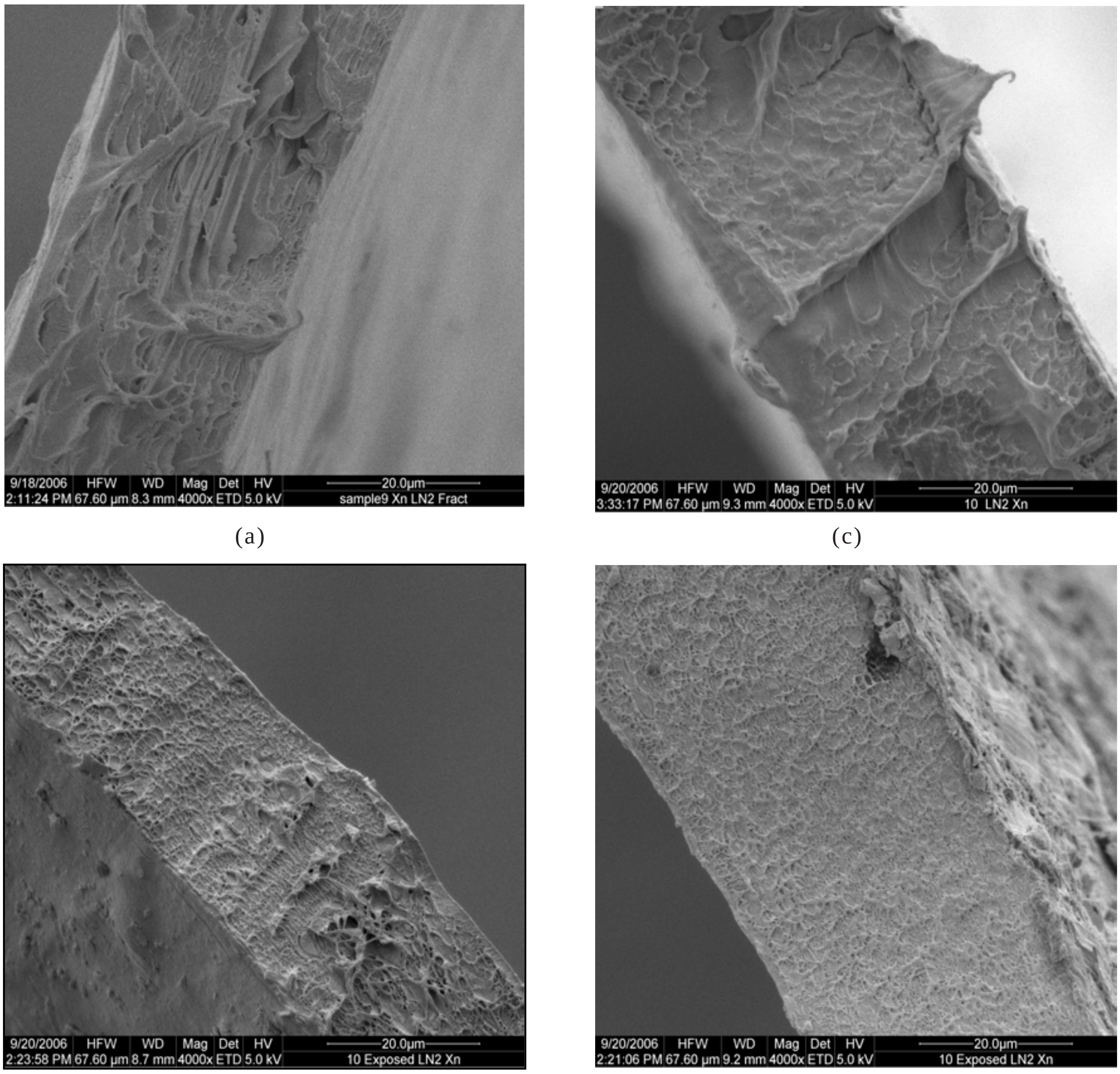
(b)

Figure 3. FT IR spectra films: (a) unexposed and solar-exposed PE:PP control, and (b) unexposed and solar-exposed PE: PP: clay.

solar exposure. The fracture surface was smooth and had minute but separated bundles of microfibrils. The height of these substructures was very small and that perhaps indicates catastrophic nature of the break. The stress-strain curves (Fig. 1) indicate good correlation between the fracture morphology and the mechanical behaviour of the films.

4. CONCLUSIONS

The films made from the composition having PE, PP, and clay, registered superior mechanical properties as compared to the film without clay. The solar-exposed films indicated brittleness as reflected by their stress-strain behaviour. The clay-containing films show higher degradation in the mechanical properties. The Raman studies revealed reduced



(a) (c)

(b) (d)

Figure 4. Scanning electron micrograph of liquid nitrogen-fractured film surface (4000X): (a) unexposed PE:PP, (b) exposed PE:PP, (c) unexposed PE:PP: clay, (d) exposed PE:PP: clay.

scattering due to changes in the morphology after the solar exposure. The IR spectra indicated formation of oxidation products in the solar-exposed films. Scanning electron microscopy revealed degradation-induced brittle fracturesin these films.

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