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

Part I *Halohydrocarbon solvents*

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The strength properties of solvent vapour-treated pre-tensioned polypropylene (PP) films have been investigated. The results showed that the variation of properties (yield stress, draw stress, initial modulus, tensile strength and breaking factor) were determined by the net-balance of two opposing effects: orientation crystallization from pre-tensioning and solvent presence one the hand, and plasticization by residual solvent defined by the interaction parameter, χ, or non-specific cohesion force, *D*, of the halo-solvents, on the other. The greater influence of crystallizaton was shown in the draw stress initial modulus and yield stress for chloroform- and carbon-tetrachloride-treated PP films. The tensile strength and breaking factor seemed invariant with solvent-vapour treatment but still showed a greater influence of stretching orientation brought about by the greater pre-tensioning. © *1999 Kluwer Academic Publishers*

1. Introduction

Polypropylene (PP) is used in piping, fittings, crates, containers and various packages. Fibrillated PP films are also woven on circular looms for use as bags and sacks for packaging of various items.

Li *et al.* [1] reviewed the diverse application of liquid transport in polymer films while Michaels *et al.* [2] have achieved enhanced permeability of 15 times that of untreated PP membranes with reduced selectivity towards the permeants by employing solvent annealing in an organic solvent at 60–100 °C. While Michaels *et al.* [2] correlated changes in properties with the absolute difference between the solubility parameters of polymer and solvent $|\delta_B - \delta_S|$, other workers [3–7] correlated changes in tensile strength of some polymers to the liquid Hildebrand parameter.

Some of the earliest investigations on environmental stress cracking, craze initiation growth and failure by liquids, were explained in terms of the wetting of the polymer surface, diffusion into the polymer and swelling/plasticization due to liquid sorption by the polymer [8, 9].

To a first approximation, the equilibrium sorption depends on the activity of the adsorbed vapour molecules and the interaction between the vapour and the polymer, given by

$$\ln a = \ln \phi_V + \phi_B + \chi_H \phi_B^2 \qquad (1)$$

where a is the activity, ϕ_V and ϕ_B are equilibrium volume fractions of vapour and polymer, respectively, and χ_H is the Flory–Huggins enthalpic interaction parameters [10]; χ_H is given by

$$\chi_H = V_S/RT(\delta_B - \delta_S)^2 \qquad (2)$$

where δ_B and δ_S are solubility parameters of the polymer and solvent respectively, V_S is the molar volume of solvent, R and T are the gas constant and Kelvin temperature, respectively. It has been suggested that χ_H values thus estimated correlate well with other properties [11]. Thus the interaction parameter can be estimated from a knowledge of solubility parameter of the polymer and the solvent. Secondly, the mobile order theory of Huyskens and Siegel [12] expresses the enthalpic cohesive energy by the non-specific cohesion force term, *D*, given by

$$D = -\phi_S^2 V_B(\delta'_B - \delta'_S)/RT \qquad (3)$$

where δ'_B and δ'_S are the modified non-specific cohesion parameters of polymer and solvent, respectively, V_B is the molar volume of polymer, ϕ_S the volume fraction of solvent, and R and T are as defined above. The modified non-specific cohesion parameter is the modified form of solubility parameter δ' in that it consists of dispersion and dipolar forces of the molecule.

It is the object of this study to present results of the effect of pre-tensioning and solvent vapour treatment at room temperature on the strength properties of PP films. The changes in the dimensions, the effect of interaction parameter, χ_H, the non-specific cohesion force term, *D*, of the solvent–polymer system as well as the effect of

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TABLE I The solubility parameter, δ, non-specific solubility parameter, δ', molar volume, V_S, boiling point (BP), interaction parameter, χ_H, and non-specific cohesion force, D, of solvents[a]

Solvent	δ_S (MPa$^{1/2}$)[b]	δ'_S (MPa$^{1/2}$)[c]	V_S (cm^3 mol^{-1})[c]	BP (°C)	χ_H	D
Chloroform	11.0	18.77	80.7	61	0.0013	−0.0000
Carbon tetrachloride	17.8	17.04	97.1	75.6	0.0392	−0.0584
Dichloromethane	20.3	20.53	64.5	39.8	0.0585	−0.0564

[a] $\delta_B = \delta'_B = 18.8$ MPa$^{1/2}$ [13], $V_B = 46.7$ cm^3 mol^{-1}.
[b] [14].
[c] [12].

boiling point/vapour pressure of the solvent, will be discussed.

2. Experimental procedure

2.1. Materials

The polypropylene films (0.012 mm thick, 0.90 g cm^{-3} density) were supplied by the Bag Manufacturing Company (BAGCO) Nigeria Limited, Lagos Nigeria. The solvents used were reagent-grade chloroform, carbon tetrachloride and dichloromethane, and were used without further purification.

2.2. Methods

Fixed lengths of pre-tensioned polypropylene films were immersed in saturated vapours of liquids of differing molar volumes, boiling points (vapour pressures) and wetting (cohesion) properties at room temperature. The pre-tensioning was done by suspending weights 5 g (49 mN) and 10 g (98 mN) before immersion into saturated vapour for a period of 30 min. Data on the solubility parameter, δ, molar volume, V_S, boiling point (°C), the interaction parameter, χ, and the non-specific cohesion force, D, and readings on length on the marked portion of the PP film were taken *in situ* at 2, 5, 7, 10, 12, 15, 20, 25 and 30 min using a Vernier microscope are reported in Table I.

The mechanical properties of the treated PP films were determined on the Instron tensile testing machine model 1122 using a gauge length of 5 cm, crosshead speed 5 cm min^{-1}. Five samples of PP films from each treatment were tested and the mean value taken. The strength properties, such as yield stress, σ_y, initial modulus, E, draw stress, σ_d, tensile strength, σ_b, and breaking factor, BF, were determined from the stress–strain curve (ASTMD 882-81). The film thickness before and after treatment was measured with a Shirley Portable Thickness Gauge SDL 253. The mean of ten successive measurements made along the film and per cent increase in thickness are reported in Table II. The change in the strength properties of the solvent vapour-treated PP films at the two pre-tensions are recorded in Table III. All film samples were first washed in acetone and conditioned at 25 °C, 65% r.h. in calcium nitrate hydrated desiccator.

3. Results

3.1. Variation of film thickness with treatment

There is strong evidence in support of changes in polypropylene film thickness following solvent vapour treatment of pre-tensioned films. Although film thickness in employed in stress calculations (stress = force/area), the changes are so significant that they deserve some comment here. Table II shows the increase in film thickness with vapour treatment and the interaction parameter of liquids. From Table II, it is evident that increase in the interaction parameter of a liquid corresponds to increasing film thickness of vapour-treated PP films. However, pre-tensioning has no effect on the film thickness. It is suggested that after liquid vapour treatment and removal of stress, the differently tensioned films relaxed to the same thickness.

TABLE II Variation of polypropylene film thickness after treatment with vapours of various liquids: χ_H is the interaction parameter; untreated film thickness = 0.0120 mm

		98 mN		49 mN	
Liquid	χ_H	Thickness (mm)	Increase (%)	Thickness (mm)	Increase (%)
Chloroform	0.0013	0.0120	0	0.0120	0
Carbon tetrachloride	0.0392	0.0126	5	0.0126	5
Dichloromethane	0.0585	0.0130	8	0.0130	8

3.2. Elongation of vapour-treated pre-tensioned PP films

The data on elongation and per cent elongation at the two pre-tensions (49 and 98 mN) of PP on exposure to solvent vapours for different time intervals at 25 °C, are reported in Table III and plotted in Fig. 1. In Fig. 1 it is evident that the per cent elongation followed parabolic kinetics in particular for dichloromethane and chloroform at the two pre-tensions. Following an initial primary elongation, a steady state or saturation level condition was reached, with the primary elongation and a steady state condition varying for different pre-tensions for the same liquid vapour and also for different solvent vapours. The saturation level conditions were reached between 10 and 20 min, with the 49 mN pre-tensioned PP film attaining the equilibrium state earlier than the 98 mN pre-tension film. The saturation level was higher for the chloroform vapour-treated (7.4%) and approximately constant for the two pre-tensions than for the dichloromethane vapour-treated PP film, being lower for 49 mN (4.9%) but 5.5% for the 98 mN pre-tensioned PP film. The kinetics of elongation of the pre-tensioned PP film in carbon tetrachloride vapour seemed irregular. While the 98 mN pre-tensioned PP film in this solvent vapour reached the equilibrium state at 12 min,

TABLE III Increase in length, Δl, and per cent elongation, (%E), of pre-tensioned PP films in solvent vapours at 25 °C: CCl_4 = carbon tetrachloride, CH_2Cl_2 dichloromethane

	Chloroform				CCl_4				CH_2Cl_2			
	49 mN		98 mN		49 mN		98 mN		49 mN		98 mN	
Time (min)	%E	ΔL	%E	ΔL	%E	ΔL	%E	ΔL	%E	ΔL	%E	ΔL
2	2.3	0.25	2.4	0.26	0.15	1.4	0.14	1.2	0.20	1.8	0.31	2.8
5	5.5	0.60	3.6	0.40	0.25	2.3	0.19	1.7	0.40	3.6	0.53	4.8
7	5.9	0.65	4.5	0.50	0.29	2.6	0.28	2.5	0.51	4.6	0.55	5.0
10	6.5	0.72	5.5	0.60	0.34	3.1	0.50	4.6	0.51	4.6	0.55	5.0
12	—	—	—	—	0.49	4.4	0.58	5.3	0.52	4.7	0.60	5.5
15	7.3	0.80	6.3	0.70	0.57	5.2	0.65	5.9	0.53	4.8	0.60	5.5
20	7.3	0.80	7.2	0.79	0.63	5.7	0.65	5.9	0.53	4.8	0.60	5.5
25	7.4	0.82	7.3	0.80	0.70	6.4	0.65	5.9	0.55	5.0	0.60	5.5
30	7.4	0.82	7.3	0.80	0.73	6.6	0.65	5.9	0.55	5.0	0.60	5.5

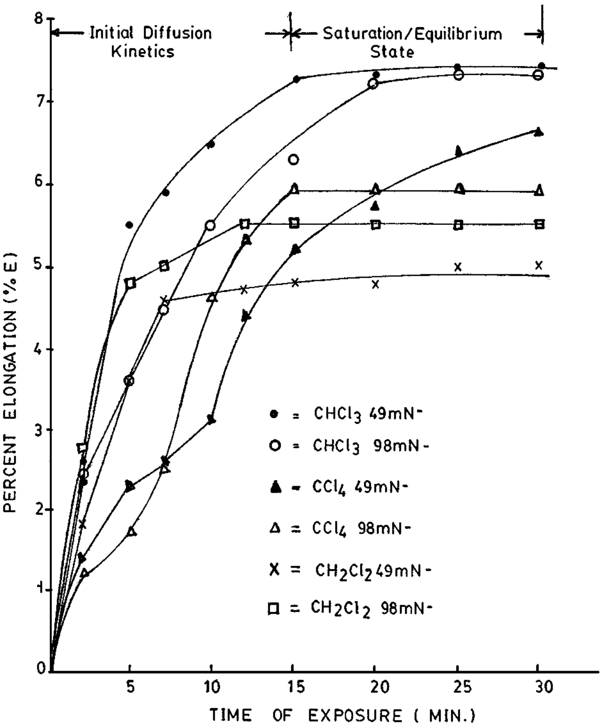


Figure 1 Per cent elongation (%E) of pre-tensioned PP film plotted against time of exposure in solvent vapours. The initial diffusion kinetics and saturation/equilibrium state for $CHCl_3$-treated 49 mN pre-tensioned PP film are shown. (●) $CHCl_3$, 49 mN, (o) $CHCl_3$, 98 mN, (▲) CCl_4, 49 mN, (△) CCl_4, 98 mN, (×) CH_2Cl_2, 49 mN, (□) CH_2Cl_2, 98 mN.

with a saturation level corresponding to 5.9% elongation, the 49 mN pre-tensioned film had not reached the saturation level at 30 min exposure time, with the latter attaining larger per cent elongation from about 16 min exposure. In our previous publications the initial rates were compared [15] and expressions were developed for the maximum per cent elongation and reciprocal boiling point, K, of the solvent [16]. Comparison of Table I and Fig. 1 shows that equilibrium state per cent elongation can be explained by either an interaction parameter, χ_H, or the non-specific cohesion force, D. The smaller the values of these enthalpic forces the larger is the equilibrium state per cent elongation. Thus the interaction between pre-tensioned PP film with solvent vapour is most favourable for chloroform and least favourable for dichloromethane. It must be emphasized that the deviation of the initial slope of the per cent elongation–time curve from 0.5, suggests a non-Fickian diffusion kinetics. The sorption behaviour of solvent vapour can roughly be related to the molar volume of the solvents. During the initial diffusion process, the smaller molecules of dichloromethane ($V_S = 64.5$) are more easily sorbed by pre-tensioned PP film than the larger molecules of carbon tetrachloride ($V_S = 97.1$).

3.3. Strength properties

The data on strength properties (yield stress, σ_y, draw stress, σ_d, tensile stress, σ_b, initial modulus, E, breaking actor, BF) for the solvent vapour treatments of pre-tensioned PP films in addition to those of untreated PP films, are presented in Table IV.

First, one notes that the stress–strain curves over the whole range of deformation of vapour-treated pre-tensioned PP film are typical of semi-crystalline polymers, showing a sharp yield peak, but with width and height differing for the various solvent vapour-treated pre-tensioned films. Pre-tensioning and solvent vapour treatment have a significant effect on the stress–strain curve of the deformed PP films. These effects are manifested in the differing values of the named strength properties of the solvent vapour treated pre-tensioned PP films (Table IV). The normalized strength property: ratio of treated film strength property to that of the untreated film are presented in Figs 2–6 for the 49 mN$^-$ and 98 mN$^-$ pre-tensioned PP films.

In Fig. 2, it is evident that for the 49 mN$^-$ pre-tensioned PP films exposed to chloroform and dichloromethane solvent vapours exhibited lower yield stress than the untreated PP film, which however had similar yield stress value as the 49 mN$^-$ pre-tensioned carbon tetrachloride vapour. On the other hand, solvent vapour 98 mN$^-$ pre-tensioned PP film behaved differently. For this system, the carbon tetrachloride and dichloromethane vapour treated films exhibited lower yield stress value than the untreated PP film, while the chloroform vapour treated film had slightly larger yield stress value than the untreated PP films. It is clear therefore that solvent property e.g. interaction parameter χ_H or non-specific cohesion parameter D alone or amount of pre-tensioning alone cannot explain the observed changes in the yield stress.

TABLE IV Strength properties (yield stress, σ_y, draw stress, σ_d, tensile stress, σ_b, initial modulus, E, breaking factor, BF) and the enthalpic interaction functions, χ_H, D, for pre-tensioned solvent vapour-treated PP films[a]

Solvent	Pre-tension (mN)	χ_H	D	σ_y (MPa)	σ_d (MPa)	σ_b (MPa)	E (MPa)	BF (N m^{-1})
Chloroform	49	0.0013	−0.0000	17.4	15.6	32.7	250	3.90
	98			22.9	18.8	33.5	500	4.0
Carbon tetrachloride	49	0.0392	−0.0584	19.9	16.8	32.7	215	4.1
	98			15.3	14.8	37.7	340	4.8
Dichloromethane	49	0.0585	−0.0564	18.3	15.2	31.7	200	4.1
	98			18.0	15.2	32.4	380	4.2
Untreated PP				19.8	15.6	41.2	179	4.9

[a] First row for each solvent is for 49 mN$^-$, 2nd row 98 mN$^-$.

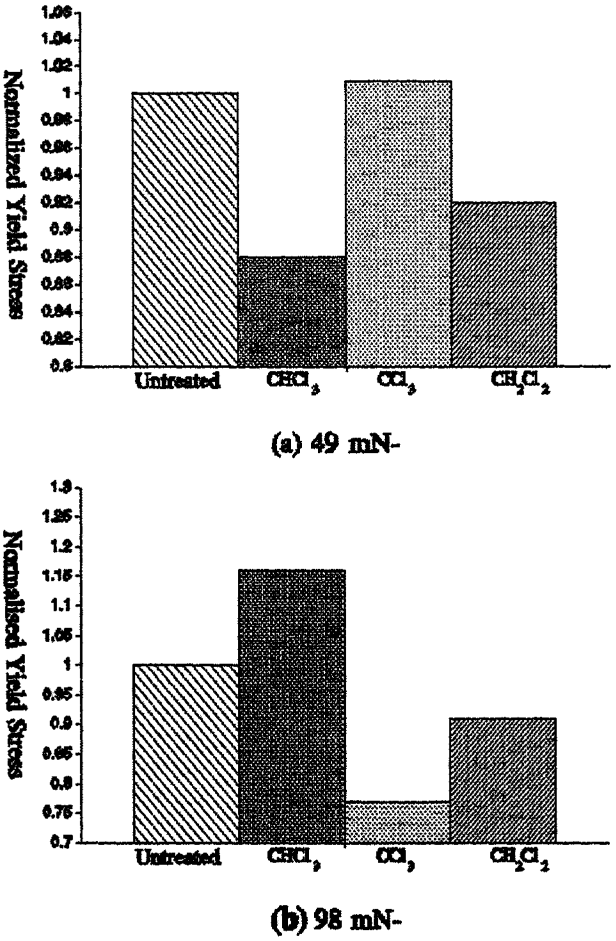


Figure 2 Normalized yield stress for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.

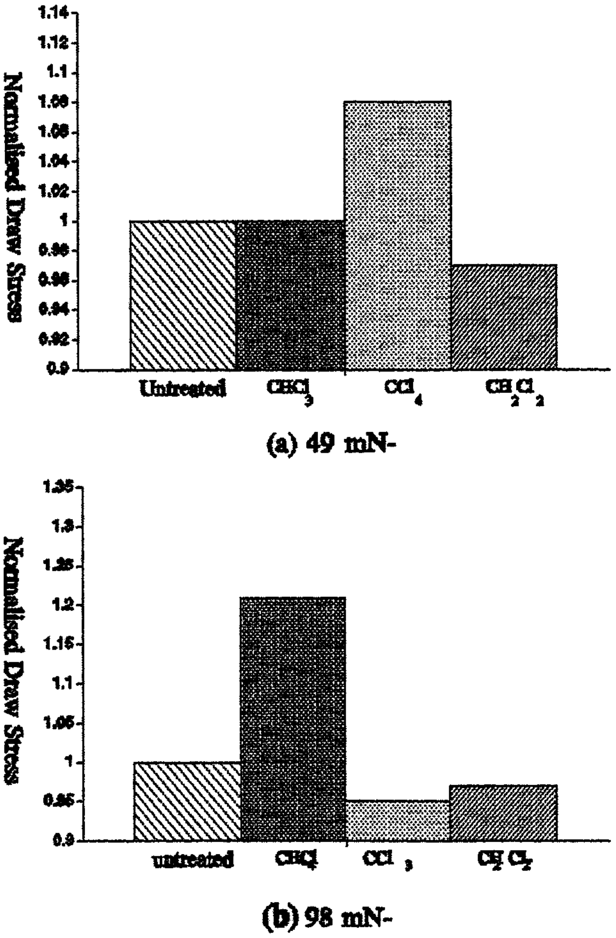
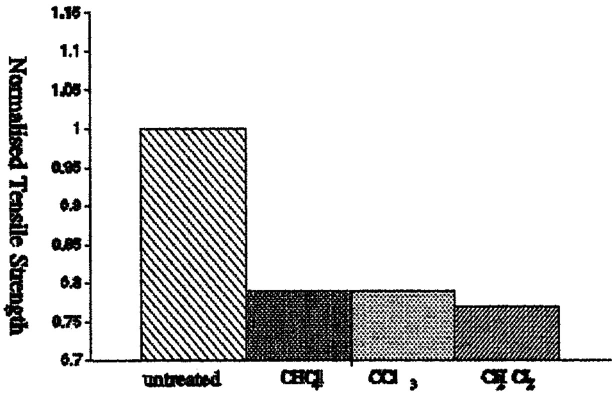


Figure 3 Normalized draw stress for solvent vapour-treated (a) 49 mN, and (b) 98 mN pre-tensioned PP films.

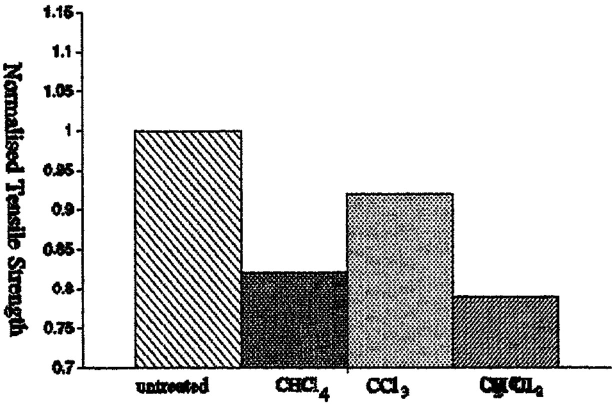
Fig. 3 represents the normalized draw stress of solvent vapour treated pre-tensioned polypropylene films for different solvent vapours. For the 49 mN$^-$ pretensioned PP film, the draw stress decreases with increase in the interaction parameter χ_H or non-specific cohesion force D of the solvent. However at higher pretension 98 mN$^-$, the observed decrease in draw stress (lower than that of the untreated PP films) exhibits an irregular dependence on the interaction parameter χ_H or non-specific cohesion force D.

In addition, Fig. 3, shows that the draw stress for any particular solvent vapour was larger for the 98 mN pre-tensioning than the 49 mN pre-tensioning. It is clear, therefore, that the influence of tension during solvent vapour diffusion which leads to orientation and hence improved crystallinity shows up in the draw stress.

In Fig. 4, we present the normalized tensile strength for solvent vapour-treated pre-tensioned polypropylene film for the three solvents under study. In Fig. 4a it is clear that the normalized tensile strength for the 49 mN pre-tensioned PP for all solvent vapour-treated films have tensile strength larger than that of the untreated film, the observed tensile strength values decreasing with increase in solvent property (interaction parameter, χ_H, or non-specific cohesion force, D). Thus, at this level of pre-tensioning, the greater solvent–polymer interaction represented by smaller solvent property has aided orientation and, consequently enhanced the crystallinity of the treated PP films. However, at 98 mN pre-tensioning, there is drastic reduction in the tensile strength with solvent vapour treatment relative to both the untreated PP film and the 49 mN pre-tensioned

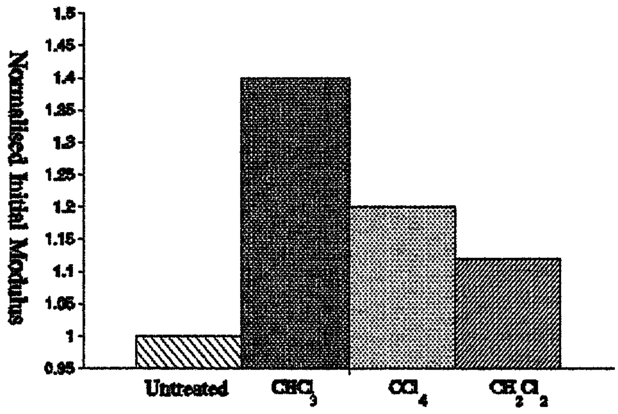


(a) 49 mN-

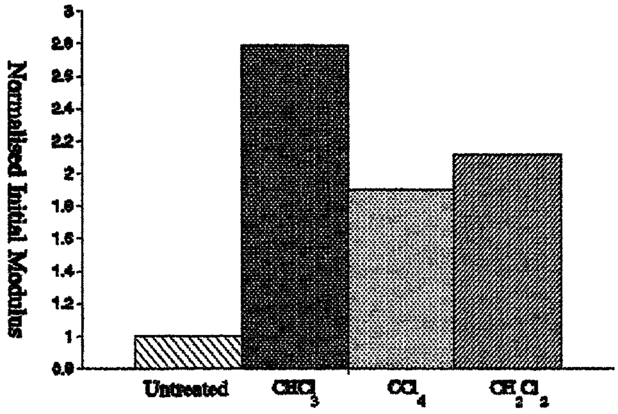


(b) 98 mN-

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



(a) 49 mN-



(b) 98 mN-

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

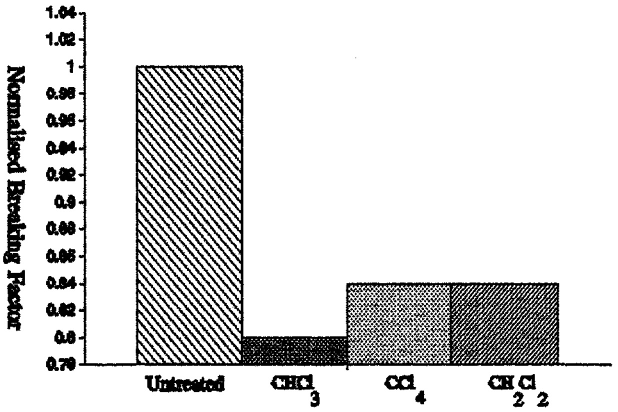
PP film. The observed decrease in tensile strength with respect to the untreated PP films are ×3.6 for chloroform-, ×5.3 for carbon tetrachloride-, and ×4.8 for dichloromethane-treated PP films. It is evident that a decrease in tensile strength of solvent vapour-treated 98 mN pre-tensioned PP correlates somewhat with increase in solvent property (interaction parameter, χ_H, and non-specific cohesion force, D). In Fig. 5, the overriding influence of stretching orientation over plasticization effect on initial modulus at the two pre-tensions is clearly shown.

The breaking factor, BF, is not a measure of strength *perse* but it defines the tension in the drawn film at the moment of rupture, and therefore is related to tensile strength. The data on breaking factor against solvent property (Table IV) are presented as the normalized breaking factor for the solvent vapour-treated pre-tensioned PP films in Fig. 6. The solvent vapour-treated 49 mN pre-tensioned PP films have values practically independent of the solvent property (interaction parameter, χ_H, and non-specific cohesion force, D Fig. 6a). For the normalized breaking factor for the 98 mN pre-tensioning, again there is only marginal difference between the solvent vapour-treated 98 mN pre-tensioned PP film and the untreated PP film breaking factor (Fig. 6b), the decrease being irregular with increasing interaction parameter/non-specific cohesion force, D.

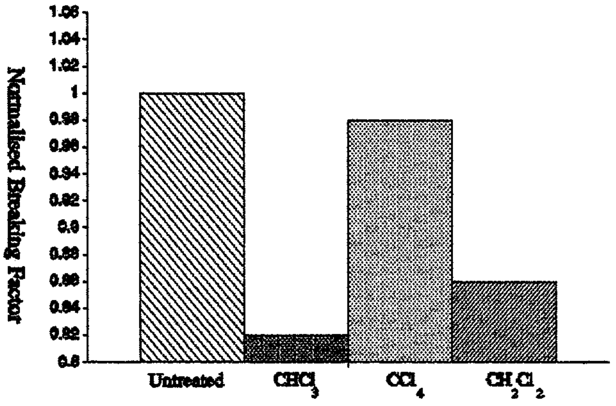
Thus from the above, it is clear generally that neither pre-tensioning alone nor solvent property alone can explain the observed changes in the studied strength properties of solvent vapour-treated pre-tensioned PP films. An explanation for the observed strength properties must be sought in the combined effects of pre-tensioning and solvent property which may both contribute positively, or may have opposite effects, so that the observed property will be a net balance of the two counter-effects.

4. Discussion

To understand the transport of molecules through films, it may be necessary to discuss briefly the modes and factors that affect the process. Previous studies have shown that transport of molecules takes place essentially in the non-crystalline regions of the polymer [17–23]. The original "free volume model" of Cohen and Turnbull [17], the modified "free volume model" of Fujita [18] and Vrentas and Duba [19, 20] and the modified "dual mode sorption model" of Mauze and Stern [21–23] are established models of transport of gases/vapours in polymers that take into consideration the plasticizing effect of the solvent. It is assumed that the solubility parameters and the modified non-specific solubility parameters of solvents in the liquid state at 25 °C will be proportional to those in the gaseous state at the same temperature. Hence, the use of the solubility parameters and non-specific solubility parameters of solvent vapour treatment of pre-tensioned polypropylene films affects the strength



(a) 49 mN-



(b) 98 mN-

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

properties of the films, altering the crystalline texture of the spherulites and re-ordering and re-orienting the crystallites.

Weigmann and Ribnick [24] showed that the initial modulus of solvent-treated polypropylene fibre decreased with increase in the single value solubility parameter of the polymer. However, it was quickly pointed out that some solvents with specific interactions, e.g. hydrogen-bonding or dipolar forces, also exhibited high initial modulus. Michaels *et al.* [2] correlated the absolute difference in the solubility parameter of polymer and solvent, $|\Delta\delta|$, to properties of solvent-treated polypropylene. In the same study, the authors showed that the organic vapour diffusivity in polypropylene film at 40 °C was time-dependent, exponentially dependent on concentration (i.e. vapour pressure) and activated transport for liquids of similar boiling points, polypropylene films being reported to be permselective to *p*-xylene relative to *o*-xylene, methyl cyclohexane and toluene relative to iso-octane, and explained this behaviour on the basis of small $|\Delta\delta|$ effects.

After pre-tension stress removal and equilibrium desorption of solvent from the treated film, the residual solvent molecules give rise to plasticization and induced crystallization. These two solvent presence effects are antagonistic to the polymer property. While induced crystallization, a result of decreased glass temperature, is rapid and irreversible, and persists for long time, plasticization is a reversible process. In addition to improved crystallization owing to the presence of solvent, pre-tensioning, which can be seen as uniaxial cold drawing, is an even more significant contributor to the improvement of crystallization. Pre-tensioning introduces stretching orientation of polymer chains. For a hydrocarbon polymer like polypropylene, stretching orientation gives rise to four simultaneous processes: (i) molecular alignment parallel or nearly parallel to the film axis; (ii) molecular unfolding; (iii) molecular slippage over each other, all leading to improved alignment and orderly close-packing that are manifest in; (iv) improved crystallization. Improved orderly close-packing and crystallization lead to improved stress, and also to improved chemical stability because solvent molecules under this condition have less diffusivity into the PP film as the amorphous zone is decreased. The greater the pre-tensioning, the greater is the induced crystallization and the less the solvent vapour diffusivity.

On the other hand, plasticization due to the presence of solvent decreases stress. This is expected for an only solvent-treated PP film, and it has been reported that, in these cases, the stress properties decrease with time of exposure and the yield stress may even disappear [25]. However, in this study, because of the strong antagonistic effect of plasticization (solvent presence) and crystallization (due mainly to pre-tensioning), the effect of one is reduced by the opposite effect of the other. Thus, the reduction in stress expected from plasticization is less than what is expected for the solvent-only treated PP sample, while the improvement of stress resulting from only pre-tensioning is less than expected. The observed variations in the strength properties at any particular pre-tension are determined by the interaction the parameter, χ_H, or the non-specific cohesion force, *D*, of the solvent.

From Table IV and Figs 2–6 it is seen that the yield stress and draw stress at both pre-tensions exhibited slightly larger or equal values than the untreated PP film for chloroform- and carbon tetrachloride-treated samples. The favourable interaction parameter implies loosening and plasticizing of the polymer chains, giving ample opportunity for simultaneous drawing orientation by pre-tensioning that gave values greater than those of untreated PP films.

The results for the initial modulus for 49 and 98 mN pre-tensioning clearly support this explanation, as the initial modulus decrease is of the order of the increase in interaction parameter, χ_H, values (chloroform 0.0013, carbon tetrachloride = 0.0392, dichloromethane 0.00585), the order of disfavouring the solvent property. It is also clear by comparison of Fig. 5b, that greater pre-tensioning results in improved crystallization. The results for draw stress and breaking factor, BF (Eqs. 3–6 respectively) no where exhibited higher values than the untreated PP film. Even though there is apparent insensitivity to solvent treatments, it is clear that the 98 mN pre-tensioned PP films exhibited a net balance of the significance of orientation crystallization to plasticization effects than the 49 mN pre-tensioned

PP film, with values close to those of the untreated PP films. Orientation may lead to brittleness which may reduce tensile strength and the breaking factor.

Stretching orientation by pre-tensioning and solvent presence, both lead to improved crystallization, while plasticization defined by the interaction parameter, χ_H, and non-specific cohesion force, D, by residual solvent give rise to reduced strength. Because both effects have the opposite effects, the deformation characteristics of the solvent vapour-treated pre-tensioned PP films will depend on the net balance of the two effects. When crystallization effects are more significant, the strength property is improved and may even be higher than that of the untreated PP film, but when the plasticization is more preponderant, the properties are reduced to values even below those of untreated PP films. The type of solvent, and extent of pre-tensioning are important in influencing the strength-related property of the solvent vapour-treated pre-tensioned PP films.

5. Conclusion

Studies have been made on solvent vapour-treated pre-tensioned PP films. The results indicate that the treated film thickness increased with the interaction parameter of the solvent, but was independent of the amount of pre-tensioning. The elongation kinetics of the film assumed a parabolic pattern for dichloromethane and chloroform for the two pre-tensions but was irregular in the case of carbon tetrachloride. The strength properties of treated PP films were determined by two opposing factors: stretching orientation from pre-tensioning and also solvent presence on the one hand and plasticization from residual solvent, defined by interaction parameter, χ, and non-specific cohesion force, D, on the other. While the former increase a strength properties by improved crystallization, the latter decrease them. The observed strength properties, therefore, depended on which of the two factors was more predominant, in any particular treatment.

For yield stress and draw stress at both pre-tensions, the influence of crystallization was found to be more significant for chloroform- and carbon tetrachloride-treated PP films when the strength property is slightly larger or equal to that of untreated PP film. This result was clearly supported by the data for initial modulus, where the values were progressively lower (though larger than that of untreated PP film) with increasing interaction parameter, i.e. decreasing plasticizing effects.

The data for tensile strength and breaking factor seemed to be insensitive to variation of solvent vapour treatment at the same pre-tension, but it is still shown that these values are larger for the 98 mN pre-tensioning than the 49 mN pre-tensioning, indicating the greater influence of stretching orientation by the greater pre-tensioning.

References

1. N. N. LI, R. B. LONG and E. J. HENLEY, *Ind. Eng. Chem.* **57** (1965) 18.
2. A. S. MICHAELS, W. VIETH, A. S. HOFFMAN and H. A. ALCALAY, *J. Appl. Polym. Sci.* **13** (1969) 577.
3. C. A. BERNIER and R. P. KAMBOUR, *Macromolecules* **1** (1968) 393.
4. S. A. WHITE, S. R. WEISSMAN and R. P. KAMBOUR, *J. Appl. Polym. Sci.* **27** (1982) 2675.
5. R. P. KAMBOUR, C. L. GRUNER and E. E. ROMAGOSA, *Macromolecules* **7** (1974) 248.
6. *Idem, J. Polym. Sci. Polym. Phys. Ed.* **11** (1973) 1879.
7. P. I. VINCENT and S. RAHA, *Polymer* **13** (1972) 283.
8. G. MARKOWSKI, H. A. STUART and D. JESCHKE, *Mateiapruff* **6** (1964) 236.
9. H. A. STUART, G. MARKOWSKI and D. JESCKE, *Kunststoffe* **54** (1964) 618.
10. A. R. BERENS, *J. Appl. Polym. Sci.* **37** (1989) 901.
11. L. H. SPERLING, "An Introduction to Physical Polymer Science" 2nd Ed. (John Wiley, New York, 1992) p. 96.
12. P. L. HUYSKENS and G. G. SIEGEL, *Bull. Soc. Chim. Belg.* **97** (1988) 821.
13. R. A. HAYES, *J. Appl. Polym. Sci.* **5** (1961) 318.
14. A. F. M. BARTON, "Handbook of Solubility Parameters and Other Cohesion Properties" (CRC, Boca Raton, FL, 1983).
15. T. C. UZOMAH and S. C. O. UGBOLUE, *J. Appl. Polym. Sci.* **55** (1995) 1.
16. S. C. O. UGBOLUE and T. C. UZOMAH, *J. Appl. Polym. Sci.* **62** (1996) 1693.
17. M. H. COHEN and D. TURNBULL, *J. Chem. Phys.* **31** (1959) 1164.
18. H. FUJITA, *Forchr. Honch. Polym. Forsh.* **3** (1961) 1.
19. J. S. VRENTAS and J. L. DUBA, *J. Polym. Sci. Polym. Phys. Ed.* **15** (1977) 403.
20. *Idem, ibid.* **15** (1977) 417.
21. G. R. MAUZE and S. A. STERN, *J. Membr. Sci.* **12** (1982) 51.
22. *Idem, Polym. Eng. Sci.* **23** (1983) 548.
23. *Idem, J. Membr. Sci.* **18** (1984) 99.
24. H. G. WEIGMANN and A. S. RIBNICK, *Text. Res. J.* **44** (1974) 165.
25. A. ARZAK, J. I. EGUIAZABAL and J. NAZABAL, *J. Mater. Sci.* **28** (1993) 3272.

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