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Photo-irradiation induced morphological changes in nylon 66

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Abstract

Nylon 66 films were photo-irradiated at 60°C for different time intervals up to 200 h. Photo-irradiated samples were characterized by XRD, DSC and optical microscopy. XRD results showed that there was increase in crystallinity with increase in exposure time during initial period of photo-exposure. However, there was no change in X-ray diffraction pattern upon photo-irradiation. DSC results showed that there was formation of new crystalline morphology upon photo-irradiation. This formation of new crystalline morphology was observed to be at the expense of existing morphology. Optical microscopy showed that there was formation of cracks at the center of spherulites as photo-irradiation proceeds. Cracks were increased in size with photo-irradiation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photo-irradiation; Nylon 66; Morphological changes

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1. Introduction

Photo-oxidation in nylon 66 has been studied widely. Several authors have characterized photo-oxidation in polyamides using various analytical techniques. Moore [1] characterized photo-oxidation by intrinsic viscosity changes, UV absorption and end-group analysis. Surface oxidation in nylon 66 was also characterized [2] by ESCA. The effects of photo-irradiation were studied in detail [3,4] by FT-IR spectroscopy. Morphology is one of the major factors, which marginally affects the degradation kinetics of the polymeric materials [5–8]. Moreover, all useful mechanical properties of a polymeric material depend on the morphology. The studies of changes in polymer morphology upon degradation have always been remained as an important area of research [9–17]. In the present study, we have discussed the morphological changes in nylon 66 induced by photo-irradiation.

2. Experimental

2.1. Materials

Nylon 66 (Zytel 101 L NC 10) was received from M/s Dupont de Nemours (USA) and used without further purification.

2.2. Experimental procedure

Thin films of (thickness ~50 μm) of nylon 66 were prepared by pressing the polymer in between two preheated platens in a hydraulic press at 270°C under ~14 kg/cm^2 pressure for 2 min and cooled rapidly by water circulation in the press under pressure. The film samples thus obtained were semicrystalline in nature. The films for optical microscopic study were prepared on glass slides by heating slides at 270°C on hot plate and forming a thin film of nylon 66 over it. All the samples were irradiated in accelerated photo-irradiation chamber (SEPAP 12/24, $\lambda \geq 300$ nm) at 60°C for different time intervals. Details of this equipment are given elsewhere [17].

2.3. X-ray diffraction measurements

The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide-angle power goniometer. The generator was operated at 40 kV and 150 mA. The samples were scanned between $2\theta = 10$ to 35° and the scan speed was 1°C/min. The crystallinity was calculated from the X-ray diffractogram as the ratio of the area of the crystalline peaks to the total area.

2.4. DSC measurements

The calorimetric measurements were done using Perkin–Elmer DSC-7. The samples were heated/cooled at a rate of 10°C/min under nitrogen environment. The melting

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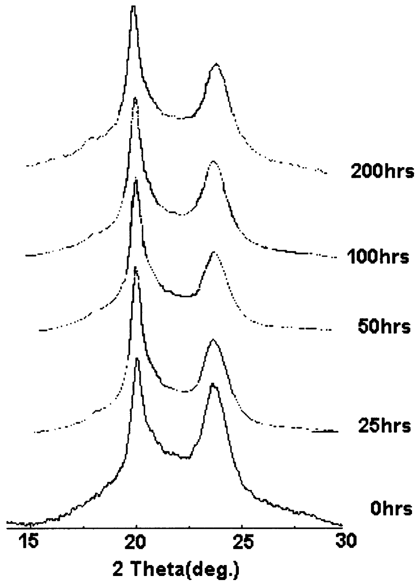

Fig. 1. Change in X-ray diffraction patterns of nylon 66 with exposure time.

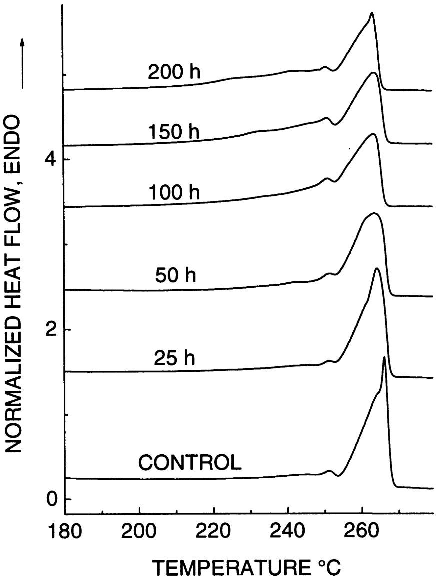

Fig. 2. Melting thermograms of nylon 66 photoirradiated for different time intervals.

temperature and heat of fusion were obtained from the heating thermogram.

3. Results and discussions

Photo-oxidation processes in polyamides consist of chain scissions, formation of hydroxy/hydroperoxy and various carbonyl species [18–20]. It was observed [4] that initiation of photo-oxidation starts with a proton abstraction from methylene group adjacent to –NH– group and amorphous region was identified as an initial site of photo-oxidation in nylon 66. The morphological changes that occurred as a result of photo-oxidative processes in nylon 66 samples were analyzed by wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC) and Polarizing Optical microscopy.

The room temperature X-ray diffraction patterns of the various samples are shown in Fig. 1. The positions of the characteristic peaks of nylon 66 at $2\theta = 20$ and 24° remain unchanged. The intensity of the peak at $2\theta = 24°$ shows a decrease during initial stages of photo-irradiation as seen from the pattern of the sample irradiated for 25 h and further increase in radiation time does not induce any additional changes. The intensity of the peak at $2\theta = 20°$ is not affected by irradiation. The crystallinity calculated from the pattern of the various samples are shown in Table 1 and showed that crystallinity increases marginally during very early stages of irradiation and then remains unchanged. The general shape and d-spacings of the 100 and 010/110 reflections suggest that the photo-irradiation does not induce any variation to the α-phase crystalline structure of nylon 66.

Table 1
Change in crystallinity with exposure time measured using XRD technique

No.	Exposure time (h)	% Crystallinity (XRD)
1.	0	36
3.	50	40
4.	100	42
5.	150	43
6.	200	44

The DSC heating thermograms of nylon samples photo-irradiated for different time intervals are shown in Fig. 2. These thermograms show systematic variation in the melting peak with irradiation time. The melting endotherm of the control sample shows two peaks, a broad peak starting from 220°C and a sharp peak at 265°C. The sharper peak at higher temperature corresponds to the melting of the lamellae that is formed at the crystallization temperature on cooling during sample preparation and can under go partial melting and recrystallization resulting in double peak. A careful inspection of the sharper peak indeed reveals that the sharper peak is composed of two peaks. The broad peak starting at 220°C corresponds to the melting of thin lamellae that crystallize at a lower temperature than the normal crystallization temperature on cooling to room temperature. This lamellae, in general, reside within the spherulites and between the thicker lamellae and cannot undergo reorganization and melts at lower temperature. The partial areas of the low-temperature broad peak and the high-temperature sharper peak are shown in Fig. 3 as a function of irradiation time. It is seen from the figure that the area under the low-temperature peak increases while the high-temperature peak decreases, however, the total area remains constant. This indicates a modification of semi-crystalline morphology due to photo-irradiation. The melting temperature also

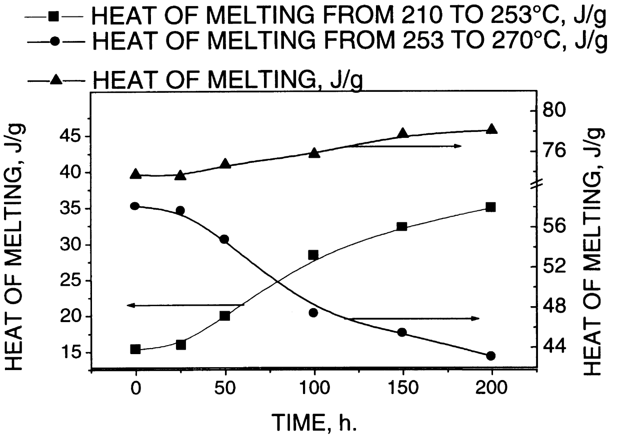

Fig. 3. Changes in heat of melting with exposure time.

shows a small decrease with exposure time and is given in Table 2.

The DSC studies on polymer degradation show emergence of new melting peak as a result of modification of morphology by degradation processes [13,16,21–25] and can be explained by chemi-crystallization phenomenon. In the present case, the irradiation experiments had been performed at 60°C, which is very close to the T_g of nylon 66. Under normal circumstances, the thermal crystallization at this temperature is rather limited because the sample has been already crystallized. Hence, the increase in crystallinity observed during initial stages of irradiation can be attributed to chemi-crystallization during irradiation. When semi-crystalline nylon 66 is exposed to UV light in presence of oxygen, oxidation reactions occur resulting in chain scissions. Since amorphous region has higher oxygen permeability and diffusivity, photo-oxidation preferentially takes place in the amorphous phase of polymer. The entangled molecules are released as a result of chain scission. These released molecular segments crystallize by rearrangement.

In this study, we observed a decrease in the heat of fusion of the high-temperature peak and increase in the heat of fusion of low-temperature peak. This indicates that the radiation affects the crystalline region as well. However, there is no decrease in crystallinity (Fig. 1) even after 200 h of photo-irradiation (see X-ray data) where as chemi-crystallization is known to increase the crystallinity [26]. Aslanian et al. [23] showed the emergence of a low-temperature melting peak when LDPE is irradiated with γ-radiation. Kostoski et al. [13] found that for oriented PP with increasing γ-irradiation dose the melting temperature decreases and the area under the lower melting peak increases at the expense of the area under the higher melting temperature. It is observed [4] in case of nylon 66 that photo-oxidative processes are prevailing in amorphous phase. The damage observed in crystalline region, the decrease in the melting peak area of high-temperature peak, are due to scission of tie molecules and chain folds at crystal surfaces and subsequent cleavage of chains from

Table 2
Melting temperature of irradiated nylon 66 samples

No.	Exposure time (h)	Melting temp. (°C)
1.	0	266
2.	25	264
3.	50	264
4.	100	264
5.	150	264
5.	200	263

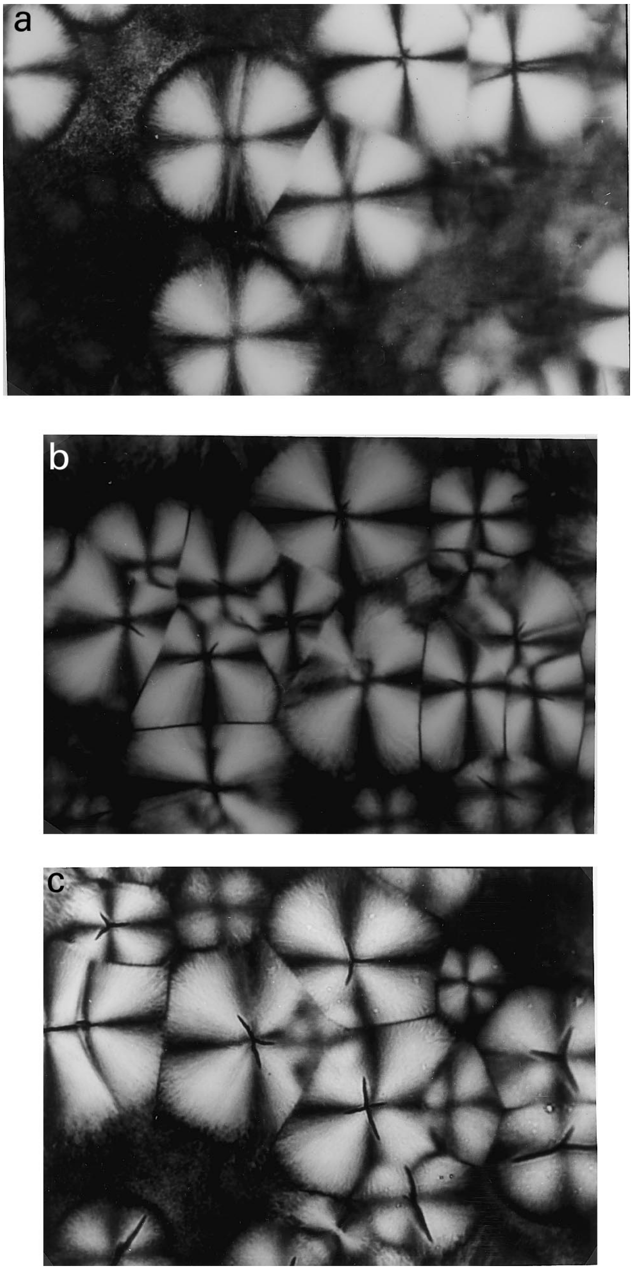

Fig. 4. Optical micrographs of nylon 66 films: (a) controlled; (b) 50 h photoirradiated; (c) 100 h photoirradiated.

the crystal surface during heating in DSC. Moreover, both tie molecules and chain folds are likely to contain heavily strained bonds and making them prone to photo-oxidation. These oxidative processes will cause bond breaking and lead to the lowering of melting point. Ogier et al. [14] also observed the similar phenomenon during photo-oxidation studies on PP. Increase in the area under lower melting peak with irradiation time is mainly due to the formation of new thin lamellae by the scissioned chains.

Kostoski et al. [13] suggested that increase in crystallinity with absorbed dose can probably be attributed to the scission of highly strained molecules followed by recrystallization. The crystals formed as a result of photo-irradiation [9] grew with the same orientation distribution as pre-existing ones. This occurs if the overgrowth predominates over formation of new crystals. This is in agreement with the theory of chain scissions to occur within or near to the interphase, suggesting the involvement of short-range movements of the molecules during molecular ordering upon photo-exposure.

Fig. 4a–c shows effect of photo-irradiation on the spherulites of nylon 66. The formation of cracks with photo-irradiation is evident from the figure. It is interesting to note that all the cracks originated from the center of the spherulites and grew in size with exposure time. Cracks formation was observed after 50 h of photo-exposure, when there is an increase in crystallinity, change in DSC thermogram and decrease in amorphous phase [4]. This indicates a correlation between chemi-crystallization process and formation of cracks at the center of the spherulites.

4. Conclusion

Photo-oxidative degradation in nylon 66 shows chemi-crystallization of cleaved chains in the amorphous region. The X-ray diffraction studies and melting behavior show modification in the morphology due to photo-irradiation. This change is due to re-organization of cleaved chains in the amorphous space. Cracks formation exhibited by optical microscopy is due to contraction forces developed upon the chemi-crystallization of entanglement free chains within the spherulites.

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