

Accelerating Role of Clay in Photo-Oxidation of Polypropylene/Clay Multifilament Yarns

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Abstract Photo-oxidative degradation of polypropylene/clay multifilament yarns containing different amounts of clay was investigated. These samples and pure polypropylene (PP) multifilaments were exposed to long wavelength radiations ($\lambda > 300$ nm) under atmospheric condition of constant temperature and relative humidity. The photo-oxidative stability was studied using FTIR spectroscopy, tensile testing and microscopy. The results indicate that the addition of clay particles decreases the stability of PP/clay composites to photo-oxidative degradation according to comparison with pure PP. From FTIR study and tensile properties, it was also found that the multifilaments with higher clay loading reveals a faster loss of mechanical properties, higher photo-oxidative product formation and more reduction in the induction time of photo-oxidation. Moreover, the crack formation on surface of irradiated filaments corresponds well to the conclusions in tensile properties and FTIR characterization.

Keywords: Photo-oxidation; Polypropylene; Multifilament yarns; Nanoclay; UV radiation.

INTRODUCTION

Polypropylene (PP) is a thermoplastic polymer used in a wide range of applications, including packaging and labeling, textiles (carpets, nonwovens, ropes and thermal underwear), stationery, automobile industry, plastic parts and reusable containers of various types, non-durable goods, construction materials, laboratory equipment, loudspeakers and polymer banknotes. As a result, polypropylene has become one of the most versatile polymers.

Pure polypropylene does not absorb radiation with wavelengths longer than 200 nm. However, the photo-oxidation of polypropylene has been the subject of many publications. The absorption is believed to be due to the chromatographic groups such as double bonds, carbonyl groups, hydroperoxy groups introduced during processing, traces of polymerization-catalysts, and charge transfer (CT) complexes formed between PP and oxygen^[1, 2].

Micro-and macro-composites are made from polymers filled with synthetic or natural inorganic particles to improve the properties or to cut the costs of the end product. Polymer/layered silicate nanocomposites (PLSN) such as organic modified montmorillonite (OMMT) have recently received considerable attention, both in polymer industries and in academia due to remarkable enhancement in the improvement of properties at very low loading levels^[3–5].

Similar to the pure PP, the photo-oxidative damage of polyolefin/clay nanocomposites is the key subject for outdoor use. The photo-oxidation of polyolefin/clay composites has been the subject of many publications^[6, 7] because of environmental durability. These studies included nanocomposites with montmorillonite (MMT) and

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different polyolefins such as *i*PP^[8–16], PE^[17–27], *s*PP^[28–30] and PPgMA^[31–34]. It was clearly illustrated that the presence of the clay particles causes a higher instability of PLSNs to photo-oxidative degradation with respect to the pure polymers. The existence of iron impurities in clay particles is able to accelerate the reactions of the chain branching step^[1, 12, 31]. The presence of the structural elements in the clay, such as Fe²⁺ and Fe³⁺ and also the thermal degradation of organic modifier of OMMT accelerate the photo-oxidation rate of the composite.

In spite of photo-oxidation of PP in the environment, the timescale is too long for it to be considered an environmentally friendly degradable polymer. The solution lies in accelerating the natural photo-oxidation of the polymers^[35]. There are many methods to obtain safe waste disposal like the photo-oxidation before exposure to the biotic environment^[36]. Adding clay particles could lead to increase the rate of photo-oxidation before exposure to the biotic environment.

As discussed in the literatures^[12, 37–39], the photo-oxidation of PP depends upon several intrinsic and extrinsic factors. Extrinsic factors involve UV radiation wavelength and intensity, temperature, exposure time, oxygen pressure and melt-processing conditions. Intrinsic factors are thickness, shape, size, chromophores (impurities or produced during melt processing), physical and chemical structure.

Physical structure includes two important parameters: molecular orientation and degree of crystallinity. These two parameters have a significant influence on the restriction of oxygen or radical mobility. It is difficult to predict whether the restriction of oxygen or radical mobility will dominate, and there are examples in the literature where the overall degradation rate increases with crystallinity and orientation, and others in which the opposite effect occurs^[37].

Photo-oxidation is known to be more prominent on the surface than in the bulk^[40]. The fibers have a considerably larger specific surface (surface area per volume) in comparison with moulded articles and films. As a result, it can be expected that the fibers are more prone to photo-oxidation^[41]. Photo-oxidation leads to extensive chain scission in the surface layers of filaments, resulting in the rapid loss in elongation at break^[42]. Significant morphological and structural changes accompany photo-oxidation. Fibrillar zones in filaments are more resistant to photo-oxidative scission than the surrounding non-fibrillar matrix^[43].

It is reported that the addition of nanoclay resulted in significant changes in the structure, morphology and mechanical properties of nanoclay/PP fibers. There is an example in the literature that the addition of clay particles resulted in a reduction in molecular orientation of the fibers. This reduction in the molecular orientation of the fibers highly impacted the mechanical properties of fibers^[44]. As a result, the changes in the structure, morphology, shape, size and mechanical properties of nanoclay/PP fibers have a significant influence on the photo-oxidation process.

Up to our knowledge, most of the studies on photo-oxidation of PP/clay nanocomposites have been performed on polymers in the film or mold form and there are just a few studies on the photo-oxidation of multifilament yarns from polypropylene/clay composites^[45]. In form of fiber, much research has been reported on the preparation, characterization and application PP/clay, focusing on the dispersed morphology of the clay particles, their excellent properties, and their rheological behavior, *etc.*^[44, 46–58]. Therefore, in this paper, we focus on the photo-oxidation of polypropylene/clay multifilaments, in which the concentration of the clay loading was studied.

EXPERIMENTAL

Materials

Commercial PP/PPgMA/OMMT master batch was supplied by Notrino Co. (Iran). The OMMT loading and compatibiliser (PPgMA) content in this master batch are the same and equal to 30% and the rest is fiber-grade polypropylene with melt flow index of 17 g/10 min (230 °C/2.16 kg). All data were given by the supplier. For dilution of master batch, polypropylene homopolymer, 512P, with a melt flow index of 25 g/10 min (230 °C/2.16 kg), was obtained from Sabic Co. (Saudi Arabia). As quoted by producer, there is no UV stabilizer in this granule.

Compounding and Sample Preparation

For producing composite multifilaments, the PP granule and master batch were first physically blended and then fed to extruder. The composite multifilament yarns containing 0.5 wt%, 1 wt%, 2 wt%, and 3 wt% clay were obtained by dilution of master batch. Abbreviated names, the amount of OMMT and compatibiliser used for different samples are shown in Table 1. Pure PP and PP/PPgMA/OMMT multifilament yarns were prepared with melt spinning by an Automatik pilot plant-spinning machine (Germany). This machine has an extruder using two spinning nozzles. Two 36 holes spinnerets of 0.25 mm hole diameter were used for spinning of partially oriented multifilament yarns at the spinning temperature of 240 °C and the take-up speed of 2000 m/min.

Table 1. Composition of the samples

Sample code	OMMT ^a (wt%)	PPgMA ^b (wt%)
PP0	0	0
PP0.5	0.5	0.5
PP1	1	1
PP2	2	2
PP3	3	3

^a OMMT = organo-modified montmorillonite;

^b PPgMA = maleic anhydride-grafted polypropylene copolymer

Ultraviolet Exposure

Irradiation was carried out in a covered, open-air chamber at room temperature (25 °C and 55% relative humidity). Samples were exposed to irradiation at $\lambda > 300$ nm (UVA irradiation) from two EVERSUN L40W/79 K Osram fluorescent lamps. Samples were laid parallel to the longitudinal axes of the lamps in a fixed place. The distance between the light source and samples was 35 cm. The samples for mechanical tests were exposed to irradiation under the tension of 200 g weight.

Characterization Methods

X-ray diffraction (XRD) analysis was done with an XPert Pro MPD (PANalytical) Diffractometer. The X-ray beam was nickel-filtered CuK α radiation of wavelength 0.154 nm operated at 40 kV and 30 mA. Diffraction spectra were obtained over a 2θ range of 1°–10° at a scanning rate of 0.02°/s and the interlayer spacing (d) for (001) plane was calculated using Bragg's equation $\lambda = 2d\sin\theta$, where λ is the wavelength of X-ray radiation.

A Nicolet 670 FTIR spectrometer was used to record the spectra between 4000 cm⁻¹ and 400 cm⁻¹ in transmission mode. The nominal resolution of the spectrometer was 4 cm⁻¹, averaging 40 scans. Following the published works^[37, 59], the band at 2720 cm⁻¹ was taken as reference peak. The range of 2750–2694 cm⁻¹ centered at 2720 cm⁻¹ was not affected by photo-oxidation^[59]. The carbonyl [CO] and hydroxyl [OH] indices of the samples were determined from the ratio of the areas of the absorbance bands in the ranges of 1850–1654 cm⁻¹ and 3600–3250 cm⁻¹ regions to the range of 2750–2694 cm⁻¹, respectively.

Mechanical properties of multifilament yarns, including tensile strength and elongation at break, were measured at room temperature with a constant rate of extension (EMT 3050 tensile tester, Iran). The gauge length and the cross-head speed were 4 cm and 200 mm/min, respectively.

Surfaces of filaments were examined through a low power Karl Zeiss light microscope.

RESULTS AND DISCUSSION

Wide-angle X-ray Diffraction (WAXD)

The master batch film and PP/PPgMA/OMMT filaments with different clay loading are characterized by wide angle X-ray diffraction in the range of $2\theta = 1^\circ$ – 10° and their patterns are shown in Fig. 1.

The X-ray diffraction pattern of the master batch film exhibits a sharp peak at $2\theta = 3.25^\circ$ that is referred to d_{001} ^[3–5], corresponding to an interlayer d -spacing of 2.7 nm. Another peak at $2\theta = 6^\circ$ – 8° region is due to the incomplete ion exchange originated during the modification process of clay^[60] (see inset in Fig. 1). The X-ray patterns for the fiber composites are considerably different from that of the master batch film. Figure 1 shows the sharp peak at $2\theta = 3.25^\circ$ and the broad feature in the $2\theta = 6^\circ$ – 8° range of clay in the samples PP0.5 and PP1

disappeared. The absence of sharp peaks denotes that exfoliation and/or disordering of the clay may have occurred. The diffuse nature of the pattern suggests either a form of intercalated nanocomposite or a mixed intercalated-exfoliated system (or simply a disordered system). The XRD traces suggest that the samples PP0.5 and PP1 are probably a mixture of micro- and nanocomposite; in the other words, the fractions of micro- and nano-dispersed components are present. As shown in Fig. 1, the (001) base peak position shifts to a lower angle, from $2\theta = 3.25^\circ$ ($d = 2.7$ nm) for OMMT to $2\theta = 2.1^\circ$ ($d = 4.2$ nm) for the samples PP2 and PP3, indicating poor clay dispersion in the samples with higher clay loading. Moreover, an increase in height of peak with increasing in clay loading shows that decreasing in the amount of exfoliated clay platelets in higher clay loading.

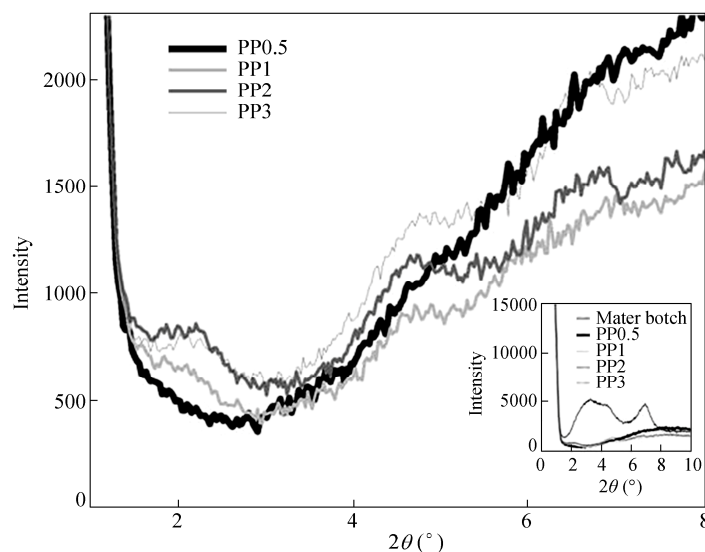


Fig. 1 XRD patterns of master batch film containing clay (inset) and PP/clay multifilament yarns

Infrared Analysis

Figure 2 depicts a typical FTIR spectrum of pure PP multifilament yarn (PP0) in the region of 4000 cm^{-1} to 400 cm^{-1} , irradiated for different period with UVA radiation. There are no main changes occurred in the regions of FTIR spectrum characteristic of carbonyl, $\text{C}=\text{O}$ ($1850\text{--}1654\text{ cm}^{-1}$) and hydroxyl, POH and/or hydroperoxide, POOH ($3600\text{--}3250\text{ cm}^{-1}$) groups. Even after 1400 h of exposure to long wavelength radiation (UVA), the FTIR spectrum of PP0 sample does not show any change with time.

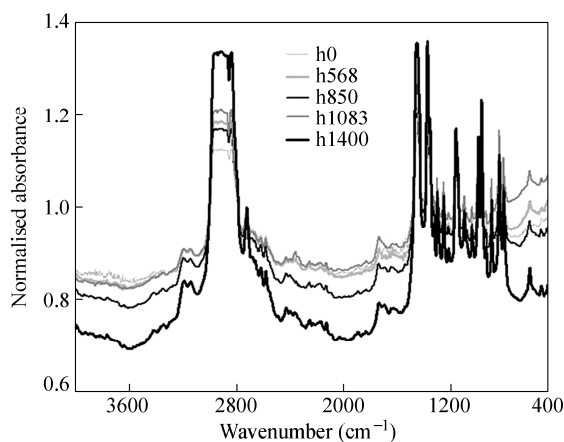


Fig. 2 Typical FTIR spectra of pure PP multifilament yarns: (h0) not irradiated, (h568) irradiated for 568 h, (h850) irradiated for 850 h, (h1083) irradiated for 1083 h and (h1400) irradiated for 1400 h with UVA lamps

However, the FTIR spectra of PP/PPgMA/OMMT multifilaments show changes with time of UV exposure. Figure 3 depicts typical FTIR spectra of the samples PP0.5, PP1, PP2, and PP3 in the region of 4000 cm^{-1} to 400 cm^{-1} , irradiated for different period with UV lamps. Similar to the photo-oxidation of PP^[38, 39], the main changes occurred in the regions of FTIR spectra characteristic of carbonyl, C=O ($1850\text{--}1654\text{ cm}^{-1}$) and hydroxyl, POH and/or hydroperoxide, POOH ($3600\text{--}3250\text{ cm}^{-1}$) groups.

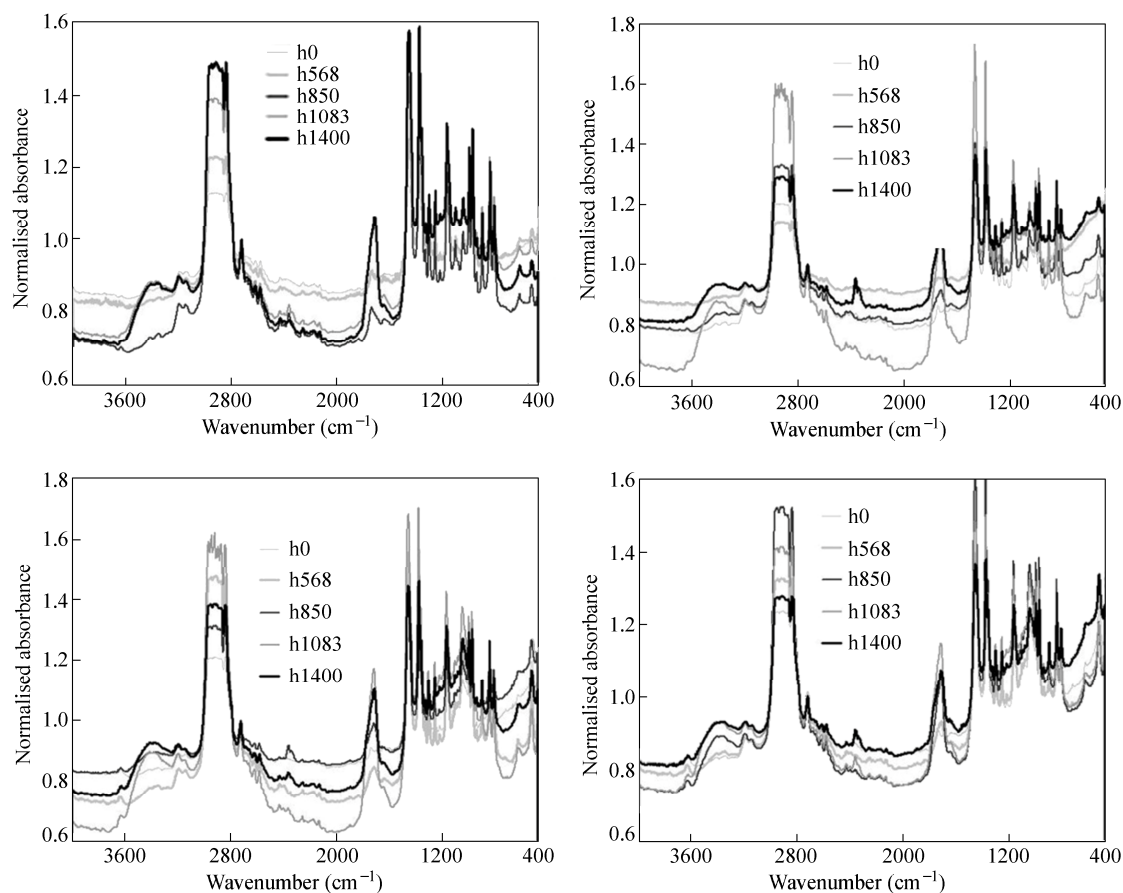


Fig. 3 Typical FTIR spectra of PP/clay multifilament yarns: (h0) not irradiated, (h568) irradiated for 568 h, (h850) irradiated for 850 h, (h1083) irradiated for 1083 h and (h1400) irradiated for 1400 h with UVA lamps

As the photo-oxidation proceeds, the amount of photo-oxidative products in PP/PPgMA/OMMT multifilaments increases, where the kinetics of the evolution of C=O groups and —OH groups are illustrated in Figs. 4 and 5, respectively. As shown in Fig. 2, there are no significant changes of carbonyl index and hydroxyl index with time in pure PP during photo-oxidation. Thus, the presence of clay particles causes the formation of C=O and —OH products during photo-oxidation. In addition, after an initial period of 850 h, the increase of the oxidation products is considerable for the sample PP0.5. Nonetheless, this initial period, called induction time, is much longer than that of the samples PP1, PP2, and PP3. Therefore, there is a decrease in an induction time by increasing the amount of clay in PP according to Figs. 4 and 5.

Consequently, the presence of the clay and PPgMA reduce the photo stability of PP/PPgMA/OMMT multifilaments as compared to the pure PP fiber in photo-oxidative degradation. This results in a shortening of the induction time. This finding is in agreement with previous investigations^[9, 10, 22, 23, 31, 34]. Moreover, by increasing the amount of clay in PP fibers, more photo-product forms.

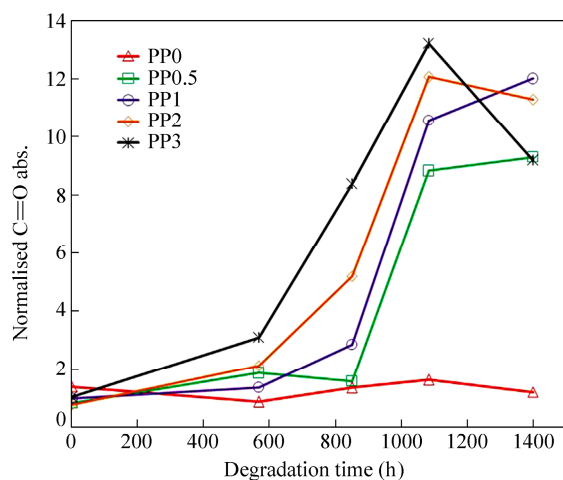


Fig. 4 C=O index of FTIR absorbance as a function of photo-oxidation time for pure PP and PP/clay multifilament yarns

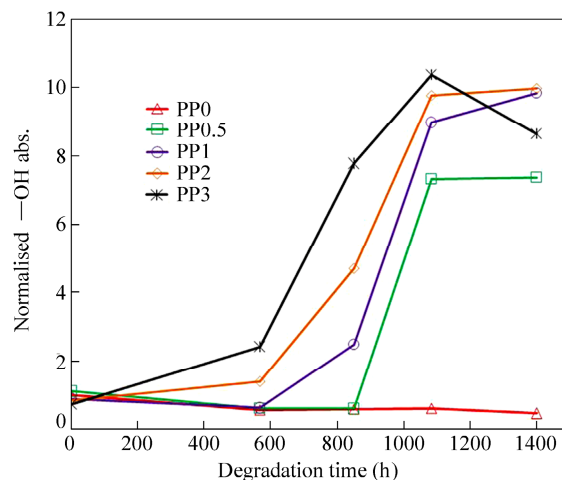


Fig. 5 —OH index of FTIR absorbance as a function of photo-oxidation time for pure PP and PP/clay multifilament yarns

As mentioned in the literatures^[8–34], it is proved that the presence of structural elements such as Fe^{2+} and Fe^{3+} in MMT, the thermal decomposition of alkyl ammonium salts in OMMT, photo- and thermo- instability of PPgMA and melt processing conditions lead to accelerate the photo-oxidation of PP/PPgMA/OMMT multifilaments in comparison to the pure PP fiber. Among them, the presence of structural elements such as Fe^{2+} and Fe^{3+} in MMT has a strong effect on the photo instability of PP/PPgMA/OMMT samples^[21].

Tensile Properties

Figure 6 gives information about the changes of tensile strength of the pure PP fiber and PP/PPgMA/OMMT multifilament yarns against exposure time in UV chamber. Before UV exposure, the tensile strength of the pure PP fiber is about 20.2 cN/tex and the tensile strength of the fiber exhibits decreasing trend with clay loading. The tensile strength of the samples PP0.5, PP1 and PP2 has an 18%, 25% and 36% decrease over that of the pure PP fiber. This behavior was explained previously in the literature^[44]. Upon 1005 h UV exposure, tensile strength of the pure PP fiber remains unchanged while tensile strength of the samples PP0.5, PP1 and PP2 decreases dramatically after 620 h UV irradiation. For the more, Fig. 7 shows the ratio of tensile strength of the samples at the different times of photo-oxidation to the tensile strength of original ones. The reduction of tensile strength in the sample PP0.5 is less intense than that of in the samples PP1 and PP2 upon photo-oxidation time. This indicated that the rate of tensile strength reduction increased with increasing the clay content from 0.5% to 1%. Besides, this reduction in tensile strength is almost the same for higher clay loadings in the samples PP1 and PP2. As a result, drop in the tensile strength of the PP/PPgMA/OMMT multifilaments is very sharp and occurs at photo-oxidation times much shorter than that of the pure PP fiber.

Generally, the elongation at break is a parameter to monitor the photo-oxidation of polymers as it is very sensitive to the molecular and morphological changes undergone by the polymer during irradiation^[20, 22, 23]. Figure 8 illustrates the alterations of the elongation at break of the pure PP fiber and PP/PPgMA/OMMT multifilaments against exposure time. Before UV irradiation, there is no significant difference in elongation of the pure PP fiber and PP/PPgMA/OMMT multifilaments. After 290 h UV irradiation, it is clearly seen that the elongation almost doubles for both samples PP0 and PP/PPgMA/OMMT multifilaments. However, after 620 h UV irradiation, there can be seen different trend in the changes of elongation at the different times of photo-oxidation for the pure PP and PP/PPgMA/OMMT multifilaments. After 1005 h UV irradiation, the elongation of the sample PP0 remains almost constant whereas the elongation of PP/PPgMA/OMMT multifilaments decreases against exposure time. In agreement to the drop in the tensile strength, the elongation of the PP/PPgMA/OMMT multifilaments reveals a continuous decrease upon UV irradiation. Finally, after 1005 h UV irradiation, the

elongation of PP/PPgMA/OMMT multifilaments reaches to fewer than 10%. As a result, the presence of clay particles reduces the photo-oxidation induction time and this result is in agreement with the other findings^[9, 10, 22, 23, 31, 34].

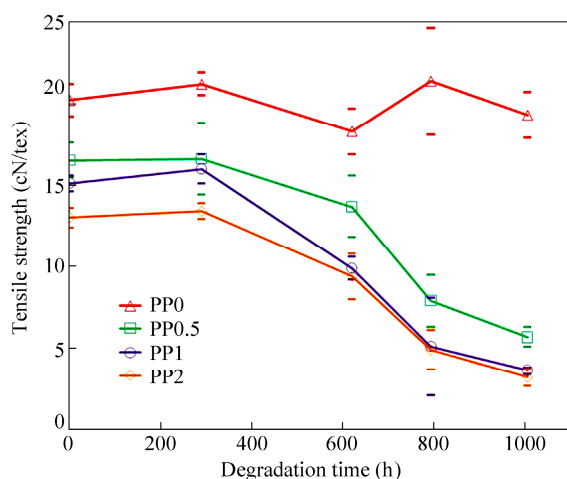


Fig. 6 Tensile strength as a function of photo-oxidation time for pure PP and PP/clay multifilament yarns

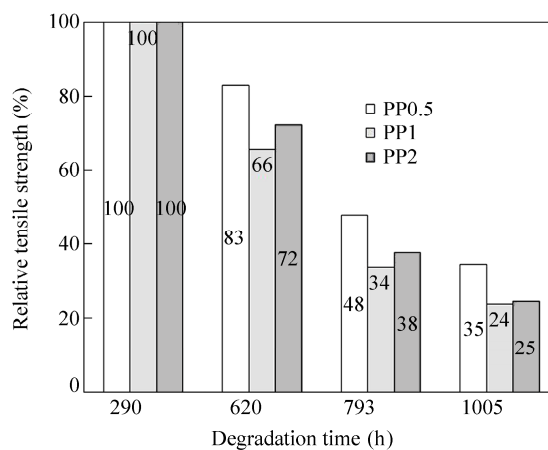


Fig. 7 Relative tensile strength as a function of photo-oxidation time for PP/clay multifilament yarns

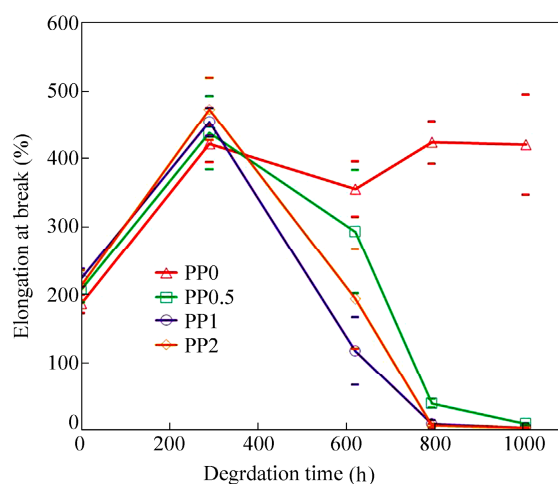


Fig. 8 Elongation at break as a function of photo-oxidation time for pure PP and PP/clay multifilament yarns

Moreover, Figure 9 illustrates the ratio of elongation of PP/clay fibers at the different times of photo-oxidation to the elongation of original ones. The reduction of elongation in the samples PP1 and PP2 is more drastic than that of in the sample PP0.5 upon photo-oxidation time. Besides, this reduction is almost the same for the samples PP1 and PP2. After 290 h UV irradiation, the elongation at break of the pure PP fiber and PP/PPgMA/OMMT multifilaments increases dramatically. The pure PP fiber is endurable to photo-oxidation; therefore the elongation of this sample remains unchanged after the initial increase during UV exposure. In previous research, this behavior is attributed to the stretching of tie molecules, which are located between crystalline lamellae^[61]. However, it seems that there is no evidence to apply this theory for our work and therefore we still do not fully understand the reason behind these changes.

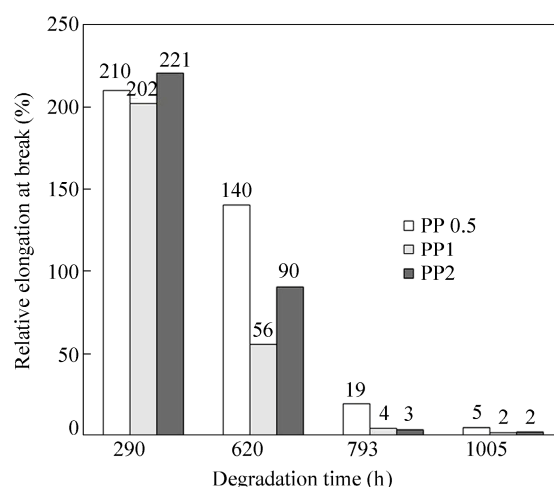


Fig. 9 Relative elongation at break as a function of photo-oxidation time for PP/clay multifilament yarns

The results of mechanical properties indicate that drops of tensile strength and the elongation at break correspond well to the results obtained by FTIR characterization. The much higher rate of photo-oxidation of PP/PPgMA/OMMT multifilaments is supplementary supported by a similar trend detected in the changes of tensile strength and elongation at break.

Table 2 illustrates the slope of C=O and —OH indices versus time of UV exposure between the 568 h and 1083 h. The results show that the rate of photo-oxidation of PP/PPgMA/OMMT multifilaments depends on clay loading. The rate of photo-oxidation increases as the clay loading increases from 0.5 wt% to 1.0 wt%. However, there is no significant difference in the photo-oxidation rate between the samples PP1, PP2, and PP3. In addition, this is confirmed by the mechanical properties (Figs. 7 and 9), where the drops in tensile properties for the samples PP1 and PP2 is the same. As the clay concentration in the polymer matrix increases, the rate of UV degradation enhances which is in agreement with previous investigation^[13, 27].

Table 2. Slopes of C=O and —OH indices versus photo-oxidation time

Sample	$\Delta(\text{C=O index})/\Delta(t) \times 10^2 \text{ (h}^{-2}\text{)}$	$\Delta(\text{—OH index})/\Delta(t) \times 10^2 \text{ (h}^{-2}\text{)}$
PP0.5	1.35	1.30
PP1	1.79	1.62
PP2	1.93	1.63
PP3	1.97	1.55

According to literature review^[9, 11, 13, 14], the rate of photo-oxidation of polyolefin/clay is higher than that of pure matrix. In addition, it is reported that the observed acceleration is not due to faster photo-oxidation but rather due to a reduction of the oxidation induction time^[22, 26]. Our results demonstrate that the rate of photo-oxidation of PP/PPgMA/OMMT multifilaments depend on clay concentration.

Light Microscopy

Figure 10 shows optical micrographs of PP/PPgMA/OMMT multifilaments irradiated for different times captured by the optical microscope. When the time of UV exposure is less than 850 h, no transverse crack is detected. However thereafter, cracks are observed on the surface of the samples PP2 and PP3. It should be noted that the cracks are detected on the surface of the samples PP1 and PP0.5 after 1083 h and 1400 h UV irradiation. These are common on the surface of the photo-degraded polymers^[38, 39].

Moreover, the formation of cracks proves the loss in the mechanical properties due to photo-oxidation. By considering Figs. 8 and 10, it can be concluded that the cracks are observed when the elongation at break in PP/PPgMA/OMMT multifilaments is less than 9%.

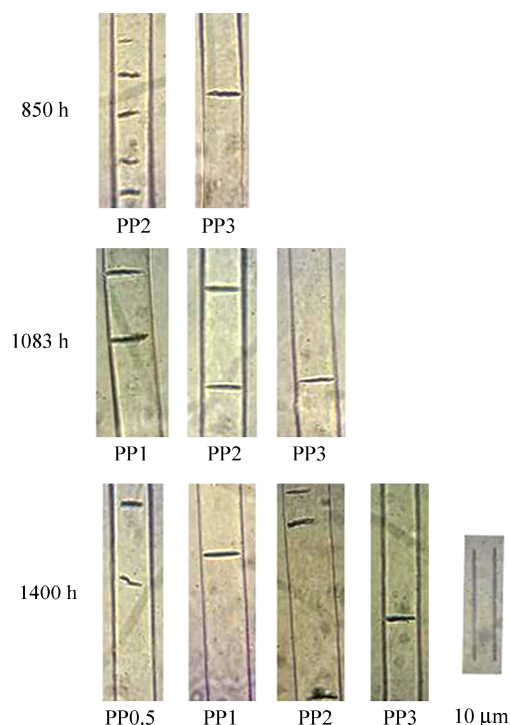


Fig. 10 Light microscope micrographs of PP/clay multifilament yarns in longitudinal view, photo-degraded for different times

Fayolle *et al.*^[62] put forward an argument for crack formation in the process of thermal oxidation. According to their view, PP oxidation results in a mass loss due to volatile emission, and density increase due to oxygen incorporation to the hydrocarbon macromolecular skeleton. The combination of these two factors causes the volume reduction and hence the crack formation. Moreover, there is a similar argument for crack formation in photo-oxidation of PP fibers^[39]. In our experimental results, the cracks appear after the accumulation of C=O and —OH as detected by FTIR and therefore it can be concluded that the volatile products emit during the accumulation of carbonyl and hydroxyl groups.

In addition, there is a dramatic increase in the C=O and —OH indices after 568 h UV irradiation and then after 1083 h UV irradiation these indices level off (see Figs. 4 and 5). This could be an evident for volatile emission of photo-products leading to formation of cracks.

CONCLUSIONS

The effect of clay content on photo-oxidation of PP/clay multifilament yarns upon UVA exposure was investigated. The presence of the clay particles promotes the degradation of PP fiber during photo-oxidative degradation. The presence of iron impurities in clay particles would be the main cause of this behavior. The most interesting finding from this research is the effect of the clay loading on the rate of photo-oxidation of PP fiber. Up to 1.0 wt% clay, there is a significant increase in the rate of photo-oxidation and decrease in the induction time while no more change is observed at higher clay loadings.

The crack formation on the surface of the filaments is also dependent on clay concentration in composite fibers in which the cracks appear faster in filaments containing higher clay loadings. Moreover, the crack formation begins when significant chemical modification occurs as detected by FTIR. Significant drop in tensile properties of the irradiated samples happens before crack formation.

REFERENECES

- 1 Rabek, J.F., "Polymer Photodegradation: Mechanisms and Experimental Methods", Chapman & Hall, London, 1995
- 2 Allen, N.S. and Edge, M., "Fundamental of Polymer Degradation and Stabilization", Elsevier Applied Science Publishers, New York, 1992
- 3 Alexandre, M. and Dubois, P., *Mater. Sci. Eng.*, 2000, 28: 1
- 4 Ray, S.S. and Okamoto, M., *Prog. Polym. Sci.*, 2003, 28: 1539
- 5 Pavlidou, S. and Papaspyrides, C.D., *Prog. Polym. Sci.*, 2008, 33: 1119
- 6 Pandey, J.K., Reddy, K.R., Kumar, A.P. and Singh, R.P., *Polym. Degrad. Stab.*, 2005, 88: 234
- 7 Kumar, A.P., Depan, D., Tomer, N.S. and Singh, R.P., *Prog. Polym. Sci.*, 2009, 34: 479
- 8 Mailhot, B., Morlat, S., Gardette, J.C., Boucard, S., Duchet, J. and Gerard, J.F., *Polym. Degrad. Stab.*, 2003, 82: 163
- 9 Morlat, S., Mailhot, B., Gonzalez, D. and Gardette, J.L., *Chem. Mater.*, 2004, 16: 377
- 10 Morlat-Therias, S., Mailhot, B., Gonzalez, D. and Gardette, J.L., *Chem. Mater.*, 2005, 17: 1072
- 11 Qin, H., Zhang, S., Liu, H., Xie, S., Yang, M. and Shen, D., *Polymer*, 2005, 46: 3149
- 12 Aslanzadeh, S., Haghighat Kish, M. and Katbab, A.A., *Polym. Degrad. Stab.*, 2010, 95: 1800
- 13 Singala, K.J., Mungray, A.A. and Mungray, A.K., *Ind. Eng. Chem. Res.*, 2012, 51: 10557
- 14 Morreale, M., Dintcheva, N.Tz. and La Mantia, F.P., *Polym. Int.*, 2011, 60: 1107
- 15 Silvano, J.R., Rodrigues, S.A., Marini, J., Bretas, R.E.S., Canevarolo, S.V., Carvalho, B.M. and Pinheiro, L.A., *Polym. Degrad. Stab.*, 2013, 98: 801
- 16 Morreale, M., Dintcheva, N.Tz. and La Mantia, F.P., *Express. Polym. Lett.*, 2013, 7: 703
- 17 Redhwi, H.H., Siddiqui, M.N., Andrady, A.L. and Hussain, S. J., *Nanomater.*, 2013, Article ID 654716, doi:10.1155/2013/654716
- 18 Sanchez-Valdes, S., Martinez Colunga, J.G., Lopez-Quintanilla, M.L., Yanez Flores, I., Garcia-Salazar, M.L. and Gonzalez Cantu, C., *Polym. Bull.*, 2008, 60: 829
- 19 Qin, H., Zhao, C., Zhang, S., Chen, G. and Yang, M., *Polym. Degrad. Stab.*, 2003, 81: 497
- 20 Qin, H., Zhang, Z., Feng, M., Gong, F., Zhang, S. and Yang, M., *J. Polym. Sci. Part B: Polym. Phys.*, 2004, 42: 3006
- 21 Morlat-Therias, S., Fanton, E., Gardette, J.L., Dintcheva, N.Tz., La Mantia, F.P. and Malatesta, V., *Polym. Degrad. Stab.*, 2008, 93: 1776
- 22 La Mantia, F.P., Dintcheva, N.Tz., Malatesta, V. and Pagani, F., *Polym. Degrad. Stab.*, 2006, 91: 3208
- 23 Botta, L., Dintcheva, N.Tz. and La Mantia, F.P., *Polym. Degrad. Stab.*, 2009, 94: 712
- 24 Dintcheva, N.Tz., Al-Malaika, S. and La Mantia, F.P., *Polym. Degrad. Stab.*, 2009, 94: 1571
- 25 Ghafor, W.A., Halley, P.J., Hill, D.J.T., Martin, D.J., Rasoul, F. and Whittaker, A.K., *J. Appl. Polym. Sci.*, 2009, 112: 381
- 26 Grigoriadou, I., Paraskevopoulos, K.M., Chrissafis, K., Pavlidou, E., Stamkopoulos, T.G. and Bikiaris, D., *Polym. Degrad. Stab.*, 2011, 96: 151
- 27 Kumanayaka, T.O., Parthasarathy, R. and Jollands, M., *Polym. Degrad. Stab.*, 2010, 95: 672
- 28 Chmela, S., Kleinova, A., Fiedlerova, A., Borsig, E., Kaempfer, D., Thomann, R. and Mulhaupt, R., *J. Macromol. Sci. A.*, 2005, 42: 821
- 29 Mouzakis, D.E., Kandilioti, G., Elenis, A. and Gregoriou, V.G., *J. Macromol. Sci. A.*, 2006, 43: 259
- 30 Kandilioti, G., Elenis, A., Macchiarola, K.A. and Gregoriou, V.G., *Appl. Spectrosc.* 2006, 60: 1285
- 31 Tidjani, A. and Wilkie, C.A., *Polym. Degrad. Stab.*, 2001, 74: 33
- 32 Diagne, M., Gueye M., Vidal, L. and Tidjani, A., *Polym. Degrad. Stab.*, 2005, 89: 418
- 33 Diagne, M., Gueye, M., Dasilva, A., Vidal, L. and Tidjani, A., *J. Mater. Sci.*, 2006, 41: 7005
- 34 Diagne, M., Gueye, M., Dasilva, A. and Tidjani, A., *J. Appl. Polym. Sci.*, 2007, 105: 3787
- 35 Billingham, N.C., Bonoro, M. and De Corte, D., In "Biodegradable Polymers and Plastics", Chiellini, E., Solaro, R., Eds., Plenum Publishers: New York, 2003, p. 313
- 36 Sivan, A., *Curr. Opin. Biotech.*, 2011, 22: 422
- 37 Rabello, M.S. and White, J.R., *Polym. Degrad. Stab.*, 1997, 56: 55

- 38 Aslanzadeh, S. and Haghighat Kish, M., *Polym. Degrad. Stab.*, 2005, 90: 461
- 39 Aslanzadeh, S. and Haghighat Kish, M., *Fiber. Polym.*, 2010, 11: 710
- 40 Blais, P., Carlsson, D.J. and Wiles, D.M., *J. Polym. Sci. Part A-1*, 1972, 10: 1077
- 41 Barish, L., *J. Text. Inst.*, 1989, 80: 107
- 42 Carlsson, D.J., Garton, A. and Wiles, D.M., *J. Appl. Polym. Sci.*, 1977, 21: 2963
- 43 Blais, P., Carlsson, D.J., Clark, F.R.S., Sturgeon, P.Z. and Wiles, D.M., *Text. Res. J.*, 1976, 46: 641
- 44 Rangasamy, L., Shin, E. and Pourdeyhimi, B., *J. Appl. Polym. Sci.*, 2011, 121: 410
- 45 Marcincin, A., Hricova, M., Ujhelyiova, A., Brejka, O., Michlik, P., Dulikova, M., Strecka, Z. and Chmela, S., *Fibers Text. East. Eur.*, 2009, 17: 29
- 46 Joshi, M. and Viswanathan, V., *J. Appl. Polym. Sci.*, 2006, 102: 2164
- 47 Toshniwal, L., Fan, Q. and Ugbolue, S.C., *J. Appl. Polym. Sci.*, 2007, 106: 706
- 48 Horrocks, A.R., Kandola, B.K., Smart, G., Zhang, S. and Hull, T.R., *J. Appl. Polym. Sci.*, 2007, 106: 1707
- 49 Mlynarcikova, Z., Kaempfer, D., Thomann, R., Mulhaupt, R., Borsig, E. and Marcincin, A., *Polym. Adv. Technol.*, 2005, 16: 362
- 50 Smart, G., Kandola, B.K., Horrocks, A.R., Nazare, S. and Marney, D., *Polym. Adv. Technol.*, 2008, 19: 658
- 51 Zhang, S., Horrocks, A.R., Hull, R. and Kandola, B.K., *Polym. Degrad. Stab.*, 2006, 91: 719
- 52 Zhang, S., Hull, T.R., Horrocks, A.R., Smart, G., Kandola, B.K., Ebdon, J., Joseph, P. and Hunt, B., *Polym. Degrad. Stab.*, 2007, 92: 727
- 53 Houphouet-Boigny, C., Plummer, C.J.G., Wakeman, M.D. and Manson, J.A.E., *Polym. Eng. Sci.*, 2007, 47: 1122
- 54 Pavlikova, S., Thomann, R., Reichert, P., Mulhaupt, R., Marcincin, A. and Borsig, E., *J. Appl. Polym. Sci.*, 2003, 89: 604
- 55 Joshi, M., Shaw, M. and Butola, B.S., *Fiber. Polym.*, 2004, 5: 59
- 56 Zhang, X., Yang, M., Zhao, Y., Zhang, S., Dong, X., Liu, X., Wang, D. and Xu, D., *J. Appl. Polym. Sci.*, 2004, 92: 552
- 57 Mlynarcikova, Z., Borsig, E., Legen, J., Marcincin, A.N. and Alexy, P., *J. Macromol. Sci. A.*, 2005, 42: 543
- 58 Marcincin, A., Marcincin, K., Hricova, M., Ujhelyiova, A., Janicki, J. and Slusarczyk, C., *Fibers Text. East. Eur.*, 2013, 21: 18
- 59 Castejon, M.L., Tiemblo, P. and Gomez-Elvira, J.M., *Polym. Degrad. Stab.*, 2000, 70: 357
- 60 Zhang, J. and Wilkie, C.A., *Polymer*, 2006, 47: 5736
- 61 Torikai, A., Shirakawa, H., Nagaya, S. and Fueki, K., *J. Appl. Polym. Sci.*, 1990, 40: 1637
- 62 Fayolle, B., Audouin, L., George, G.A. and Verdu, J., *Polym. Degrad. Stab.*, 2002, 77: 515