

Effect of Exposure Time on the Mechanical Properties of Solvent Vapor-Treated Polypropylene Films

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SYNOPSIS

This investigation seeks to establish the effect of pretensioning and solvent vapor treatment on polypropylene films. There are observed changes in the thickness of the polypropylene films. It is surmised that relatively small molecules such as chloroform, petroleum ether, dichloromethane, and toluene diffused into the polymer film more easily and resulted in maximum percent elongation in the shortest possible time. Decalin and tetralin, which are good solvents for polypropylene, brought about low percent elongation value at 27°C and their behavior is explained in terms of the high boiling point of the liquid and their ability to contribute low vapor pressure on the polypropylene film at the temperature of investigation. Attempts to relate the absolute difference between the solubility parameter of the polymer and the various solvents, $|\Delta\delta|$, with the mechanical properties of the polypropylene film showed complex relationships. However, chloroform and reformate with $|\Delta\delta| = 0.2 \text{ MPa}^{1/2}$ are most soluble, whereas naphtha and petroleum spirit with $|\Delta\delta| = 1.7 \text{ MPa}^{1/2}$ are least soluble for the pretensioned polypropylene films. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene (PP) is an important polyolefin polymer used in the manufacture of containers and different types of packaging items. As containers and in packaging, it is meant to handle liquids, solids, and foods, etc., which emit vapors.

de Phillipi¹ and Choo² showed that solvent annealing of polyethylene increased film permeability. Krewinghauss³ demonstrated the increased permselectivity of uniaxially cold-drawn polyethylene to benzene relative to cyclohexane. Li and colleagues⁴ reviewed the diverse applications of liquid transport in polymer films while Michaels and coworkers⁵ have achieved enhanced permeability 15 times that of untreated PP membranes with reduced selectivity toward the permeants by employing solvent annealing in organic solvent at 60–100°C. Also, solvent treatments^{6–14} could have such effects on polymers as to lead to deterioration in use and to be associated with such phenomena as environmental stress

cracking and environmental stress crazing which are typical visual signs of failure of polymer films. Changes in tensile strength of some polymers have also been correlated with the liquid Hildebrand parameter.

This investigation seeks to establish the effect on the mechanical properties by the combined effect of pretensioning and solvent vapor treatment. This is important because the polymer material is useful in carrying organic liquids (load) whose vapors are also in contact with the container/materials. The 49- and 98-mN pretensioned PP films treated at various times up to 10 h are used for this study.

EXPERIMENTAL

Materials

The PP films were supplied by Bag Manufacturing Company (BAGCO) Nigeria Limited, Lagos, Nigeria. The solvents used were either Nigerian National Petroleum fractions [naphtha, reformate, and petroleum motor spirit (PMS)] or reagent-grade chloroform, toluene, carbon tetrachloride, *o*-xylene,

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tetralin, petroleum ether, and dichloromethane, and were used without further treatment.

Methods

Solubility Parameters

Some properties of the liquids are given in Table I. The solubility parameters of the petroleum fractions—reformate, naphtha, petroleum motor spirit, and petroleum ether—were determined from the aniline point, ASTM D 1012.

Vapor Treatment of Pretensioned Films

Fixed lengths of pretensioned PP film (thickness, 0.012 mm) were immersed in saturated vapor of liquids of varying boiling points (vapor pressures) and solubility parameters at room temperature using 49 mN (5 g) and 98 mN (10 g) pretensioning forces. The changes in length with time at each pretensioned force were measured *in situ* using a Vernier microscope. Readings were taken at 2-, 4-, 5-, 9-, 15-, 25-, 30-, and 60-min, and after 10-h intervals.

Mechanical Properties

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, cross-head speed of 5 cm min⁻¹ and chart speed of 5 cm min⁻¹. Five samples of PP films from each treatment were tested and the mean value taken. The mechanical properties such as initial modulus (IM), yield stress (σ_y), % extension at yield (% E_y), % extension at break (% E_b), tensile strength (tensile stress at break) (σ_b), and draw stress (σ_d), were determined from the stress-strain curves (ASTM D882-81). The thickness of the film before and after treatment was measured with Shirley Portable Thickness Gauge SDL 253. The mean of ten successive measurements made along the film was recorded. All film samples were first washed in acetone and conditioned at 25°C, 65% rh in calcium nitrate-hydrated charged desiccator.

RESULTS AND DISCUSSION

Variation of Film Thickness with Treatment

Table I shows the increase in film thickness with vapor treatment and the absolute difference of the solubility parameter of polymer and solvent $|\Delta\delta|$.

There is strong evidence in support of changes in PP film thickness following solvent vapor treatment

Table I Properties of Vapor-treated and Pretensioned Polypropylene Films

Liquid	Boiling Point (°C)	Molar Heat of Vaporization ΔH_v (KJ mol ⁻¹)	Solubility Parameter at 25°C δH (MPa)	$ \Delta\delta $ (MPa ^{1/2})	98 mN Pretension			49 mN Pretension		
					%E	Thickness (mm) $\times 10^{-2}$	Increase (%)	%E	Thickness (mm) $\times 10^{-2}$	Increase (%)
Reformate	115-118	—	19.0	0.2	5.0	1.30	8	6.0	1.30	8
Chloroform	61	29.6	19.0	0.2	7.3	1.20	8	7.6	1.20	8
Toluene	110.6	33.2	18.2	0.6	5.9	1.30	8	5.8	1.30	8
O-xylene	144.4	36.8	18.0	0.8	5.6	1.30	8	4.0	1.24	3
Tetralin	204-207	—	18.0	0.8	1.6	—	—	1.1	—	—
Carbon tetrachloride	75.6	29.9	17.8	1.0	6.4	1.26	5	6.6	1.26	5
Dichloromethane	39.8	36.3	20.3	1.5	5.5	1.30	8	5.1	1.30	8
Petroleum motor spirit	94-96	—	17.1	1.7	4.6	—	—	5.9	—	—
Naphtha	126-130	—	17.1	1.7	2.7	1.26	5	3.5	1.26	5
Petroleum ether	60-80	—	15.2	3.6	6.4	1.30	3	5.7	1.30	3

Untreated polypropylene (control): solubility parameter,¹⁵ δH 18.8; film width, 0.5 mm; thickness of film, (mm $\times 10^{-2}$) 1.2; % Elongation; 10.4.

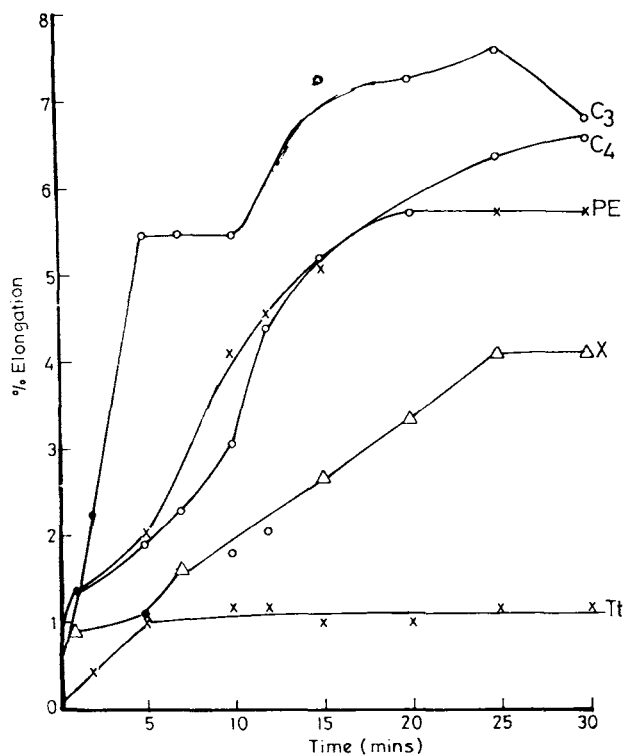


Figure 1 Plot of percentage elongation against time (min) at 49 mN pretension. Tt, tetralin; X, xylene; PE, petroleum ether; C₄, CCl₄; C₃ = CHCl₃.

of pretensioned films, as has been described in greater detail elsewhere.¹⁶

Changes in Elongation with Times of Exposure of Pretensioned and Solvent Vapor-treated PP

From Figures 1, 2, 3, and 4 it can be observed that percent elongation depends more on the time of exposure to solvent vapor and the nature of the solvent treatment. It also appears that pretensioning at 49 mN and 98 mN had no significant effect on the percent elongation results after samples had been exposed for about 1 h.

Generally, the plot of the percent elongation, %E, versus time of exposure of the pretensioned PP films exhibited similar shapes regardless of the extent of pretensioning. However, of importance is the initial elongation percent (at 2 min exposure time) which is high for reformat, petroleum motor spirit, toluene, dichloromethane, and chloroform.

Of the solvent vapors studied, the percent elongation was least for decalin and tetralin; the curves were steep for reformat, petroleum motor spirit, naphtha, *o*-xylene, carbon tetrachloride, and petroleum ether, while the films had reached vapor saturation level for tetralin.

The diffusion of vapor into polymer film is determined in part by molecular size, vapor pressure, and plasticizing effect of the permeant.¹ Michaels and coworkers⁵ have reported that for liquids with similar boiling points, toluene and cyclohexane diffuse faster than isooctane; *p*-xylene faster than *o*-xylene in untreated polypropylene. Also, small molecules have larger diffusion coefficient than large molecules in drawn polyethylene.³ Brandt¹⁷ established the dependence of diffusivity in PP on the square of the molecular diameter of the permeant and explained this dependence of transport of relatively large permeants on the rigidity imparted to the PP material by the pendant methyl groups. Hence it is surmised that relatively small molecules such as chloroform, petroleum ether, dichloromethane, and toluene diffused into the polymer film with ease and gave maximum percent elongation in the shortest possible time. The large molecules of decalin and tetralin had a decreased effect. The low percent elongation observed for petroleum motor spirit, reformat, and naphtha may be due to the fact that these are composite liquids, where the smaller molecular components diffuse faster whereas the larger ones have a slower diffusion rate and on the average the elongation percent is reduced. However, from

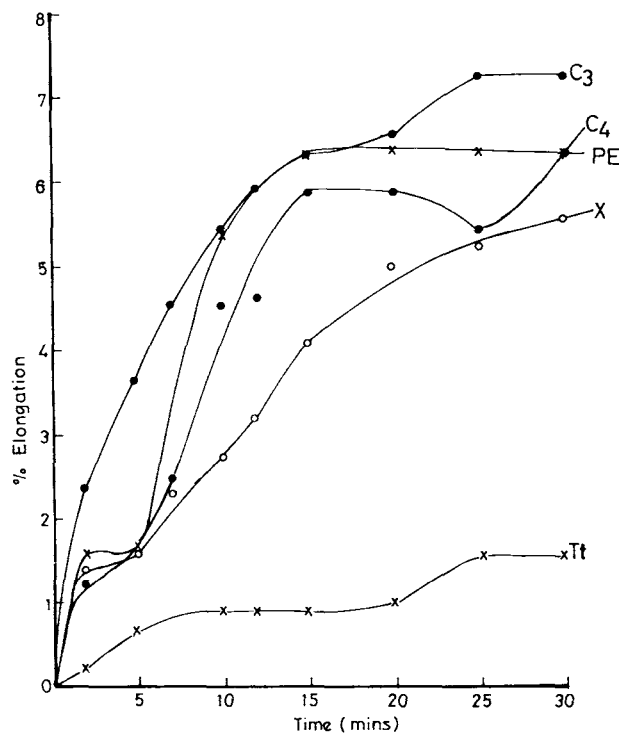


Figure 2 Plot of percentage elongation against time (min) at 98 mN pretension. Tt, tetralin; X, xylene; PE, petroleum ether; C₄, CCl₄; C₃, CHCl₃.

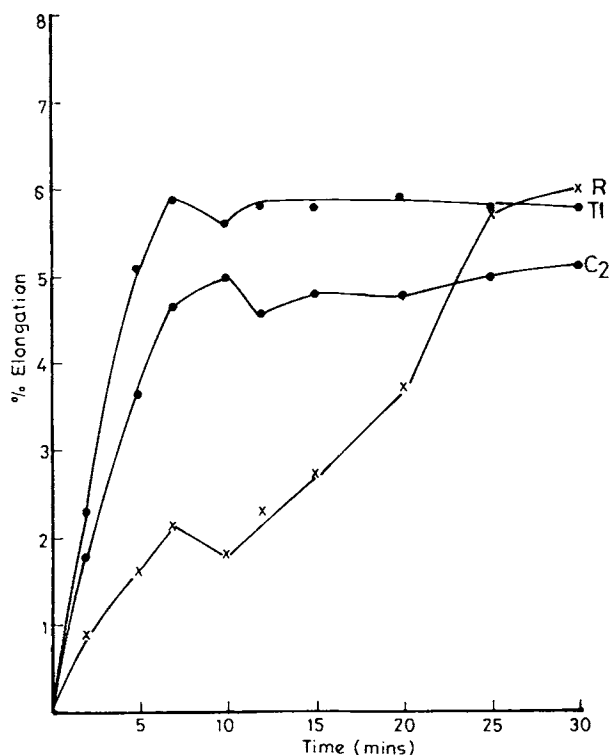


Figure 3 Plot of percent elongation against time (min) at 49 mN pretension. C₂, CH₂Cl₂; Tl, toluene; R, reformate.

Figures 1, 2, 3, and 4, and Table I, the maximum elongation percent, $E\%$, at the end of 30 min investigation time of the PP film in reformate, *o*-xylene, and carbon tetrachloride, had improved quite remarkably, suggesting that the plasticizing effect of these solvents had improved the permeability of the vapors into the PP. Decalin and tetralin are known solvents for PP but have exhibited extremely low percent elongation value at 27°C under the conditions of this study. This observation is explained in terms of the high boiling point of these liquids and their ability to contribute low vapor pressure (low molecular concentrations) on the PP films at the temperature of investigation. This is further discussed in the following section.

Effect of Boiling Point (Vapor Pressure)

The plots of maximum percent elongation versus reciprocal boiling points of liquids given in Figure 5 brings out the linear dependence of the parameters clearly. The proposed relationship is

$$\% E_m = mT^{-1} + c \quad (1)$$

where m is the slope and c is a constant.

This means that the maximum percent elongation is inversely proportional to the boiling point of the liquid of treatment. The vapor pressure (concentration) of liquid is also known to be inversely proportional to the temperature. Thus the maximum elongation percent will be directly affected by the vapor pressure (concentration) in contact with the pretensioned PP films. Complications may arise in the cases of reformate-, naphtha-, and petroleum motor spirit-treated PP films at ambient temperatures because of their multicomponent nature. The smaller molecules will be more in the vapor than the heavier molecules.

Generally, at ambient temperatures, there will be more molecules of dichloromethane, chloroform, petroleum ether, and carbon tetrachloride (liquids with low boiling points), while fewer molecules of tetralin, *o*-xylene, naphtha, reformate, toluene, and decalin are expected in the vapor on a boiling-point basis. Since the diffusivity into PP film is partly vapor pressure/concentration-dependent,¹⁸⁻²⁰ the larger vapor pressure (higher concentration of vapor molecules) will favor the transport of liquid vapors of the low-boiling-point liquids—dichloromethane, chloroform, carbon tetrachloride, and petroleum ether. This is borne out in practice, as the elongation

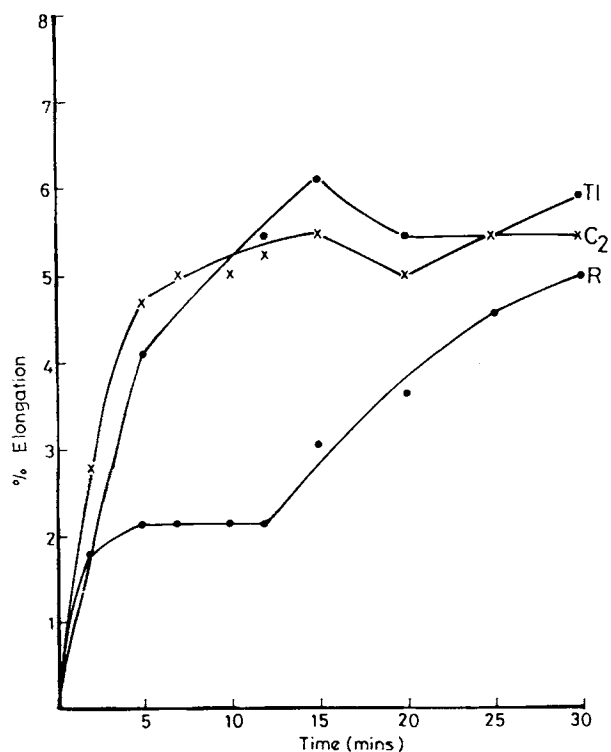


Figure 4 Plot of percent elongation against time (min) at 98 mN pretension. R, reformate; C₂, CH₂Cl₂; Tl, toluene.

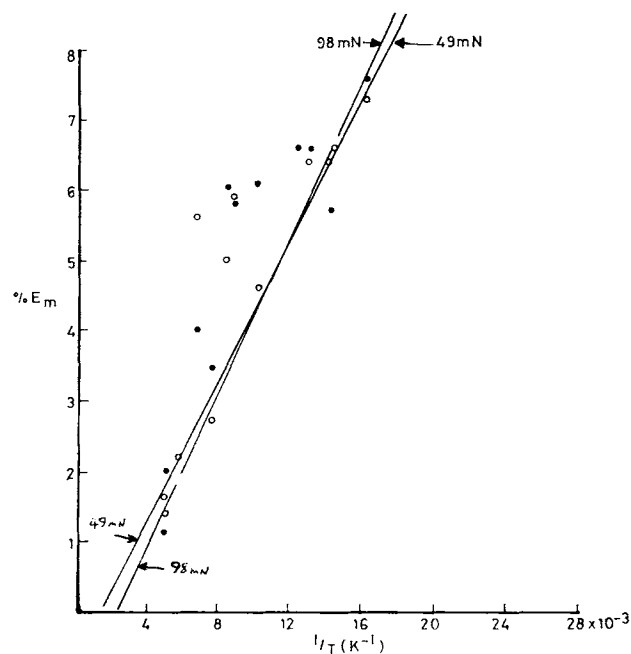


Figure 5 Maximum percentage elongation ($\%E_m$) of vapor-treated pretensioned PP films against reciprocal boiling points of liquids (K^{-1}): (O) 49 mN pretension; (●) 98 mN pretension.

percent exhibited by these low-boiling-point liquids is several times larger than that of high-boiling-point liquids at the early stages of exposure.

Effect of Exposure Time on the Yield Properties

The yield properties, namely yield stress (σ_y), initial modulus (IM), and percent elongation at yield

($\%E_y$), of the solvent vapor-treated, 49 mN-pretensioned PP film at 10-h and 1-h exposure times, respectively, are presented in Table II.

It would appear from Table II that percent elongation at yield ($\%E_y$) is greater after the 10-h exposure time. This is expected because longer time of exposure would increase the number of available plasticizing gas molecules, which would subsequently increase the $\%E_y$ appreciably. Similarly, the pretensioning would increase the orientation of the crystallites which, in effect, would reduce the number of diffusing molecules through the amorphous region; the longer exposure time would enhance the swelling of the polymer material and thus increase the diffusivity.

Table II shows that the yield stress (σ_y) is generally higher for the 1-h exposure than for the 10-h exposure over the $|\Delta\delta|$ studied, except for the small and very large $|\Delta\delta|$ value, < 0.5 and > 3.36 $MPa^{1/2}$. This is attributable to the fact that during the time interval of 1 h, a smaller amount of organic vapor diffused into the polymer vis-à-vis the 10-h solvent treatment. The longer period of exposure resulted in an improved effect of the plasticizing ability of the solvents. Consequently, the yield stress value after 10-h exposure would generally be reduced except for the small and very large $|\Delta\delta|$ values, < 0.5 and > 3.6 $MPa^{1/2}$.

The data for variation of IM (MPa) of solvent-vapor-treated PP films for 49 mN-pretensioned film at different time intervals given in Table II shows that for the 10-h exposure, details of variation of initial IM include a gradual decrease to $|\Delta\delta| = 1.0$ $MPa^{1/2}$, increasing gently to $|\Delta\delta| = 1.7$ $MPa^{1/2}$ before finally

Table II Comparison of the Yield Properties of Solvent-vapor-treated 49 mN-pretensioned Polypropylene Films at Different Times of Exposure

Solvent	$ \Delta\delta $ ($MPa^{1/2}$)	10-h Exposure			1-h Exposure		
		σ_y (MPa) $\times 10^{-1}$	IM (MPa)	$\%E_y$	σ_y (MPa) $\times 10^{-1}$	IM (MPa)	$\%E_y$
Reformate	0.2	208	23.8	19.0	196	25.0	1.6
<i>o</i> -Xylene	0.8	195	16.0	21.7	206	20.0	2.0
Decalin	0.8	196	23.5	16.8	—	—	—
CCL	1.0	186	12.3	27.0	199	21.5	2.2
Acetone	1.5	221	17.0	26.5	—	—	—
Naphtha	1.7	182	21.8	19.2	218	21.9	2.3
Isoamyl acetate		204	14.0	22.9	—	—	—
Petroleum ether	3.6	204	14.0	21.1	196	36.0	2.6
Control sample (No tension; non-solvent-treated)		198	17.9	17.2	—	—	—

decreasing to $|\Delta\delta| = \text{around } 3.6 \text{ MPa}^{1/2}$. The general decrease in IM for $|\Delta\delta|$ in the range $< 1.40 \text{ MPa}^{1/2}$ is consistent with the proposal that the plasticizing ability of the solvents has an overriding influence at low $|\Delta\delta|$ values.

CONCLUSION

Studies on the absolute difference between the solubility parameter of PP and various solvents, $|\Delta\delta|$, have been carried out. There are observed changes in the thickness of PP films following treatment of the pretensioned films. It is surmised that relatively small molecules such as chloroform, petroleum ether, dichloromethane, and toluene diffused into the polymer film more easily and resulted in maximum percent elongation in the shortest possible time. Generally, chloroform and reformate with $|\Delta\delta| = 0.2 \text{ MPa}^{1/2}$ were found to be most soluble while naphtha and petroleum motor spirit with $|\Delta\delta| = 1.7 \text{ MPa}^{1/2}$ were least soluble for the pretensioned PP films.

The longer period of exposure of the PP to various solvents resulted in improved effect of the plasticizing ability of the solvents. It is thus concluded that the general decrease in the initial modulus for $|\Delta\delta|$ in the range $< 1.4 \text{ MPa}^{1/2}$ was consistent with the proposal that the plasticizing ability of the solvents has an overriding influence at low $|\Delta\delta|$ values.

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