

FT-Raman analysis of the effects of γ -radiation on nylon 6-12 filaments

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SUMMARY

FT-Raman spectroscopy of commercial amorphous and crystalline nylon 6-12 filaments subjected to various γ -radiation doses are presented. The results show that a difference exists in the interaction of γ -radiation with these polyamides, depending on the crystallinity which can be evaluated by measuring the CH-stretching/CH-bending Raman band intensity ratio as a function of applied γ -dose.

INTRODUCTION

Nylons constitute a big family of versatile engineering polyamides with a wide range of applications in various fields [1]. In particular, fibers produced by different types of crystalline and semi-crystalline nylons are routinely used as reinforcing elements in FRP (Fiber-Reinforced Plastics) and as bristle materials [1,2]. In every case, physical, chemical and mechanical properties are considerably dependent on the degree of cristallinity of the specific nylon employed and various methodologies, including DSC [2], WAXS [3] and spectroscopic approaches [4-5] have been explored for understanding and predicting nylon properties.

Various nylons present a temperature-induced crystalline phase transition, the so-called Brill transition [6-7], whose precise mechanisms are still to be determined. Polyamides are also relevant because of their structure is a close relative to that of peptides or proteins [8] and various vibrational spectroscopies are used as tools for understanding some of the characteristics of both nylons and biomolecules [9-11]. Specifically, Raman spectroscopy offers promising analytical possibilities because a number of the most relevant molecular events taking place in nylons are Raman-active. Until recently, however, the use of Raman spectroscopy was limited because of strong fluorescence overlapping the significant peaks. The development of FT-Raman instruments in which the laser-excitation of the sample is within the near IR range, allows now to renew the interest in exploring Raman effects in polymeric materials [8-12]. Irradiation of polymers is an active area of research because radiation modification of polyamides can lead to an improvement in their properties [13,14] and because these studies can provide insight into the

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amorphous-to-crystalline transitions in nylons. In this contribution we report our FT-Raman spectroscopy studies on commercial nylon 6-12 filaments subjected to various doses of γ radiation.

EXPERIMENTAL

a) Materials

Commercial nylon 6-12 filaments (Dupont, ZYTEL 158TM) were purchased in two forms: nearly amorphous and crystalline. The amorphous filaments had a diameter of 0.425 mm whereas the crystalline ones had a diameter of 0.20mm. The fibers were cut to 40 cm length and placed in the radiation chamber.

b) γ Radiation procedure

The radiation of the fibers was carried out by a JS 6500 gamma irradiator from Atomic Energy of Canada Limited (now Nordion International INC). The dosimetry control of the irradiation was carried out continuously using a red acrylic dosimeter L9C1

c) Characterization techniques

Single crystal x-ray diffractometry was done by a Siemens D-5000 diffractometer in the 2 to 70° range at a scanning rate of $4^\circ/\text{min}$. FT-Raman was performed by a Nicolet Raman 910 bench equipped with a Nd:YV04 (neodymium yttrium vanadate) laser, emitting at 1064 nm. In every case, the spectra were obtained across the fiber. The resolution of the equipment is 4 cm^{-1} , and the spectral range is $100\text{-}3400\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffractogram of the crystalline nylon 6-12 filaments prior to irradiation. It was observed that the amorphous specimens showed a broad peak at around 20° , identified, according to previous studies [3,14-16], as the typical amorphous reflection as well as a (hkl) peak, whereas the (100) and (010) reflections are clearly defined in the crystalline filaments, as seen in Figure 1. This constitutes an important starting point, because it has been reported in some previous studies of γ -damage nylons, that the hydrogen plane (010) is more susceptible to radiation interaction [16]. Figures 2(a) and 2(b) correspond to the FT-Raman spectra of amorphous and crystalline fibers, respectively, before irradiation. A number of vibration bands have been identified and reported in the literature, especially for wavenumbers between 500 and 3500 cm^{-1} [16,17]. Here we shall briefly review only the main bands: For example, the N-H stretching

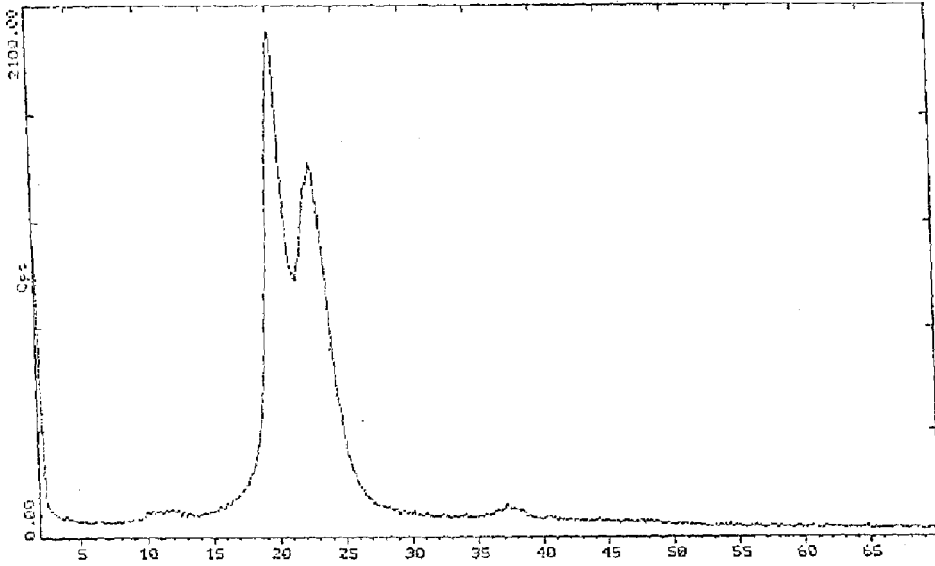


Figure 1.- X-ray diffractograms of crystalline nylon 6-12 filaments.

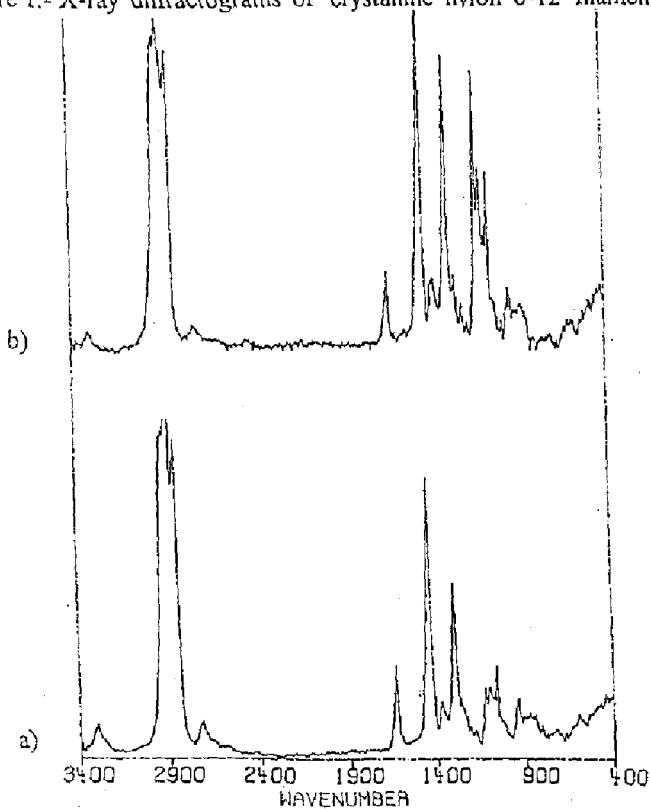


Figure 2.- FT-Raman spectra of non-irradiated fibers. a) Amorphous and b) Crystalline.

vibration at around 3230 cm^{-1} is observed clearly in the amorphous filaments whereas in the crystalline ones it is considerably weaker or, more likely, displaced towards Raman shifts beyond the detector response (3500 cm^{-1}). This can be understood by recalling that the well-known β -sheet structures of linear aliphatic polyamides are due to intermolecular $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonds between amide groups in adjacent chains [18, 19]. Thus, because of the anisotropic character of nylon 6-12 triclinic crystals [16], those groups are not detected across the fiber, as the present measurements were performed, but have indeed been detected along the fiber by spectroscopic methods which will be reported separately [20].

The C-H stretching vibration bands appear in both amorphous and crystalline samples between 2800 to 3000 cm^{-1} . However, two important differences exist between the two types of nylons: First, the most intense bands for the amorphous sample are the C-H asymmetric stretching ones, whereas for the crystalline fibers the C-H bending modes produce the most intense bands at around 1440 cm^{-1} . The second difference is the absence of a weaker band at around 2830 cm^{-1} , likely corresponding to the CH symmetric stretching mode in the crystalline filaments.

Figures 3(a) through 3(d) show now the FT-Raman spectra of amorphous filaments irradiated at 4 different doses of γ -radiation. Often, the methylene bending bands of nylons are employed as intensity self-standards for quantitative analysis since these vibrations are independent from intermolecular interactions [8]. However, it has been reported [10] that the bands in the 1400 to 1500 cm^{-1} range consist of a number of overlapping peaks. Nevertheless, it seems reasonable to include in the analysis all the bands with slight frequency differences caused by small changes in the precise molecular sites, and it has been concluded by the present and by the previous authors [10] that the integrated intensities of these overlapping bands can be used for standard purposes.

By comparing the series of spectra of Figure 3, spanning an order of magnitude in radiation dose, it seems at first glance that no evident difference in the Raman response is detected. However, a closer examination reveals that the relative intensity of the CH-bending at 1440 cm^{-1} , as compared to the 2900 cm^{-1} CH-stretching vibration, changes with dose, as shown in Figure 5(a), where the relative CH-stretching / CH-bending intensity is plotted against the dose. It is interesting to compare these results with previous works in which similar relative intensities were plotted as a function of the number of CH contained in a number of nylons [10], which indicate that some chain scission is taking place. This conclusion is further supported by reports which indicate that the bond energy for crosslinking or scission goes inversely with the γ -dose [13].

The results for the crystalline filaments are altogether different, as observed in the series of plots of Figure 4, which shows FT-Raman spectra of the crystalline specimens as a function of the applied γ -dose. In this case, the changes in the CH-stretching / CH-bending relative intensities show very little changes with dose, as can be better appreciated in the plot of Figure 5(b). This difference with respect to

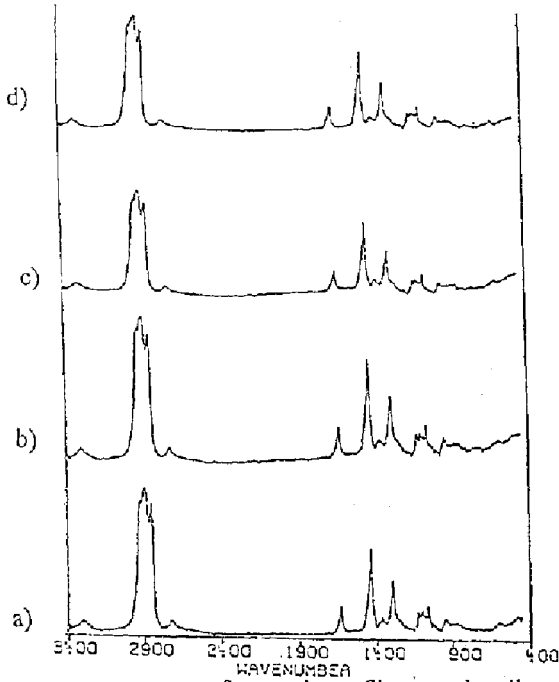


Figure 3.- FT-Raman spectra of amorphous filaments irradiated at: a) 20 kGy; b) 110 kGy; c) 250 kGy and d) 400 kGy.

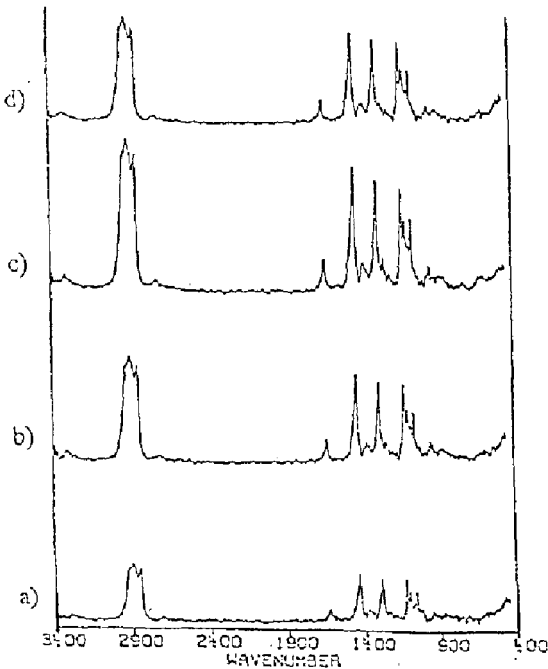


Figure 4.- FT-Raman spectra of crystalline filaments irradiated at: a) 20 kGy; b) 110 kGy; c) 250 kGy and d) 400 kGy.

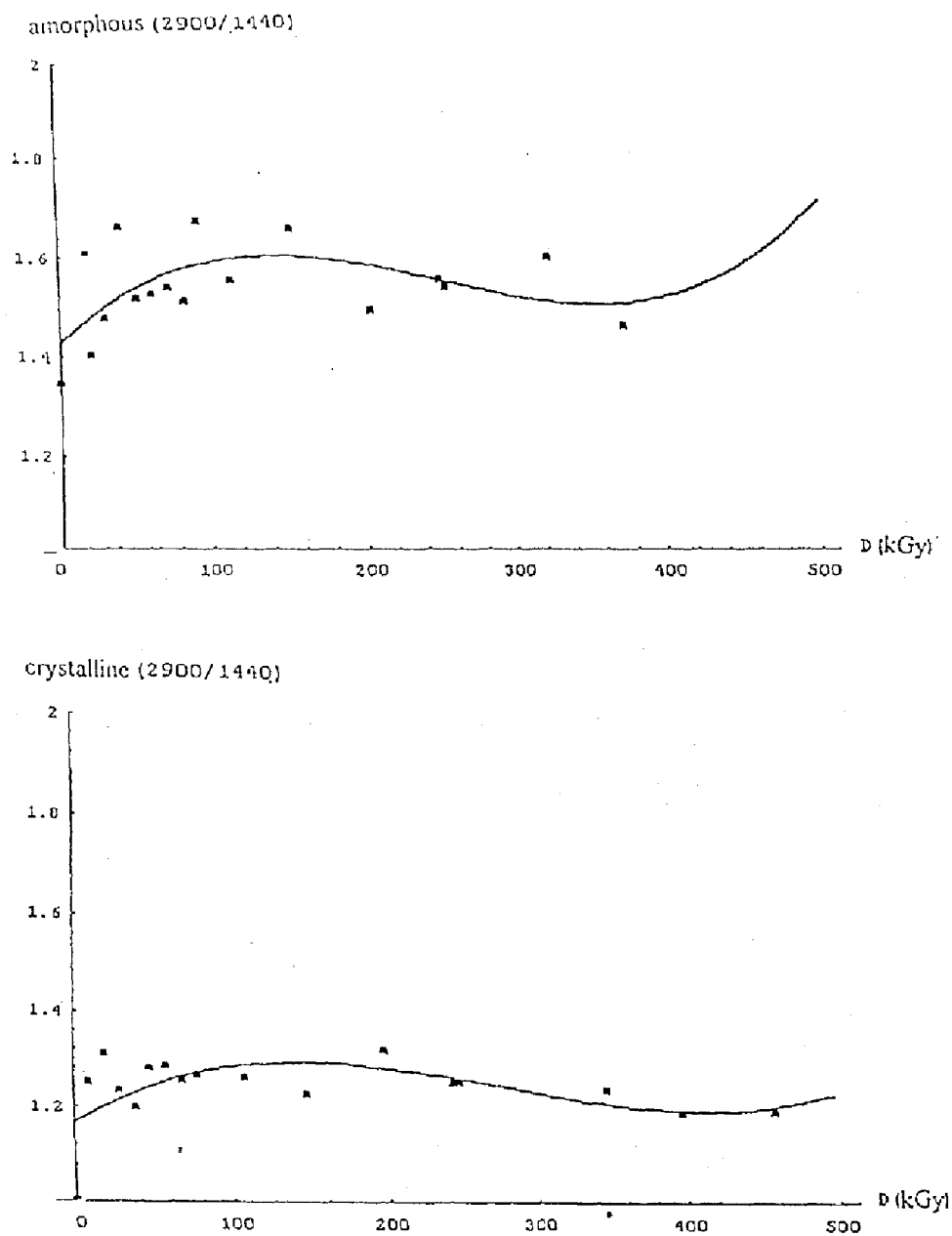


Figure 5.- Plots of the CH-stretching / CH-bending relative intensities as a function of γ -irradiation dose for: a) amorphous and b) crystalline filaments.

the amorphous case can be explained in terms of the mobility of free radicals produced during irradiation, which is higher in the amorphous regions. Thence, in the crystalline fibers, the probability of these radicals, terminating by a coupling thus producing crosslinking, is considerably smaller than in the amorphous regions, because of the constrictions to the movement of the radicals in a crystalline structure. This difference in the interaction of γ -radiation between crystalline and amorphous regions has been repeatedly found by X-ray, DSC, and mechanical measurements in different types of nylons [13-16].

CONCLUSIONS

A number of points can be drawn from the results presented. First, that there exists a difference in the nature of the interaction of γ -radiation with nylon 6-12 filaments depending on whether or not the material is crystalline. Second, that Raman Spectroscopy, laser-exciting in the infrared region, is a sensitive technique for studying the above phenomena, provided an adequate internal intensity standard is chosen. In this respect, interesting anisotropy effects have been detected with FT-Raman methodologies and a corresponding report is being prepared [20]. Finally, besides the potential insight into the basic physico-chemical mechanisms of the radiation-matter interaction these results may offer, it is also worth exploring their application in designing a novel radiation dosimeter, an aspect which is being also studied in our laboratory.

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