

STUDY ON THE MECHANISM OF STAINING BY ALLYLAMINE/ OsO_4 ON PET FILM

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ABSTRACT

It was proposed that in the staining process allylamine diffuses into amorphous region of PET film, reacting slightly with ester bond on PET chain and connecting with it and remaining in the amorphous area, then OsO_4 reacts with $\text{C}=\text{C}$ group in allylamine, deposits in that region and hence, increases the contrast between amorphous and crystalline regions.

The transmission electron microscopy and the scanning electron microscopy are the most important methods for observing the morphology of the bulk polymer. Most of polymers consisted of light elements such as carbon, hydrogen, oxygen, nitrogen, which have less electrons. The contrast between different regions of bulk polymer are very small. It is quite difficult to obtain the micrograph of polymers. How to enhance the contrast has become a longstanding problem in polymer morphology studies.

Kato^[1] was the first to use OsO_4 on staining unsaturated polymers for enhancing the contrast. This is a milestone in polymer morphology study. Unfortunately, this technique is only limited to unsaturated polymer.

Kanig^[2] developed a two-step staining method. First, the polyolefin was treated with chlorosulfonic acid, then stained by uranium acetate. The fine structure of polyolefin was obtained in this way.

Recently, a new staining technique has been established by Wegner and Zhu Lilan^[3]. They used allylamine etching polymer having ester bonds, and then stained the sample with OsO_4 . The contrast between amorphous regions and crystalline one in those materials was enlarged dramatically. This opened a new route to investigate morphology of the polymer having ester bonds. Many fruitful results on poly-ester-ether-amide^[3], polyester-polyether multiple segment copolymer^[4], and PET films experienced different thermal-mechanical history^[5] have been obtained.

In this paper, we report studies on the process of etching PET films by means of infrared spectroscopy and scanning electron microscopy, for understanding the action of allylamine and OsO_4 staining on contrast in polymer having ester bonds.

EXPERIMENTAL

1. Sample preparation

PET has been investigated extensively in various respects. For example, the vibration spectrum of PET has been assigned in detail by many researchers^[6]. But few work have been done

on its morphology for lack of a suitable staining agent. It is of more importance that many copolymers contain PET segments. If the etching process of PET by allylamine are understood well, it would also be useful to other polymer having ester bonds. So, the PET film having different thermal-mechanical history was chosen as sample in this study.

Allylamine was supplied by Shanghai Chemical Agent Company. The raw PET film was obtained from Shanghai Chemical Factory and then was processed in different thermal-mechanical history Conditions.

(1) Solution-casting film

A few pieces of raw films were dissolved in trifluoroacetic acid, and after the vaporization of the solvent, formed a homogenous film, which then was put into a vacuum oven for removing the residues of solvent. The film was melted at 280°C and quenched quickly in ice-water to amorphous state. The density of the film is 1.34g/cm³.

(2) Uniaxial stretched film.

The raw PET film was stretched at 110°C with strain rate 60.7%/min. The stretching ratio is 7.6. The density of the film is 1.34g/cm³.

(3) Biaxial stretched film

The biaxial stretched film was the same as sample B, but was stretched simultaneously in two directions at 100°C and at strain rate of 25.9%/min, with stretching ratio 3.4. The density of sample C is 1.357g/cm³.

2. Etching of PET film

The prepared samples were put into a container where there is an ampule of liquid allylamine. Then the ampule was broken to fill the container with allylamine vapor. After preset time of etching, the samples were taken out to remove residual allylamine in a vacuum oven at room temperature for an hour and then measured by infrared spectroscopy and scanning electron microscopy.

The IR instrument is PEKIN-ELMER 180. Resolution was set to 2cm⁻¹ at 1000cm⁻¹. The SEM is DX-3A produced by the Scientific Instrument Work of the Academia Sinica.

RESULTS AND DISCUSSION

Figure 1 shows a group of micrographs which represent the morphologies of PET films during etching. With the increasing of etching time, the surface morphology of the films was revealed clearly. Micrograph 1 is the surface morphology of specimen 1 of film C after 12hrs etching. There is no evident etching effect on the micrograph. Micrograph 2 is the one after 22hrs etching. There is only a little effect can be seen on it. Micrograph 3 is the one etched for 35hrs. Part of the surface area have been etched seriously, The network morphology was disclosed clearly in that area. After 46hrs etching, all of the surface area have been etched, and the typical morphology of PET film appeared on the micrograph 4.

Figure 2 shows that there are some new bands appearing on the IR spectrum of etched film A. The 3300cm⁻¹, 1680cm⁻¹ 1540cm⁻¹ bands are due to the vibrations of N—H group, C = O group, amide II respectively. It is evident that new structures have been formed in the film after etching by allylamine. It may participate in the following reaction with the ester bonds of PET chain.

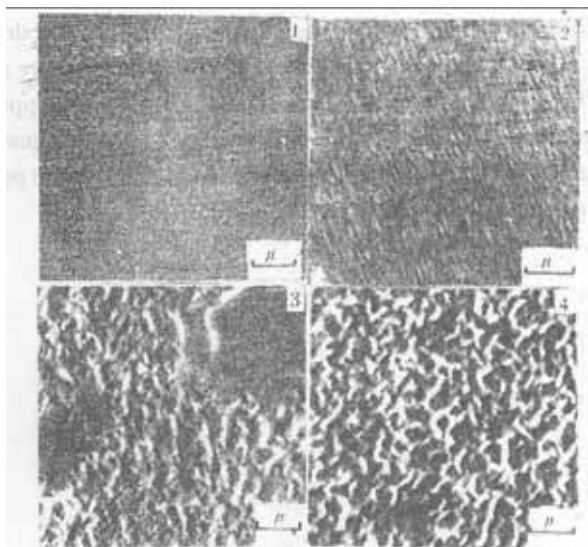
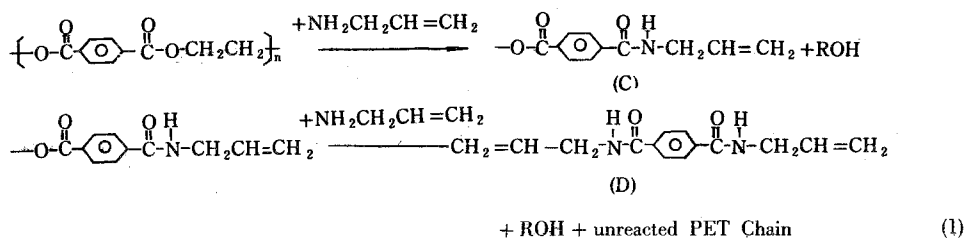


Fig 1 The morphology revealed on the surface of PET film with the increase of etching time of sample C
1, 12h; 2, 22h; 3, 35h; 4, 46h.

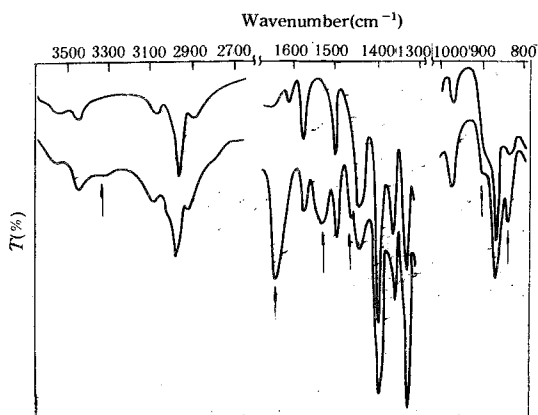


Fig 2 The PET spectrum after 2 h etching of sample A.

Compound C is PET chain connected with one allylamine molecule. D is the final product of the complete degradation of a PET chain. For further verification, some other PET films were over-etched with liquid allylamine. The etched products were dissolved in distilled water. After filtration, separation, crystallization of the solution, a yellow needle-like crystal was obtained. It is the exact compound D by IR and MS characterization. As a matter of fact, some bright points on the micrograph C and some black point on TEM micrograph in ref. [3] can be observed, which are

the aggregates of degraded products of PET chain.

There are many significant changes for the bands which are associated with vinyl-glycidol chain conformation states. The 845cm^{-1} , 1340cm^{-1} , 1473cm^{-1} , trans conformation bands increased, and the 898cm^{-1} , 1372cm^{-1} , 1455cm^{-1} , gauche bands decreased with the increase of the etching time. This means that there is conformation change in PET chain during etching process.

For characterizing the whole etching process, the amide II band 1540cm^{-1} was chosen as an analysis band and the 2965cm^{-1} band as an internal standard band for it does not change during etching. From Fig.3, it is evident that although all of the three samples were subjected etching, the rate of etching are different. For sample C, the 1540cm^{-1} band only appeared after long time etching. However, the amorphous film A has a relatively much higher intensity of the band after 1 hr etching. The etching rate of sample B is between A and C. This order is parallel to the results^[7] about the hydrolytic rate of PET film by HCl.

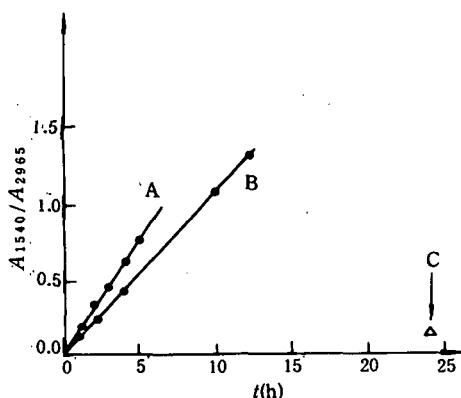


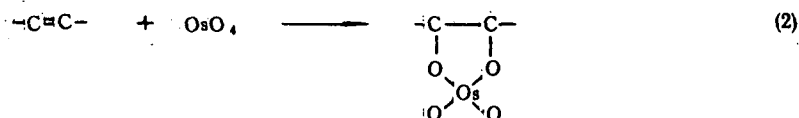
Fig 3 The different etching rate of samples which have different thermal-history

A, amorphous film. B, uniaxial stretched film. C, biaxial stretched film.

It may be interpreted by that the etching effect depends on the thermal-history of the sample. In light of the chemical reaction, the reaction rate depends on many factors, and for the bulk polymer there is an additional factor which is important in etching, that is the thermal-mechanical history of polymer.

From the above results, it can be concluded that the mechanism of enhancing contrast of PET by allylamine is the amidation reaction on the ester bond of PET chain. But the reaction is not violent. In the PET film there are two different regions in microscopic level. The chain in crystalline regions are in stable trans-conformation, and the density of chain is greater than amorphous one. Chains are arranged in order. When the allylamine diffused into the surface of PET film, it is easier to enter the amorphous area and amidate with the ester bonds in that regions. As the etching rate is quite slowly, only a few ester bonds on the chain participated in the reaction with allylamine at the preset time, e.g., only the chains on the surface in the amorphous region have been affected, and the chains in the crystalline region and in the core of bulk polymer remained without etching. As a few ester bonds are connected with allylamine, the chains now have vinyl groups in the amorphous regions. The strong interchain-interaction held the chains at their original place.

There is a very important difference between the sample preparation for SEM and TEM. For samples to be observed by SEM, it is not necessary to be stained by OsO_4 after etching with allylamine. As a matter of fact, other amines may also be used in this purpose. However, for TEM, it must be stained by OsO_4 after etching. The SEM uses the secondary electrons emitting from sample surface to form the image which depends on the roughness of surface. It shows clearly on the micrographs that the etching time should be relatively longer in order to reveal the surface morphology. But for samples in TEM, the etching conditions should be well-defined and over-etching be prohibited^[8]. It is necessary to stain the sample with OsO_4 . In the second step, the vinyl groups reacted with OsO_4 as follows:



and the heavy metal osmium deposited in that regions finally enhanced the contrast between the amorphous state and crystalline one. The difference between these two staining processes can be illustrated in Fig. 4. A is the case for TEM, and B is for SEM.

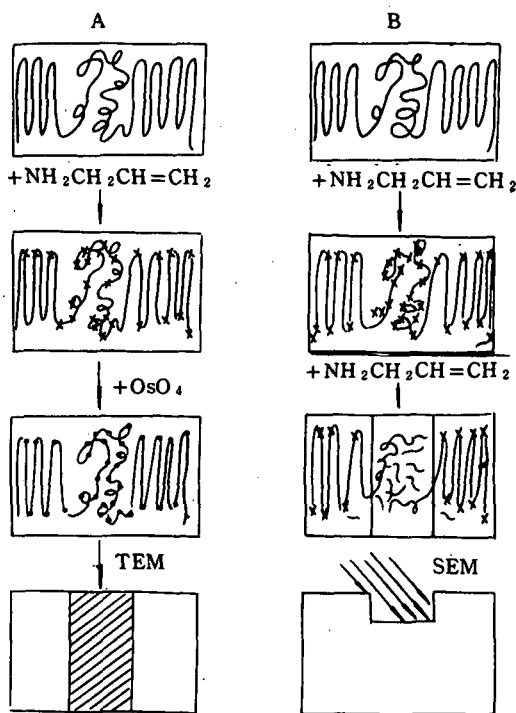


Fig 4 The proposed model of the etching process and staining process on PET film for SEM, TEM respectively

A, the two step etching/staining method for TEM. B, the etching process for SEM.

× indicates the position of allylamine; ● indicates the position of OsO_4

Keywords:

Staining allylamine/ OsO_4 ; morphology; SEM; IR

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