

Some Mechanical Properties of Solvent-Treated Polypropylene Films

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SYNOPSIS

The amount of polypropylene (PP) extracted by hot solvent extraction increased with increasing naphtha in a naphtha/reformate solvent blend. The stress-strain curves formed the basis for the calculation of several mechanical properties of the residual film. The yield stress, the natural draw ratio, secant modulus, breaking factor, and work expended in drawing were maximum at a 10/90 naphtha/reformate composition. These were explained in terms of extraction of low molecular weight and atactic materials leaving a more stereoregular block, giving maximum properties with the least removal of polymer materials. Further increases in the naphtha component, however, decreased these properties, possibly due to the greater solubilizing effect of naphtha for the PP chains. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The chemical resistance of polypropylene (PP) is well known.¹ It is only soluble at elevated temperatures in a few solvents, for example decalin, *o*-xylene, benzene, and trichloroethylene.² Researchers adopt the hot extraction method under nitrogen atmosphere.³ Extraction of stabilizers also occurs during hot extraction. The temperature of extraction and the plasticizing effect of the solvent molecules also affect the leachability of the stabilizers. Extraction with organic solvents has been shown to have greater effect than washing with water and a detergent-water mixture.⁴ Rejection of additives to the spherulite boundaries, which is dependent on the crystallization mechanism, the degree of ordering of the crystallites being formed within the polymer film, or on the surface, may well increase the loss of stabilization.

Extraction of low molecular weight polymer materials and loss of stabilizers from the polymer film affect the mechanical properties of the polymer films. PP is extensively used for containers for veg-

etable oils, petroleum products of various kinds, etc. and may leach stabilizers and extraction of low molecular weight fractions with consequent deterioration of useful mechanical properties, notably the tensile strength, yield stress, draw stress, natural draw ratio, etc.

There is little or no report on the solubility of PP in the Nigerian National Petroleum Corporation (NNPC, Warri, Nigeria) petroleum fraction: naphtha, reformate, and their blends. This article gives details of recent experimental investigation on PP films aimed at obtaining information not only on its solubility in these solvents or their blends but also on establishing criteria for developing PP films with improved mechanical properties. This study also dwells on the percent elongation of pretensioned PP films in some common solvents. The mechanical properties of the residual PP films after hot extraction are also discussed.

EXPERIMENTAL

Materials

PP films (0.012-cm thickness) were supplied by the Bag Manufacturing Company (BAGCO) Nigeria Limited (Lagos, Nigeria). The petroleum fractions, naphtha (bp 126–130°C) and reformate (bp 115–

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Table I Fraction of PP Films by Hot Extraction for 10 h

Solvent	Original Mass of PP Film (g)	Mass % Extracted	Temperature (°C)	
			Hot Solution	Phase Separation
Naphtha	0.740	48.0	—	75
Naph/Ref 90/10	0.775	27.7	61	—
Naph/Ref 80/20	0.820	19.8	83.5	82
Naph/Ref 70/30	0.815	21.5	82	—
Naph/Ref 60/40	0.840	11.9	85	88
Naph/Ref 50/50	0.775	8.4	—	58
Naph/Ref 40/60	0.830	18.7	76	71
Naph/Ref 30/70	0.830	7.2	—	65
Naph/Ref 10/90	0.820	5.5	64	59
Reformate	0.835	5.3	—	59
Decalin	0.800	100	108	84
<i>o</i> -Xylene	0.850	100	114	79

Naph, naphtha; Ref, reformate; film thickness = 0.012 cm; width = 0.5 cm.

118°C) were obtained from NNPC. Other solvents were Grade A laboratory reagents. All solvents were used without further purification.

Method

Hot Extraction

A known mass (0.774–0.850 g) of PP film was extracted in hot solvent (150 cm³) using a Soxhlet extractor for a period of 10 h under nitrogen atmosphere. The residual polymer film was air dried for a couple of days and weighed. The temperatures

of hot extraction solvent, phase separation of solution, and the percent mass of polymer film extracted are recorded in Table I.

Vapor Treatment of Pretensioned PP Film

Fixed length, 11.0 cm, width, 0.5 cm, and thickness, 0.012 cm, of pretensioned PP films were suspended in saturated vapor at room temperature. The elongation of pretensioned films after exposure at various times (2, 5, 7, 10, 15, 20, 30, 50, 60 min) was measured *in situ* with a Vernier microscope. Similarly, the percent elongation in different solvent vapors

Table II Percent Elongation of PP Film at Different Pretensions for Solvents with Time

Time (min)	Load (g)							
	Decalin		Naphtha		Reformate		PMS	
	5	10	5	10	5	10	5	10
2	0.45	0.45	0.75	0.50	0.90	1.8	1.50	1.1
5	0.90	0.90	1.7	1.0	1.6	2.1	1.8	1.6
7	—	0.90	—	—	2.1	2.1	—	1.9
10	—	0.90	1.8	1.6	1.8	2.1	2.7	2.1
15	1.3	1.4	2.1	1.9	2.7	3.1	4.3	2.7
20	—	—	2.4	2.3	3.7	3.6	5.9	3.2
25	—	—	—	—	5.7	4.6	—	4.2
30	2.0	1.7	3.5	2.7	6.0	5.0	6.1	4.6
40	2.1	2.1	5.0	3.1	—	—	6.2	—
50	—	—	5.7	4.0	—	—	5.9	—
60	2.3	2.3	5.9	4.7	—	—	5.9	—

PMS, petroleum motor spirit.

Table III Percent Elongation at 5-g Pretension of PP Film at 27°C and 10-h Time

Solvent	% Elongation
Decalin	8.9
Carbon tetrachloride	8.5
Naphtha	7.1
Reformate	6.2
Petroleum ether (60–80°C)	6.1
<i>o</i> -Xylene	5.5
Acetone	2.0

and maximum elongation percent in solvent vapors at 27°C for 10 h were determined. The data are presented in Tables II and III, respectively.

Mechanical Properties

Neat and residual PP films were measured on the Instron tensile testing machine, model 1122, using a gauge length of 5 cm, cross-head speed 5 cm/min, and chart speed 5 cm/min. Five samples of films from each treatment were tested and the mean values of each specific property reported. The initial modulus (IM) extension-at-break (EB) yield stress (YS), tensile strength (TS), natural draw ratio (NDR) etc. were determined from the stress-strain curves (ASTM D 882-81). Other important properties such as work (energy) expended in plastic deformation, U , and the draw stress (DS), which are important in the description of the free energy of melting of polymer, were also determined. The data are presented in Tables IV and V.

$$U = DS(NDR - 1). \quad (1)$$

Table IV Mechanical Properties of Residual PP Films from 10-h Hot Extraction

Solvent	YS $\times 10^{-1}$ (MPa)	E% at Break	IM (Nm ⁻¹)	BF (MPa)	%E at Yield	TSB $\times 10^{-1}$ (MPa)	SM at 100% E $\times 10^{-1}$ (MPa)
Reformate	172	930	71	4631	19.9	365	175
Naph/Ref 10/90	222	877	30	4949	19.5	351	217
Naph/Ref 30/70	188	857	18	4263	13.7	296	160
Naph/Ref 40/60	195	723	18	3920	12.3	269	176
Naph/Ref 50/50	174	790	20	3508	10.6	265	160
Naph/Ref 60/40	182	428	15	2261	9.6	196	170
Naph/Ref 70/30	198	420	12	2989	10.2	160	^a
Naph/Ref 80/20	196	168	10	2381	8.5	125	^a
Naph/Ref 90/10 ^b	—	—	—	—	—	—	—
Naphtha ^b	—	—	—	—	—	—	—

Ref, reformate; Naph, naphtha; YS, yield stress; IM, initial modulus; BF, breaking factor; TS, tensile strength; SM, secant modulus.

^a Film broke before 100% E.

^b Film destroyed by hot solution.

All samples were first washed in acetone, kept frozen prior to treatments to minimize the possibility of physical ageing of polymer films, and then conditioned at 24.5°C, relative humidity (RH) 65% in calcium nitrate. The stress refers to cross sectional area of residual films.

RESULTS AND DISCUSSION

Hot Extraction

Judging from the distribution of percent mass of films extracted (Table I) it would appear that naphtha is a better solvent for PP than reformate: there is a gradual decrease in the amount extracted with increasing reformate component in the binary blend. The extraction involved a separation of low molecular weight polymer fractions from the more stereoregular block with higher molecular weight.^{3,5} Hot extraction with decalin and *o*-xylene dissolved PP films completely.

The high temperature of the extraction solvent favored dissolution. This is expected as the extraction of polymer should occur at a temperature close to the melting point of the solvated polymer fraction. The higher temperature of hot solution for decalin (108°C) and *o*-xylene (114°C) are significant for the solvency power for PP.

For the temperature of phase separation, the solvency power of a liquid, and the amount of polymer in the hot extract solution compete in giving the observed temperature. A solvent with high solvency power is expected to give a solution with a low phase separation temperature, while a large concentration of polymer in solution should favor a high phase

Table V Composition of NDR, DS, MDR, U for Residual PP Films

Solvent	NDR	DS $\times 10^{-1}$ (MPa)	MDR	$U \times 10^{-1}$ (MPa)
Untreated PP	6.33	156	5.33	831
Reformate	2.88	181	1.88	340
Naph/Ref 10/90	4.62	216	3.62	782
Naph/Ref 20/80	4.56	208	3.56	741
Naph/Ref 30/70	4.24	206	3.24	667
Naph/Ref 40/60	4.16	196	3.16	619
Naph/Ref 50/50	2.49	189	1.49	282
Naph/Ref 60/40	2.66	188	1.66	302
Naph/Ref 70/30 ^a	—	184	—	^b
Naph/Ref 80/20 ^a	—	182	—	^b
Naph/Ref 90/10 ^c	—	—	—	—
Naphth a ^c	—	—	—	—

Naph, naphtha; Ref, reformate; NDR, natural draw ratio; DS, draw stress; MDR, measured DR; U , energy of drawing.

^a Film broke before reaching NDR.

^b Values cannot be estimated from eq. (1) because NDR is not known.

^c Film destroyed by hot extraction.

separation temperature. From Table I this was proved in practice.

It must be pointed out that in using a binary mixture of naphtha (bp 126–130°C) and reformate (bp 115–118°C), the vapor would always contain more of the lower boiling liquid, reformate. Thus, the hot condensate in the Soxhlet apparatus would contain more reformate than has been indicated in the percent binary composition.

Vapor Treatment

Generally, the percent elongation at the same time interval appeared to be more for the less pretensioned (5 g) film than for the more pretensioned film (10 g) for naphtha, petroleum motor spirit (PMS), and to an extent, for reformate (Table II). This is attributed to the effect of increased residual crimp present in the less pretensioned film. Also the sigmoid nature of the profile is observed for PP films at different pretensions for the different solvent vapors. But of significance is that the initial elongation percent (at 2 min) is high for reformate and PMS and least for decalin (Figure 1). From Table II it appears that pretension had significant effect on elongation percent for naphtha, reformate, and PMS vapors but not for decalin vapor.

Of the solvent vapors studied, the percent elongation was least for decalin but the curves are steep for reformate, PMS, and naphtha; but the films reached vapor saturation levels for PMS at 5-g film pretension (Figure 1). The diffusion of vapor into

polymer film is determined in part by molecular size and plasticizing effect of the permeant.^{6,7} Hence, as it is observed, smaller hydrocarbon molecules of PMS diffused into the polymer film with ease and gave maximum elongation percent in the shortest possible time. The large molecules of decalin had a decreased effect. However from Table III, the elongation percent at saturation for decalin vapor became the largest for the solvent vapors studied. It can therefore be proposed that the plasticizing effect of decalin improved the permeability of the vapor into the PP film. The same proposition may be put forward in the case of naphtha.

Again, the higher boiling point of decalin compared to other solvents would give rise to its lowest vapor pressures at 27°C, which would explain the lower elongation observed during the early stages of the diffusion.

The trend in Table III also supports the fact that hydrocarbon solvents (e.g., decalin, *o*-xylene) with approximately zero dipole moment have greater capacity to plasticize PP when compared to more polar solvents, for example acetone.

Mechanical Properties

Several mechanical properties of the residual PP films from the hot extractions were determined from the stress-strain curve. The following: Y_S , the maximum tensile force, the tensile stress-at-break (TSB), and the IM are listed in Table IV. It can be seen clearly from Table IV that hot extraction of

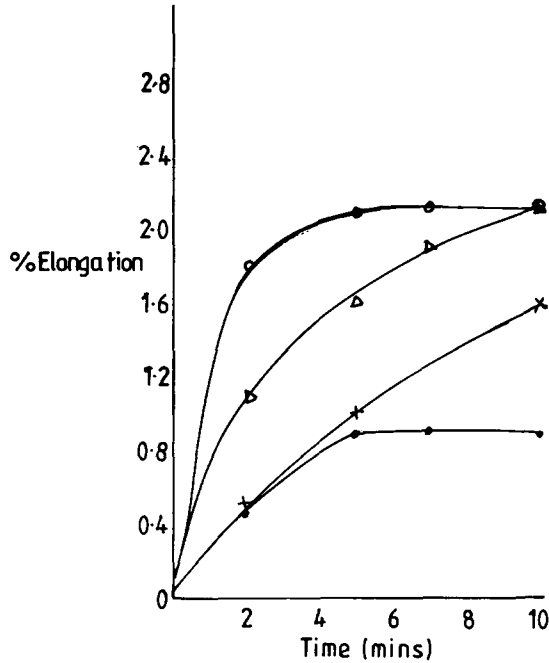


Figure 1 Percent elongation vs. time (mins) of film treatment (10 g.-pretention) in solvent vapour. ● Decalin, × Naphtha, ○ Reformate, △ PMS.

PP films with naphtha/reformate blends had significant effect on the mechanical properties. From Figure 2 the yield stress and secant modulus (SM) increased fairly regularly, attaining maxima at 10/90 naphtha/reformate composition before decreasing to minima at 50/50 naphtha/reformate composition and then increasing with increasing naphtha in the blend composition.

However, the relative increase was larger for the secant modulus than for the yield stress. The variation of percent EB and TSB with increasing naphtha composition in the naphtha/reformate blend plotted in Figure 3 shows that the TSB exhibits a gentle decrease initially and then dips after 50/50 naphtha/reformate blend composition, reaching very low values at 80% naphtha composition. In addition, percent EB decreased monotonically with an increase in percent naphtha in the blend, for up to 80% naphtha. From Figure 4, IM decreased rapidly with increasing volume percent of naphtha up to 20/80 naphtha/reformate composition, and then the decreases become more gentle. On the other hand, percent extension-at-yield decreased fairly regularly with increases in the volume percent naphtha in the

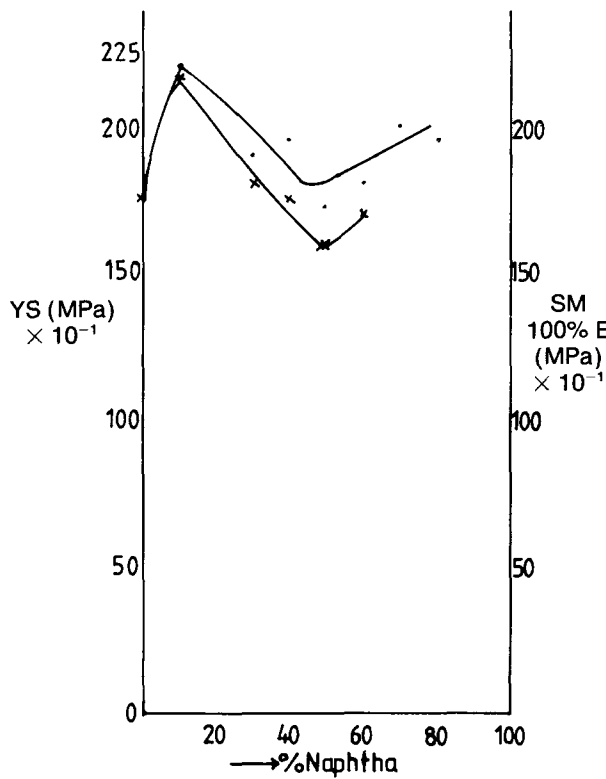


Figure 2 Yield stress YS (MPa) (●) and secant modulus SM (MPa) (×) versus %naphtha in naphtha/reformate blend.

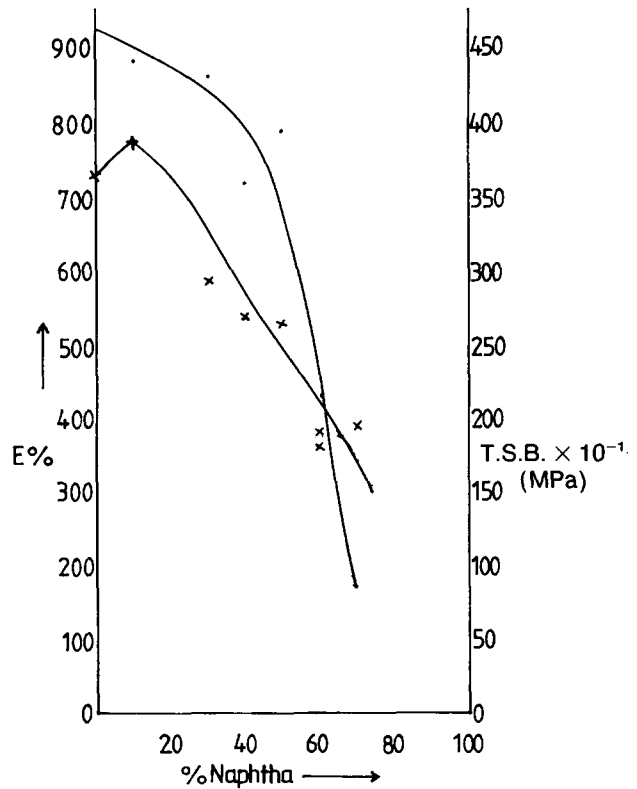


Figure 3 Variation of percent strain E% at break (●), and tensile strength at break T.S.B. (×) with increasing percent naphtha in naphtha/reformate blend.

naphtha/reformate blend. From Figure 5, the breaking factor (BF) is maximum for 10/90 naphtha/reformate composition before decreasing at higher naphtha percent composition in the binary blend.

The observed increases in SM, YS (Fig. 3), and breaking factor (BF) (Fig. 5) for residual PP film, from the 10/90 naphtha/reformate composition especially, may be attributed to least extraction of polymer materials giving maximum properties. Any possibility of chain restructuring leading to increased orientation and enhanced crystallinity of the residual polymer film must await further confirmation of increased crystallinity by density measurements and/or infrared studies. However, the present data suggest that 10% naphtha in the naphtha/reformate blend is probably needed to improve the strength of PP film even though minute amounts of low molecular weight and atactic materials must have been extracted. Further increases in naphtha composition in addition to the extraction of more polymer materials, did swell and plasticize the polymer and in the process resulted in the reduction of all the mechanical properties studied. It is therefore, proposed that even the low molecular weight oligo-

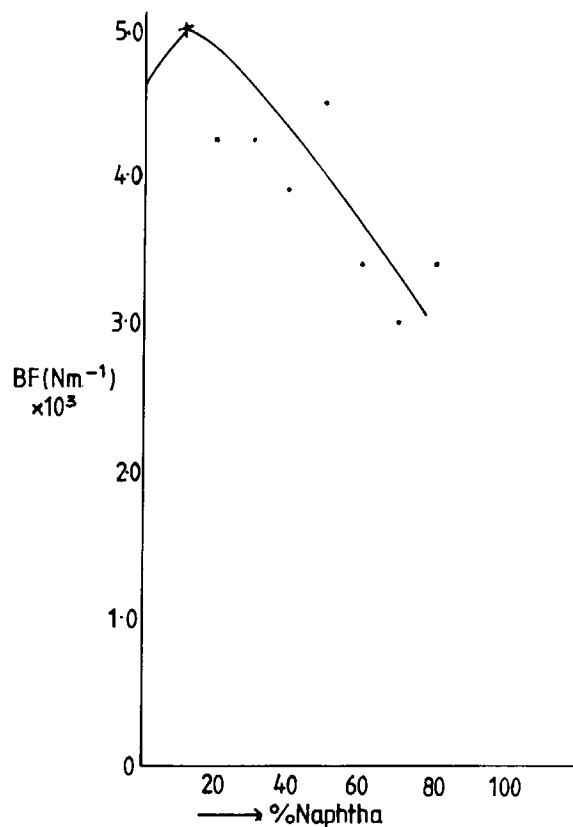


Figure 5 Breaking factor BF (Nm⁻¹) vs. increasing naphtha in naphtha/reformate blend.

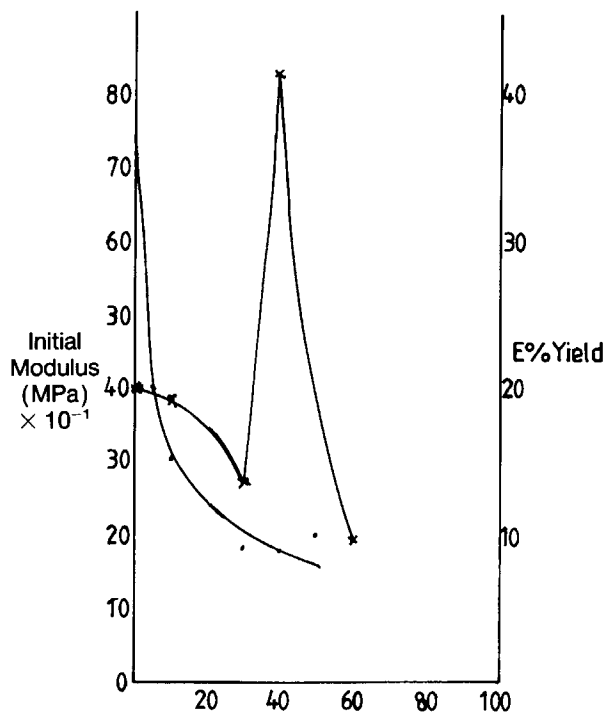


Figure 4 Initial modulus (IM) (●) and strain at yield (E%) (×) as a function of increasing naphtha in naphtha/reformate blend.

mers extracted played a significant role in maintaining these mechanical properties.

Variation of NDR, DS, and U with Blend Composition

Generally PP like other melt-spun fibers is subject to drawing that increases its strength and modulus and decreases its elongation.⁸ The detailed study of further mechanical properties of NDR, given by the constant extension ratio in the drawn part of the film as the neck grew to the final drawn state, and the DS, the minimum value of stress developed as the neck was fully stretched, are useful in the description of other properties of film deformation.⁹ Properties such as the measured draw ratio (MDR) = NDR - 1, and the energy expended in drawing polymer film, U , [eq. (1)] are also listed in Table V. Examination of Table V and Figure 6 (plots of natural DR and DS versus solvent blend composition) shows that the NDR, MDR, and the U , appear to be maximum for the 10/90 naphtha/reformate blend composition and then decrease with further increases in naphtha in the solvent blend. The NDR

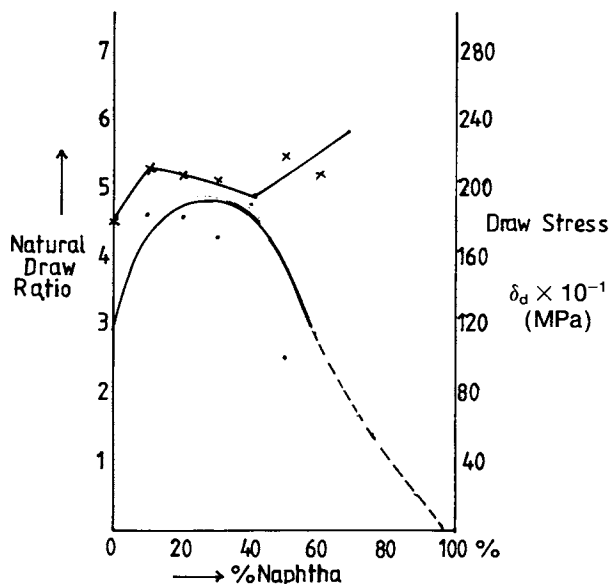


Figure 6 Natural draw ratio NDR (●), draw stress (×) versus increasing naphtha in naphtha/reformate blend.

of 0 can be obtained by extrapolation close to neat naphtha, possibly achieved at the boiling point. In practice, PP pellets were found soluble in refluxing naphtha at 128–130°C. However, the DS reached local maximum at 10/90 naphtha/reformate composition but decreases gently with further increases in naphtha in the blend composition. Moreover, these properties are less than as found in untreated PP films. These are attributed to the effect of hot extraction on PP films. The data in Table V and Figure 6 support our earlier proposition that hot extraction with solvent or solvent blends removed low molecular weight and atactic polymer materials that contribute to observed higher mechanical properties for the untreated polymer films. Again, the relatively higher values of these mechanical properties for the 10/90 naphtha/reformate blend treated PP films compared to those of the other treated polymer films indicate improved properties with the least removal of polymer materials.

Gent and Madan⁹ have proposed that the mechanical work of drawing breaks the crystallites for melting to occur. They developed the theory of stress-induced melting that depends upon the crystallinity and free energy of melting of a polymer. The more crystalline the polymer, the larger the NDR. Because YS and DS decrease with increasing temperature, and plasticization decreases the melting point, the YS and DS will also decrease with increasing naphtha in the naphtha/reformate blend.

CONCLUSIONS

PP film is shown to be more soluble in naphtha than in reformat, and the amount of PP extracted by blends increased with increasing naphtha in the naphtha/reformate blend. The higher temperature of the hot solution seemed to favor extraction.

Variation in the pretension of PP films affected the percent elongation of films in solvent vapors. Generally the 5-g pretensioned films exhibited more elongation than the 10-g pretensioned films in the solvent vapors over the period of time of study. Again PP films exposed to smaller molecular vapors attained maximum elongation in a shorter time interval.

The mechanical properties of polymer film residues were fractions of those for neat PP. Whereas the IM, percent elongation at yield, percent EB, and tensile stress-at-break all decreased with increasing naphtha in the blends, many other mechanical properties, including YS, DS, NDR, U , SM, and breaking factor seemed to be maximum at 10/90 naphtha/reformate composition. These maxima have been explained in terms of improved properties with the least removal of polymer materials. Further increases in percent naphtha in the binary blends decreased these properties and have been explained in terms of the solubilizing effect of naphtha in these blends.

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