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THERMAL ANNEALING AND REFRACTIVE INDEX MONITORING OF POLYPROPYLENE FILM

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ABSTRACT

Isothermal annealing technique was used to accelerate the ageing process on prefabricated highly crystalline polypropylene thin films to investigate the specification failure of such films. Samples were held at a constant temperature of 125 °C, for different periods of time ranging from 1 to 10 hours. A mechanism to describe the observed variations has been proposed. A model for the macrostructure is introduced which explains the observed data. The suggested model helps to identify the role of relaxation processes by ageing. The periodic changes of the polymer structure were proven by infra-red technique. Infra-red dispersion properties of the samples were measured in the wavelength range 2-6.5 micron. The technique exhibited a structural periodic time of 4 hours.

KEY WORDS: Polypropylene, Annealing Technique, Infra red

INTRODUCTION

All polymers can be found in two major structural states: crystalline and/or amorphous state. The most important feature of polymers in the crystalline state is that they are not generally composed of crystallites alone; they also contain amorphous regions. Therefore, the term "crystalline polymer" in fact means that it is only partially crystalline (1).

The effect of annealing increases drastically with temperature, and also depends on the time for which sample is held at the annealing temperature. To understand annealing effects, their molecular source must be known. In the case of a highly crystalline polymer, thermal treatment strongly affects its crystalline state, including degree of crystallinity, orientation and distribution of crystals throughout the amorphous region. Many authors have studied this subject from different points of view (2-4).

In the majority of cases, the degradation of polymers is not desirable because it detracts from the physico-mechanical and other properties of polymers. Selection and modification of suitable thermal stabilizers for polymers are also directly dependent on results of such studies. On the other hand, most polymers suffer degradation by aging at a continuous operation temperature, or even at room temperature during storage.

Aging can be defined as any change in the molecular, supermolecular, or phase structure of polymers and materials resulting in a change in the physicomechanical properties during storage or service of the relevant articles(5). Annealing of a polymer for long time at a constant temperature (isothermal annealing), few degrees below its softening temperature, may be referred to as accelerated ageing process.

In this work, a study of the origin of the variations due to aging of a polymer has been made. It is expected to be helpful in finding a treatment for increasing the durability of polymeric end products, which allow these products to be stored or used for longer time without serious failure.

EXPERIMENTAL METHODS

A. Sample preparation

The specimens used in this investigation were rectangular pieces cut in parallel to the machine direction from a polypropylene film manufactured by TECHNOPOCK CO., EGYPT, labeled BOPP of Poly.P. film-OCS. Samples were left in an electric oven for different periods of time ranging from one to ten hours, and then quenched in air at room temperature 23°C. The temperature of the oven was fixed at 125 ±1 °C. This was carefully selected in view of the following criteria:

1. Well above the glass transition temperature (-20°C for polypropylene)(6) .
2. Within the sample's range of continuous use temperature (120-160 °C)(7) .
3. Fairly, away from the softening temperature (140-170 °C)(7) .
4. Some degrees higher than the temperature needed to develop enhanced mobility to the crystals of isotactic polypropylene (110°C)(8) .

B. Measurement of film thickness

The thickness of samples was measured using a calibrated high power traveling microscope. The calibration was done using a standard gratitule 100 divisions per 5 mm. The microscope's micrometer scale is 100 divisions per one millimeter on the horizontal direction so, the minimum measurable horizontal shift was 0.2 micron. A long section from the sample was examined at about 50 positions through 12 cm of its length, and the average thickness was calculated and found to be 20±0.2 micron.

C. Determination of the IR-Dispersion properties

The transmission spectra of the annealed samples were measured by the IR-Nicolet model Magna FT-IR spectrometer 550 (7000-200 cm^{-1}). Figure 1 is a typical print of the obtained spectrum, in the range of interest, for a polypropylene film annealed at 125 °C for 5 hours.

A beam of light which falls normally on a thin film, bounded on either side by semi-infinite nonabsorbent layers, will be divided into reflected and transmitted parts. Such division occurs each time the beam strikes an interface so that the transmitted and reflected beams are obtained by summing the multiply reflected and multiply transmitted elements. The multiply transmitted elements interfere with each other forming bright and dark fringes. For bright fringes (maximum transmission)

$$2\mu d = n\,\lambda \qquad (1)$$

Where μ is the refractive index of the film material at the wavelength λ, while $n = 0, 1, 2, 3, \ldots$ is the order of the fringe and d is the film thickness. In finding the refractive index from interference fringes, there is the problem that in general the order of the fringe, n, is not known. The usual method of overcoming this problem is to measure the wavelength λ_1, λ_2 for two adjacent transmissions maxima and apply the equation (9):

$$2\mu d = (\lambda_2^{-1} - \lambda_1^{-1})^{-1} \qquad (2)$$

In this method, the calculated value of μ may be considered as the average of $\mu(\lambda_1)$ and $\mu(\lambda_2)$ when the dispersion is effective. By successive application of Eq.(2) to a train of transmitted bright fringes, one can obtain values for the function $\mu(\lambda)$ where $\lambda = (\lambda_n + \lambda_{n+1})/2$.

Figure 2 shows the dispersion curve characterizing the unannealed polypropylene film. The figure shows a fair normal optical dispersion either in the neighborhood of the present characteristic absorption bands or between bands. This normal behavior was violated by annealing. A serious abnormality (anomalous feature) began to appear just after one hour of annealing. The amount of the shift from the normal dispersion behavior was found dependent on the annealing time Fig. 3. The size and positions of the anomalous peaks in the characteristic dispersion curve of a polymeric medium were related to the degree and type of the anisotropy generated in the medium due to the applied treatments (10-12).

RESULT AND DISCUSSION

Stability is a major task of researchers in the field of industrial production of polymeric articles. Some aspects of the problem of polymer stability have been solved chemically by adding stabilizers, inhibitors,...etc. Such chemical treatments of polymers act on either the chain interaction forces or on the bond strength of the chain components. Both of these characterize the physical state of the final polymeric article just after the production or for some finite range of time after production. Other sides of the problem of polymer stability are still under active consideration and a lot of polymeric products, especially films and fibers, degrade their specifications, as a second stage raw material, during storage or by aging. The physical and mechanical conditions during fabrication appear to be responsible for the unsatisfactory long range stability of polymeric products. The following data analysis is an attempt to identify to which degree does the processing of films and fibers affects their stability of the final product.

Recalling figures 1, 2, and 3, one can record the following behaviors:

(1) All observed variations are damped periodic variations (note: the magnitude of the recorded variations may be included within the experimental error limits. However, this probability was discarded; because, random errors do not exhibit systematic behavior, oscillatory or periodic or otherwise. In addition, similar data from other authors showed the same behavior, but was not identified as fine periodic variations [8,9],taking into account the time-temperature superposition principles .

(2) The periodically varying crystallographic parameters have nearly the same periodicity, although Bragg's angle and the reflected intensity are independent.

(3) Most variation of parameters occur during the first two hours of the annealing process.

(4) By increasing the annealing time, values of all parameters are found to tend to stabilize at values only slightly different from the starting values.

Considering the above notes one may decide that, all the recorded observations should be a physical response to either a single or a set of simultaneous mechanisms. To determine this / these mechanisms, the relations in Figs. 1,2 and 3 should be analyzed to its proper functions as assisted with the variation in XRD structure[14] .Then one may consider that each obtained function component should describe an independent mechanism . A numerical analysis was done using commercial software. The analysis clarified that the annealing time functions, including lamellar thickness, XRD and inter planer spacing[14] have shown that these are summation of only two functional components. These are: (1) a continuous function and (2) a damped sinusoidal wave function. The net form that describes any of the annealing time functions is the sum of these functions.

Practically, the drawing process may be defined as one where the sample's successive transverse sections are subjected to a velocity gradient field. Such sections are considered extremely dense so that any point in the polymer should lie within a section. Hence, every micro structural element in the polymer will share in the overall observed variations, each according to its nature and its location with respect to the direction of the driving force (15-17).

Hence, it can be safely proposed that the observed variations of the crystallographic parameters are all due to recovery of the strained molecular system, through two different and simultaneous mechanisms. Moreover, during recovery, all mechanical responses of the polymeric molecular structure, due to drawing, would be reversed but damped due to the viscosity of the system. Thus, the structural behavior on recovery (on aging) may be deduced from the careful description of the mechanism followed by the structure during the drawing processes. This structural behavior on recovery and drawing was previously discussed [5,8] .

Peterlin gave more details about the response of a crystalline polymer undergoing tensile stress in the region of the neck (12). He also suggested a model for the formation and orientation of fibrils during necking. From the current authors point of view, two points are unclear in Peterlin's model. Primarily, according to the mentioned model the crystallites, at necking, were rotated about some axis by 90 ° to form the fibrils. Such rotation needs, of course, a torque, i.e. two non- axial forces in opposite directions. The drawing force is one of them, but the model didn't define the second one. The resistance force due to the viscosity of the interlamellar regions should not be considered this second force, because the resultant resistance due to viscosity acts coaxially with the drawing force but in opposite direction. Secondly, the mentioned model does not define the structural element which releases the stored strain if the sample, at necking, is left free to relax and how?

On isothermal annealing (accelerated ageing), the frozen strained fold tips would be relaxed. During such relaxation, the defolded tips will follow the same straining sequence but in the opposite direction. Thus periodic variations in the crystallographic parameters can be obtained by ageing. With time the number of strained folds tips decreases, so the occurrence of the periodic variations should be damped, since measurements are for the average values of the crystallographic parameters. Hence, the damping factor may represent the average relaxation time of a fold tip.

The current author used a previous notation [10] where the dependence of the size and shape of shifting in the far IR-dispersion properties of a polymeric medium from the known normal dispersion, on the macro-structure of the medium. So, the repetition of the whole polymeric structure means repetition of the IR-dispersion properties measured in the IR-range where there are no characteristic absorption bands.In Figs. 3 the graphs for the times(3,4h) (5,7h) and (8,9h) show the coincidence of the dispersion properties of the annealed polypropylene films where the annealing time difference was exactly 4 hours. This implies that the periodic structural variation of the polymers by ageing is a physical fact. It also provides strong evidence for the validity of the concept introduced by ref. [10] when the determination of the average structural variation of a polymer is a main task.

CONCLUSION

From the above discussion, the following conclusion is evident. Measurement of the far IR-dispersion properties for a polymer film can give clear view for the whole structural variations caused due to various external effects. This technique still needs further theoretical work to link the observed dispersion characteristics to other measurable physical parameters.

In order to define the stable specifications of polymeric products, the author recommends carrying out the quality test on polymeric products after isothermal heat treatment at suitable temperature and time. In fact this study was carried out on highly crystalline sample only. Study of other samples with marked amorphous regions may lead to limited modifications to the mechanism of crystalline relaxation process presented and discussed here.

ÖZET

Kristalin yapıda hazırlanmış polipropilen filmlerin ayırdedilmesinde karşılaşılan güçlükleri incelemek amacıyla bu tür filmlerin hızlı bir şekilde yaşlandırılmalarını gerçekleştirmek üzere izotermal tavlama yöntemi kullanıldı. Numuneler bir saat ile on saat arasında değişen sürelerde 125 santigrad sabit sıcaklıkta tutuldu. Gözlenen değişiklikleri açıklayabilen bir mekanizma önerildi. Elde edilen verileri betimleyen makroyapısal bir model öne sürüldü. Bu model, yaşlanma ile relaksasyon süreçlerinin rolünü açığa kavuşturmakta yardımcı olmaktadır. Polimer yapının periyodik değişimleri kırmızı altı tekniklerle gösterildi. 2 – 6,5 mikron dalgaboyları için numunelerin kırmızı altı dispersiyon özellikleri ölçüldü. Uygulanan bu teknikler 4 saatlik bir yapısal periyoda işaret etmektedir.

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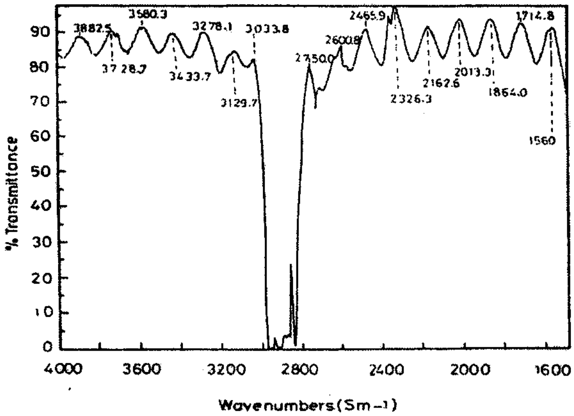

Fig. 1 – A typical print of the spectrophotometer transmittance spectrum for a used polypropylene film annealed at 125 o c in air for 5 hours.

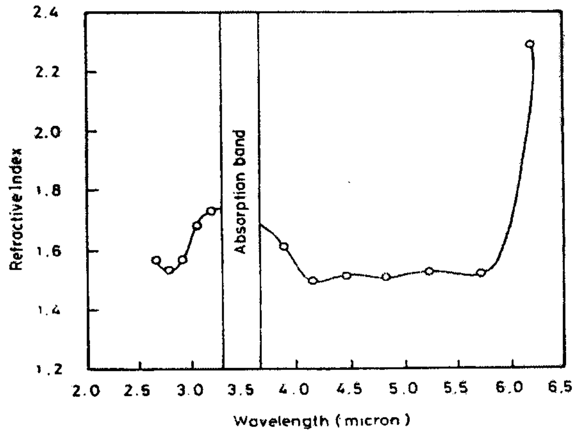

Fig. 2 – The dispersion characteristics of untreated polypropylene film.

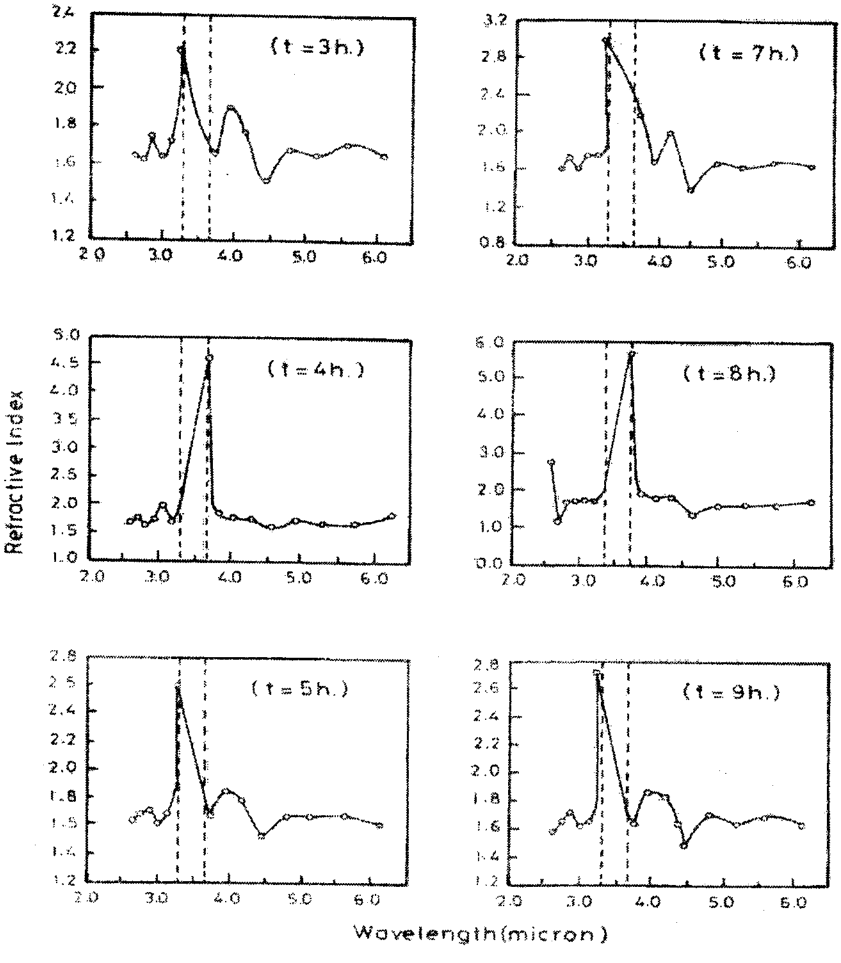

Fig. 3 - The dispersion characteristics of annealed polypropylene films at 125 o c for different period of time.

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