Effect of uncoated calcium carbonate and stearic acid coated calcium carbonate on mechanical, thermal and structural properties of poly(butylene terephthalate) (PBT)/calcium carbonate composites

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MS received 13 January 2009; revised 22 August 2009

Abstract. PBT/CaCO₃ composites were prepared in a single screw extruder with particle content varying from 0–30% by weight. The influence of surface treatment of the particles, with and without stearic acid (SA), on the mechanical, thermal and structural properties was studied. The experiments included tensile tests, impact tests, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy. The composite systems containing SA coated CaCO₃ were found to exhibit better mechanical properties as compared to composite systems containing uncoated CaCO₃, with the S3 system (20% of SA coated CaCO₃) exhibiting best combination of mechanical properties. Thermal study revealed that particle type and content had no influence on the melting temperature but the crystallization temperature, % crystallinity and thermal stability increased on increasing the CaCO₃ content in PBT matrix. Morphological observation indicated that in PBT composites containing SA coated CaCO₃, the coupling agent favours a better polymer filler interaction rendering inorganic polymer interface compatible, which is also evident from better mechanical and thermal properties.

Keywords. Polymer–matrix composites; mechanical; thermal analysis.

1. Introduction

During the last few decades polymer composites have attracted much attention from both industry and academia because of their superior mechanical and thermal properties, light weight, and favourable cost/performance ratio, and hence appear to be suitable replacements for metals and alloys in many industrial applications in fields such as automotive, structural plastics, electronics, packaging, and so on.

Among the various fillers, calcium carbonate (CaCO₃) is used as important reinforcing filler in thermoplastic industry and has been studied by many researchers who have reported large improvements in mechanical properties such as strength, modulus and toughness. Also it has been reported that the coating of CaCO₃ surface with low molecular weight organic compounds like stearic acid changes the interfacial interactions between particles and matrix polymer which modifies the debonding mechanism, failure behaviour and thus, the overall performance of composites. Although there is extensive literature on the

use of CaCO₃ in polyolefins, such as polyethylene and polypropylene, but studies dealing with use of CaCO₃, as filler in polyesters are not much reported.

Poly(butylene terephthalate) (PBT) is an important semicrystalline engineering thermoplastic with many valuable properties including a high rate of crystallization, good solvent resistance, thermal stability, and excellent processing properties. However, pure PBT has low impact strength and heat distortion temperature, which obstruct its application. Much work has been done on PBT blending but few data are reported in the scientific literature on polyester-based composites. As a reinforced method, many researchers have worked extensively on PBT/glass fibre composites. Other fillers used as reinforcements in PBT include oxidized single wall carbon nanotubes, montmorillonite and SiO₂.

The present work deals with calcium carbonate (CaCO₃)/[poly(butylene terephthalate) (PBT)] composites involving two types of filler particles: one was plain CaCO₃, the other was stearic acid (SA) coated CaCO₃. The study presents a detailed analysis of the effect of filler on the mechanical, thermal and structural properties of PBT based composites, and in particular, to determine the efficiency of the stearic acid coating in improving dispersion

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of CaCO₃ into the polyester matrix and promoting interfacial adhesion between the phases.

2. Experimental

2.1 Materials

The PBT used in this work was supplied by BASF Ultradur, grade ultradur B 2550 having density and melt flow index as 1.30 g/cm³ and 18 g/10 min, respectively. Calcium carbonate particles, plain and coated with stearic acid, were kindly supplied by 20 MICRONS Limited having particle size, *D* (50) 3.47 microns.

2.2 Composite preparation

Two sets of PBT composites (sets C and S) containing two different types of CaCO₃ were prepared by melt blending method in a single screw extruder and the filler loadings of both types of CaCO₃ were varied as 5%, 10%, 20% and 30% by weight. Prior to compounding, all the materials were dried at 110°C in an oven for at least 6 h before use, to minimize the effects of moisture. The temperature of the four heating zones was set to 220, 230, 240, and 250°C, and the screw speed was fixed at 30 rpm. Upon completion of melt blending, the extruded strands were allowed to cool in the water bath, and then cut into pellets using a pelletizer. The two sets of PBT composites which were produced in the present investigation and their corresponding compositions are shown in table 1.

Finally, the tensile and impact test specimens were prepared, by using Ferromatic Milacron (Model-Omega 80W) injection-molding machine from the pellets, which were again dried in an oven at 110°C for 3 h prior to molding. The geometry of the tensile and impact test specimens was according to ASTM D 638 and ASTM D256 specifications, respectively.

2.3 Mechanical testing

The tensile strength and elongation at break were measured with a universal testing machine (LLOYD-EZ-20) at a crosshead speed of 50 mm/min. Five specimens were sampled from each composite for measurement. The five test results were averaged and then reported.

The Izod notched impact resistance of the composite system was measured using Izod Impact Testing Machine (International Engineering Industries).

2.4 DSC analysis

A differential scanning calorimeter (model DSC821, Mettler Toledo) was used to examine the thermal properties of the PBT/CaCO₃ composites. About 10 mg of samples were two-stage-heated as follows: first, the sample was heated from 30–250°C at a heating rate of 10°C/min and then held there for 5 min. Subsequently the sample was cooled to room temperature at a cooling rate of 10°C/min. Then in order to observe melting after crystallization it was reheated from 30–250°C at a heating rate of 10°C/min.

2.5 Thermogravimetric analysis

The thermal stability of the samples was measured by means of thermogravimetric analysis (TG) with a Perkin Elmer Diamond TG/DTA. Each sample was heated from 30–500°C at a scanning rate of 10°C/min under Argon atmosphere. The thermal parameters like thermal degradation, onset temperature, the temperature at the maximum rate of weight loss (*T*_{max}), and the % weight loss of PBT/CaCO₃ were calculated from the obtained TGA and DTA thermograms.

2.6 X-ray diffraction

XRD pattern of as molded PBT composite was recorded on Philips X'Pert Pro PANalytical PW 3040/60 diffractometer. Ni filtered CuK α radiation ($\lambda = 1.54 \text{ \AA}$) generated at 45 kV and 40 mA was used for the angle (2θ) range from 10–80°. The scan step size and time per step was 0.01° and 15 s, respectively.

2.7 Scanning electron microscopy

Scanning electron microscopic (SEM) pictures were taken to study the morphology of the composites. Samples were immersed into liquid nitrogen and then fractured. The morphology of fractured surfaces was then studied with JEOL 6380A scanning electron microscope after the samples were sputter-coated with a thin platinum layer.

2.8 FT-IR spectroscopy

Infrared spectra of PBT/CaCO₃ composite were recorded using a Perkin Elmer Spectrum One FTIR. As the state of samples was thin film (5 mm thickness), the attenuated total reflectance (ATR) technique using zinc selenide (ZnSe) crystal having incident angle at 45° and scan number, 20 was used.

Table 1. Compositions of PBT/CaCO₃ composites.

C set compositions		S set compositions	
PBT/uncoated CaCO ₃ (w/w)		PBT/SA coated CaCO ₃ (w/w)	
C1	95/5	S1	95/5
C2	90/10	S2	90/10
C3	80/20	S3	80/20
C4	70/30	S4	70/30

3. Results and discussion

3.1 Mechanical properties

Table 2 presents the results of tensile and impact tests for both the composite systems. As can be seen, composite system containing uncoated CaCO_3 shows lower tensile strength values as compared to the composite system containing SA coated CaCO_3 and neat PBT. Also, here the % elongation value decreases with the increasing content of CaCO_3 . In case of composite systems containing SA coated CaCO_3 the tensile strength and % elongation initially decreases and then increases. In the S3 composite (20 weight%) the tensile strength increased from 56–58.9 MPa which is about 5% higher than pure PBT and has a % elongation value better than all other composites.

In case of notched Izod impact strength, the impact value decreases by about only 18% in the composite system containing uncoated CaCO_3 and also this decrease is constant for all the weight % of CaCO_3 added. Whereas in case of composite system containing SA coated CaCO_3 , again the S3 system shows impact strength value better than all other composites and similar to that of pure PBT.

The better mechanical properties of S3 system among all the composites can be attributed to the fact that the stearic acid coating imparts hydrophobic characteristics on CaCO_3 surface, thereby promoting adhesion between the particles and PBT matrix and thus improving the dispersion and compatibility between the phases.

3.2 Differential scanning calorimetry (DSC)

DSC measurements were carried out to determine the thermal properties such as melting temperature (T_m), heat of crystallization (H_c), degree of crystallinity, onset crystallization temperature (T_{on}), and peak crystallization temperature (T_c) of PBT composites. The DSC heating, cooling and heating curves are shown in figure 1. From the recorded heating and cooling curves, thermal properties were calculated which are tabulated in table 3. The

Table 2. Mechanical properties of PBT/uncoated CaCO_3 and PBT/SA coated CaCO_3 composites.

Sample	Tensile at yield (MPa)	% Elongation at break	Izod impact strength (J/m)
PBT	56.408	27.4	39
C1	51.166	7.85	32
C2	51.362	6.56	32
C3	53.299	6.45	32
C4	50.406	5.54	32
S1	52.711	4.97	32
S2	53.397	6.15	32
S3	58.938	8.53	39
S4	50.235	5.03	29

crystallinity percentage of PBT constituent in composite was determined by (Liu *et al* 1997)

$$\chi_c (\% \text{ Crystallinity}) = \Delta H_m / \Delta H_m^0 w \times 100,$$

where ΔH_m^0 is the heat of fusion (140 J/g) for 100% crystalline PBT (Brozaa 2005) and w the mass fraction of PBT in the composites.

From figures 1a and d it is observed that melting point of first heating is not affected by the presence of CaCO_3 in both the composite systems. However, CaCO_3 did accelerate crystallization during cooling which is evident from the higher crystallization peak temperatures in both the composite systems (about 6°C higher when compared to neat PBT) (figures 1b and e) which increased with the increasing content of CaCO_3 .

Also the % crystallinity of both the composite systems was found to be greater than virgin PBT, which indicates that CaCO_3 acts as a nucleating agent during the crystallization of composites. But between the two composite systems, the crystallinity of PBT composites containing uncoated CaCO_3 was found to be higher than that of the other system containing SA coated CaCO_3 . This is because, the treatment of CaCO_3 with stearic acid, apparently reduces the surface energy of the CaCO_3 particles and therefore, it cannot act as strong nucleating species as has been reported earlier (Papirer *et al* 1984).

However, the 2nd heating shows some differences (figures 1c and f). The composites and neat PBT show double melting peaks, which is interpreted in terms of reorganization processes occurring during the 2nd heating and has been reported earlier also (Xiao and Hu 2005). The results confirm that the addition of a CaCO_3 enhances the nucleation process on PBT crystallization.

3.3 Thermogravimetric analysis

TGA was used to study the thermal stability of PBT composites and the results are listed in table 4. Figure 2 shows the % weight loss vs temperature curves for PBT and SA coated CaCO_3 . From the thermogram, it is observed that PBT undergoes degradation at about 375°C, whereas in CaCO_3 light weight loss is observed between 350 and 400°C which is associated with the degradation of stearic acid, after which it is stable up to 600°C and finally degrades to CaO at 600°C. Figure 3 shows the TGA and DTA thermograms of two sets of PBT/ CaCO_3 composites and PBT polymer.

As can be seen, the incorporation of the uncoated and coated CaCO_3 into the PBT matrix has enhanced the thermal stability of both the composites, which is evident from the increased onset of thermal degradation temperature. Also in both the composite systems, the T_{max} increased with the increasing content of CaCO_3 . This can be interpreted in terms that the initial degradation products of PBT, which accelerate further degradation process, are

Figure 1. DSC curves of 1st heating, cooling and 2nd heating of PBT/CaCO₃ composites. (a) 1st heating, (b) cooling, (c) 2nd heating of C composite system; (d) 1st heating, (e) cooling and (f) 2nd heating of S composite system.

absorbed by the CaCO₃ surface thus increasing the temperature of the point of maximum degradation ($T_{\max}$).

3.4 X-ray diffraction

Figure 4 shows X-ray diffractogram for pure PBT and CaCO₃. In virgin PBT the diffraction peaks are observed

at 2θ Bragg's angle of 15.5°, 16.8°, 20.2°, 22.9° and 24.2°, corresponding to diffraction planes (0 1 1), (0 1 0), ($\bar{1}$ 0 1), (1 0 0), (1 1 1) which are characteristic of the α form (Hall and Pass 1976; Desborough and Hall 1977) of PBT with triclinic crystal structure, whereas CaCO₃ shows the calcite crystal structure which is confirmed by the 100% intensity peak appearing at about 29.4°.

Table 3. Thermal parameters of PBT/CaCO₃ composites.

Sample	First heat			Cooling			Second heat	
	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_c onset (°C)	T_c peak (°C)	ΔH_c (J/g)	T_{m1} (°C)	T_{m2} (°C)
PBT	228.5	48.1	34.3	198.3	194.4	46.99	214.4	224.1
C1	226.3	52.5	39.4	201.7	199.6	49.5	215.1	223.2
C2	227.5	49.1	38.9	202.1	200.4	41.4	215.3	223.1
C3	227.4	43.2	38.5	203.3	201.4	39.88	216.1	223.4
C4	226	37.4	38.1	202.9	200.7	35.6	215.2	222.8
S1	227.7	49.01	36.8	202.7	200.1	42.1	215.9	223.7
S2	227.4	46.2	36.6	203.1	201.3	38.04	215.7	223.3
S3	227.7	40.8	36.4	204.1	201.9	32.3	216.7	223.7
S4	226.8	35.7	36.4	204.9	202.6	29.5	216.6	223.1

Table 4. Thermal degradation of PBT/CaCO₃ composites.

Sample	PBT	C1	C2	C3	C4	S1	S2	S3	S4
Onset T (°C)	377.1	382.1	384.2	384.1	381.1	379.2	381.6	380.8	379.5
T_{max} (°C)	395.8	399.8	402.5	406.9	407.6	398.1	403.1	405.3	405.3
Residual wt. %	2.1	6.7	11.3	24.4	34.9	4.1	17.7	24.5	35.9

Figure 2. TGA curves of PBT and SA coated CaCO₃.

Figures 5a and b present the X-ray diffractograms of two sets of PBT/CaCO₃ composites. Apparently, apart

from those of pure constituents, no new diffracting peaks were observed in the diffraction pattern of the composites. Moreover, all composite systems showed the same XRD patterns with varying peak intensity in proportion of the constituent's weight fraction. The absence of new diffraction peaks showed that the presence of CaCO₃ did not change the crystal structure of PBT.

3.5 Morphology

Figure 6 shows the SEM micrographs of uncoated and SA coated CaCO₃. As can be seen in case of uncoated CaCO₃, there is strong particle–particle interaction with a tendency to form aggregates whose dimensions are higher than that of isolated particles. In figure 7, the scanning electron micrographs of the composites are exhibited.

In the samples reinforced with uncoated CaCO₃ (figures 7a and c) it is observed that CaCO₃ particles are poorly welded to the PBT matrix, that is also evident from the SEM micrographs of C3 composite at higher magnification (figure 7e). Here fracture lines and air voids are observed at the borderline of filler, which are formed as a result of detachment of the unembedded particles during fracture in liquid nitrogen, indicating that there is poor adhesion between the filler and the matrix. In samples containing SA coated CaCO₃ (figures 7b and d) the particles are found, better welded to the PBT matrix and also no fracture lines and voids are present at the interface suggesting that the coating of CaCO₃ with stearic acid promotes adhesion between the particles and PBT matrix thus improving the compatibility between the phases.

Figure 3. TGA and DTA curves of PBT/CaCO₃ composites: (a) C composite system and (b) S composite system.

Figure 4. X-ray diffractogram of PBT and CaCO₃.

3.6 FTIR

Figure 8 shows FTIR spectra of PBT and CaCO₃. The typical IR bands of PBT appear at 2925, 2853 (CH₂ stretching), 1707 (C=O stretch), 1456 (C–H bending in CH₂ group), 1407 (arom. ring), 1241 (CO–O stretch in esters), 1115 (O–CH₂), 1018 (arom. ring) and 723 cm⁻¹ (aromatic C–H bending). The calcium carbonate spectrum shows IR bands at 1084, 878, 1455, 713 cm⁻¹ corresponding to ν_1 -symmetric stretching, ν_2 -symmetric

Figure 5. X-ray diffractograms of PBT/CaCO₃ composites: (a) C composite system and (b) S composite system.

Figure 6. Scanning electron microscopic images of CaCO_3 particles: (a) uncoated and (b) SA coated particles.

Figure 7. Scanning electron micrographs of the PBT/ CaCO_3 composites: (a) and (e) C3 composite, (b) and (f) S3 composite, (c) C4 composite and (d) S4 composite.

Figure 8. Infrared spectra of PBT and CaCO_3 .

Figure 9. Infrared spectra of PBT/ CaCO_3 composites: (a) C composite system and (b) S composite system.

bending, ν_3 -asymmetric stretching and ν_4 -asymmetric bending vibrations, which are characteristic of the calcite structure (Alder and Kerr 1962).

Figure 9 presents FTIR spectra for PBT/ CaCO_3 composites. It is observed that in both composite systems

with the addition of CaCO_3 , the IR band at 1455 cm^{-1} appeared in the spectrum, which is typical of CaCO_3 and its absorption increased with the increasing content of CaCO_3 . But apart from this no new IR band was observed in the composites indicating that no bonding has taken place between CaCO_3 and PBT matrix.

Thus from the FTIR analysis it can be concluded that stearic acid coating on CaCO_3 helps in improving the compatibility between the filler and matrix but as such does not help in binding the filler with the PBT matrix and this improved compatibility is responsible for the better mechanical properties of composites containing stearic acid coated CaCO_3 as compared to composite containing uncoated CaCO_3 .

4. Conclusions

The mechanical, thermal, and structural properties of PBT/ CaCO_3 composites were studied by addition of two different types of CaCO_3 , uncoated and SA coated CaCO_3 . The results of different tests clearly demonstrate that PBT composites containing SA coated CaCO_3 exhibit better mechanical properties, with the S3 composition showing the best combination of properties where the tensile strength has increased from 56 MPa to 58.9 MPa and has an impact strength similar to that of neat PBT. A better polymer–filler interaction with increased adhesion between the polymer and filler particles has resulted in enhancing the mechanical properties of the S system. Also the thermal studies show an increase in % crystallinity, crystallization temperature and thermal stability in both the composite systems. All of the results indicate that CaCO_3 is a good candidate for use as a reinforcing agent in PBT for future applications in electronics and automobile sector.

Acknowledgements

The author is thankful to the Visvesvaraya National Institute of Technology, Nagpur, for providing a research fellowship to work on this area of polymer composites.

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