Effects of Compatibilization of Oxidized Polypropylene on PP Blends of PP/PA6 and PP/Talc

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ABSTRACT: The influence of compatibilization on the dynamic mechanical properties of polypropylene (PP) binary blends with polyamide-6 (PA6), Talc, and oxidized PP (OPP) was investigated. The oxidation of PP homopolymer was performed in a internal mixer by using air as a oxidizing agent (under atmospheric pressure) and dodecanol-1 as an accelerator at 180°C for 6[1–2] h [Abdouss, M.; Sharifi-Sanjani, N.; Bataille, P. J Appl Polym Sci 1999, 36, 10]. In the blends, OPP was used as a blend component and compared with PP over the whole concentration range. Pressed film blends of PP/OPP, PP/OPP/Talc, and PP/OPP/PA6 were examined by dynamic mechanical analyzer, thermal gravimetry analysis, and scanning electron microscopy. Mechanical properties such as tensile strength, modulus of elasticity, elongation, melt flow index, and hardness of the blends were measured. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2871–2883, 2004

Key words: polypropylene homopolymer; blends; oxidized polypropylene; compatibilization; PA6

INTRODUCTION

Polypropylene (PP), among polyolefins (PO), is a most important polymer for its intrinsic properties such as a high melting temperature, a low density, and the capabilities of being produced with different morphological and molecular structures, of being reinforced with high amounts of fillers, and of being toughened with elastomers.[2–5]

Pressed films of PP with poly(*cis*-butadiene) rubbers (PcBR) of grafted copolymer of ethylacrylate (EA) onto PcBR (PcBR-*g*-EA) was studied.[6–9]

In addition, PP can be modified by grafting on functional groups[10] to make it possible that PP can be blended with some polar polymers such as polyamides (PAs), poly(ethylene terephthalate),[11–12] and polycarbonate[12] for exploring its ability to further compete with technopolymers in some important, rapidly growing application sectors.[14–18]

Oxidized PP (OPP)[1] can be used as a compatibilizer, lubricant, or processing aid in certain alloys or composite systems. PP is nonpolar, whereas polyamide and Talc are polar, and PP/PA, PP/Talc are incompatible with each other. However, they may become compatible or semicompatible in PP/OPP/PA and PP/OPP/Talc blends. In this article, the phase structure and morphology of PP/OPP, PP/OPP/PA, and PP/OPP/Talc blends are discussed.

EXPERIMENTAL

Materials

The PP homopolymer without any additives of grade PIO105 were supplied by Bandar Imam (Mahshahr) Petrochemical Co. Ltd. (Iran) [Melt flow index (MFI) = 1.5 (190°C/2.16 kg) g/10 min, isotacticity index = 94–97%, d^{20} = 0.91 g/cm^3]. The following materials were used: Talc Esfahan-Iran with mesh 1500; OPP[1] M_n = 4565, MFI = 4.32 (105°C/1.2 kg) g/10 min, T_m = 137.40°C, d^{20} = 0.87 g/cm^3; and polyamide 6 (PA6) made by Iran Fibers Co. (Tehran-Iran), fiber grade.

Preparation of blends

Binary PP/PA, PP/OPP/PA, PP/OPP, PP/Talc, and PP/OPP/Talc blends were prepared by melt mixing the polymer in a internal mixer (Brabender, plasticorder PLE 331) at temperatures of 180–250°C with a residence time of 5 min at 30 rpm.

The compositions of the investigated blends are reported in Table I.

Specimen preparation

From the blends prepared earlier, sheets of 2.94 mm thickness were obtained by compression molding in a heated press equipped with a water-cooling system.

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TABLE I
Compositions of Blends

Trial number	PP (%) (w/w)	PA (%) (w/w)	OPP (%) (w/w)	Talc (%) (w/w)	Temperatures (°C)	Other conditions
Reference	100	—	—	—	180	Pure N_2 only
1	80	—	20	—	180	Pure N_2 only
2	85	—	15	—	180	Pure N_2 only
3	85	—	—	15	190	Pure N_2 only
4	70	—	15	15	190	Pure N_2 only
5	85	15	—	—	250	Pure N_2 only
6	70	15	15	—	250	Pure N_2 only
7	50	—	50	—	180	Pure N_2 only

The samples were heated to 180–250°C (Table I) and kept 4 min between plates without any applied pressure, allowing for complete melting.

After this period, a press of 20 tons was applied at the 180–250°C temperatures (Table I) for 5 min. The samples then slowly cooled in another unheated press to room temperature for about 15 min. From the sheets so prepared, the rectangular specimens were cut to perform the dynamic mechanical tests.

Mechanical properties

Mechanical properties of the samples were measured by using a tabletop Instron 1435 (Zwick) traction machine. All tests were in conformity with ASTM D-1505; that is, they were performed at 23°C and an elongation speed of 5 mm/min. The results are given in Table II.

Contact angle measurements

The advancing contact angles (θ adv.) were determined by using a telescope goniometer (measuring system G2/G40) (solvent: water; time: 2 min; sample volume = 10 μL). The results are given in Table II.

Characterization

The following instruments were used for characterization: scanning electron microscope (SEM; Cambridge Instrument STEREOSCAN 360); DMA, DuPont Instruments, 983 Dynamic Mechanical Analyzer; thermogravimetric analyzer V5.1 A DuPont 2000; FTIR-4300 (Shimadzu Co.); Instron 1435 (Zwick), ASTM-D-1505; MFI-592 (Motor-Heizug); contact angle (Measuring system G2/G40; Kruss).

RESULTS AND DISCUSSION

FTIR spectra of oxidized PP by air showed sharp bands at 3448-, 1776-, 1714-, and 1164-cm^{-1} regions. These absorption bands are attributed to alcoholic or OH intramolecular bonding, anhydride, ketonic groups, and stretching band of anhydride or etheric C—O, respectively.

The thermal decomposition of PP and OPP was studied in air (Fig. 1). A characteristic thermogram was recorded with OPP; onset of decomposition was lower (16.7%) than for PP and owing to the presence of thermolabile groups. This increase in thermal stability of OPP may be attributed to abstraction of labile hy-

TABLE II
Elongation, Hardness, Tensile Strength, Modulus of Elasticity, Contact Angle, and Chemical Property Data for Blends

No.	Blends	Tensile strength at yield (MPa)	Elongation at yield (%)	Hardness (shore A)	modulus of elasticity (MPa)	θ adv. deg.	Tg (DMA) (°C)
1	PP(100%)	29.58	6.557	92	1417	80.8	−4.759
2	PP(80%) + OPP(20%)	25.42	4	93	1662	69.1	—
3	PP(85%) + OPP (15%)	26.9	4.32	93	—	72	8.396
4	PP(85%) + Talc(15%)	23.6	1.2	95	—	73.4	4.07
5	PP(70%) + OPP(15%) + Talc(15%)	29.1	14.35	98	—	67.3	4.338
6	PP(85%) + PA(15%)	1.042	5.476	97	2118	79.5	2.934
7	PP(70%) + OPP (15%) + PA(15%)	16.88	46.29	99	1271	74	4.625
8	PP(50%) + OPP(50%)	—	—	95	—	53	—
9	OPP(100%)	—	—	—	—	45	—
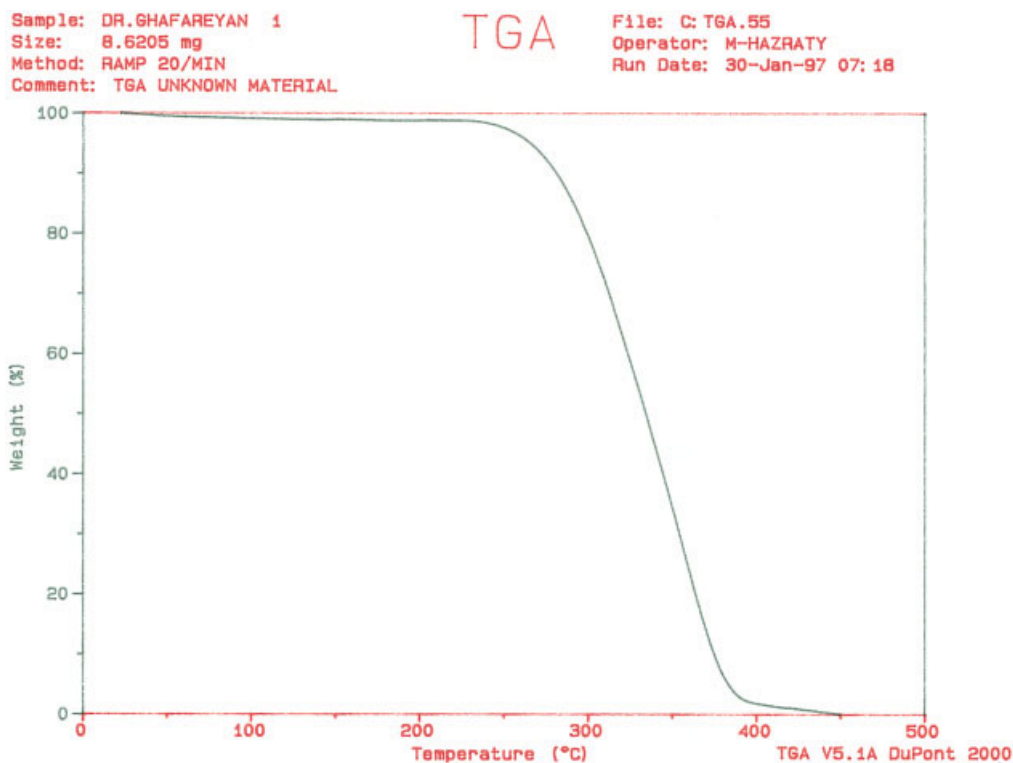
(a) PP
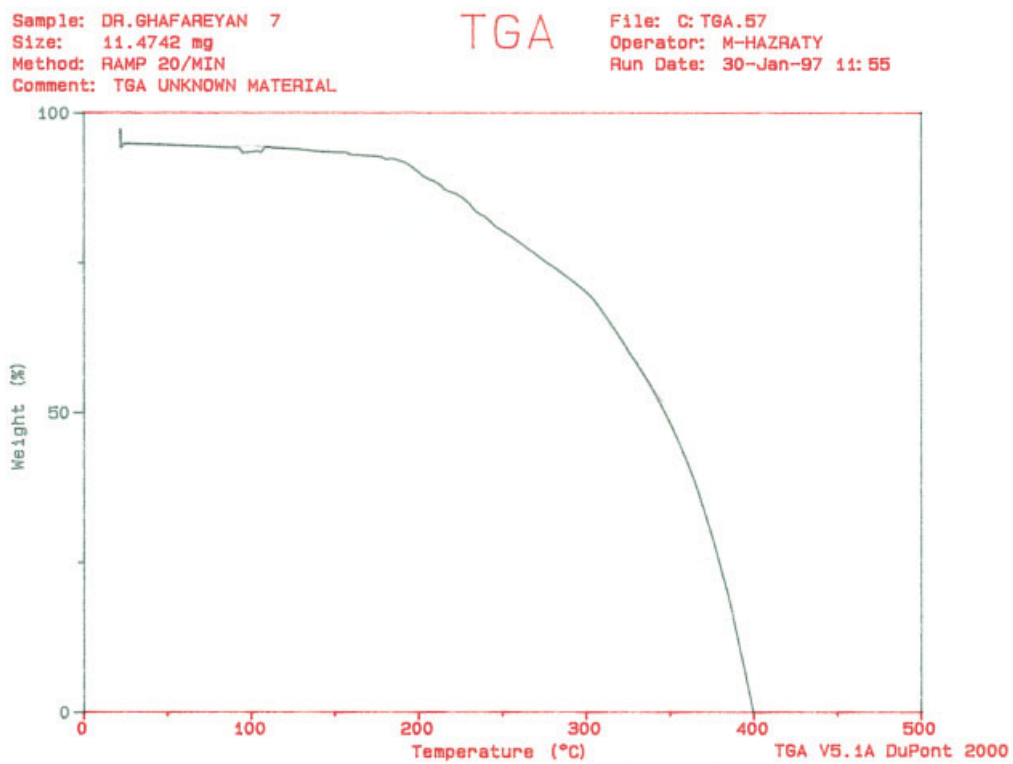
(b) opp

Figure 1 (a) PP; (b) OPP

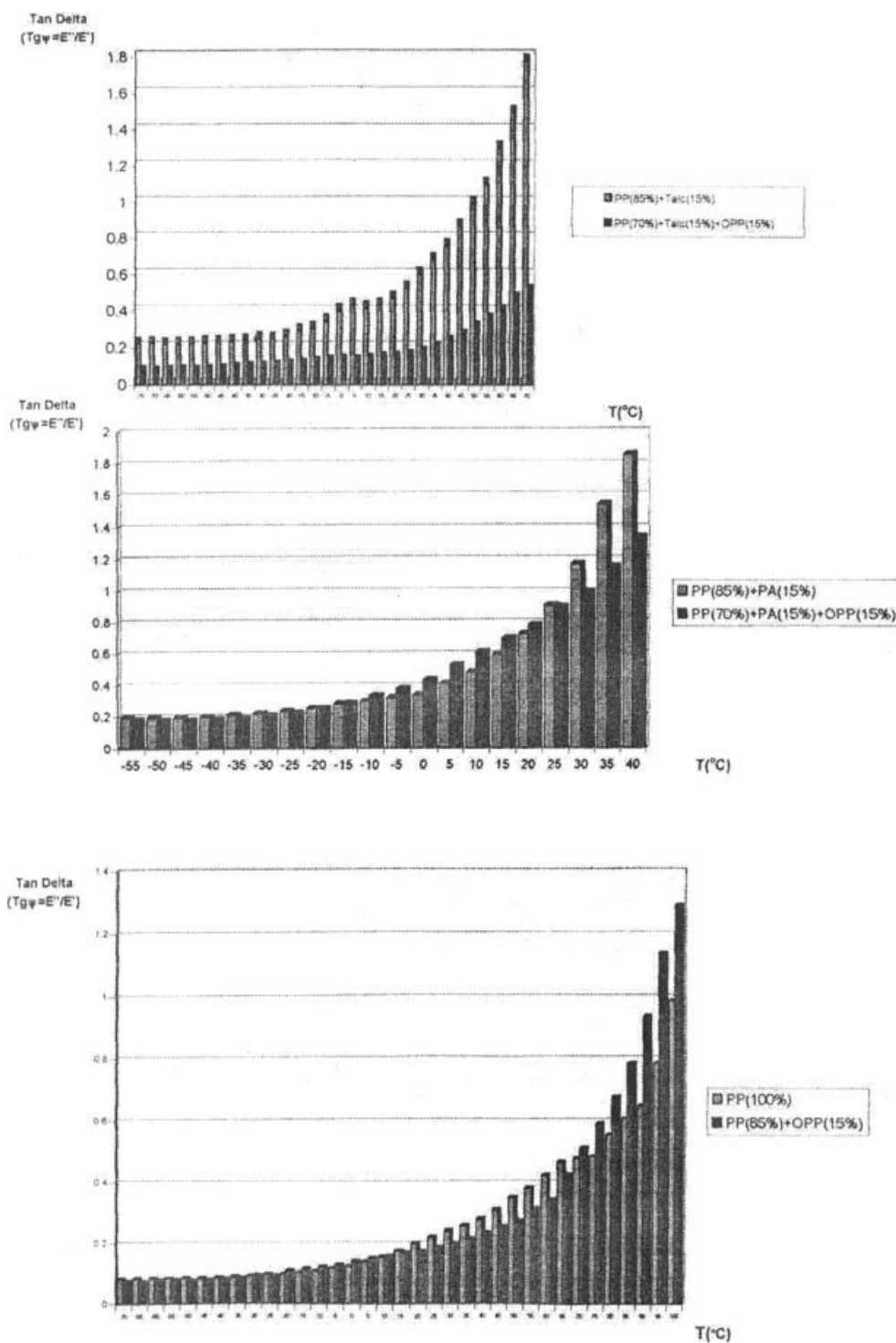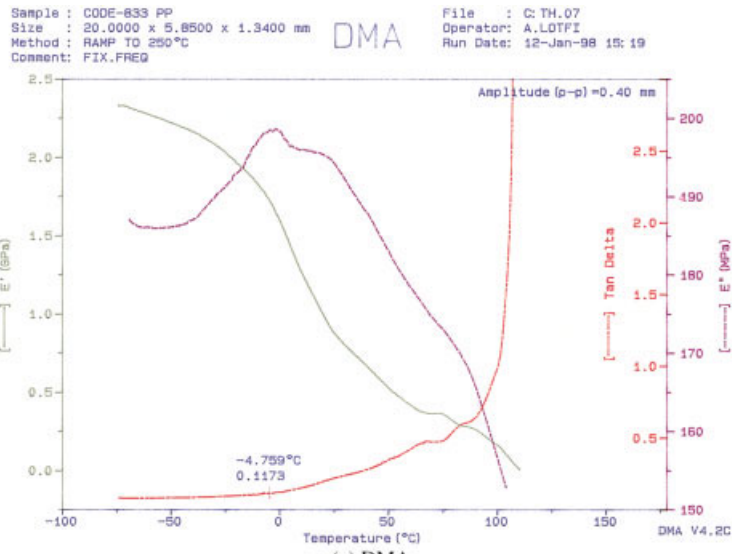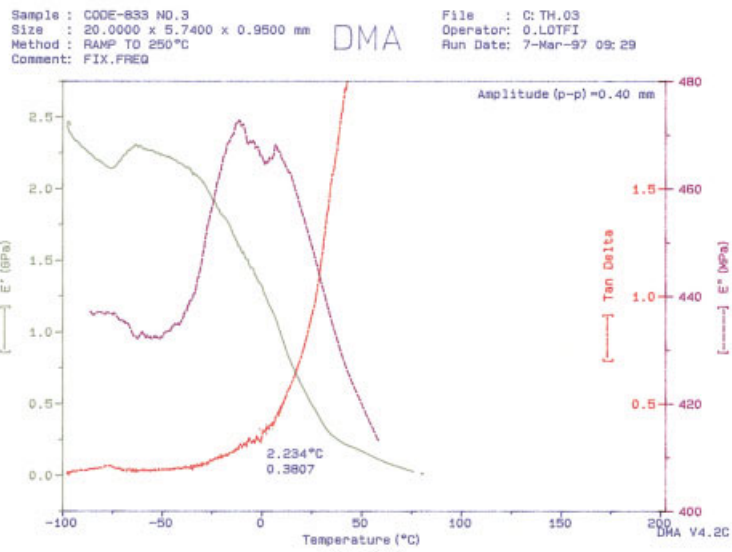**Figure 2**   Temperature dependence of loss factor (tan δ) at 1 Hz for blends.

drogen from the tertiary carbon atom, followed by the grafting (oxidation reaction) chain at the site generated, which produced an increased thermal stability to the polymer.[19]

After the decomposition of alcoholic, anhydride, and ketonic bonds in OPP, further thermolysis is prob-
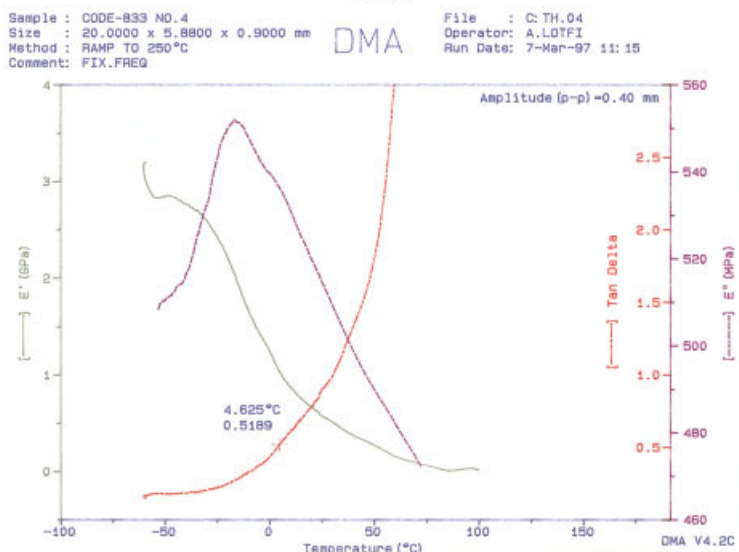
ably similar to PP. Despite the thermal decomposition, the TGA thermogram OPP in comparison with PP shows more thermal resistance in the temperature range of 305–400°C. This result probably arises from the decrease of tertiary hydrogens in OPP. OPP can be used as wax or as compatibilizer in certain applica-
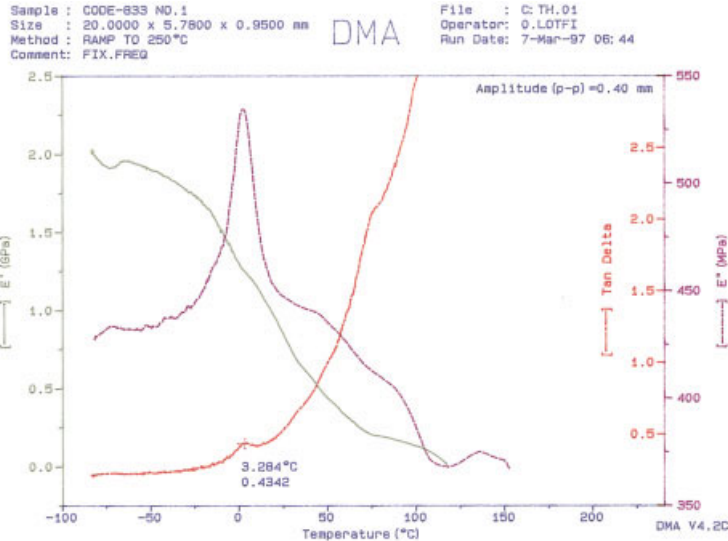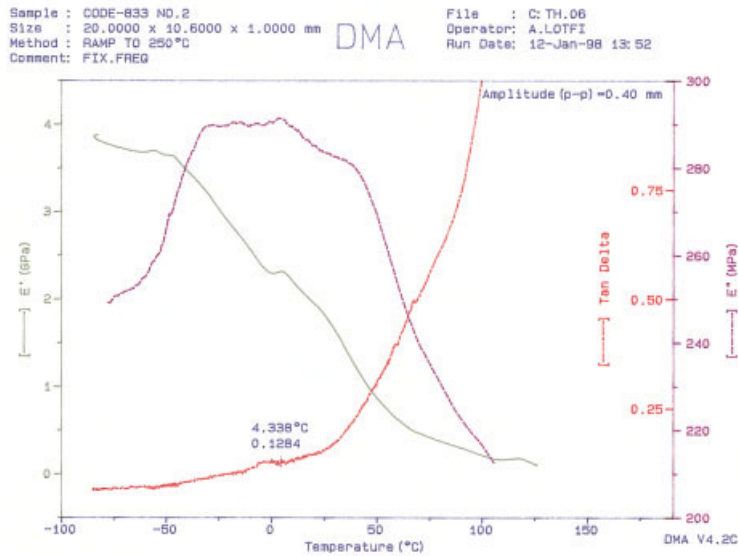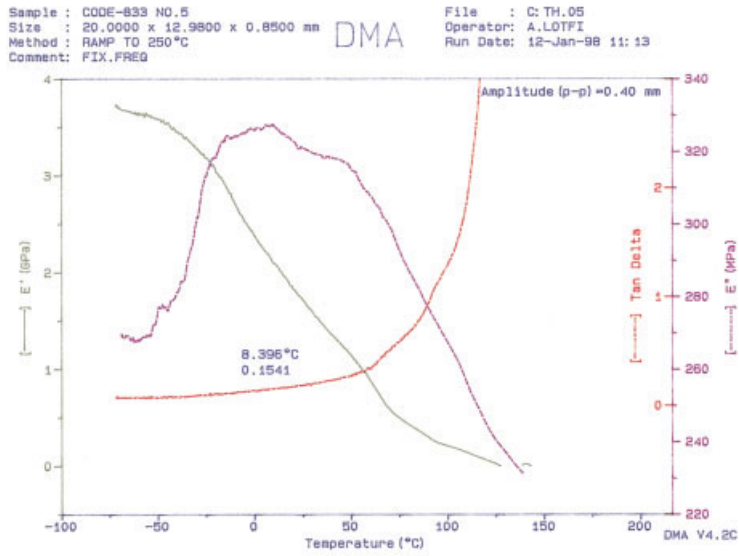
Figure 3 (a) DMA PP; (b) DMA PP/PA; (c) DM PP/OPF; (d) DMA PP/Ta; (e) DMA PP/OPP TaLc; (f) DMA PP/O

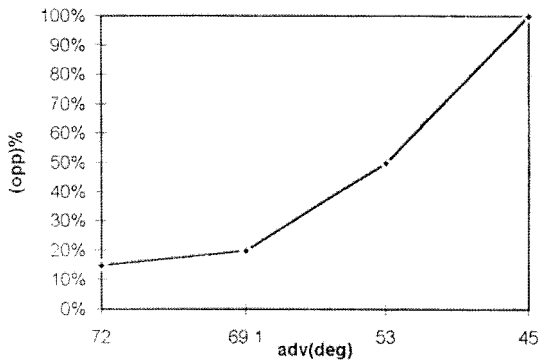**Figure 3** *(Continued from the previous page)*

Figure 4 Curve of the OPP% versus contact angle.

tions. The results of the solubility of OPP and PP in boiling toluene indicated that PP/OPP blends are compatible.[18] In Figure 2, the temperature dependence of the dynamic storage and loss moduli (E' and E'') and the factor (tan σ) at 1 Hz for blends are given. The loss factor curves (tan σ) shown in Figure 3 for the noncompatibilized blend PP/PA exhibit two fairly sharp relaxation peaks, exactly corresponding to the glassy transition temperatures of PP ($-11°$C) and PA ($+3.5°$C), respectively, while the compatibilized PP-PA, PP-OPP, and PP-Talc blends exhibited only one transition in the glassy transition temperature blends (Table II, Fig. 3).
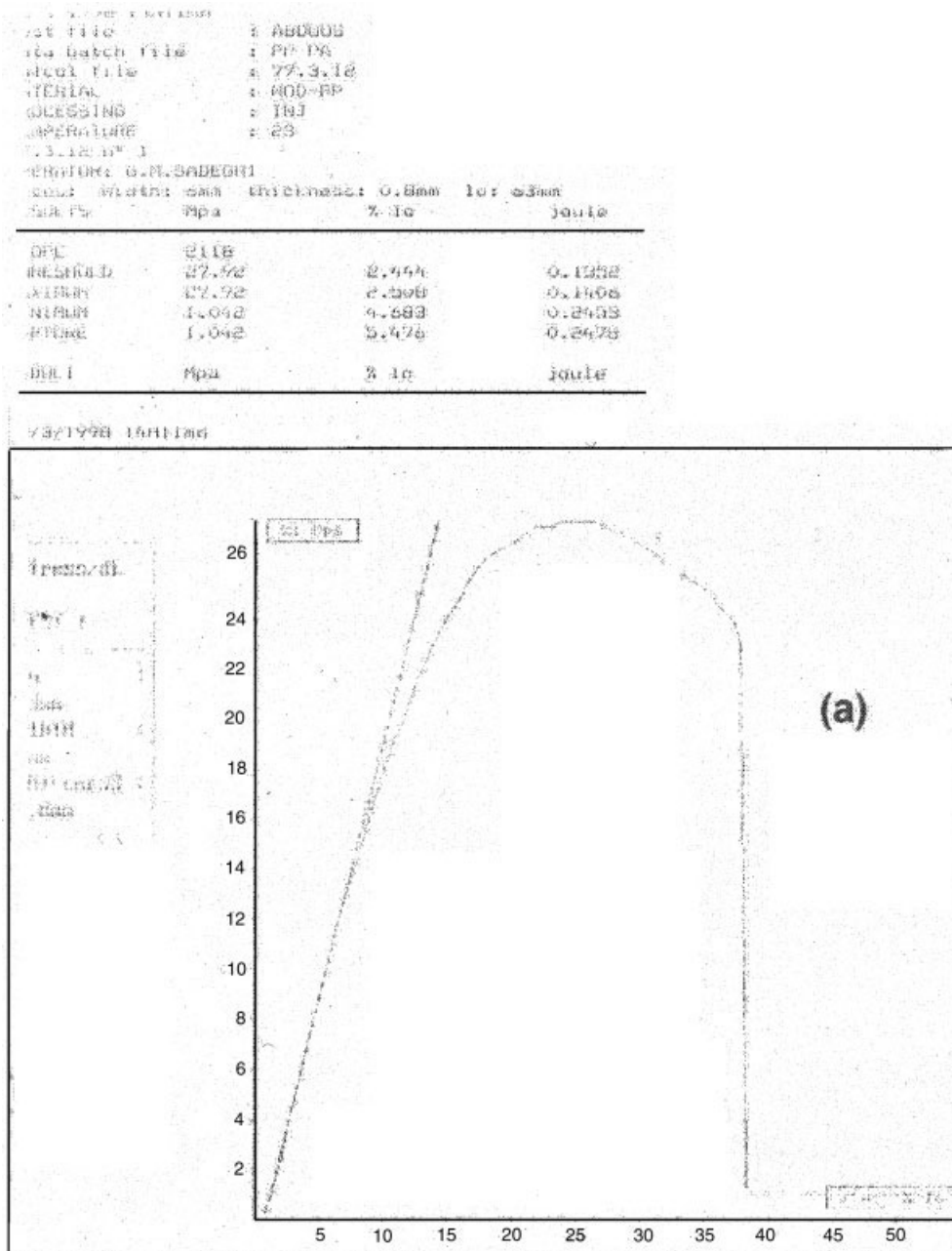

Figure 5 The stress-strain curves for (a) PP; (b) PP/OPP

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12/3/1998 13H49mn
test file          : ABDOOS
data batch file    : PP-PA-OPP
calcul file        : 77.3.12
MATERIAL           : MOD-PP
PROCESSING         : INJ
TEMPERATURE        : 23
77.3.12 n° 2
OPERATOR: G.M.SADEGHI
Sizes:  width: 6mm  thickness: 0.8mm  lo: 59.5mm
RESULTS       Mpa           % lo            joule
------------------------------------------------------
SLOPE         1271
THRESHOLD     22.71         4.672          0.2301
MAXIMUM       22.71         4.739          0.2345
MINIMUM       1.25          47.97          2.374
RUPTURE       16.88         46.29          2.305

MODULI        Mpa           % lo            joule
------------------------------------------------------
12/3/1998 13H48mn
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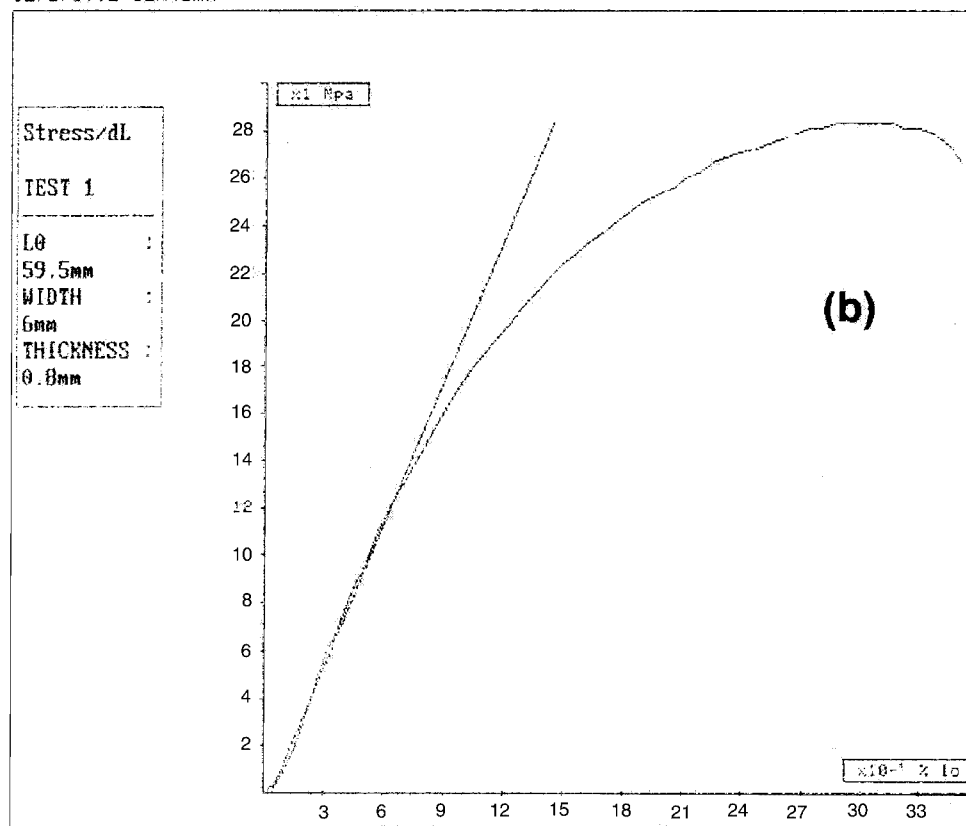

Stress/dL

TEST 1

LO   :
59.5mm
WIDTH   :
6mm
THICKNESS :
0.8mm

(b)

Figure 5 (*Continued from the previous page*)

TABLE III
Melt Flow Index (MFI) for Blends in Different Conditions

No.	Blends	MFI (190°C/2.16kg)(g/10 min)	MFI (195°C/2.16kg)(g/10 min)	MFI (255°C/2.16kg)(g/10 min)
1	PP(100%)	1.5	—	—
2	PP(80%) + OPP(20%)	2.15	—	—
3	PP(85%) + OPP(15%)	1.94	—	—
4	PP(85%) + Talc(15%)	—	1.62	—
5	PP(70%) + OPP(15%) + Talc(15%)	—	2.3	—
6	PP(85%) + PA(15%)	—	—	3.35
7	PP(70%) + OPP(15%) + PA(15%)	—	—	5.8
8	PP(50%) + OPP(50%)	2.42	—	—
9	OPP(100%)	2.8	—	—
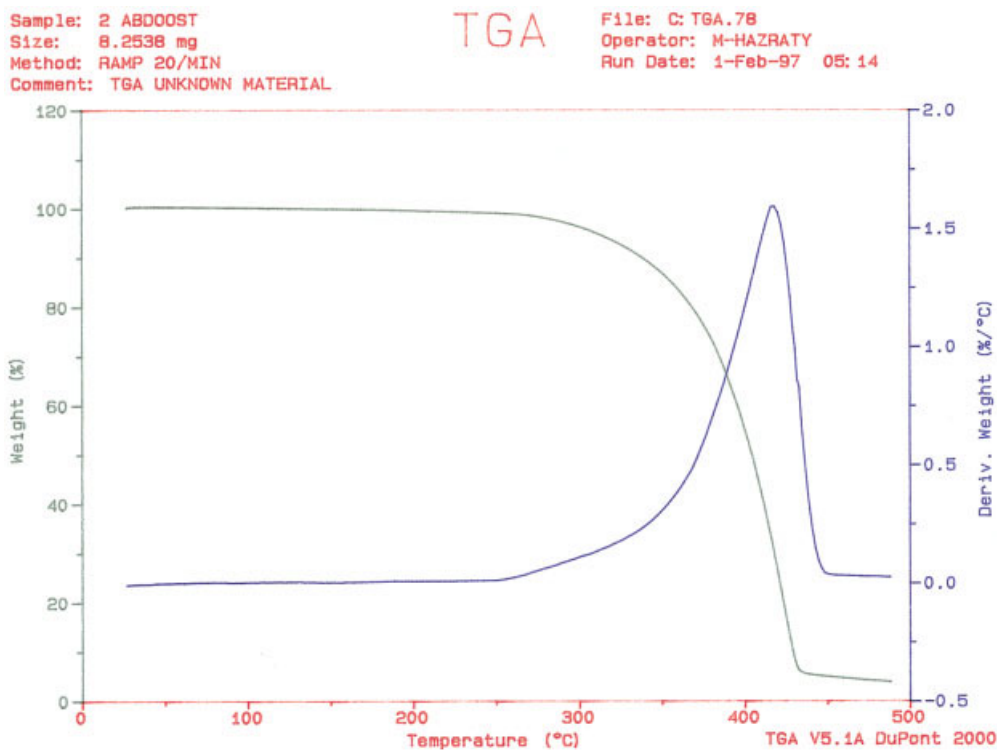
(a) TGA
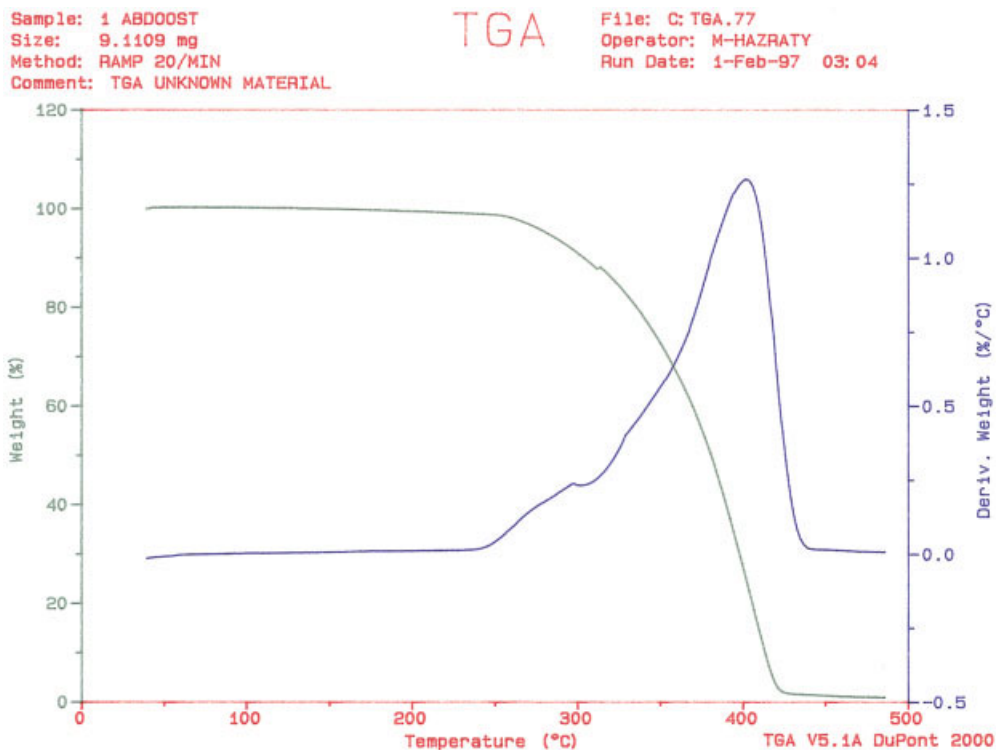PP/OPP/PA
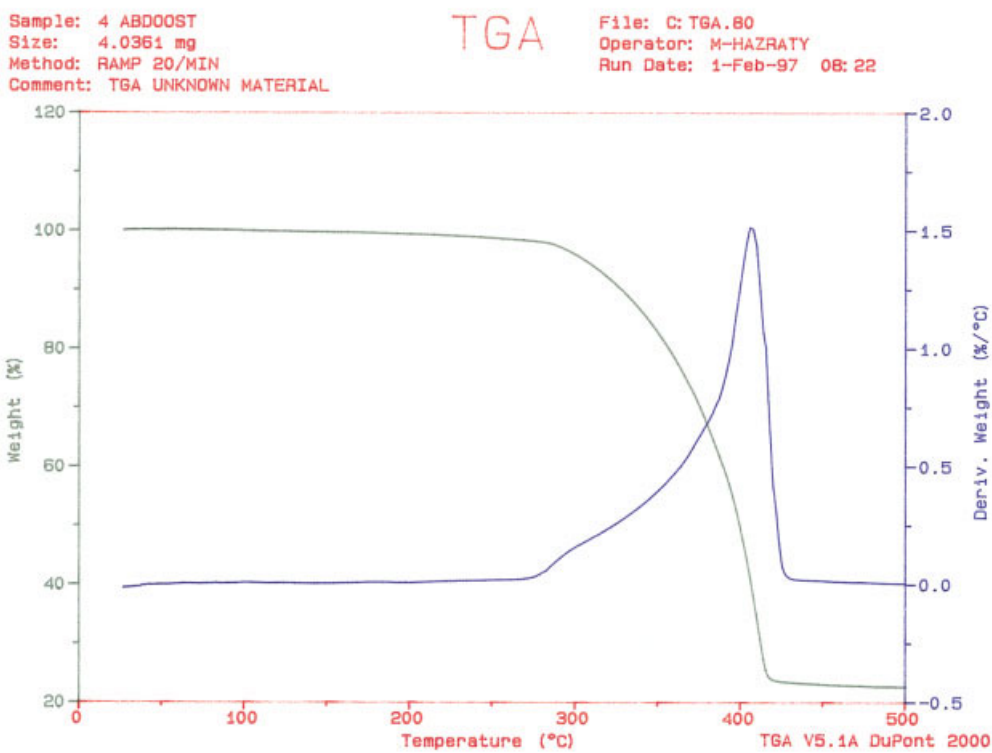
(b) TGA
PP/OPP/Talc

Figure 6 (a) TGA PP/OPP/PA; (b) TGA PP/OPP/TaLc; (c) TGA PP(85%)/OPP(15%); (d) TGA PP(50%)/OPP(50%)

Sample: 1 ABDOOST   TGA   File: C: TGA.77
Size: 9.1109 mg   Operator: M-HAZRATY
Method: RAMP 20/MIN   Run Date: 1-Feb-97 03:04
Comment: TGA UNKNOWN MATERIAL

(c) TGA
PP(85%) OPP(15%)

Sample: 3 ABDOOST   TGA   File: C: TGA.79
Size: 11.3727 mg   Operator: M-HAZRATY
Method: RAMP 20/MIN   Run Date: 1-Feb-97 06:03
Comment: TGA UNKNOWN MATERIAL
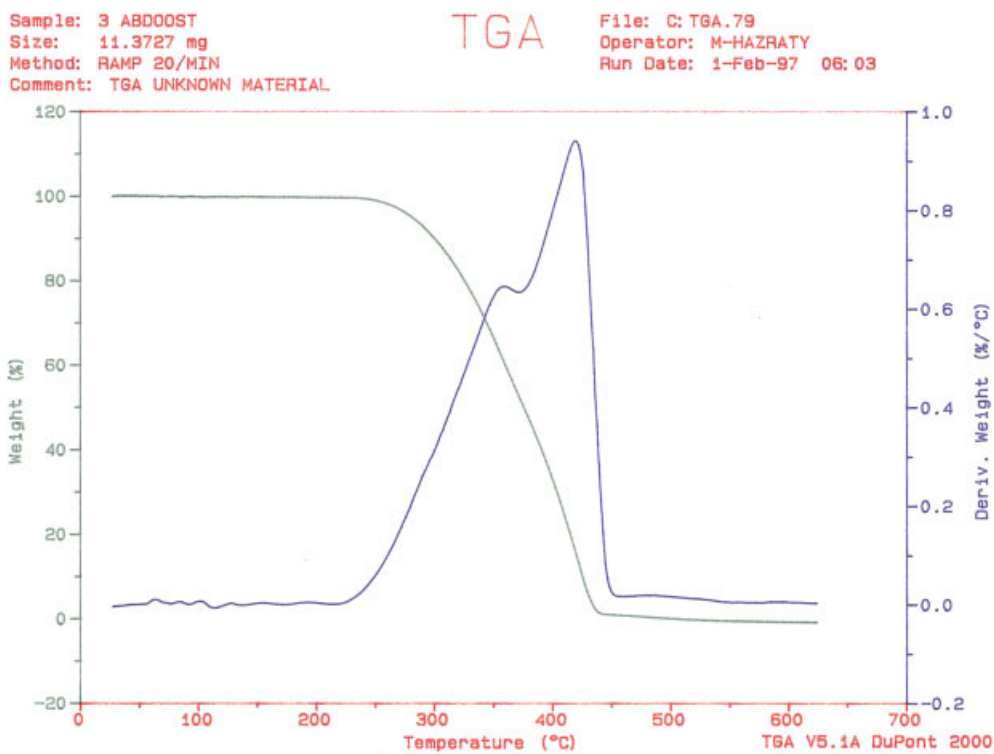
(d) TGA
PP(50%) /OPP(50%)

Figure 6 (*Continued from the previous page*)

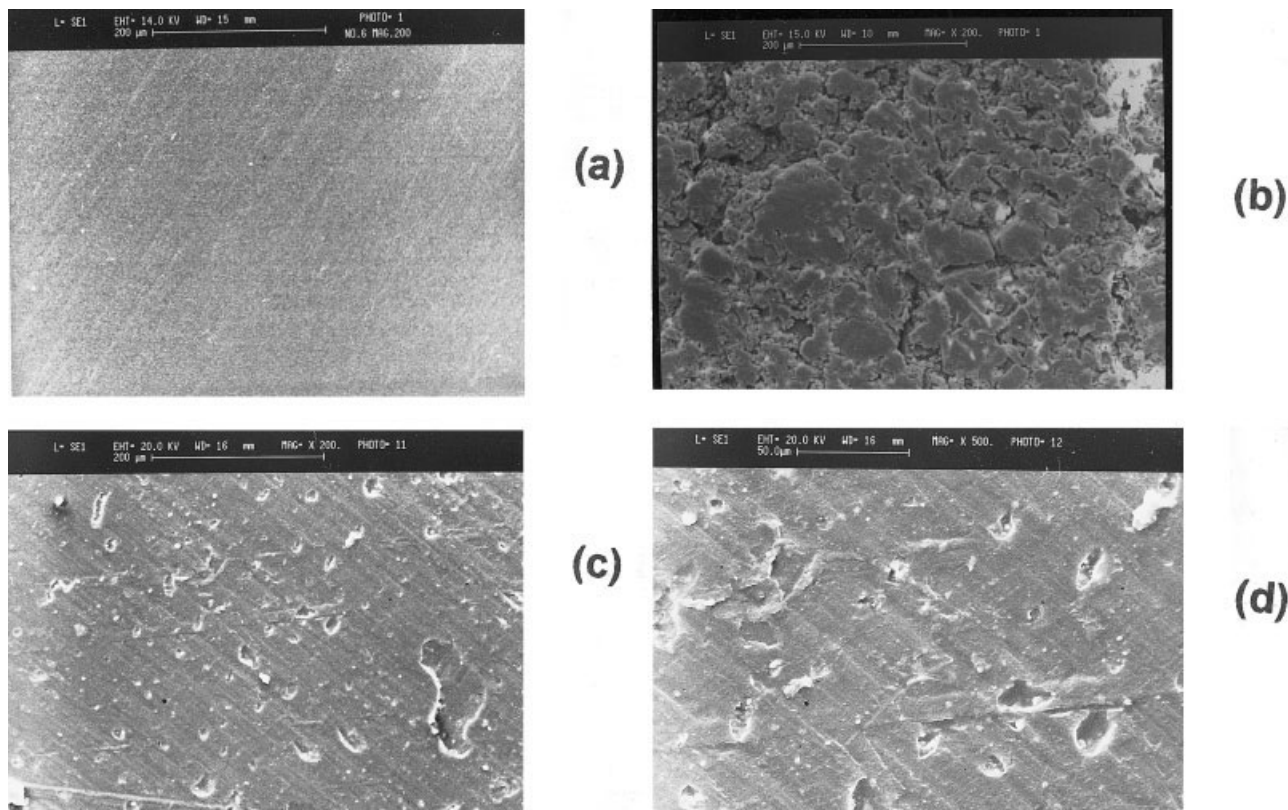**Figure 7** Scanning electron microscope results: (a) unoxidized PP; (b) oxidized PP; (c) PP/Talc; (d) PP/PA; (e) PP/OPP/PA; (f) PP/OPP/Talc; (g) PP (85%)/OPP (15%).

In the blend of PP/OPP/PA, the glass transition temperature (T_g) is nearly zero; the difference between two points of T_g decreased about 7°C and two points were closer to each other. This shows the relative compatibility of the PP/OPP/PA system (Fig. 3). In addition, the peaks are broader and then drag a shoulder on the high-temperature side, especially obvious for the PP/OPP blends.

Increasing the polarity of the polyblends increases its T_g (Table II). The reduction in contact angle blends seems large in view of the small increase in polarity as determined by DMA (T_g) (Table II). Also, the curve of OPP% versus contact angle is shown. According to this curve, by increasing the OPP percent, the contact angle increases (Fig. 4).

Previous studies have shown that degradation[19] and oxidation of PP during processing is mainly chain scission and decreases the molecular weight from 181,000 to 4565.[1] This explained the decrease of tensile strength and elongation in PP/OPP systems, while mechanical properties increase in PP/OPP/PA and PP/OPP/Talc blends (Table II). The tensile strength in PP is nearly 29.58 MPa and has decreased to 23.6 MPa with 15% Talc, but by adding 15% of OPP, increases to 29.10 MPa. This means the tensile strength in the PP/OPP/Talc blend has increased. This is the remarkable role of OPP in the compatibility between PP and

Talc. This role is especially significant in the PP/PA blend, so that the PP/PA blend (15% PA) showed a tensile strength of 1.04 MPa. By adding 15% of OPP (with the same amount of PA), the tensile strength increases to 16.88 MPa. Also, the elongation in PP/PA increased from 5.476 to an order of 8.4 in the PP/OPP/PA blend. These results show the role of OPP in the compatibility between PP and PA. There is also an increase in hardness (shore A, Table II).

It is noticeable that by adding 15% of Talc (PP/Talc blend), the elongation in PP decreased from 6.557 to 1.2%, but increased to 14.35 by adding 15% OPP (in the PP/OPP/Talc blend). The increases in both tensile strength and elongation show the compatibility of the system and toughness in the blend.

As the surface tension and contact angle increase by adding OPP to PP, the compatibility of PP/OPP/Talc and PP/OPP/PA composite is confirmed in both mechanical resistance and morphology; the T_g of PP and PA are close to each other and a new T_g point in DMA appears. This confirms the compatibility in the PP/OPP/PA blend.

The T_g of PP/OPP, PP/Talc, and PP/OPP/Talc blends are 8.4, 4.0, and 4.3°C, respectively. Although the OPP increases the T_g of PP to 13°C, the T_g of PP/OPP/Talc blend is close to the T_g of PP. This result
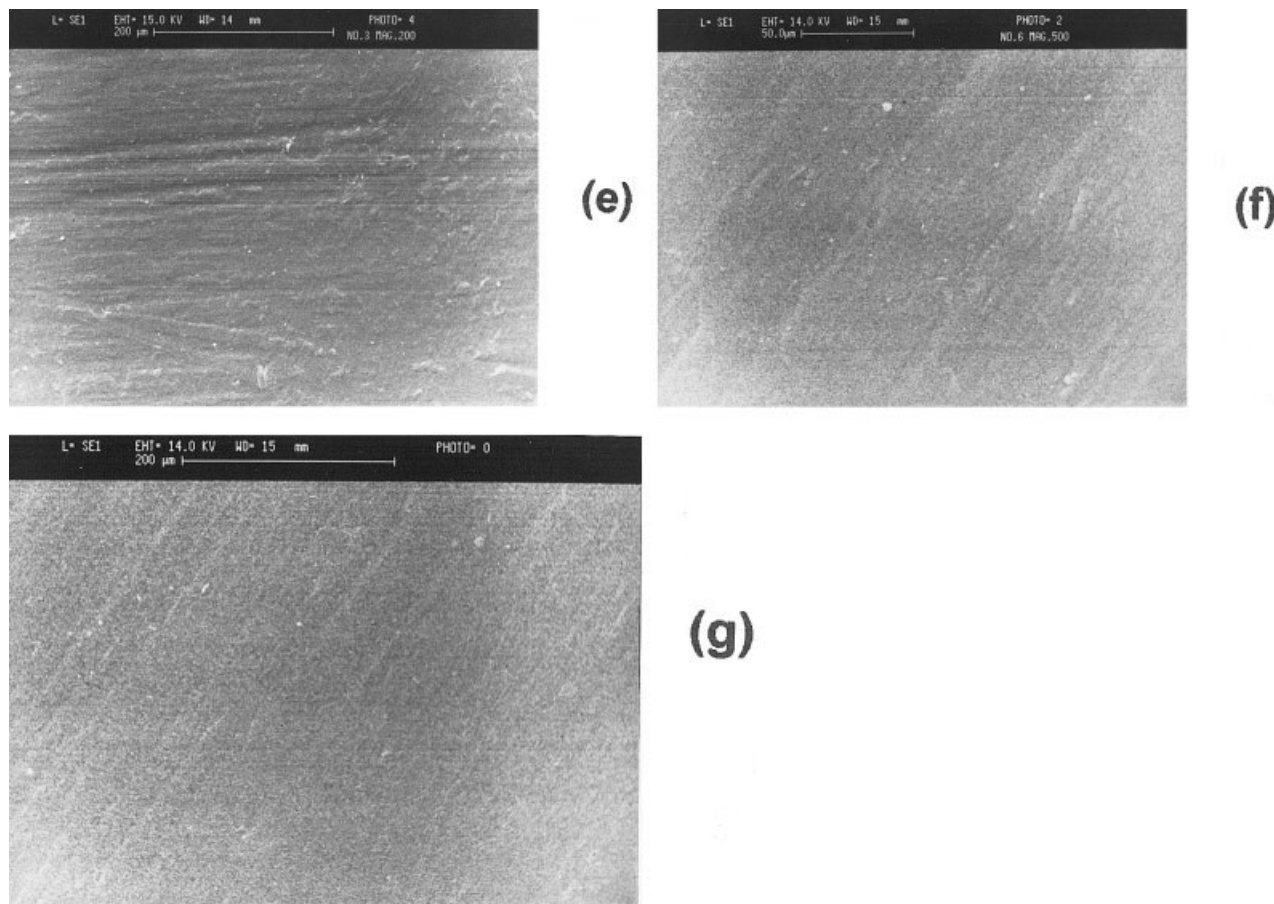
Figure 7 (*Continued from the previous page*)

shows the compatible role of OPP between PP and Talc.

The stress–strain curves of different blends are shown in Figure 5. These curves show that PP/OPP/Talc and PP/OPP/PA blends are tougher than PP.

The MFI of PP at 190°C and 2.16 kg is 1.5 g/10 min and increases with OPP%. In other blends, MFI increases with polarity (Table III).

The TGA thermograms of PP/PA and PP/Talc blends with compatible OPP shows that decomposition proceeds for one step, while without OPP decomposition proceeds for two steps. The TGA thermograms of different blends are shown in Figure 6.

In the temperature range of 380–420°C, the thermal decomposition of PP/OPP/PA and PP/OPP/Talc shows more thermal resistance in comparison with PP/Talc and PP/PA. Also, the increase of thermal resistance, tensile strength, and elongation shows the compatibility of OPP in PP/OPP/Talc and PP/OPP/PA blends.

SEM studies

The overall morphology of blends was investigated on the surface of specimens broken in liquid nitrogen.

SEM micrographs of cryogenically fractured surfaces of the blends are shown in Figure 7. SEM blends without compatibilizers and blends compatibilized with OPP might be explained in the following way: In the uncompatibilized blend (PP/PA), the dispersion is so coarse that practically every PP droplet contains the heterogeneities that usually nucleate PP (Fig. 7). In the case of compatibilization with OPP, despite the fineness of the morphology, the nucleation apparently occurs as efficiently as in the bulky uncompatibilized blends.

The compatibilizer OPP is expected to be compatible with both PP and PA6 (PP/PA, PP/Talc) and form, therefore, an interlayer between the components.

CONCLUSION

1. The OPP changed the morphologies of the surface and introduced incompatible polar groups.

2. The addition of OPP as a compatibilizing agent into blends modifies the properties of the latter to a significant extent.

3. Dynamic mechanical tests are especially sensitive to morphological changes and structural changes in polyblends.

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