Effect of Calcium Carbonate on the Mechanical and Thermal Properties of Isotactic Polypropylene/Ethylene Vinyl Acetate Blends

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ABSTRACT: The effect of calcium carbonate ($CaCO_3$) on the mechanical properties (with heat treatment) and thermal properties of polypropylene and isotactic polypropylene (i-PP)/ethylene vinyl acetate (EVA) blends was investigated. $CaCO_3$, in five different concentrations (3, 6, 9, 12l, and 15 wt %), was added to i-PP/EVA (88/12) to produce ternary composites. The mechanical properties, including the yield and tensile strengths, elastic modulus, Izod impact strength for notch radii of 0.25 and 1 mm, and hardness with and without an annealing heat treatment, and the thermal properties, such as the melting point and melt-flow index, of the composites were investigated. The annealing heat treatment was carried out at 100°C for three different holding times: 75, 100, and 150 h. On the basis of the results, attempts were made to establish a relationship between the $CaCO_3$ content, the annealing holding time, and the mechanical and thermal properties to obtain the best results. The tensile test results showed that the heat treatment was not effective for the ultimate tensile strength, and the yield strength and tensile strength decreased gradually as the $CaCO_3$ content increased. However, $CaCO_3$ was effective for higher elastic modulus, impact strength, and hardness values. A consid- erable increase in the elastic modulus was found with a 3% $CaCO_3$ concentration for a holding time of 100 h. The max- imum impact strength for a notch radius of 1 mm was obtained with 3% $CaCO_3$ with annealing for a holding time of 100 h, whereas a 9% $CaCO_3$ concentration produced higher toughness values for a notch radius of 0.25 mm. The fracture surfaces also supported the results from the Izod impact tests. Similarly, hardness values increased with the annealing heat treatment and increasing $CaCO_3$ content. However, different holding times showed similar effects on the hardness values. The increased $CaCO_3$ content caused the melting point to increase 5°C, whereas the melt-flow index showed a sharp decrease as the $CaCO_3$ content in- creased to 3%. Taking into consideration the mechanical and thermal properties and the annealing holding time, we rec- ommend a $CaCO_3$ concentration of 3% with an annealing heat treatment for 100 h for optimum properties of such ternary composites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1126–1137, 2005

Key words: compounding; injection molding; mechanical properties; poly(propylene) (PP); structure

INTRODUCTION

Isotactic polypropylene (i-PP) is a semicrystalline and multipurpose thermoplastic with a wide range of characteristics, such as good mechanical properties, corrosion resistance, low cost, easy processing, low density, and easy design. It has, however, a simple molecular structure. Its structure and properties de- pend on the crystalline structure, the ratio of amor- phous and crystalline phases, the crystal size, the molding conditions, the chemical compositions of the additives, the fillers, the fiber content, and so forth.[1,2]

Polypropylene has a low impact strength under low service temperatures. For this reason, both the price and performance characteristics and the low-service- temperature characteristics could be improved gener- ally with elastomers, particularly ethylene–propylene copolymers, ethylene–propylene–diene terpolymers, and ethylene vinyl acetate (EVA). Although the tough- ness characteristics are improved by the addition of an elastomer to the polymeric structures, this causes a decrease in the elastic modulus, tensile strength, and yield strength and an increase in the elongation and impact strength properties. For this reason, multipur- pose fillers and reinforcements could be used to over- come this problem because they would ensure better dimensional stability and rigidity.[3–5]

Particle-filled polypropylene compounds are used in many applications in the automotive, houseware, packaging, and electric industries for the reduction of the production costs of final products formed by in- jection molding. Molding particle-filled polypro- pylene blends is easier than molding fiber-reinforced blends. However, the material properties of blends molded by injection molding can vary, depending on various parameters, such as the blend matrix, the

TABLE I
Characteristic Properties of i-PP, EVA, $CaCO_3$, and Additives Used to Produce the Ternary Composites

Material	Supplier	Trade name	MFI	d	T_m	Shape
i-PP	Petkim	Petoplen MH 418	4–6[a] g/10 min[a]	0.925 g/cm^3	166°C	Pellet
EVA	Greenflex	18 EVA	8–10 g/10 min[b]	—	—	Pellet
$CaCO_3$	Omya	Hydrocarb 95 T	—	—	—	Powder
Stabilizer	Ciba	Irganox B 225	—	530–630 g/L[c]	—	Powder
PE wax	Eral	—	—	—	—	Powder

[a] 230°C, 2.16 kg.
[b] 190°C, 2.16 kg.
[c] Bulk density.
[d] d = density.

types of fillers and reinforcements, the surface characteristics, the ratios, and the molding conditions. Parameters such as the crystallite size, the tendency toward crystallization, and the properties of the matrix and fillers play important roles for the final product. The size of the filler plays an important role for polymer blends. If the filler is very large, the processability of the polymer into the mold, the crystallization behavior, and the orientation of matrix molecules become difficult. The negative effects on the properties of blends are obvious. Calcium carbonate ($CaCO_3$) is the second most widely used mineral filler after talc. The use of $CaCO_3$ with a suitable hardness (Mohr hardness ~ 3) does not cause short-term failure in processing machinery.[6] Although fillers are used mostly to reduce costs, some mechanical properties, such as the modulus, yield strength, and tensile strength can increase. However, the toughness decreases and the rigidity increases in polypropylene, just as they do in plastics containing mineral fillers.[1,2,6–10]

Inorganic reinforcements and fillers are used to improve the mechanical and structural properties of polypropylene. Glass fiber, mica, talc, and $CaCO_3$ play important roles in the properties of composites. Polymer blends reinforced with glass fiber have higher strength and rigidity. Particle-filled polypropylene blends are generally used in engineering applications for which high-strength properties are not required.[6–18]

The adhesion between the filler and the matrix is very important for polypropylene composites. If the adhesion is strong in the interface, the modulus, rigidity, strength, and toughness of a particulate composite will be increased. Many mineral fillers and $CaCO_3$ are based on inorganic materials that do not exhibit good adhesion to thermoplastic matrices. Therefore, the surface modification of filler particles with suitable coupling agents is often recommended to enhance filler-particle dispersion into polypropylene matrices to improve strong bonding with the matrix and molding.[2]

In this study, the effects of the $CaCO_3$ concentration on the mechanical and thermal properties of i-PP/

EVA blends were investigated. To this end, i-PP/EVA/$CaCO_3$ composites containing 3, 6, 9, 12, or 15 wt % $CaCO_3$ were produced, and the properties of the ternary composites were investigated.

EXPERIMENTAL

Materials

The i-PP, EVA, fillers, and additives used in this study were all commercial products. The characteristics properties of the materials, provided by the suppliers, are listed in Table I. The i-PP homopolymer, used as the matrix phase in this study, was Petoplen MH 418 in a pellet form (Petkim, Izmir, Turkey). EVA in a pellet form (18 EVA), supplied by Greenflex (Italy), was used with 18 wt % vinyl acetate (VA). The melt-flow index (MFI) of EVA also increased with increasing VA content. $CaCO_3$ was used as a filler material and was supplied by Omya (Germany) (calcium stearate coated Hydrocarb 95 T). The ratio of i-PP to EVA was fixed at 88/12. The concentration of $CaCO_3$ with respect to i-PP/EVA was varied (0, 3, 6, 9, 12, and 15 wt %). The characteristic properties of i-PP/EVA/$CaCO_3$ used in this investigation are also listed in Table I. The materials and blends were dried at 75°C for at least 1 h in an oven before being compounded. The compositions of the blends used in this study are listed in Table II. Irganox B 225 (Ciba, Basel, Switzerland; 0.3 wt %) was added as the stabilizer (synergistic

TABLE II
Compositions of Blends Used to Produce i-PP/EVA/$CaCO_3$ Composites

Material		
i-PP (wt %)	EVA (wt %)	$CaCO_3$ (wt %)
88.00	12.00	0
85.36	11.64	3
82.72	11.28	6
80.08	10.92	9
77.44	10.56	12
74.80	10.20	15

TABLE III
Processing Parameters in Extrusion Used to Produce
i-PP/EVA/CaCO$_3$ Composites

Parameter	Value
Screw diameter (mm)	30
Length-to-diameter ratio	25
Screw speed (rpm)	40
Extrusion pressure (bar)	5
Extrusion temperature profiles from the feed zone to the die (°C)	210–225

processing and long-term thermal stabilizer system), whereas 0.4 wt % polyethylene (PE) wax was added to the i-PP/EVA/CaCO$_3$ blends during the melt processing.

Processing and specimen preparation

Extrusion

i-PP/EVA/CaCO$_3$ blends were prepared with a Microsan MTV single-screw extruder (Izmit, Turkey). The processing parameters used for the extrusion of the blends are given in Table III. The extrudate was frozen in-line in a water bath (~15°C), pelletized, and dried in an oven at 105°C for 2 h.

Injection molding

Tensile and impact specimens (ISO 527.2 and 180) were prepared by injection molding on a Yonca YMS 70-ton machine (Istanbul, Turkey); the processing parameters are listed in Table IV. Before the molding, the pellets were dried at 105°C for 2 h.

Mechanical characterization

The effects of CaCO$_3$ on i-PP/EVA (18% VA) blends were evaluated through the mechanical properties, such as the yield stress, tensile stress, elastic modulus, Izod impact resistance, and hardness (Shore D), and the thermal properties. The tensile testing of the blends was carried out on a Zwick Z010 tensile test machine (Ulm-Einsingen, Germany) according to the ISO 527.2[19] test procedure at a crosshead speed of 50 mm/min at room temperature. A computer was connected to the Zwick load cell, and a data-acquisition program recorded the force measured by the load cell. At least seven specimens were tested for each blend, and average values were found. Izod impact strength values of the blends and composites were evaluated with a Zwick impact test instrument according to the ISO 180[20] test procedure at room temperature. Izod impact tests were carried out for two different notches [notch radius (r) = 0.25 or 1 mm]. Seven impact test specimens were tested, and average values are re-

ported for the blends. Before the mechanical tests, all specimens were kept at room temperature for at least 72 h. The hardness of the i-PP/EVA/CaCO$_3$ composites were determined with a Zwick hardness test machine according to the ISO 868[21] test method at room temperature.

Scanning electron microscopy (SEM)

The fracture surfaces of Izod impact test specimens were evaluated with Jeol SEM (5410LV, JSM) (Tokyo, Japan). The surfaces of the specimens were coated with a thin gold film (25 Å). SEM investigations were performed at 20 kV after the samples were coated with gold for better conductivity.

Thermal analysis

The melting temperatures (T_m's) of the i-PP/EVA/CaCO$_3$ blends were measured with a Mettler–Toledo differential scanning calorimeter (Barcelona, Spain). The weight of the specimen was 10 mg. The differential scanning calorimetry (DSC) curve was obtained for a temperature range of 70–200°C at a heating rate of 20°C/min. The experiments were carried out in an N$_2$ atmosphere. The MFIs of the i-PP/EVA/CaCO$_3$ composites were determined with a Zwick 4100 MFI test instrument according to the ISO 1133[22] method. The annealing of i-PP/EVA/CaCO$_3$ was carried out in a Binder 115 hot-air oven (Tuttlingen, Germany) at 100°C for holding times of 75, 100, and 150 h.

RESULTS AND DISCUSSION

Tensile test results

The changes in the yield and tensile strengths of the composites with and without CaCO$_3$ are shown in Figure 1(a,b), respectively. The yield and tensile strengths tended to decrease in direct proportion to the increase in the CaCO$_3$ content in the i-PP/EVA/CaCO$_3$ ternary composites, and the expected increases in the yield and tensile strengths after the specimens were subjected to the heat treatment were not observed. The yield and tensile strengths of the specimens not subjected to the heat treatment were lower

TABLE IV
Processing Parameters in Injection Molding Used to
Produce i-PP/EVA/CaCO$_3$ Composites.

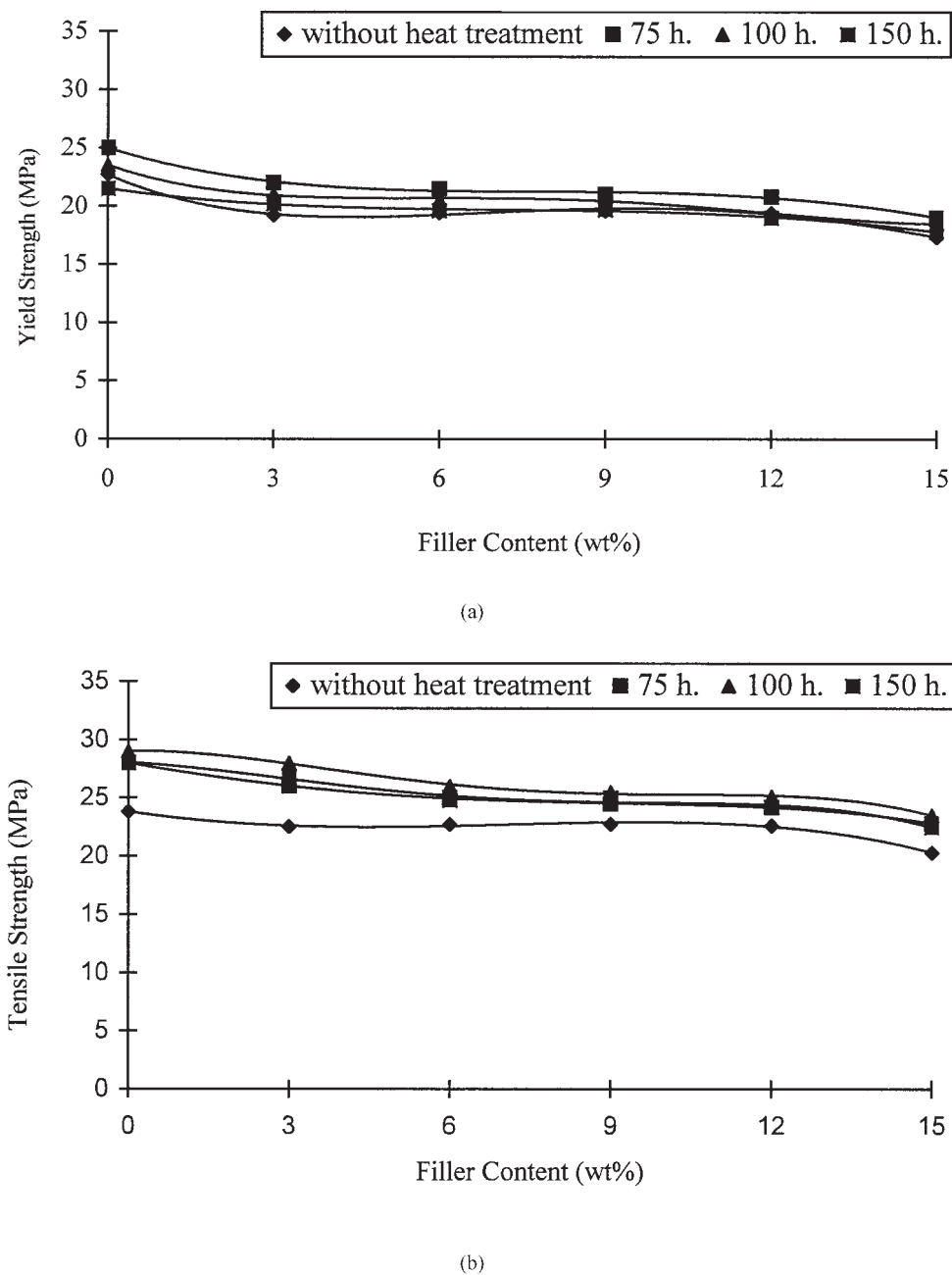| Parameter	Value
Injection pressure (bar)	500
Injection pressure time (s)	10
Mold temperature (°C)	40
Dwell time in the mold (s)	10
Temperature range (°C)	210–230

(a)

(b)

Figure 1   (a) Yield strengths and (b) tensile strengths of i-PP/EVA/CaCO$_3$ ternary composites.

than those of the i-PP/EVA/CaCO$_3$ specimens subjected to the heat treatment. However, the effect of the annealing heat treatment on the tensile strength was much more significant than the effect on the yield tensile strength.

Figure 1(a,b) shows that although the addition of 6–12% CaCO$_3$ had a minimal effect on the yield and tensile strengths, the addition of 15% of CaCO$_3$ caused the reduction to become more pronounced. The yield and tensile strengths of the thermoplastic matrix varied as the amount of the filler increased. However, the form of the material used as the filler

was most important. If the filler was a fiber, then the yield and tensile strengths of the matrix increased, and so the transfer capability of the composite improved.[1,2] If the filler was powder, the strength of the matrix decreased.[1,2,18] In our study, the decrease in the yield and tensile strength was directly related to the filler type (powder). However, the decrease in the yield and tensile strength was not so significant. This was also related to the interfacial characteristics of i-PP, EVA, and CaCO$_3$. The CaCO$_3$ used in the study was coated with stearic acid. Therefore, especially for lower filler contents, the homoge-
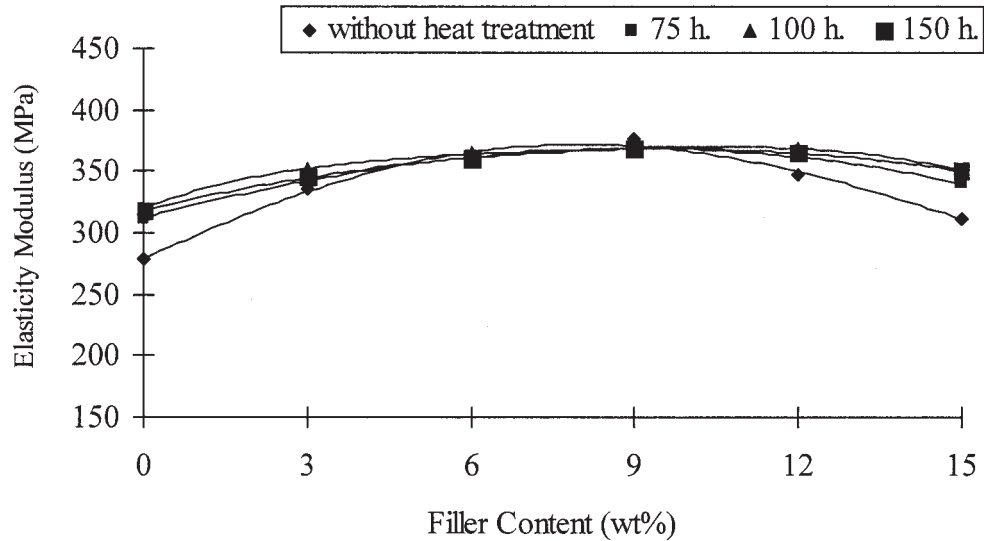
Figure 2   Elastic moduli of i-PP/EVA/CaCO$_3$ ternary composites.

neous distribution of CaCO$_3$ in the matrix was ensured, and the adhesion between the matrix and the filler was increased.[1,2,18,23]

Weak interfacial properties were not the only reason that the yield and tensile strengths decreased in the particle-filled composites. A nonhomogeneous distribution of filler particles in the matrix also caused the properties to weaken. When the filler was distributed homogeneously in the matrix (this was quite difficult most of the time) and a strong interaction was sufficiently improved, then the composite could transfer higher loads. Therefore, in our study, decreases in the yield and tensile strengths for the 15% CaCO$_3$ concentration were directly related to weak adhesion or lower molecular interactions as the filler content increased, as pointed out by other researchers.[1,2,23]

Figure 2 shows the effect of CaCO$_3$ on the elastic modulus of i-PP/EVA. A significant increase in the elastic modulus was observed for 3% CaCO$_3$, and beyond 9% CaCO$_3$, the values started to decrease. The elastic modulus of the i-PP/EVA blend subjected to the heat treatment slightly increased. An important decrease was observed with the addition of 15% CaCO$_3$. The decrease was related to the weak bond strength, adhesion, or lower molecular interaction caused by the higher content of the filler (CaCO$_3$) in the i-PP/EVA matrix structure.[1,2,9,23] Usually, CaCO$_3$ increased the stiffness and elastic modulus. Although CaCO$_3$ increased the bond strength and the molecular interaction decreased because of excessive stress, there was shrinkage between the filler and i-PP/EVA. However, in this study, the addition of more than 9%
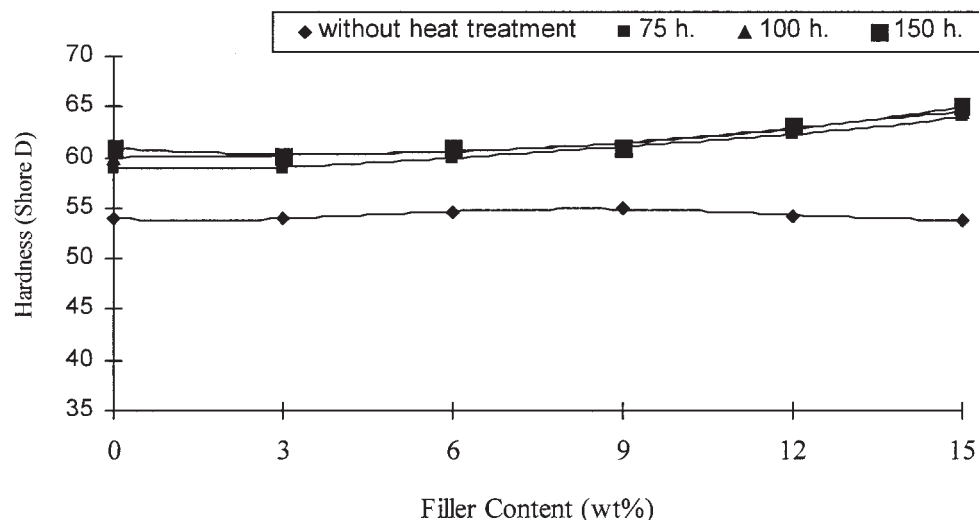

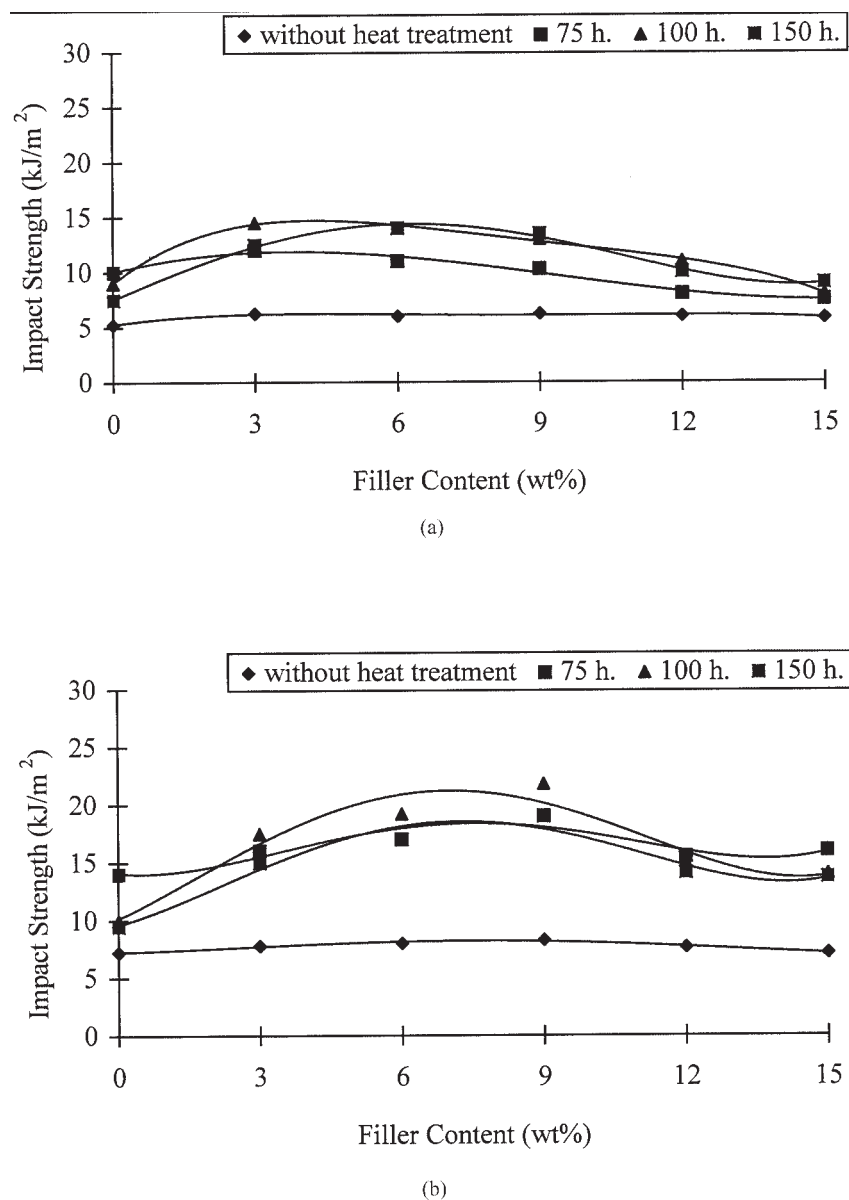**Figure 3**   Hardness of i-PP/EVA/CaCO$_3$ ternary composite.

(a)

(b)

Figure 4 Impact strength of i-PP/EVA/CaCO$_3$ ternary composites: (a) $r = 0.25$ mm and (b) $r = 1$ mm.

CaCO$_3$ to i-PP/EVA reduced the modulus. For strong molecular interactions, a lower filler content (CaCO$_3$) had to be used. The addition of more than 9% CaCO$_3$ not only increased stress but also increased microcracks and provided weak adhesion between the filler and matrix. Especially when the filler content was greater than 9%, the modulus decreased.

Hardness

Figure 3 shows the hardness values of the i-PP/EVA/CaCO$_3$ ternary composites. No significant changes dependent on the CaCO$_3$ increase were observed in the hardness values of the specimens not subjected to the heat treatment. The hardness values of the composites

subjected to the heat treatment increased in direct proportion to the CaCO$_3$ increase. This was perhaps due to less degradation of the small and macromolecular parts or segments of the blends from annealing. Figure 3 also shows that different holding times produced similar effects.

Impact strength

Figure 4 shows the variations in the impact resistance for the i-PP/EVA/CaCO$_3$ composites. Here, if we consider the i-PP/EVA blend as a reference, it becomes apparent that the impact resistance significantly depended on the amount of CaCO$_3$ and r. Figure 4(a) shows the Izod impact resistance of
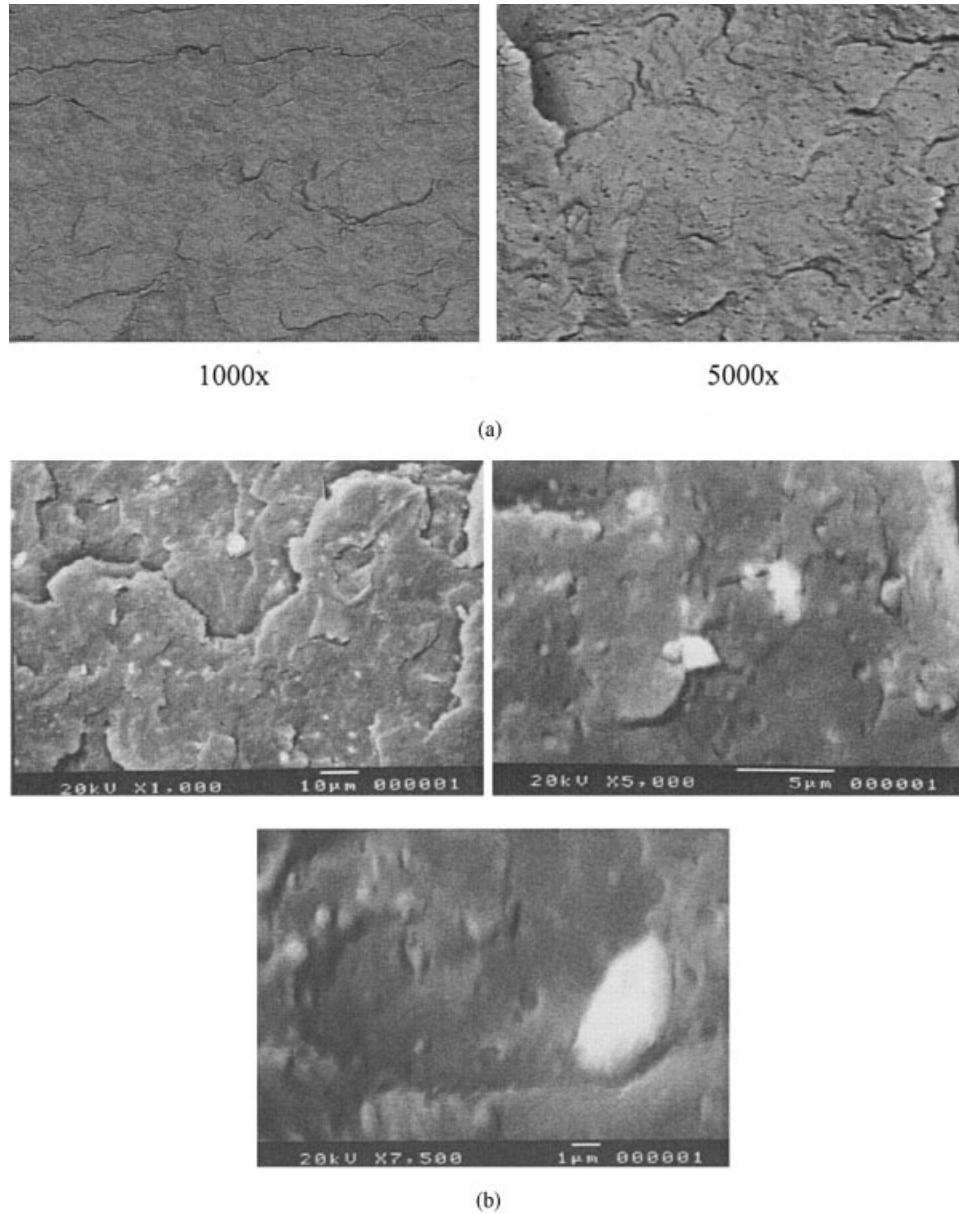
Figure 5 SEM fracture surfaces of i-PP/EVA/CaCO$_3$ blends: (a) i-PP/EVA, (b) i-PP/EVA/3% CaCO$_3$, (c) i-PP/EVA/6% CaCO$_3$, (d) i-PP/EVA/9% CaCO$_3$, (e) i-PP/EVA/12% CaCO$_3$, and (f) i-PP/EVA/15% CaCO$_3$.

specimens with $r = 0.25$ mm. The addition of 3% CaCO$_3$ caused the impact resistance to increase significantly. However, the Izod impact resistance decreased in the composites containing 6–15% CaCO$_3$. When the effects of the heat treatment were examined, it became apparent that the impact resistance of the specimens not subjected to the heat treatment did not change in a significant manner, whereas the impact resistance of the specimens subjected to the heat treatment tended to increase. The impact resistance of the composites with $r = 0.25$ mm was lower because of the excessive stress around the notch tip. A sharp notch not only increased the stress but also provided microcracks and prevented high load

transfer. The microcracks that occurred during fast breaking (plastic deformation) reduced the impact resistance and service performance of the materials. Figure 4(b) shows the Izod impact resistance of specimens with $r = 1$ mm. The Izod strength of the composites not subjected to the heat treatment changed as the CaCO$_3$ concentration increased. However, the impact resistance of the specimens subjected to the heat treatment increased in the 3–9% range according to the increase in the CaCO$_3$ concentration. The reason for the increase was thought to be the high level of adhesion between the i-PP/EVA matrix and CaCO$_3$ particles during the heat treatment and the growth of r. During the experimental studies, all the specimens
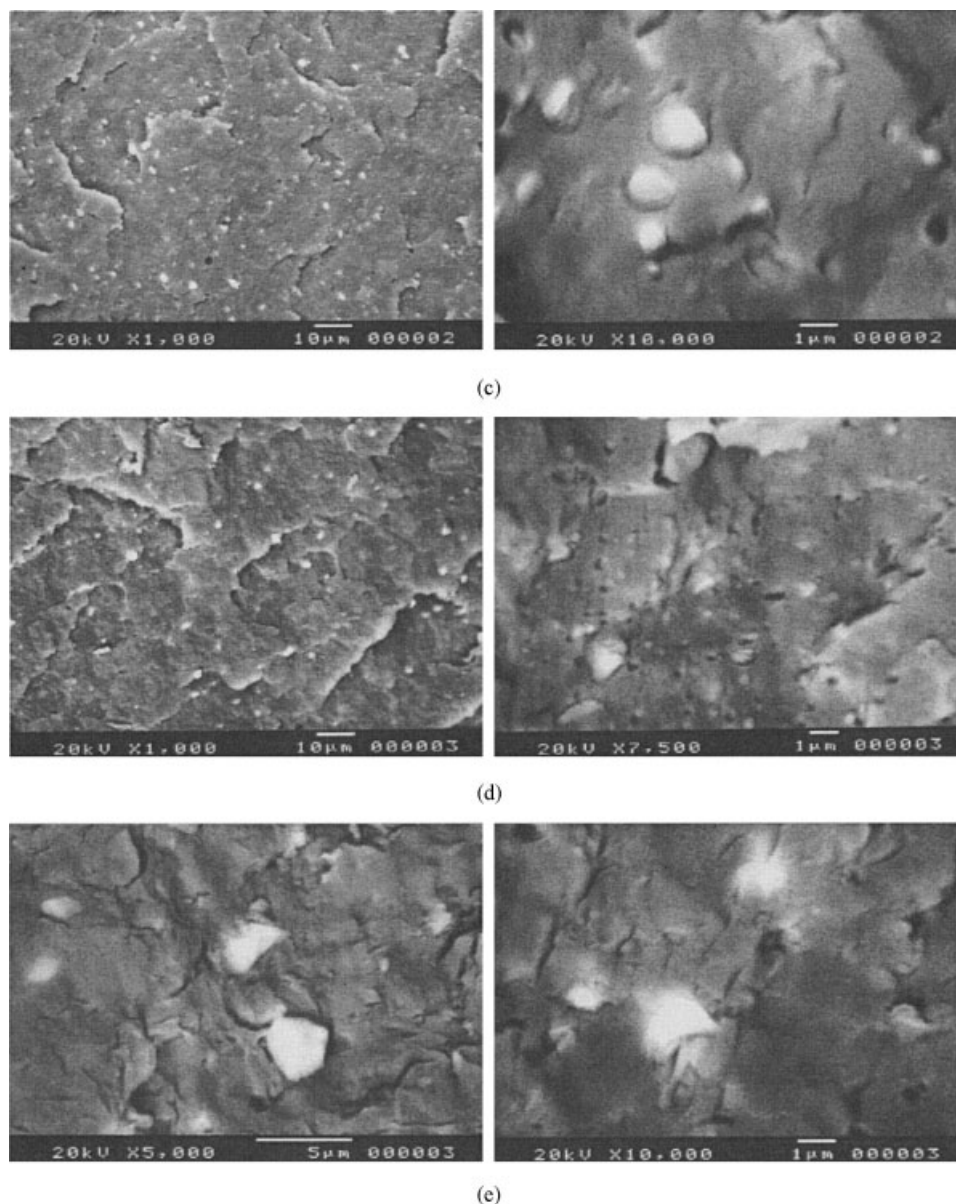
(c)

(d)

(e)

Figure 5 (*Continued from the previous page*)

were molded under similar conditions and were subjected to the heat treatment. Therefore, the higher impact resistance of the specimens with a larger r value was thought to stem from the fact that the energy was distributed to a larger area during the impact. In a blend containing 15% $CaCO_3$, the reduction of the Izod impact resistance was the result of inefficient adhesion between i-PP/EVA and $CaCO_3$ particles despite the heat treatment. The impact resistance of the composite samples with $r = 1$ mm was higher than that of the samples with $r = 0.25$ mm because there was not excessive stress around the notch tip. A large r value not only reduced stress but also provided high load transfer. Sharp notches reduced the impact resistance and service performance

of the materials. Especially when the filler concentration was greater than 9%, the impact resistance decreased. This was perhaps due to insufficient interaction or bond strength. Also, r indicated the importance of the impact resistance of the composites.

Figure 5 shows SEM micrographs of Izod impact fracture surfaces of specimens with various $CaCO_3$ contents. EVA and $CaCO_3$ had fine distributions in the i-PP matrix. The fracture surface topologies of Izod impact test specimens were dependent on the filler content. The fracture surfaces were quite smooth with lower filler contents, and there was more plastic deformation on the fracture surfaces [Fig 5(a–d)]. Figure 5(a–d) shows that there was quite strong adhesion between the matrix material and the filler material.
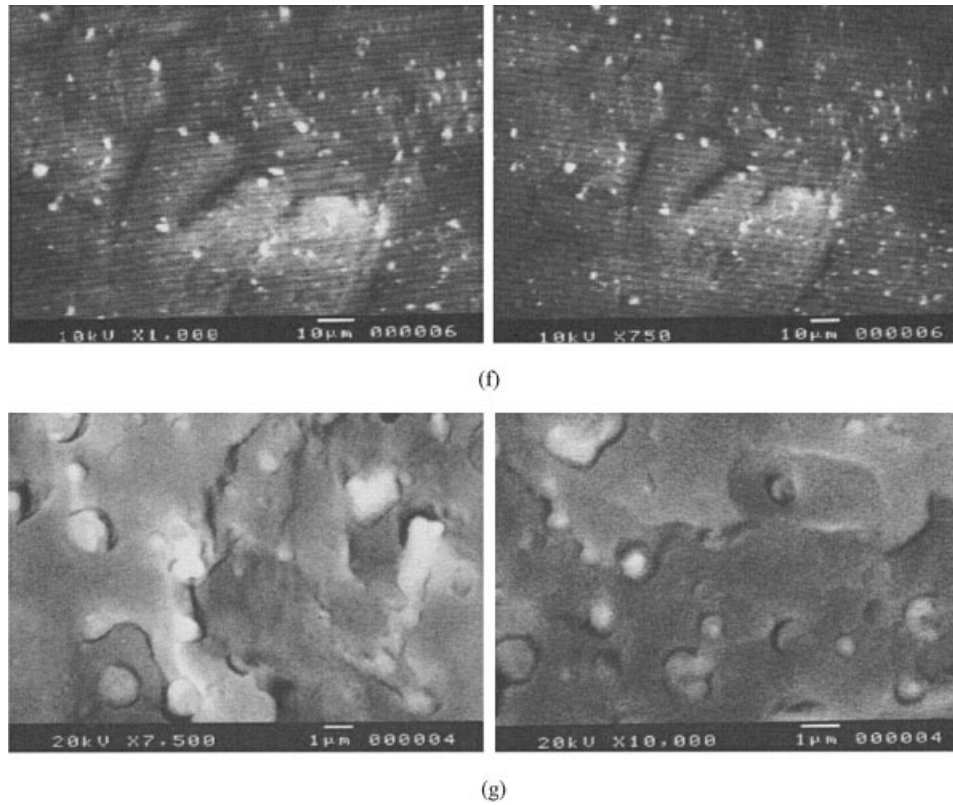
(f)

(g)

Figure 5   (*Continued from the previous page*)

Figure 5(e,f) shows the fracture surfaces of blends containing 12 or 15% CaCO$_3$. Lines defined as microcracks or phase separation formed between the matrix and the filler as the amount of CaCO$_3$ increased in the matrix. As shown by the tensile strength properties [Fig. 1(a,b)], the reduction of the impact resistance properties in direct proportion to the increase in the amount of CaCO$_3$ was thought to be the reason for the aforementioned defaults. Furthermore, an increase in

the amount of CaCO$_3$ also made the distribution within the matrix more difficult and thus weakened the adhesion between the matrix and filler.[2,18,23]

MFI

Figure 6 shows the changes in the MFI values of i-PP/EVA/CaCO$_3$ blends. The MFI values decreased in direct proportion to the increase in the amount of
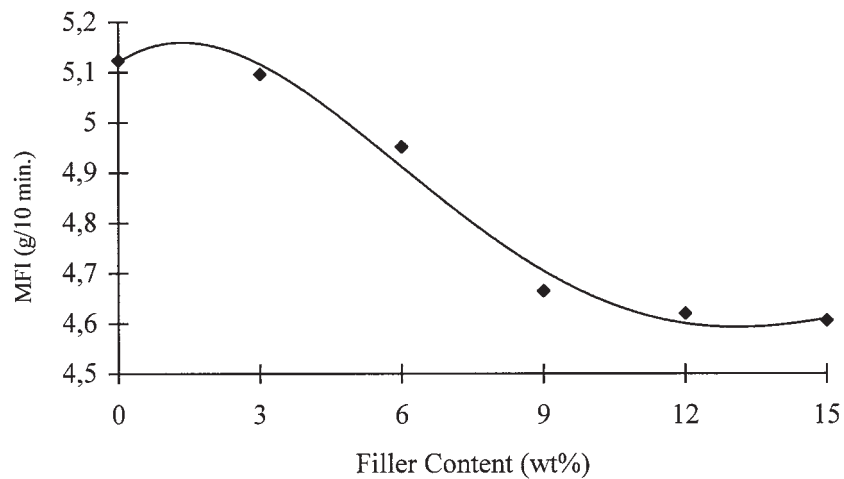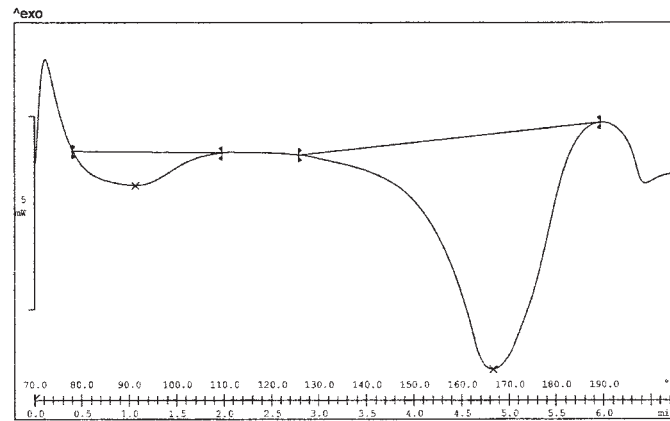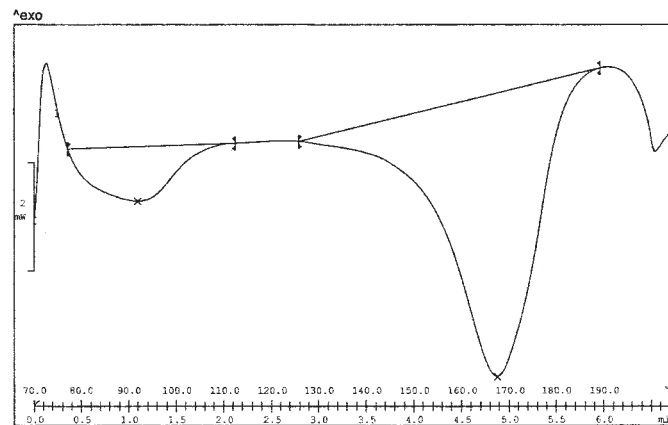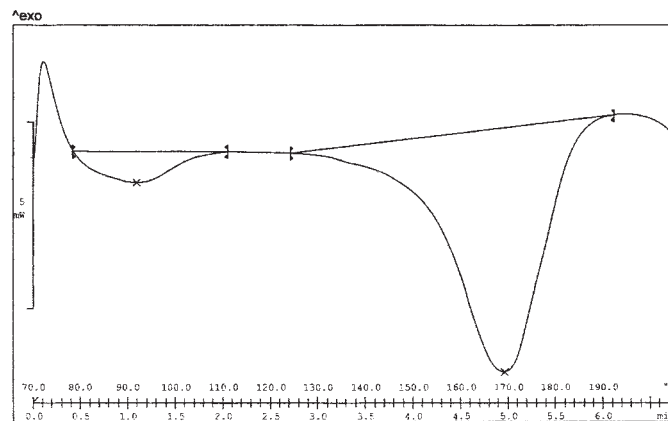

**Figure 6**   MFI values of i-PP/EVA/CaCO$_3$ ternary composites.

Figure 7 DSC thermographs of i-PP/EVA/CaCO$_3$ blends: (a) i-PP/EVA/3% CaCO$_3$, (b) i-PP/EVA/6% CaCO$_3$, (c) i-PP/EVA/9% CaCO$_3$, (d) i-PP/EVA/12% CaCO$_3$, and (e) i-PP/EVA/15% CaCO$_3$.

CaCO$_3$. With the 0% CaCO$_3$ point considered as the reference point, the MFI value decreased insignificantly with the addition of 3% CaCO$_3$. A significant decrease was observed in the 3–12% range, and an insignificant decrease was observed in the 12–15% range. Increasing the amount of CaCO$_3$ in an i-PP/EVA material increased the shear stress and viscosity. The polymer flow into the mold decreased according
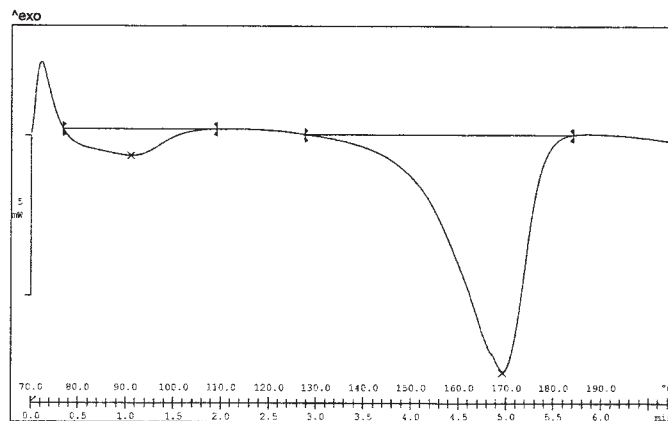
(d)
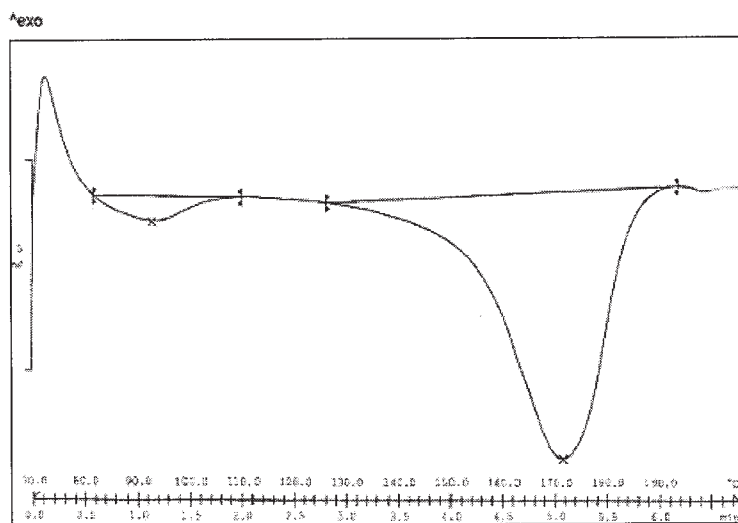
(e)

Figure 7 (*Continued from the previous page*)

to the filler concentration. Therefore, the polymer processes were affected by the influence of particulate materials on the flow properties of the material. The flow properties could also be adversely affected by numerous phenomena related to the presence of the filler in the formulations.[24]

Figure 7(a–e) shows DSC curves of the i-PP/EVA/CaCO$_3$ composites. T_m's of the blends tended to increase in direct proportion to the increase in the content of CaCO$_3$ in the i-PP/EVA matrix. The measurements indicated that T_m of polypropylene was 166°C, whereas T_m of the i-PP/EVA blend was 165°C. However, as shown by the DSC curves, the addition of CaCO$_3$ increased T_m's of blends up to 170°C. Because CaCO$_3$ hindered the molecular mobility of the crystallite segments of the blends, T_m of the blends increased up to 170°C.

CONCLUSIONS

The effects of CaCO$_3$ on the mechanical properties, such as the yield and tensile strengths, elastic modulus, hardness, and Izod impact strength with and without heat treatment, and the thermal properties, such as T_m and MFI, of i-PP/EVA blends were investigated. The following results were obtained:

1. The yield strength decreased gradually as the CaCO$_3$ content increased. The annealing heat treatment increased the yield strength, and different holding times showed similar effects on the increased yield strength values.
2. The tensile strength decreased gradually as the CaCO$_3$ content increased, and the heat treatment did not affect the tensile strength values.
3. The annealing heat treatment increased the elastic modulus of i-PP/EVA composites by nearly

35 MPa. When 3% CaCO$_3$ was added, the increase was about 15 MPa. Different annealing holding times showed similar effects on the elastic modulus.

4. The Izod impact strength increased for both r = 0.25 mm and r = 1 mm. However, the Izod impact strengths were higher for r = 1 mm. The maximum impact strength was obtained with 3% CaCO$_3$ for r = 0.25 mm at a holding time of 100 h, whereas the maximum impact strength was obtained with 9% CaCO$_3$ for r = 1 mm.

5. The hardness values of the ternary composites increased as the CaCO$_3$ content increased. The annealing heat treatment was effective for increasing the hardness values.

6. T_m increased as the CaCO$_3$ concentration increased.

7. MFI decreased as the CaCO$_3$ content increased.

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