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DSC STUDIES OF THERMAL EVENTS AT THE GLASS TRANSITION TEMPERATURE REGION OF PARTIALLY ORIENTED POLYESTER FIBERS

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ABSTRACT

The high rate of quenching and the excessive frozen-in stresses development that take place during the spinning process of partially oriented polyester yarns brings about a thermal behavior similar to that of pressure vitrified and mechanically stressed polymeric glasses with a sub Tg exotherm preceded by an endotherm at 335°K.

Annealing at 338°K relaxes the frozen-in stresses and eliminates the sub Tg events.

Annealing above 355°K recovers the enthalpy of the aged fibers, minimizes the enthalpic recovery and drops the endothermic peak height in the DSC thermogram. The extent of enthalpic recovery during annealing of fibers containing different spin finishes indicates the plasticization efficiency of the finishes.

INTRODUCTION

Prest and Roberts observed in the DSC thermograms of pressure-vitrified and mechanically stressed polymeric glasses an exothermic event preceded by an endotherm at temperatures below the glass transition [1]. As shown in Fig. 1, aging of the polymeric glasses develops the low temperature endotherm in the fractured samples and the normal higher temperature endotherm in the regular samples.

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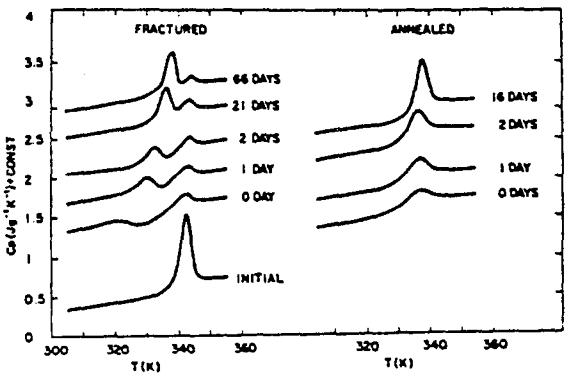

Fig. 1 Apparent heat capacity of attrited (left) and an unstressed (right) low molecular weight copolymer as a function of annealing time [1].

It has been concluded that the endothermic peak is associated with the recovery of the lost enthalpy in the aged polymers and that the internal stresses in the deformed glasses permit the normally observed endothermic process to occur significantly below the glass transition temperature [1, 2].

According to another approach, the residual stresses decrease effectively the glass transition by increasing the free volume of the polymer [3]. According to Boyer, one can consider the stressed polymers as a two phase system of strained and unperturbed molecules giving the lower and higher glass transitions respectively [4].

The high spinning speed of partially oriented yarns involves high strain rate and thread-line stress which freezes-in due to the rapid quenching.

Indications for the effect of the frozen stresses on the glass transition of polyester partially oriented yarns were obtained in studies of their shrinkage and dyeing behavior [5, 6].

In this report a DSC study characterizes the effect of frozen-in stresses on the thermal events at the glass transition temperature region of the fibers and compares them with the reports on stressed glasses.

EXPERIMENTAL

Materials: Poly(Ethylene Terephthalate) Partially oriented yarns were spun at 3300 m/min. The Polymer I.V. was 0.649. Yarn samples were finished with pure water and with 15% aqueous solutions of Poly(Ethylene Glycol)s of molecular weights 400 and 540. Differential scanning calorimetry thermograms were obtained on a Perkin Elmer DSC II. The heating rate was 20°C/min and the sample weight was 5 mg. In order to maintain a uniform geometry inside the pan, all yarns were wrapped on spools.

RESULTS AND DISCUSSION

The DSC thermogram of a Partially Oriented Polyester Yarn (POY) given in Fig. 2 shows exothermic and endothermic peaks below the 355°K glass transition endotherm.

In Fig. 3 the thermogram scales expansion at the glass transition temperature range shows an exothermic peak preceded by an endothermic peak at 335°K.

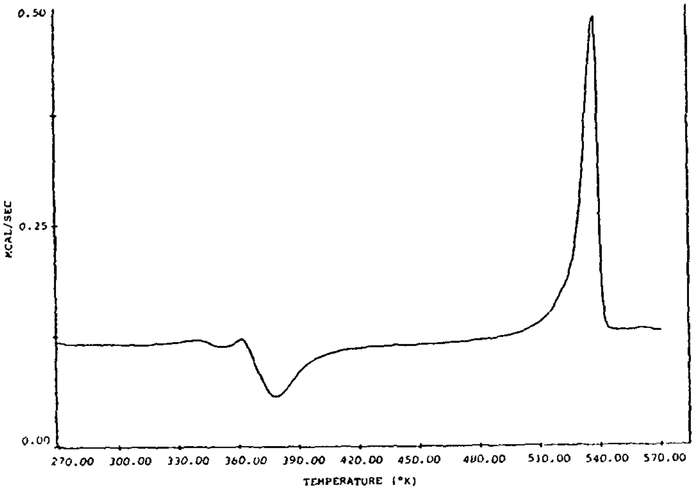

Fig. 2 DSC thermogram of Polyester partially oriented yarn.

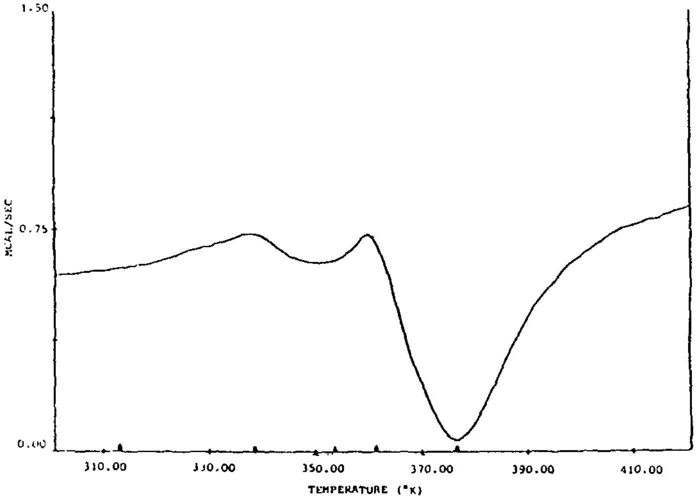

Fig. 3 DSC thermogram of Polyester partially oriented yarn. Expanded scales.

Annealing of the yarn at 338^{o}K for one hour yields in Fig. 4 a thermogram without any thermal event below the glass transition, while the endothermic peak at the glass transition (355^{o}K) becomes more excessive.

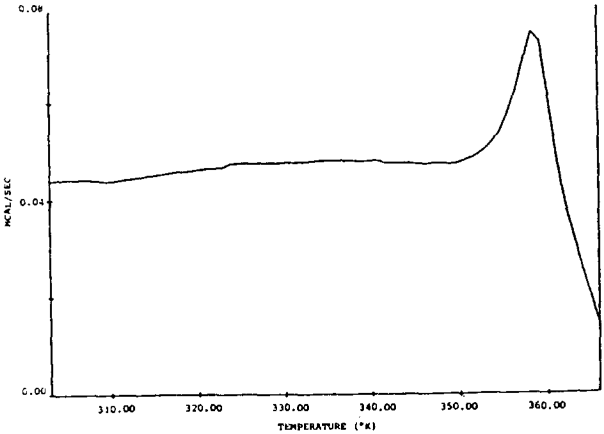

Fig. 4 DSC thermogram of Polyester POY annealed at 355^{o}K for one hour.

The observations are similar to reports by Prest and Roberts on pressure vitrified and mechanically stressed polymeric glasses, where the low temperature endotherm exists only in stressed glasses, and develops as the aging time of the stressed glasses increases [1, 2]. Accordingly, the high stress levels and rapid quenching associated with the partially oriented yarn spinning, generates a high degree of frozen stresses in the amorphous phase, which permit the normally observed glass transition endotherm to take place at lower temperatures. The endothermic peak is associated with the sudden recovery of the enthalpy that the molecules lost during their aging.

The exotherm following the lower temperature endotherm is related to the exothermic relaxation of the frozen-in stresses in the strained molecules that takes place once they reach their corresponding glass transition.

One can conclude that the POY fibers contain two glass transitions. The low glass transition is related to the stressed amorphous phase and the normal higher glass transition is related to the unperturbed phase. Lower glass transition in stressed polyester had been reported already [4].

Annealing at temperatures in the vicinity of the lower glass transition relaxes the stressed molecules and eliminates the low glass transition. Annealing above the upper glass transition temperature recovers the enthalpy of the aged molecules and drops the endothermic recovery at the glass transition: In Fig. 5 higher annealing temperatures and better plasticizers enhance the enthalpic recovery and correspondingly drop further the endothermic peak height. In Fig. 6 Poly(Ethylene Glycol)s plasticize the fibers. Apparently, PEG 400 is a better plasticizer than PEG 540.

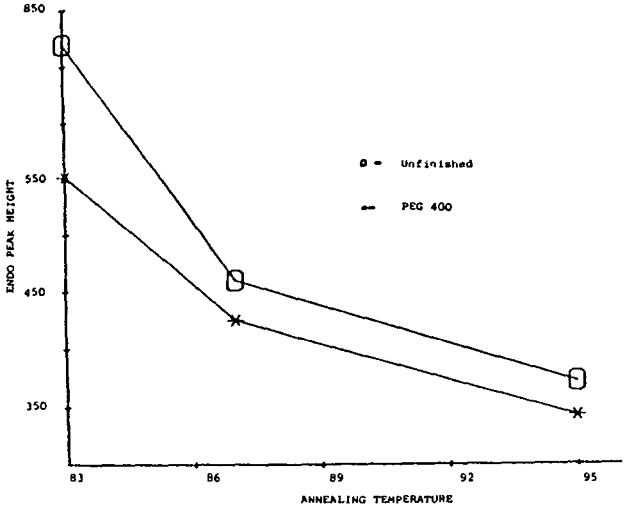

Fig. 5 Effect of annealing temperature on the endothermic peak height of Polyester partially oriented yarns finished with water and PEG 400.

CONCLUSIONS

The high threadline stresses and rapid thermal quenching that take place during high speed spinning of partially oriented polyester fibers brings about a thermal behavior similar to that of pressure vitrified and mechanically stressed polymeric glasses which have a typical

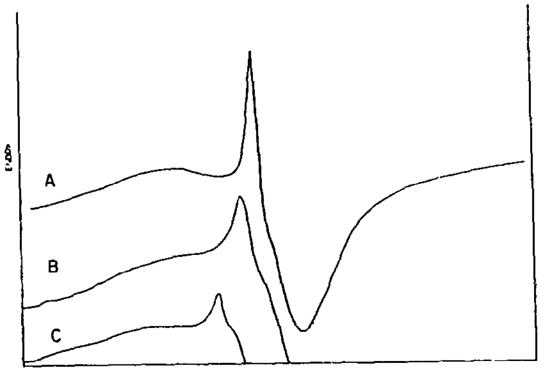

Fig. 6 DSC thermogram of Polyester partially oriented yarns with different finishes: A-deionized water. B-PEG 540. C-PEG 400.

exothermic peak proceeded by an endothermic peak, both below the observed normal glass transition endotherm. The lower temperature events are related to the excessive free volume and entropy in the stressed molecules which decrease the glass transition. Annealing at the vicinity of the lower temperature endotherm relaxes the excessive free volume and entropy and eliminates the lower glass transition. The effectiveness of enthalpy recovery during annealing above the upper glass transition temperature of the aged molecules can be evaluated by the height of the endothermic peak at the upper glass transition temperature.

Accordingly, the plasticization efficiency of additives in the fibers can be evaluated by the residual upper glass transition endothermic peak height in the DSC thermogram: The better plasticizer enhances the enthalpic recovery during annealing and minimizes the endothermic enthalpic recovery peak in the DSC thermogram.

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