

ELASTICITY OF HARD ELASTIC POLYPROPYLENE FIBRE AND SURFACE ENERGY*

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ABSTRACT

In the stress relaxation process of HEPP (Hard Elastic Polypropylene) fibre, the added liquids, e. g. ethanol and n-hexane, which can wet polypropylene, cause an abrupt decrease of stress.

By measuring the contact angles and decreases of stress and evaluating according to Young-Dupre's equation, it was found that about one-third of the initial stress is associated with the surface energy. When soaked in liquids mentioned above, HEPP fibre almost lost its elasticity. It is not the result of plasticizing or 'solvent cracking' but most likely comes from the changes of the surface energy.

INTRODUCTION

Hard elastic polypropylene (HEPP) fibre is a kind of fibre with crystalline lamellae aligned normal to the fibre direction. It has high elasticity when extended. The elasticity of this crystalline polymer is primarily not rubber-like, but is rather controlled by the energy effect. Recently many models were proposed to explain its elasticity. The simplest one is the leaf-spring model which is based on reversible bending of lamellae. Some models also consider the contribution of lamellae rotation, the entropy change of interlamellar layer, the surface energy effect of micro-voids and the surface energy effect of microfibrils^[1-5]. Each structure model explains certain aspects of hard elasticity. But they are not consistent. As to the essence of elasticity mechanism of HEPP, there is still lack of full understanding to date.

This paper tries to discuss the elasticity mechanism based on experiments of HEPP fibres extending in some liquids.

EXPERIMENT

HEPP fibre (SM-45-A, Celanese Research Company) was kindly supplied by H. D. Noether. The liquids used in experiments are all of analytical grade except liquid paraffin (chemical grade).

The tensometer used is DL-1000 made by the Second Material Testing Factory, Changchun. The extension experiments were carried out at the temperature range of 20–25°C, with sample length of 50 mm, and draw speed of 50 mm/min. The sample and clamps can be both immersed in liquids during experiments.

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The measurements of contact angles between polypropylene fibre and liquids were performed on WDS-I contact Angle Meter made by The East China Institute of Chemical Technology.

A Rigaku Geizeflex 3015 X-ray diffractometer was used for the small angle X-ray scattering measurements with experiment conditions of copper target, k_{α} ray, 40 kV and 15 mA.

RESULTS AND DISCUSSION

M. Miles et al.^[3] have found that the stress relaxation curve of hard elastic polyethylene fibre will shift to lower level if methanol is added to immerse the fibre during the process of stress relaxation and it shifts back to its original height after removing the methanol. Their experiments indicate that the retractive stress of hard elastic polyethylene is partly associated with surface energy.

In order to semi-quantitatively estimate the surface-energy-associated part of retractive stress, the stress relaxation curves of HEPP fibre was studied, curve 1 in Fig. 1 is the stress relaxation curve of HEPP fibre at 50% elongation. It tends to level off after 6 mins. When samples were soaked in liquid which can wet polypropylene surface, the stress dropped immediately as shown by curves 2 and 3 in Fig. 1. After liquids were removed and evaporated from the fibre, the stress relaxation curve went back to its previous height as shown in Fig. 2. These phenomena are similar to M. Miles' results about hard elastic polyethylene fibre.

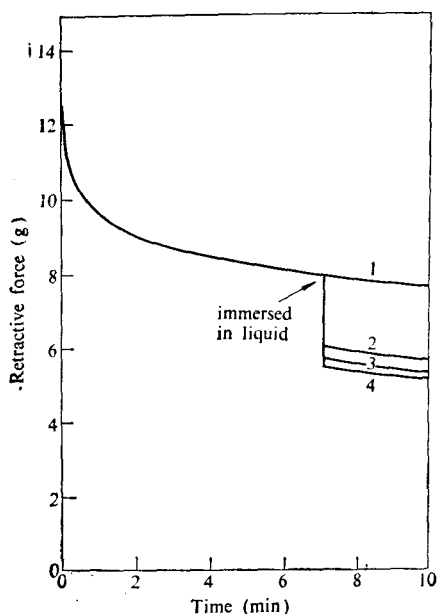


Fig. 1 The stress relaxation curve of HEPP fibre
1. Air; 2. Ethanol; 3. Butanone; 4. n-hexane

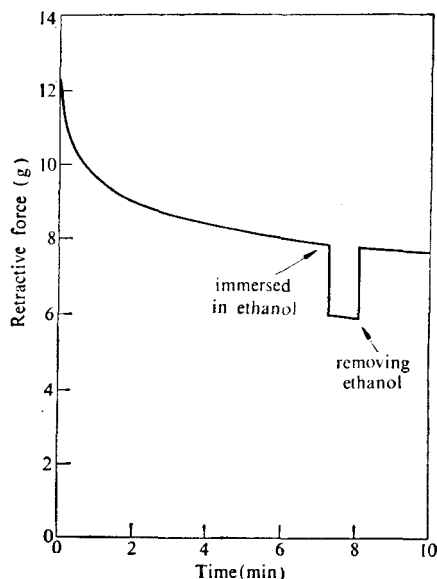


Fig. 2 The effect of ethanol on stress relaxation of HEPP fibre

According to Young-Dupre's classical equation,

$$r_s - r_{sL} = r_L \cos \theta$$

where r_s is the surface tension of solid polypropylene; r_{sL} , the interfacial tension between solid polypropylene and liquid medium; r_L , the surface tension of liquids; θ , the contact angle between polypropylene and liquid. F_s , the surface-energy-associated part of retractive stress, should be proportional to r_s ; and the stress reduction due to the addition of liquid, ΔF , be proportional to $\cos \theta$. In the calculation, r_s may take the value of the critical surface tension of polypropylene, namely 32 dyne/cm^[7]. Therefore, by measuring contact angles, it is possible to calculate the proportion of F_s in F_0 , the latter is the stress before relaxation. The results are listed below.

	r_L (dyne/cm)	θ (°)	ΔF (g)	F_s (g)	F_s/F_0
Ethanol	22.75	39	1.94	3.5	0.28
n-hexane	18.43	<15	2.39	4.2	0.34
Butanone	24.6	43	2.10	3.7	0.30

It tells us that only one third of the initial retractive stress is due to surface energy effect. After six minutes of relaxation, the value of F_s/F_0 increases to about 0.5. I. K. Park et al.^[7] measured the hard elastic fibre's retractive stress under different temperature and found that the stress decreases with increasing temperature. This is remarkably different from so-called 'entropy elasticity'. In view of that the force measurements were taken after allowing the material to relax for ten minutes we think that the major part in F_s should be surface energy's contribution and, thus, the change of retractive stress with temperature resembles very much the change of surface energy with temperature.

Fig. 3 is a comparison of the stress relaxation curves obtained for HEPP fibre in air and in n-hexane respectively. The sharp decreasing of retractive stress in the initial parts of the

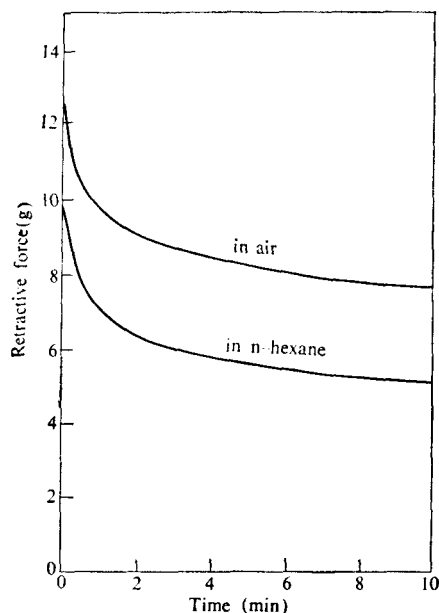


Fig. 3 The relaxation curve of HEPP fibre in different medium

curves implies that there is a certain 'viscous element' in the structure units. If we move curve 2 upwards, it can almost coincide with curve 1. This indicates that within the time scale of experiments the addition of n-hexane does not alter the 'viscous' property of the fibre.

Fig. 4 shows curves for cyclic loading of HEPP fibre performed in different liquid media, the abscissa is the relative changes of distances between clamps. It can be seen from the picture that in liquid media the elastic recovery reduces noticeably. The partial loss of elas-

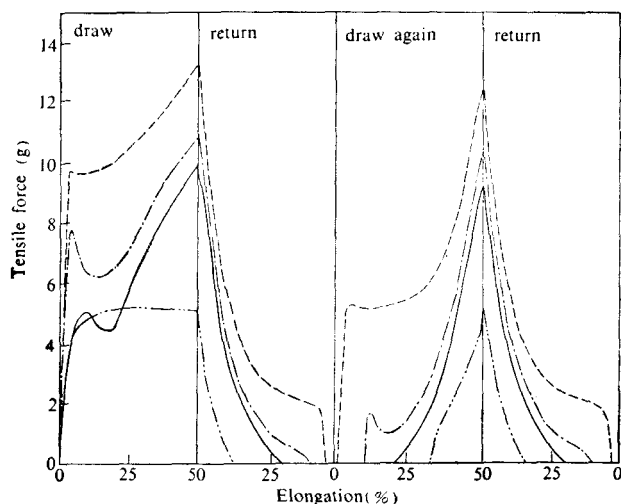


Fig. 4 Curves for cyclic loading of HEPP fibre in different medium: --- in air; - · - · - in ethanol; — in n-hexane; · · · · · non-elastic PP fibre

ticity may be caused by following factors: (a) the reduction of surface energy; (b) the partial breaking of fibre owing to 'solvent cracking' in the liquid media; (c) the plasticization due to liquid media. For finding the real cause, several experiments were designed.

One kind of experiments was that the cyclic loading were first performed with HEPP fibre immersed in *n*-hexane and then were done again immediately after the removal and evaporation of *n*-hexane. The results shown in Fig. 5 indicate that the elasticity was fully recovered and no 'solvent crack' took place during the extending process of HEPP fibre in *n*-hexane.

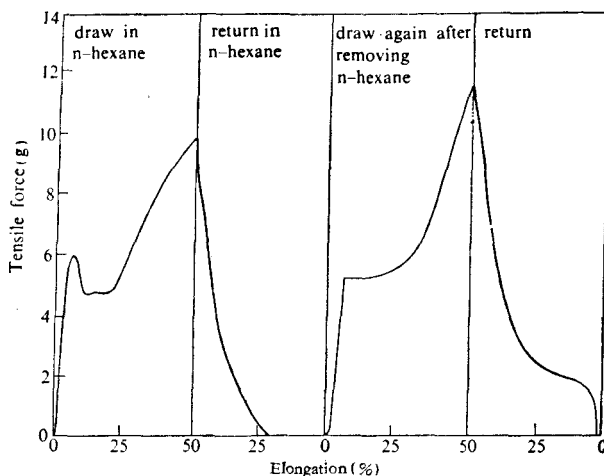


Fig. 5 The effect of *n*-hexane on curves for cyclic loading of HEPP fibre

In order to study the possible influence of plasticization by liquid, liquid paraffin which is similar to *n*-hexane in structure was chosen to replace *n*-hexane. It was found that during the extending process the loss of HEPP fibre's elasticity was also considerable. A new polypropylene fibre sample was made by mixing with 20% of liquid paraffin using screw extruder and then spun into HEPP fibre. The detailed method has been described elsewhere^[8] Curves for cyclic loading of the new fibre were shown in Fig. 6. Apparently HEPP fibre with and without liquid paraffin have same elastic recovery. Since polypropylene has high crystallinity, the percentage of liquid paraffin in the amorphous region could be very high although only 20% liquid paraffin is introduced. Liquid paraffin may have some plasticization effects on amorphous region. But this does not affect its elasticity. Therefore the partial loss of elasticity of HEPP fibre in *n*-hexane may not be originated from plasticization.

Then the elasticity loss of HEPP fibre is probably due to the change of surface energy. Although the retractive stress which relates to the change of surface energy is only one third of the total extension stress, it is the major driving force for the elasticity recovery of HEPP fibre.

In *n*-hexane, the interfacial tension of polypropylene will not disappear completely. According to Young-Dupre's equation $r_{SL} = r_S - r_L \cos \theta = 14$, which is about 40% of r_S . This interfacial energy causes HEPP fibre to retain partial elasticity when immersed in *n*-hexane.

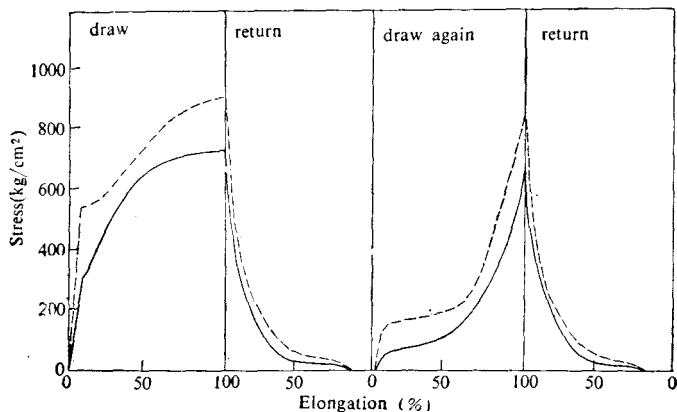


Fig. 6 Curves for cyclic loading of HEPP fibre containing 20% liquid paraffin
 — PP with liquid paraffin; --- pure PP

The interfacial tension between polypropylene and ethanol is a little bigger than that between polypropylene and n-hexane, so that the elasticity loss of HEPP fibre in ethanol is less than that in n-hexane.

It is well known that the stacked crystalline lamellae would open to form micro-voids during extending. This creates more surface area and is bound to enhance its surface energy. Fig. 7 is the SAXS curve of HEPP at meridian direction. The long period increases at 20 %

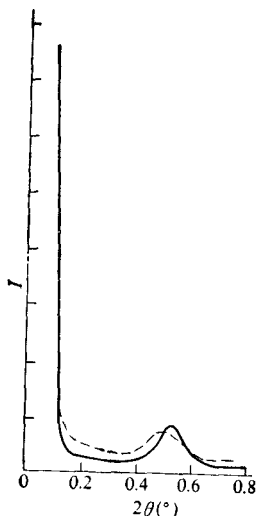


Fig. 7 SAXS curves of HEPP fibre at meridian direction
 — before elongation; --- at 20% elongation

elongation, which accounts for the spraying apart of lamellae and the formation of micro-voids. If the increase of lamellae surface area during extending is the only contribution to the increase of specific surface area then this increase should be limited when subjected to further extending. However, as shown in Fig. 4, after reaching 20 % elongation the tensile curves obtained in dif-

ferent liquids tend to be in parallel with each other and the surface energy-associated retractive stress keeps constant. It shows that the specific surface area increases continuously. It is conceivable to relate the increase of specific surface area to the formation of microfibrils during extending. Fig. 8 is Guinier plotting of HEPP fibre's SAXS curve in equator direction at 20% elongation. The part with smaller slope corresponds to structure units of dimensions in several decades of Å. These structure units may be microfibrils formed between lamellae during extending.

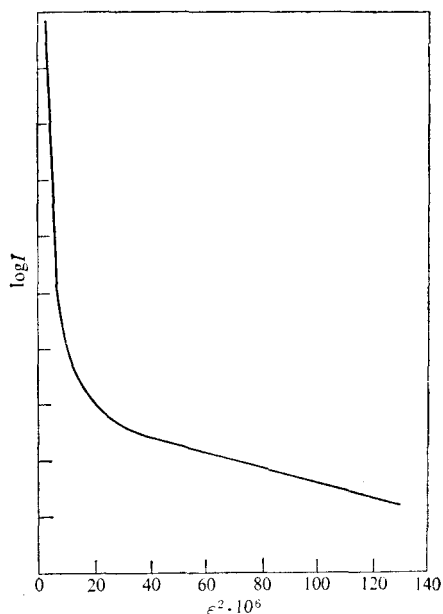


Fig. 8 Guinier plotting of HEPP fibre's SAXS curve in equator direction at 20% elongation

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