

INVESTIGATION OF THE TRAP STATES IN QUENCHED AND ANNEALED NYLON 6 FILMS USING THERMALLY STIMULATED DEPOLARIZATION CURRENT

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Abstract

Quenched and annealed nylon 6 films were prepared and their short - circuit thermally stimulated depolarization current (TSDC) has been measured using a modified thermal electric analyzer. The space charge peak in the temperature range of 90°C~180°C observed in the TSDC spectra of different samples showed that the trap state of the films shifted to lower temperature as annealing time increased. In general, the trap state became shallower in the annealed sample. The result was consistent with the structural transition of quenched β form to annealed α form. FTIR spectrum and X-ray diffraction were also used to examine the transition. According to the analysis of the phase transition, structural origin of the TSDC peaks has been proposed.

Introduction

Thermally stimulated depolarization current technique was introduced by Bucci and Fieshi in 1964[1], and since then it has been extensively used to study the dielectric relaxation phenomena in polymeric materials[2-4]. However, less attention has been paid to the high temperature TSDC of the polymer due to the much more complicated relaxation phenomena in this temperature range, probably including space charge polarization, interfacial Maxwell-Wagner-Sillars polarization, conductivity current relaxation etc[5].

Nylon 6 is a semicrystalline polymer material widely used in industry and so many reports on its crystalline structure have been published[6-11]. In general, Nylon 6 exhibits three crystalline forms that coexist in various amounts, depending on processing conditions. The polymer chains in the α form are in the extended conformation[6], while in the γ form are in the twisted helical conformation[7]. Hydrogen bonds are formed between antiparallel chains in the α form and between parallel chains in the γ form. The metastable pseudo hexagonal β form is not as well identified[8,11], and can be inverted to the α form on annealing[11].

In this article we investigate the change in trap states of nylon 6 films due to the different crystalline forms of the film by using the TSDC technique. The results were discussed in detail in terms of the structural transition of the films.

Experimental

The nylon 6 pellets are supplied by Yixing Chemicals. The film samples with a thickness of about 100 μ m were produced by hot pressing at 230°C and subsequent quenching in an ice-water bath. Annealed samples were prepared by annealing the quenched samples at 160°C for different time. The films were coated with silver electrodes of 10mm in diameter for the TSDC measurement carried out by a modified thermo-electric analyzer[12]. To get rid of any residual water, all the samples were placed

under vacuum at 300K for 12hrs. The samples were poled with an electric field $E_p=50\text{kV/cm}$ at a poling temperature $T_p=80^\circ\text{C}$ for a poling time t_p , typically 5min. The heating rate was 4°C/min .

FTIR spectra were obtained using a Vector-22 model FTIR spectrometer at a resolution of 1cm^{-1} .

X-ray diffraction experiments were performed using a Y-4Q diffractometer.

Results and discussion

Figure 1 shows the TSDC spectra for quenched and annealed nylon 6 films. The peak at $\sim 50^\circ\text{C}$ presents the dipole relaxation in the film, corresponding to the glass transition on the DSC spectra. There is only slight difference in the dipole relaxation for quenched and annealed films and they would not be discussed in this paper.

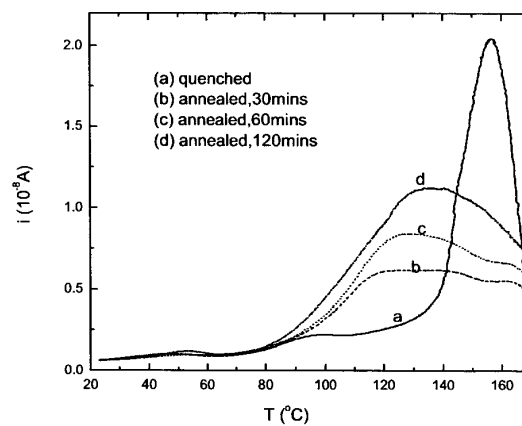


Fig. 1. TSDC spectra of different nylon 6 samples.

For the quenched sample a, it has a sharp relaxation peak at 156°C , indicating a deep trap energy. While for the sample which is annealed for 120 minutes, it has only one trap energy corresponding to a broad relaxation peak observed at $\sim 130^\circ\text{C}$. The interpretation for the change of the TSDC spectrum may be found from our FTIR spectrum and X-ray diffraction scans. It can be seen from Figure 2 that in the 930 and 1030cm^{-1} bands, the shoulder peak 960cm^{-1} increases for the annealed film, while the band at about 1120cm^{-1} shifts slightly, indicating a $\beta \rightarrow \alpha$ structural change[11]. Moreover, some authors proposed that β form can be viewed as an intermediate structure between the α and the γ forms from the standpoint of H-bond setting and chain conformations[11,13-14]. According to the X-ray experiment shown in Figure 3, two characteristic peaks at $2\theta=20.4^\circ$ and 23.6° probably showed that the β phase is similar to the metastable phase proposed by Murthy[8], with the hydrogen bonds between the chains in the β form being formed between both antiparallel and parallel chains; i.e. while the hydrogen bonds in the α and γ forms are formed exclusively within a 'hydrogen-bonded' sheet, inter-sheet hydrogen bonds may be present in the β form. So we proposed that, the deep trap energy at the range of 156°C should correspond to the inter-sheet hydrogen bonds, while for the annealed film, it has a high content of α form, so the hydrogen bonds are exclusively between the antiparallel chains. This is in agreement with the shallower trap energy observed at $\sim 135^\circ\text{C}$ in the TSDC spectrum. Moreover, it is clearly seen that TSDC technique is much more sensitive to the detection of the structural change comparing with FTIR spectrum or X-ray

diffraction scans.

The charge carrier density released to the external circuit during the depolarization is shown in Figure 4. For the sample annealed for 30 minutes, the inter-sheet hydrogen bonds disappear before the formation of the inner-sheet hydrogen bonds, so the charge trapped during the polarization process decreases obviously. Continued annealing yielded more inter-sheet hydrogen bonds, so the charge trapped during polarization increased.

More information may be arrived from the circulative TSDC spectra (Figure 5) of the same sample. Due to the thermal process the sample experiences during a complete TSDC process, it may also be regarded as an annealing course. The lower temperature range of the space charge at the second course of the TSDC spectrum and the change of the released charge during depolarization ($0.1\mu\text{C}\rightarrow 0.15\mu\text{C}$) indicated that the $\beta\rightarrow\alpha$ transition after a TSDC process may to some extent be equivalent to the annealing process at 160°C for 120 minutes or longer time. However, the shoulder peak at 145°C of the second course probably showed the structural difference deserving further study under isothermal and non-isothermal treatments.

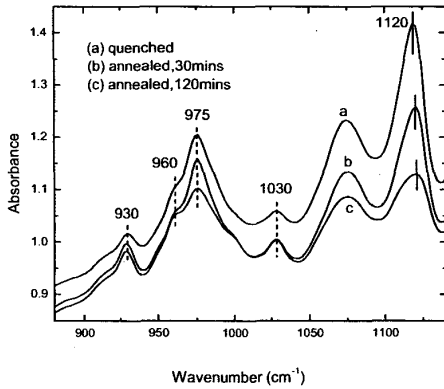


Fig. 2. FTIR spectra of nylon 6 films.

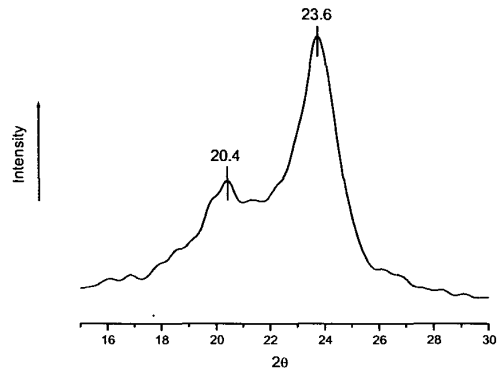


Fig. 3. X-ray diffraction pattern of quenched sample.

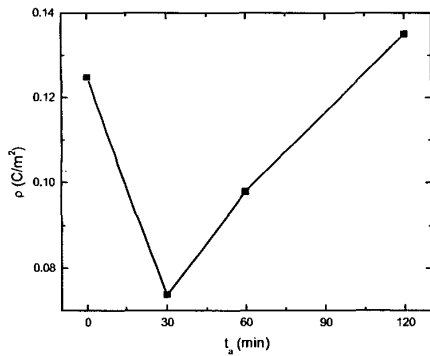


Fig. 4. The carrier density of nylon 6 films as a function of annealed time.

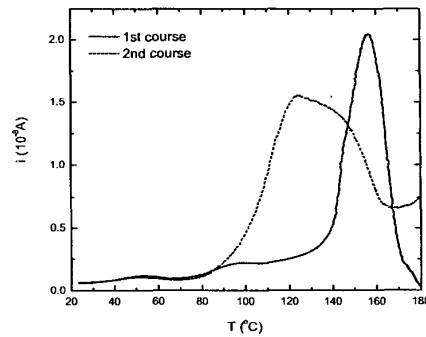


Fig. 5. TSDC spectra of quenched films for the circulative measurement.

Conclusions

Quenched and annealed nylon 6 films have been prepared and their TSDC spectrum are analyzed in terms of the transition of the crystalline forms. Corresponding to the $\beta \rightarrow \alpha$ phase transition, a change of the trap states is also observed in the TSDC spectrum for different films. For quenched films, hydrogen bonds form between both antiparallel and parallel chains, while for films annealing at 160°C for 120 minutes, a high content of β phase has transformed to α phase, so the hydrogen bonds are exclusively between the antiparallel chains, which gives rise to the shallower trap energy of the annealed films. Moreover, the TSDC technique is much more sensitive in detecting the structural change comparing with other techniques such as FTIR or XRD.

Acknowledgements

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