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Barrier properties of polyamide-6/high density polyethylene blends

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SUMMARY

The barrier properties of Polyamide-6 (PA6)/High Density Polyethylene (HDPE) blends with and without compatibilizer prepared by ribbon extrusion were studied. The results show that the toluene diffusivity was improved by the addition of an interfacial agent and by inducing orientation of the polymer chains. The presence of PA-6 in the blend results in a decrease of the toluene diffusivity. This reduction is even larger for the case of the interfacial modified system. However, the most important reduction of the toluene diffusivity is observed for pure HDPE when stretched. A six-fold decrease is observed when the draw ratio is increased two fold. In the case of the permeability of different solvents through blends a gravimetric permeation cell was used. The results show that the permeability decreases with increasing size of the penetrant molecules (CH_2Cl_2, $CHCl_3$ and CCl_4) and this decrease is more important for a compatibilized blend.

INTRODUCTION

Historically the containers used to store or transport chemical products were made of metal or glass. Currently, plastic materials are the materials of choice. The polymer wall must however have good barrier properties in order to reduce the transfer of mass to the environment. The barrier term is used to describe a material with a low diffusion coefficient and low permeability of gases and vapors. There are techniques such as, co-extrusion of laminates of two or more polymers, used of impermeable inorganic fillers, interfacially stabilized immiscible blends [1], to prepare this kind of materials. However, some of these techniques represent expensive manufacturing costs.

In the last two decades, polymer blends have been used in many commercial applications. For example, the packing industry is entering a period of high expectation and it has been the focus of intensive investigation [2-5].

Polyolefins are ideal candidates for the manufacture of a wide variety of films, containers, trays, etc., for various packaging and industrial applications. However, they have a high permeability to many organic solvents and gases, which make the undesirable for applications where high barrier properties are required. In contrast to polyolefins, polyamide is known for its excellent barrier properties to hydrocarbons. Blends of polyolefins and polyamides have been the topic of many research efforts [6-11]. This kind of blend produces a heterogeneous morphology and compatibilizer components should be introduced in order to improve the interfacial adhesion and the final physical properties. Several studies [9,10,12] have shown that the compatibilizer in inmiscible polymer blends improves the barrier properties. For example, Subramanian [6,12,13] have shown that polymer blends, where the minor phase is dispersed as thin platelets parallel to the surface of the manufactured product, have significantly improved the permeability barrier properties. Holsti-Micttinen *et al* [10] studied the oxygen barrier properties of polypropylene/PA-6 blends. They observed that the barrier properties of the blends were improved and approached those of PA-6, after the phase inversion (when the polyamide became the continuous phase). They also observed that the blending procedure had a great influence on the oxygen permeability.

This study belongs to a series of papers, which have published about this HDPE/PA6 system. The objective of these articles is to establish a relationship between the blend morphology and the physical properties. A detailed study of the system morphology, compatibilizer [14] effect and theoretical [15] analyses have been published.

The objective of this study is to measure the barrier properties of the oriented materials and to observe the morphological effect of the blends with and without compatibilizer, a rheological analysis of the blends is also included.

EXPERIMENTAL

Materials.

The HDPE used in this study was 07055 C, obtained from Dow in pellet form. The PA-6 was Zytel 211 from DuPont (in granular form) was used as the minor phase. Surlyn 9020 obtained from DuPont was used as a compatibilizer. This ionomeric resin is a random terpolymer consisting of 80% polyethylene and 20% of a mixture of methacrylic acid and isobutyl acrylate. The methacrylic acid was approximately 70 % neutralized with zinc.

Mixing.

Prior to a typical mixing experiment, the sample mixture was dried under vacuum at 90 °C overnight. The materials were blended in a ZSK-30 (Werner-Pfleiderer) intermeshing co-rotating twin-screw, extruder with a screw length to screw diameter radio, L/D, of 40. The feeding was performed under dry nitrogen. Vacuum was applied in the decompression zone. The melt temperature remained constant at 250° C and the screw speed was maintained at 250 rpm.

Blends containing 20 % vol. of PA6 in HDPE with (MIPA20s) and without (MIPA20) compatibilizer were prepared. When the blend was compatibilized, a two-step mixing was used. A master batch of HDPE with 10 % ionomer, based on the minor phase (or 3% of total), was prepared. This master batch was then compounded with the minor phase (PA6). In a recent morphological study, Willis, *et al* [16] observed a high affinity of the ionomer for the PA-6, and the migration of modifier to the interface is facilitated when it is initially mixed with the component with which it has the least affinity.

Rheological analysis

The rheological characterization of the resins was performed using two instruments. For shear rates lower than 10^2 s^{-1}, a Weissenberg rheometer was used. The tests were carried out using a plate-plate geometry of 40 mm diameter with a 2 mm gap. The measurements were performed under dried nitrogen. For high shear rates, the viscosity data were obtained with an Instron capillary rheometer model 2404, using a set of capillary dies of 0.127 mm diameter and length to diameter (L/D) ratios of 40, 60 and 80. Bagley and Rabinowitsch corrections were applied to the capillary rheometry data.

Ribbon Extrusion

Ribbons of the blends and pure materials previously compounded were extruded through a 7.6 cm slit die with adjustable gap at 250°C using a Brabender single screw extruder. The screw has a 1.905 cm diameter and a 3:1 compression ratio with an L/D of 25. The screw speed remained constant at 60 rpm and the linear velocity was calculated taking into account the melt densities. The extrudate was taken up between two water-cooled steel rolls and the linear velocity of the rolls was measured.

Diffusion experiments

A sorption/diffusion measurement system based on a Cahn electronic balance was used to measure the desorption kinetic of solvent-polymers pairs. This is a constant volume vacuum system. The desorption proceeds under a vacuum of 10^{-2} mmHg and the overall temperature variation of the sample during the desorption was controlled within 0.1K.

The accuracy of the balance is 1x 10^{-7} gr. The details of this computer-aid apparatus have been described elsewhere [17]. A solvent-saturated polymer sample was loaded into the balance at time zero. The system was subjected to vacuum at the same time .The weight change of the system as a result of desorption at a given temperature was recorded through a data acquisition unit by a computer. These data were used to determine the values of the diffusion coefficients as described elsewhere [17].

Permeation experiments

An experimental method based on a gravimetric permeation cell was used in measuring the permeability of the blends. This cell made of Teflon, is basically a liquid container with a polymeric membrane seal on its top. The use of Teflon ensures that the liquid inside the cell does not react with the surfaces of the cell. A concentration gradient across the polymeric membrane is established, and one measures a decrease in the overall weight of the cell.

RESULTS AND DISCUSSION

Rheology of polymer blends

Figure 1 shows the viscosity $\eta(\dot{\gamma})$ and the primary normal stress coefficient $\eta(\dot{\gamma})$ of the polyethylene (*Figure 1a*) and polyamide-6 (*Figure 1b*) resins at 250°C. The solid curves are predictions of the De Kee and Chan Man Fong model [18], given by Equations (1) and (2).

$$\eta(\dot{\gamma})=\eta_0\frac{1+d\dot{\gamma}^{r-m}+c\dot{\gamma}^{r}}{1+d\dot{\gamma}^{r-m}+b\dot{\gamma}^{m}+(bd-c)\dot{\gamma}^{r}} \qquad (1)$$

$$\psi_1(\dot{\gamma})=\frac{2\eta^2(\dot{\gamma})}{G(\dot{\gamma})} \qquad (2)$$

Where b, c and d are model parameters, η_0 is the limiting zero shear rate viscosity and $G(\dot{\gamma})$ is elastic modulus. We assume that G may be given by $G(\dot{\gamma}) = G_0\,(1 + \mu\dot{\gamma}^{n})$, where G_0 is the limiting zero shear rate elastic modulus, μ and n are parameters.

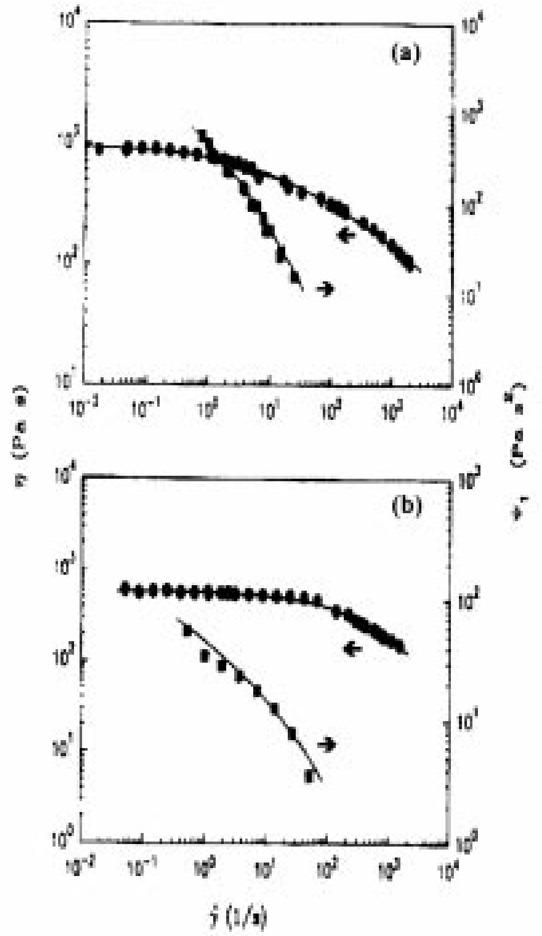

Figure 1. Viscosity and primary normal stress coefficient as a function of shear rate for: **(a)** HDPE and **(b)** PA-6 at 250 ^{0}C. •Viscosity data, ▪Primary normal stress coefficient data, ---- prediction of the De Kee and Chan Man Fong model (1994).

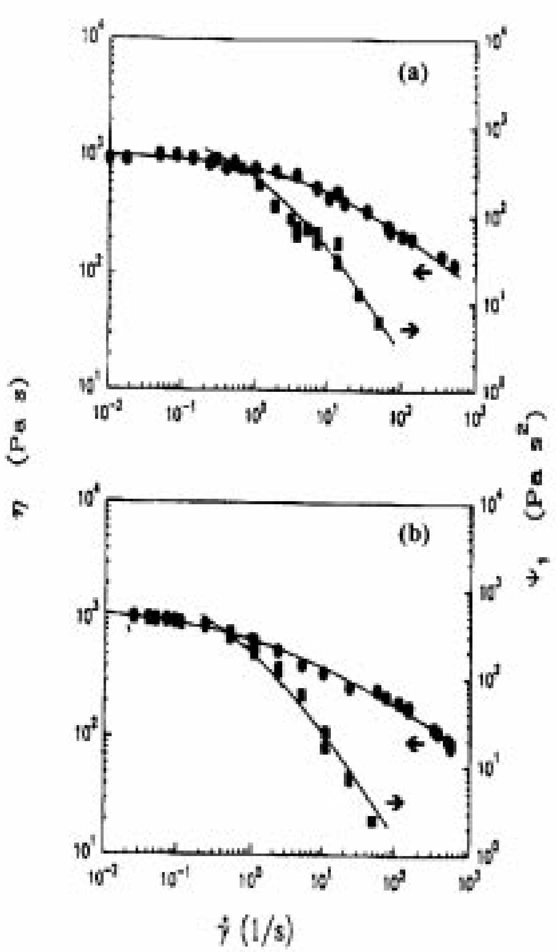

Figure 2. Viscosity and primary normal stress coefficient as a function of shear rate for: **(a)** M1PA20 and **(b)** M1PA20s at 250 ^{0}C. •Viscosity data, ▪Primary normal stress coefficient data, ---- prediction of the De Kee and Chan Man Fong model (1994).

Table 1. Parameters of De Kee and Chan Man Fong Model.

Parameters	HDPE	PA6	MIPA20s	MIPA20
η_0	969	589	1048	1248
b.	0.26	0.02	0.32	0.85
m.	0.45	0.64	0.53	0.42
G_0	1000	3450	1900	1600
n.	0.85	0.51	0.55	0.55
μ	1.50	3.20	1.50	2.00

Figure 2 shows also the viscosity and the first normal stress coefficient for M1PA20 *(Figure 2a)* and M1PA20s (*Figure 2b*) blends. The values obtained for the zero shear viscosities (η_0) were higher for the blends than the pure polyethylene at 250°C. These results indicate a positive deviation from the mixing rule for the blends. In the case of the compatibilized blends (M1PA20s), this could be explained via the interfacial modification introduced by the ionomer copolymer. Willis *et al* [19] studied the emulsifying effect of a polyethylene based ionomer on the phase size/composition relationship for PP/PA6 and PE/PA6 blends. They explained that the localization of the ionomer at the interface decreased the interfacial mobility at all dispersed-phase contents. Chang and Hwu [20] have shown that a higher viscosity of the compatibilized blend indicates a better miscibility and a molecular weight increase due to copolymer formation for a PS/PA6 blend.

On the other hand, for an uncompatibilized blend, the positive deviation from the mixing rule could be attributed to coalescence effects. Recently, Germain *et al* [21] studied the influence of a block copolymer compatibilizer, on the rheological behavior of PP/PA6 blends. A dual-flow behavior was observed. At low shear rates, the blend viscosity is higher than the viscosity of the matrix, while at high shear rates the opposite is observed.

Effect of the material orientation on the toluene diffusivity

An example of desorption kinetic curves for toluene in different films at 25 °C are presented in *Figure 3*. The rate of desorption is faster in PE films than in PA6 films.

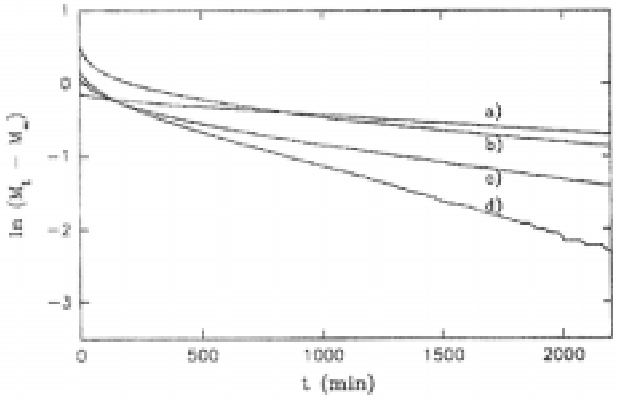

Figure 3. Kinetic curves for the desorption of toluene in different polymers films: **(a)** HDPE, **(b)** MIPA20, **(c)** MIPA20s and **(d)** PA6

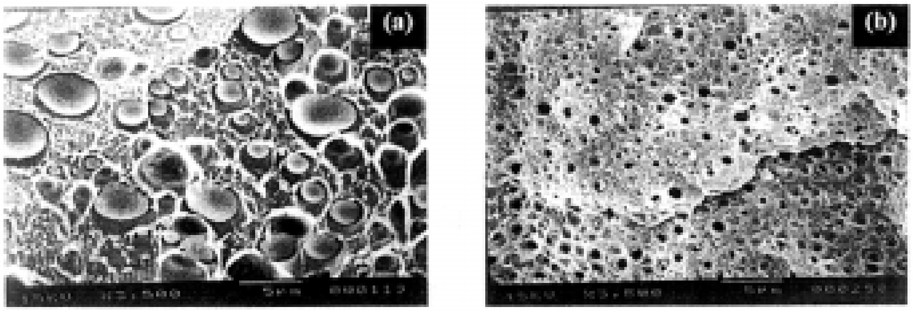

Figure 4. SEM micrographs of **a)** MIPA20 and **b)** MIPA20s

The initial straight-line parts of the curves were used to calculate the diffusion coefficient (D) at zero diffusant concentration. In general, these results show that the presence of PA-6 produces a decrease in toluene diffusity. This decrease is larger for interfacially modified systems (MIPA20s). This phenomenon may be explained from the morphological results shown in *Figure 4*. It can be seen that the blend without interfacial agent shows voids between each component. One the other hand, the compatibilized system shows a better adhesion between the phases and a decrease in voids (*Figure 4b*).

Kamal *et al* [7] also observed an improvement on the permeability properties when nylon was added to polyethylene films. Another study related to this work was developed by Subramanian [6]. They obtained materials with excellent permeability properties by controlling the morphology of polymer blends. Subramanian showed that the formation of lamella morphologies enhance the permeably properties.

In this study, the combined effect of the compatibilizer and the orientation is presented in *Figure 5*. It is interesting to observe that a low stretch-ratio there is an important difference of the diffusion coefficient of toluene through polymeric membranes. For this particular region, the presence of PA6 in HDPE produce a decrease in D, and the morphology plays an important role. Particularly, in the case of compatibilized blends a six-fold reduction of diffusion coefficient is observed. These results indicate that for immiscible polymer blends at low stretch-ratio (no orientation), the barrier properties is a function of the morphology. However, when the hot stretch ratio increases, the barrier properties are a function of the orientation. The transformation of the spherical particles of the dispersed phase in the polymer blends into laminar morphology may also have a significant effect on the diffusion of gases and hydrocarbons through the film [12]. In a recently study [14], the morphology of this system was analyzed.

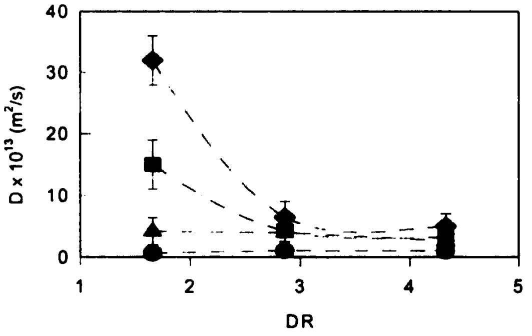

Figure 5. Diffusion coefficient versus hot-stretch ratio.
♦HDPE, ■MIPA20, ▲MIPA20s and •PA6.

The deformation of spherical particles was studied as a function of the hot stretch ratio. The diffusion coefficient (D) of toluene in HDPE decreases when the material was prepared at a high hot stretch ratio. The same results are obtained for other materials. From *Figure 5*, it is observed that the barrier properties using a compatibilier or inducing orientation. The effect of the orientation has been reviewed by Weinkauf and Paul [4]. They analyzed the factor affecting the transport process of a gas through a polymeric film. Oriented semi-crystalline membranes show improvements in the barrier properties. This improvement is produced by the fact that during the stretching, the stress applied to the ribbon orientation of the amorphous phase.

Effect of the orientation on the crystallization.

The crystallinity of the blends were measured using a Differencial Scaning Calorimeter Perkin-Elmer, analyzing the endotherm (around 130 °C) indicating the melting of the PE.

The total crystallinity was determined by the thermal energy (ΔH_f) absorbed in the melting process. *Table 2* shows the obtained values of ΔH_f and the crystallinity calculated [22] for HDPE and the blends as a function of the stretch ratio (V_R/V_E). In general, not important changes are observed for the blends, compared with HDPE values.

Table 2. Crystallinity of blends as a function of drawn ratio (V_R/V_E)

Material (V_R/V_E)	T_m (°C)	ΔH_f (J/gr)	% Crystallinity ($\Delta H_f/276*0.8$)(100)
HDPE (1.7)	131.4	179.8	65.1
(2.9)	132.5	183.1	66.5
(4.0)	130.7	176.0	63.8
(4.8)	129.6	181.6	65.8
MIPA20 (1.7)	129.7	142.5	64.5
(2.9)	129.9	140.0	63.4
(4.0)	130.1	145.1	65.7
(4.8)	131.7	138.3	62.6
MIPA20s (1.7)	129.6	143.9	65.2
(2.9)	130.0	144.9	65.6
(4.0)	129.9	142.6	64.7
(4.8)	129.1	139.6	63.2

Katio *et al* [23] also reported, in the formation of HDPE sheets, that increasing draw ratio, the degree of amorphous orientation increased and not the crystallinity. These changes are considered to be related to the formation of amorphous tie molecules in the interfibrillar and intercrystallite regions.

Effect of molar volume on the permeability.

In order to verify the efficiency of blends and alloys (compatibilized blends) as barrier materials to several solvents, a gravimetric permeation cell was used to measure the permeability of solvents through blends.

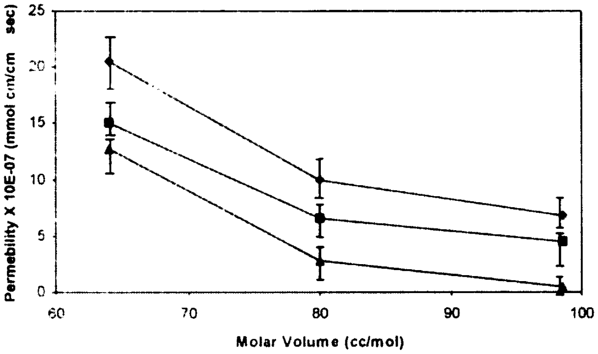

Figure 6. Permeability versus molar volume for:
◆ HDPE, ■ MIPA20, ▲ MIPA20s

The polymeric films used in this part were obtained at high stretch ratio ($V_R/V_E \cong 4.0$). In contrast to the ribbon materials obtained at low stretch ratio ($V_R/V_E < 3.0$), where the extrudate is thicker and the permeation test were difficult to perform. The results of the permeation of CH_2Cl2, $CHCl_3$ and CCl_4 in PE, M1PA20 and M1PA20s are presented in

Figure 6. The permeability decreases when the molar volume increases. The tendency is similar to that for diffusion coefficient data. The compatibilized blends (M1PA20s) always show a lower permeability. This result confirms the improvement in the barrier properties as in the case of the diffusion coefficient data.

CONCLUSIONS

The addition of PA6 to HDPE considerably improved the barrier properties. The effect was more pronounced for the compatibilized blends. The orientation of the films (stretching of the samples) also improves these properties. A six -fold decrease of the toluene diffusivity is observed for pure PE when the draw ratio is increased two folds. In the same way, the permeability decreases with increasing size of the penetrant molecule (CH_2Cl_2, $CHCl_3$ and CCl_4) and this decrease is more important for a compatibilized blend.

The rheological and barrier properties for compatibilized HDPE/PA6 blend were studied. The zero shear viscosities (η_0) for blends, show higher values than the one for the pure polymers. This result can be explained in terms of the interfacial modification, due to the compatibilizer or coalescence effects for the uncompatibilized blends.

REFERENCE

1. W. J. Koros ed., "Barrier Polymers and Structures". (1990) ACS Symposium Series.
2. M. Alger and T. Stanley, (1989) Polym Prepr 30:24
3. A-F.A, Asfour,., Saleem M. and De Kee, D. (1989) J Appl Polym Sci 38:1503
4. D. H. Weinkauf, and D. R. Paul, (1990). "Effect of Structural Order on Barrier Properties", ACS Symposium Series 423, Dallas, Tex.
5. C. J. Guo and D. De Kee, (1991) Chem Eng Sci 46:2133
6. Subramanian, P.M. , Polym. Eng. Sci., 25, 483 (1985).
7. Kamal, M.R., Jinnah, I.A. et Utracki, L.A. (1984) "Permeability of Oxygen and Water Vapor Through Polyethylene/Polyamide Films" Polym Eng Sci 24:1337
8. P. M. Subramanian and V. Mehra (1987) Polym. Eng Sci 27:663
9. Jen-Taut Yeh, Chien-Cheng Fang-Chiang and Shun-Syu Yang, (1997) J Appl. Polym. Sci 64:1531
10. R. M. Holsti-Miettinen, K. P. Perttila, J. V. Seppala and M. T. Hcino (1995) J Appl Polym Sci 58:1551
11. P. Van Gheluwe, B. D. Favis and J.-P. Chalifoux, (1988) J Mat Sci 23:3910
12. H. Garnabi and M. R. Kamal, SPE (1997) Antec Tech Papers 55:2687
13. Subramanian, P.M (1987 b) Polym Eng Sci 27:1574
14. R. Gonzalez-Nunez, D. De Kee and B. D. Favis (1996) Polymer 37:4689
15. R. Gonzalez-Nunez, C.F. Chan Man Fong, B. D. Favis and D. De Kee, (1996) J Appl Poly Sci 62:1627
16. J. M. Willis, and B. D. Favis, (1988) Polim Eng Sci 28:1416
17. Guo, C. J. and D. De Kee, (1992) J Appl Polym Sci 44:181
18. D. De Kee and C.F.Chan Man Fong, (1994) Polym Eng Sci 34:438
19. J. M. Willis V. Caldas B. D. Favis. (1991) J Mat Sci 26:4742
20. Feng-Chinh Chang and Yih-Chyun Hwu. (1991) Polym Eng Sci 31:1509
21. Y. Germain, B. Ernst, O. Genelot, and L. Dhamani. (1994) J Rheol 38:681
22. F.W.Billmeyer Jr "Textbook of Polymer Science" (1984) John Wiley & Sons Inc
23. A. Katio, K.Nakayama and H. Kanetsuna (1985) J Appl Appl Poly Sci 30:1241