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Strength properties of solvent vapour-treated pre-tensioned polypropylene films

Part II *Aromatic solvent vapours*

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The dependence of strength properties of solvent vapour-treated and pre-tensioned polypropylene films on solvent interaction parameter, χ, and non-specific cohesion force, *D*, and the amount of pre-tension force, has been studied. The five strength properties are yield stress, σ_γ, initial modulus, *E*, draw stress, σ_d tensile strength, σ_b, and breaking factor, BF. The results show that for most solvent vapour treatments, the 98 mN pre-tensioned PP film exhibited larger values of the strength properties which also increased with decreasing plasticization effect (increasing interaction parameter/non-specific cohesion force). With the exception of tensile strength and breaking factor where the untreated PP films have larger values, the other strength properties (yield stress, draw stress, and initial modulus) exhibited smaller values than the treated PP films. These results are explained by the net balance of two opposing forces: crystallization by stretching orientation and solvent presence on the one hand, and plasticization, on the other. © *1999 Kluwer Academic Publishers*

1. Introduction

The main interest in the strength properties of polypropylene (PP) is its use in various applications such as fittings, crates, containers, packaging and chordage. During use, polypropylene-based materials are exposed to solvents and vapours. Li *et al.* (1) reviewed the different applications of liquid transport in polymer films. Michaels *et al.* [2] achieved a 15-fold enhanced permeability of untreated polypropylene membranes by solvent annealing in organic solvents at 60–100 °C.

While some researchers [3–7] have correlated changes in the tensile strength of polymers to the one-term Hildebrand parameter, other workers correlated the property changes to the absolute difference between the solubility parameters of the polymer and solvent $|\delta_B - \delta_S|$ [2], and to the interaction parameter of the solvent [8]. However, the first process in polymer–solvent treatment is the sorption of liquid or vapour. Michaels *et al.* [2] showed that organic vapour diffusivity in polypropylene film at 40 °C is time dependent, and exponentially dependent on the concentration (i.e. vapour pressure). The same work [2] provided evidence of activated transport, showing that with liquids of similar boiling points, PP films was perm-selective to *p*-xylene relative to *o*-xylene, methylcyclohexane and toluene relative to *iso*-octane, the behaviour was explained on the basis of small $|\delta_B - \delta_S|$ effects. However, the combined effects of $|\delta_B - \delta_S|$ and boiling point (i.e. vapour pressure or concentration) which separately have opposing effects on the diffusivity, were not discussed.

In our on-going investigations on polypropylene (PP) film samples, we have reported marginal elongation of pre-tensioned PP films at 25 °C in a high boiling liquid, decalin [9]. The variation in the strength properties of simultaneous halohydrocarbon solvent vapour and pre-tensioning treatments of PP films have also been explained by the net-balance of two opposing effects: stretching orientation crystallization and plasticization [10]. In the present study in aromatic solvent vapours, the results of solvent vapour-treated and pre-tensioned PP films specimens on the strength properties are reported. It will be shown that the net-balance of crystallization and plasticization effects plays a major role in the observed strength properties. Variations caused by low vapour (concentration), i.e., high boiling point of solvent, lower aromatic content of the petroleum fractions reformate and naphtha, and the relative difference in molar volume of solvents, will be highlighted. In addition, the sorption kinetics and saturation level elongation will be reported.

2. Experimental procedure

2.1. Materials

The polypropylene films (0.012 mm, thick, density 0.90 g cm^{-3}) were supplied by the Bag Manufacturing Company (BAGCO) Nigeria Limited, Lagos, Nigeria.

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The solvents were either Nigerian National Petroleum Corporation (NNPC) fractions: naphtha and and reformate or reagent-grade toluene, *o*-xylene, and tetralin and were used as supplied.

2.2. Methods

The solubility parameters of the petroleum fractions naphtha and reformate were determined from the aromatic content by aniline point determination, ASTM D 1012. The molar masses of these solvents were determined from ebullioscopic measurement with urea as standard, while the molar volumes were estimated from the mass to density ratio. Data on the physico-chemical properties of solvents are recorded in Table I.

2.2.1. Vapour treatment of pre-tensioned films

Fixed lengths (11 cm) of pre-tensioned polypropylene film were immersed in saturated vapours of liquids, and the elongation of the films at different time intervals was visually observed *in situ* with a Vernier Microscope, at times of 2, 5, 7, 10, 12, 15, 20, 25 and 30 min. The per cent elongation, E was calculated from the expression

$$\%E = \frac{l - l_0}{l_0} \times 100 \tag{1}$$

where l, l_0 are the new and original lengths, respectively. The pre-tensioning was done by attaching weights 10 gf (98 mN) and 5 gf (49 mN) at one end of the film.

After equilibrium desorption, the treated films were stored in brown envelopes in a desiccator at 25 °C 65% r.h. Data on elongation at different pre-tensions and different solvents are presented in Table II.

2.2.2. Mechanical properties

The treated films were stretched at crosshead speeds of 5 cm min^{-1}, and a gauge length of 5 cm in an Instron tensile testing machine, Model 1122. The film thickness was measured with Shirley Development thickness gauge (SDL 253). The mean of ten successive measurements made along the film was taken. Five samples from each treated film set were analysed and the mean values were recorded. The strength properties of the treated PP films were obtained from the stress–strain curves. Data on the strength properties (yield stress, σ_γ, initial modulus, E, draw stress, σ_d, tensile strength, σ_b, and breaking factor, BF) are presented in Table III.

3. Results and discussion

3.1. Variation of film thickness with treatment

There is strong evidence for change in film thickness following solvent vapour treatment of pre-tensioned films. Data on the change in PP film thickness for different solvent vapour treatments at 49 and 98 mN pre-tensioning, are presented in Table IV.

In Table IV, it is evident that, except for the *o*-xylene vapour-treated PP films which exhibited larger a per cent thickness increase for the 98 mN pre-tensioning, pre-tensioning had no effect on the per cent thickness increase for the other solvent-treated PP films. This result corroborates our earlier finding using halohydrocarbon solvents [10]. The plasticization effect,

TABLE I The solubility parameter, δ_S, non-specific solubility parameter, δ_s, molar volume, V_s, boiling point (BP), interaction parameter, χ, and non-specific cohesion force, D, of solvents

Solvent	δ_S (MPa$^{1/2}$) [11]	δ'_S (MPa$^{1/2}$) [12]	V_S (cm^3 mol^{-1}) [12]	BP (°C) [14]	χ^a	D^a
Reformate	19.00	19.00	104.9	115–118	0.0017	0.0007
Toluene	18.20	18.10	106.9	110.6	0.0153	0.0091
o-xylene	18.00	17.30	123.3	144.4	0.0313	0.0417
Naphtha	17.10	17.10	126.9	126–130	0.1455	0.0535
Tetralin	18.00 [13]	19.43	137.1	204–207	0.0783	0.0074
Untreated PP	18.80 [13]	18.80	46.7	—	—	—

[a] χ and D were calculated as in [10].

TABLE II Strength properties (yield stress, σ_y, initial modulus, E, draw stress, σ_d, tensile strength, σ_b, breaking factor, BF) of treated PP films and different pretensions and in different solvent vapours. χ = interaction cohesion force parameter, D = non-specific

Solvent	Pre-tension (mN)	χ	D	σ_y (MPa)	E (MPa)	σ_d (MPa)	σ_b (MPa)	BF (kN m^{-1})
Reformate	49	0.0017	−0.0007	19.8	240	16.6	29.0	3.77
	98			19.6	210	15.4	26.6	3.46
Toluene	49	0.0153	−0.0091	20.6	160	16.6	30.0	3.90
	98			19.1	140	15.6	35.6	4.61
Tetralin	49	0.0783	−0.0074	19.8	300	14.8	37.7	4.02
	98			19.4	375	16.4	30.7	3.97
o-xylene	49	0.0313	−0.0417	18.0	250	14.8	37.7	4.75
	98			20.3	200	16.8	32.7	4.12
Naphtha	49	0.1455	−0.0535	21.8	190	18.8	29.8	3.75
	98			20.6	250	17.6	34.6	4.36
Untreated	PP			19.8	179	15.6	41.2	4.95

TABLE III Increase in length, ΔI (cm), per cent elongation, %E, and time of exposure of pre-tensioned polypropylene films (49 and 98 mN) in solvent vapours at 25 °C for a fixed length of PP film = 11 cm

Time (min)	Reformate				Toluene				*o*-xylene			
	49 mN		98 mN		49 mN		98 mN		49 mN		98 mN	
	Δl	%E	Δl	%E	Δl	%E	Δl	%E	Δl	%E	Δl	%E
2	0.10	0.9	0.20	1.8	0.25	2.3	0.20	1.8	0.10	0.9	0.15	1.4
5	0.18	1.6	0.24	2.1	0.56	5.1	0.45	4.1	0.14	1.3	0.20	1.8
7	0.24	2.1	0.24	2.1	0.64	5.8	0.55	5.0	0.18	1.6	0.25	2.3
10	0.24	2.1	0.24	2.1	0.64	5.8	0.60	5.5	0.20	1.8	0.30	2.7
12	0.25	2.3	0.24	2.1	0.64	5.8	0.60	5.5	0.23	2.1	0.35	3.2
15	0.30	2.7	0.34	3.1	0.64	5.8	0.66	6.0	0.29	2.6	0.45	4.1
20	0.41	3.7	0.40	3.6	0.64	5.8	0.65	5.9	0.36	3.3	0.55	5.0
25	0.63	5.7	0.50	4.6	0.64	5.8	0.65	5.9	0.45	4.1	0.58	5.22
30	0.66	6.0	0.55	5.0	0.64	5.8	0.65	5.9	0.44	4.0	0.61	5.66

Time (min)	Naphtha				Tetralin			
	49 mN		98 mN		49 mN		98 mN	
	Δl	%E	Δl	%E	Δl	%E	Δl	%E
2	—	—	—	—	0.05	0.5	0.03	0.2
5	0.19	1.7	0.11	1.0	0.11	1.0	0.08	0.7
7	—	—	—	—	—	—	—	—
10	0.20	1.8	0.18	1.6	0.13	1.1	0.10	0.9
12	—	—	—	—	0.13	1.1	0.10	0.9
15	0.23	2.1	0.21	1.7	0.13	1.1	0.10	0.9
20	0.26	2.4	0.25	2.3	0.13	1.1	0.11	1.0
25	—	—	—	—	0.13	1.1	0.17	1.6
30	0.39	3.5	0.30	2.7	0.13	1.1	0.17	1.6

TABLE IV Variation of Polypropylene film thickness after treatment with solvent vapours

Liquid	χ[a]	D[b]	49 mN		98 mN	
			Δt (mm)[c]	T[d]	Δt (mm)	%T
Reformate	0.0017	0.0007	0.001	8	0.001	8
Toluene	0.0153	0.0091	0.001	8	0.001	8
o-xylene	0.0313	0.0417	0.0004	3	0.001	8
Naphtha	0.1455	0.0535	0.0006	5	0.0006	5
Tetralin	0.078-3	0.0074	0.0006	5	0.0006	5

[a] Interaction parameter.
[b] Non-specific cohesion force.
[c] Increase in film thickness.
[d] Per cent thickness increase, thickness of untreated PP film = 0.0120 mm.

defined by the interaction parameter, χ, and the non-specific cohesion force, D, affect the per cent thickness increase. Generally, it can be seen that the greater the plasticization effect, i.e. smaller χ and D values, the greater is the per cent thickness increase. Therefore, it can be inferred that, on removal of pre-tension and solvent vapour stresses, the more intensely plasticized films undergo chain folding to the point that the treated film assumes more relative per cent thickness increase.

3.2. Elongation of treated polypropylene films

The data on elongation (Δl, cm) and per cent elongation of solvent vapour-treated PP films at different time intervals (min) are presented in Table II, and plotted in Fig. 1. In Fig. 1 it is evident that the over-all diffusion of solvent vapour followed a smooth parabolic kinetics for the toluene-treated 49 and 98 mN pre-tensioned PP films and tetralin vapour-treated 49 mN pre-tensioned PP film. While the 49 mN pre-tensioned PP film had a faster sorption rate (1.1 min^{-1}) than that of 98 mN pre-tensioned PP film (1.0 min^{-1}) and attained a saturation level earlier (7 min, cf. 98 mN, 15 min) pre-tensioning had no significant effect on the saturation level per cent elongation. Fig. 1 also shows that naphtha vapour-treated, and reformate vapour-treated pre-tensioned PP films, did not attain saturation sorption level during the investigated time, and generally the 49 mN pre-tensioned films exhibited larger values of per cent elongation. A possible explanation may be found in the composite nature of these petroleum

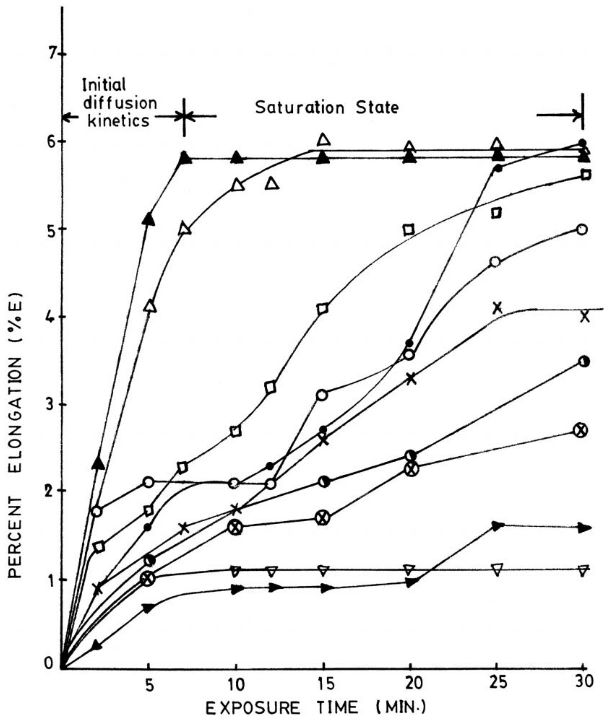


Figure 1 Per cent elongation (%E) of pre-tensioned PP film plotted against exposure time in solvent vapours. Reformate, (●) 49 mN, (○) 98 mN; toluene, (▲) 49 mN, (△) 98 mN; xylene, (×) 49 mN, (□) 98 mN; naphtha, (●) 49 mN, (⊗) 98 mN; tetralin, (▽) 49 mN, (▼) 98 mN. Initial kinetics and saturation state for reformate 49 mN pre-tensioned PP film are shown.

fractions; the smaller molecules diffuse faster and plasticize the PP chain before the larger molecules, which then have better sorption and plasticization chances.

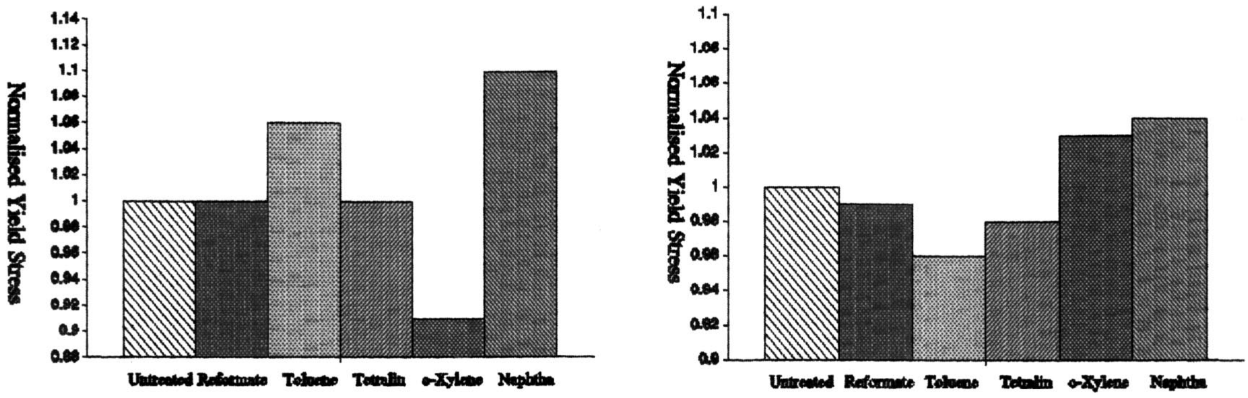
Tetralin vapour-treated 98 mN pre-tensioned PP film seemed to exhibit two saturation levels of per cent elongation, primary and secondary events between 5 and 20 min (0.90%) and greater than 25 min (1.6%) respectively, while the 49 mN pre-tensioned samples attained a saturation level at 1.05%. There is a reversal in trend for the *o*-xylene vapour-treated PP films, in that the loci of the points for the 98 mN pre-tensioned film lie above those of the 49 mN pre-tensioned film, making the kinetics of primary sorption for the former faster (0.8 min^{-1}) than that of the latter (0.6 min^{-1}). In addition to these differences, the 49 mN pre-tensioned PP film in this solvent vapour seems to have reached a saturation level of per cent elongation of 4.05% at 25 min (Fig. 1).

These results can be explained by a combination of factors: the polymer–solvent interaction parameter, χ, and/or the non-specific cohesion force, the boiling points and molar volumes of the treatment solvents. The smaller the interaction parameter/non-specific cohesion force, the smaller is the molar volume, and the lower, the boiling point of the treatment solvent, the faster is the sorption rate, and the greater the plasticization effect of the treatment solvent.

The role of the boiling point of the solvent is that, at ambient temperatures for a high boiling point solvent, e.g. tetralin, few molecules are available for sorption and hence less capillary condensation is needed for plasticization and crystallization, and hence low sorption kinetics and saturation level of per cent elongation result. Such results have, in part, been reported in the case for simultaneous halohydrocarbon treatment of pre-tensioned PP films. The results of primary sorption kinetics (at 2 min) and the expression relating the maximum per cent elongation for several solvent treated pre-tensioned PP films have been reported [9, 15]. Except for toluene vapour-treated pre-tensioned PP films, other aromatic solvent vapour-treated films generally have lower saturation levels than the chlorosolvent treated pre-tensioned films [10].

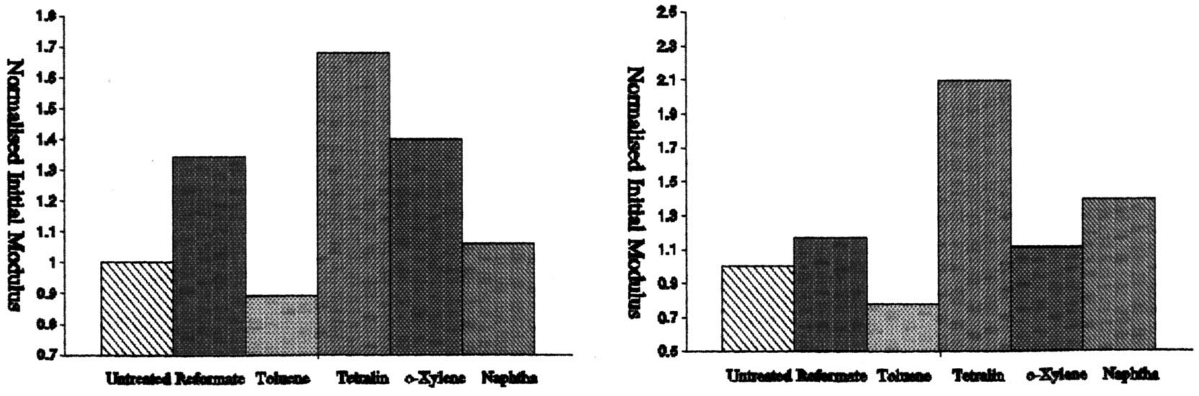
3.3. Strength properties of treated PP films

The strength properties of the solvent vapour-treated pre-tensioned polypropylene films (yield stress, σ_γ, stress σ_d, initial modulus, E, and tensile strength, σ_b were evaluated from the stress–strain curve, while the breaking factor, BF, was calculated from force/area at the moment of film rupture. First, it is noted that the stress–strain curves over the whole range of deformation for the treated PP films were typical of semicrystalline polymers showing a sharp yield peak but differing in width and height for the various solvent vapour-treatments. The data on these strength properties and their variation with solvent vapour treatments and pre-tensioning are presented in Table II. The normalized strength properties versus the interaction parameter, χ, or non-specific cohesion force, D, are plotted in Figs 2–6.



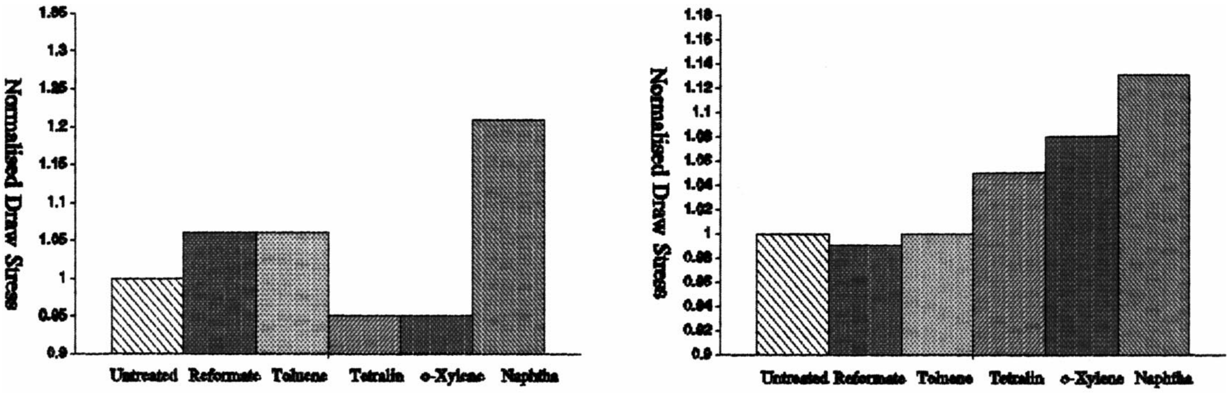
(a) (b)

Figure 2 Normalized yield stress for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.



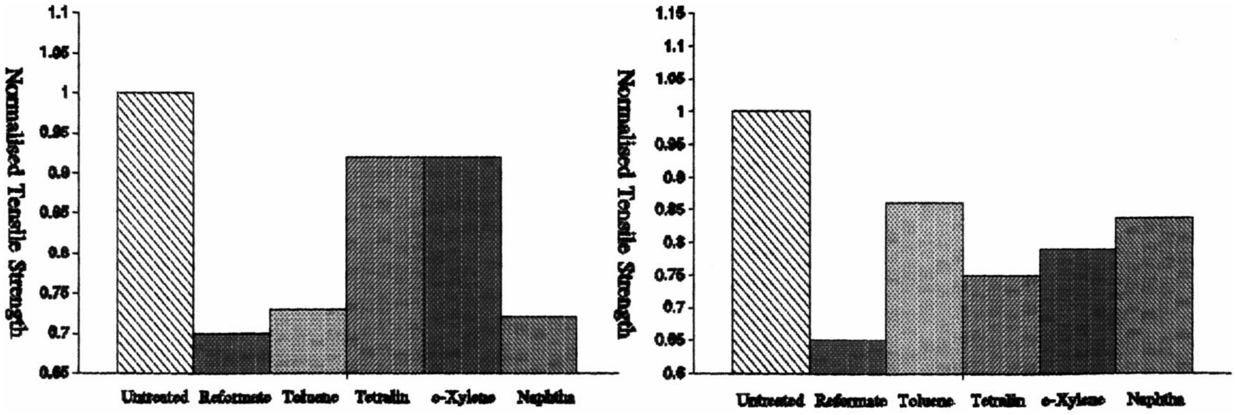
(a) (b)

Figure 3 Normalized initial modulus for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.



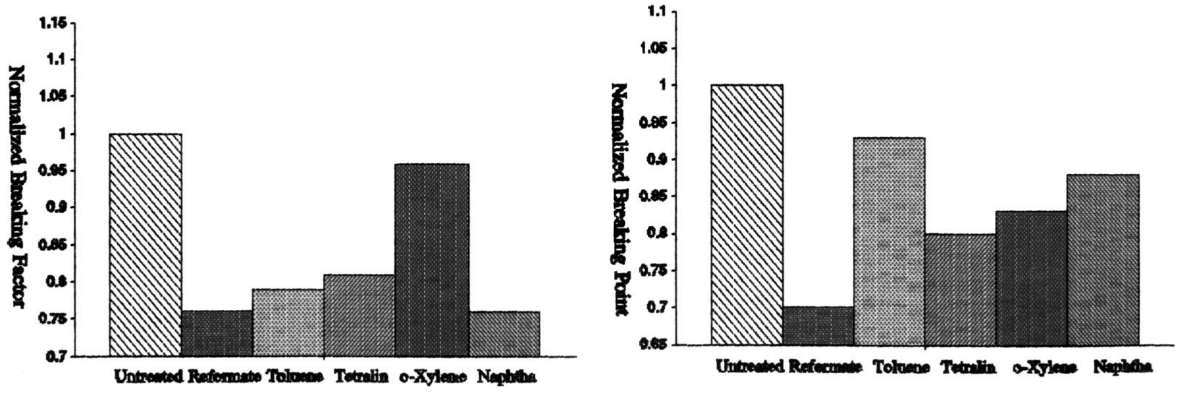
(a) (b)

Figure 4 Normalized draw stress for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.



(a) (b)

Figure 5 Normalized tensile strength for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.



(a) (b)

Figure 6 Normalized breaking factor for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.

3.4. Yield stress

The data on yield stress (MPa) reported in Table II are plotted in Fig. 2a and b for the 49 and 98 mN pre-tensioned PP films. The normalized yield stress was obtained from the ratio of yield stresses of treated to untreated PP films. In Fig. 2, it is evident that simultaneous pre-tensioning and solvent vapour treatment have a significant effect on the yield stress. Generally, the 98 mN pre-tensioned PP film had higher values of yield stress than the 49 mN pre-tension one, except in the case of *o*-xylene-treated PP films. For the 49 mN pre-tensioned PP film, the increase in non-specific cohesion force, D, rather than the interaction parameter, χ, of the solvent, correlated better with the increase in the yield stress, σ_y, suggesting a reduction in the plasticization of PP films with increase in D and concomittant increase in the crystallization of treated PP films.

Such a proposition is also applicable to the 98 mN pre-tensioned film, but the greater pre-tensioning relative to the former tends to favour crystallization effects. It should be remembered that yield stress of semi-crystalline polymers is greatly dependent on the density [16] and hence on the crystallization, and crystallite thickness. Supermolecular structures exert only slight influence and any deviation can be explained by the thermodynamic stability of the crystallites [16].

3.5. Initial modulus

The initial modulus represents the initial reaction of the deforming system to the energy input. It is a reversible response, within 2% or 3% strain, and estimated from the slope of the stress–strain curve in this small strain limit. The data on initial modulus, E (MPa) presented in Table III are plotted in Fig. 3a and b for the 49 and 98 mN pre-tensioned films and different solvent vapour treatments. Comparison of Fig. 3a and b shows that pre-tensioning has a significant influence on the initial modulus of a particular solvent vapour treatment and, with the exception of tetralin- and naphtha-treated films, the 49 mN pre-tensioned sample had lower values of initial modulus.

This deviation may be explained by low vapour concentration, i.e. higher boiling points, so that mainly stretching orientation increases the crystallinity for these solvent-treated films, while the larger values exhibited for the other three solvents (reformate, toluene and *o*-xylene) are explained by additional crystallization due to the presence of residual solvent. However, for the two pre-tension values, the initial modulus did not correlate well with either the interaction parameter or the non-specific cohesion force. What seems to be clear from Table II and Fig. 3a and b is that, except for toluene vapour-treated PP films, the initial, modulus is enhanced by the treatments relative to that of the untreated films. The remarkably higher value for tetralin vapour treatments is probably due to its low vapour concentration in contact with the pre-tensioned PP films, so that stretching orientation and crystallization become predominantly significant over plasticization effects. Popli and Mandelkern [16] have explained that the initial modulus of linear polymers, e.g. polyethylene, is a linear function of density and crystallinity, E, decreasing with increase in the thickness of amorphous region, but increasing with the crystallite thickness.

3.6. Draw stress

The data on draw stress, σ_d (MPa), for the solvent vapour-treated pre-tensioned PP films at 25 °C, and the interaction parameter, χ, and the non-specific cohesion force, D, for solvents are reported in Table II and plotted in Fig. 4a and b. Like all semi-crystalline polymers, the draw stress, σ_d, of all the solvent vapour-treated pre-tensioned PP films are less than the corresponding yield stress, σ_y. In Table II and Fig. 4b it seems that the draw stress for solvent vapour-treated 49 mN pre-tensioned PP film is either equal to or greater than the value for the untreated PP film; the decrease in draw stress, σ_d, correlating with the interaction parameter and non-specific cohesion force increase, representing a decrease in the plasticization effect of the solvent. However, for the greater pre-tensioning (98 mN), the draw stress for liquids with intermediate plasticization effect (tetralin and *o*-xylene) were found to have values less than that of the untreated PP films and the corresponding value for the 49 mN pre-tensioned PP films. The explanation for this behaviour is not clear, but the influence of stretching orientation may be assumed to be less than the plasticization effect in these cases, while for the other three solvent-treated PP films, the stretching orientation effect on enhanced crystallization relative to the plasticization, becomes more significant.

3.7. Tensile strength

Tensile strength refers to the tensile stress at the point of rupture of the polymer film. The data on tensile strength, σ_d (MPa), for the solvent vapour-treated pre-tensioned PP films at 25 °C with the corresponding plasticization property of the solvents, are presented in Table II and plotted in Fig. 5a and b. It is evident in Table II and Fig. 5a and b that simultaneous solvent treatment and pre-tensioning reduce the tensile strength to values lower than that of untreated PP films. Even though Popli and Mandelkern [16] have reported no significant difference in tensile strength due varying supermolecular structures, level of crystallinity or crystallite thickness distribution for any given polymer (the property being dependent on molecular weight, at least for polyethylene), there seems to be some noticeable variation in tensile strength that is dependent on solvent treatment and pre-tensioning. Except for the toluene vapour-treated sample, the tensile strength of solvent vapour-treated 49 mN pre-tensioned PP film decreased with increasing plasticization (i.e. decreasing interaction parameter/non-specific cohesion force) of the solvents.

For, the 98 mN pre-tensioned solvent vapour-treated PP films, however, the neat solvents (toluene, tetralin and *o*-xylene), all pure aromatic solvents with an intermediate plasticization property, exhibited higher tensile strength than the composite solvents, reformate and naphtha, that consist of aliphatic and aromatic molecules. It is probable that additional polar interactions with polypropylene as reported by Weigmann and Ribnick [17] come into play.

3.8. Breaking factor

Strictly by definition, the breaking factor measures the tension in the deformed film of the point of rupture, and therefore has some relationship with the tensile strength. The data for breaking factor, BF (kN m^{-1}) for solvent vapour-treated pre-tensioned PP films are recorded in Table II together with the plasticization property of solvents, while the normalized breaking factors for the solvent vapour-treated 49 and 98 mN pre-tensioned PP films, are presented in Fig. 6a and b, respectively.

From Table II and Fig. 6a and b, it is evident that simultaneous pre-tensioning and solvent vapour treatment have a significant effect on the breaking factor. For the 49 mN pre-tensioned PP film, except for the toluene vapour-treated specimen, the decrease in breaking factor correlates with an decrease in interaction parameter or non-specific cohesion force, i.e. increasing plasticization property. On the other hand, the 98 mN pre-tensioned specimen exhibited no simple correlation with the plasticization property; rather, solvents with intermediate property had higher values of breaking factor than those with high and low plasticization property. The same factors as in the tensile strength variation may also be operative, given the relationship between tensile strength and breaking factor. Finally, it is noted that the breaking factor, BF, of untreated PP films remains larger than that of solvent vapour-treated pre-tensioned PP films.

Diffusion of liquids and vapours in polymers takes place only in the amorphous regions. The diffusion process is governed by the molecular size of the penetrant, the temperature, the plasticization property of the penetrant, and the molecular regularity of the polymer. After equilibrium desorption of solvent from the treated film, capillary condensation leaves some residual solvent molecules, which result in plasticization and induce crystallization. These two factors have opposing effects in influencing film properties. Solvent-induced crystallization (SINC) has been well documented (18–21). While induced crystallization, a result of decreased glass temperature, is instantaneous, irreversible, and persists for a long time, plasticization is a reversible process. Pre-tensioning in the present study contributes significantly to the improved crystallization. Pre-tensioning may be considered analogous to uniaxial cold drawing and results in stretching orientation of the polymer chains. This gives rise to simultaneous molecular alignment parallel to the film axis, molecular unfolding and slippage that favour orderly close packing that are manifest in enhanced crystallinity. Enhanced orderly close-packing and crystallization lead to improved stress and improved chemical resistance because solvent molecules under this condition have reduced permeability, as there is some reduction in the amorphous regions.

Plasticization, on the other hand, decreases the stress by improving the mobility of polymer chains or the distance between them. This is perfectly true for only solvent-treated polymer film. However, because of strong opposing effects of improved crystallization due to both residual solvent and pre-tensioning and plasticization due to the presence of solvent, the observed strength property is a result of a net-balance of the two factors [10, 22]. Any variations from the normal trend may come from some unique property of the solvent, e.g. high boiling point (low vapour concentration), and the composite nature of the solvent, e.g. for reformate and naphtha.

Table II and Figs 2–6 reveal that simultaneous solvent vapour treatment and pre-tensioning have a noticeable effect on the yield stress, with 98 mN pre-tensioned PP exhibiting a larger yield stress value with respect to the 49 mN pre-tensioned specimens except for *o*-xylene vapour treatment; the increasing yield stress correlates roughly with increasing interaction parameter (decreasing plasticization effect) of the solvent for the 49 mN pre-tensioning. The draw stress with the exception of toluene vapour-treated specimens, the initial modulus, E, of the untreated PP films is less than the values for other solvent-treated pre-tensioned PP films; the observed values exhibit no simple correlation with plasticization effect of the solvents. The enhancement of initial modulus is probably due to enhanced crystallization arising from both stretching orientation and the presence of solvent relative to the lowering effects of plasticization by residual solvent presence.

The draw stress, σ_d, for the 49 mN pre-tensioned film exhibited about equal or larger values, which correlate well with decreasing plasticization property of the solvent. However, at higher pre-tensioning (98 mN) the larger and increasing draw stress that also roughly correlates with decreasing interaction parameter of solvents is rather masked by the effect of low vapour concentration from higher boiling point *o*-xylene and tetralin and the composite nature of naphtha. The larger values of draw stress in this case are probably due to greater relative contribution from pre-tensioning effects (Table II, Fig. 4a and b). Table II, Figs 5a and b and 6a and b reveal that the tensile strength and breaking factor, respectively, of the untreated PP films have larger values than the solvent vapour-treated 49 and 98 mN pre-tensioned PP films; the 49 mN pre-tensioning generally exhibits smaller values that correlate roughly with increasing plasticization effect/decreasing interaction parameter.

The greater plasticization effect relative to the stretching orientation effect results in lowered tensile strength and breaking factor. However, at the larger pre-tension (98 mN) the improved orientation crystallization becomes more dominant than the plasticization effect and hence the tensile strength and breaking factor assume higher relative values. It is also noted that pure aromatic toluene, *o*-xylene and tetralin exhibit larger values for these properties than reformate and naphtha that are only partly aromatic in composition. In all these variations, the observed strength properties are explicable by the net-balance of stretching orientation and solvent presence that enhance crystallization, and plasticization effects which depend on solubility parameter differences, the molar volume and boiling point of solvents, that reduce crystallization.

4. Conclusions

The properties of polypropylene films simultaneously pre-tensioned and treated with aromatic solvents have been studied. Results showed that the thickness of treated PP films was independent of the amount of pre-tensioning, but increased with the plasticizing effect of the solvent defined by the interaction parameter, χ, or the non-specific cohesion force, D. The sorption kinetics and saturation per cent elongation decrease with increase in molar volume and boiling point (concentration of vapour) of the solvent. For most solvent vapour treatment, the 98 mN pre-tensioned PP films exhibited larger values of strength properties which, in addition increased with the increasing interaction parameter, χ, and/or non-specific cohesion force, D (decreasing plasticization), relative to the 49 mN pre-tensioned film. Of the five strength properties studied, initial modulus, E, and draw stress, σ_d, exhibited larger values with respect to the untreated PP films, while the yield stress, σ_y the tensile strength, σ_b, and breaking factor, BF, exhibited lower values. These results can be explained by the net-balance of two opposing forces: stretching orientation due to pre-tensioning and solvent presence which improve crystallization, and the plasticization effect due to residual solvent presence which reduce it. The effect of the composite nature of reformate and naphtha and the low aromatic content, low vapour concentration of high boiling point tetralin, and their influences on properties, have been shown to be of considerable importance.

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