Effect of Particulate Fillers on Thermal Expansions and Other Critical Performances of Polycarbonate-Based Compositions

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ABSTRACT: Influence of different inorganic particulate mineral fillers on polycarbonate composites was explored. Among all the fillers assessed here only boron nitride and mica could appreciably reduce the thermal expansion of polycarbonate, particularly along the direction of flow. While measured in the normal to flow (cross-flow) direction, the coefficient of thermal expansion (CTE) values decreased marginally in presence of boron nitride and mica as compared to the unfilled specimen. The anisotropicity in CTE is presumable due to preferential orientation of boron nitride and mica along the direction of flow in the injection molded samples. The effectiveness of fillers in reducing CTE of the polycarbonate composites was correlated to the dispersion of fillers in the polymer matrix. Better dispersion of boron nitride and mica, as observed through SEM, ensured their improved interaction with the matrix and thereby reducing the CTE. It was observed that in presence of particulate fillers the impact performance of the composites decreased appreciably with an increase in tensile modulus, in general. The flow behavior of the composites was by large dependent on the types of fillers used. In presence of some of the fillers such as BaSO$_4$, ZnO, ZnS, TiO$_2$, and alumina, flow of the composites increases significantly, primarily associated to appreciable reduction in molecular weights of the polycarbonate. On the other hand, with boron nitride flow remained almost unchanged upon its addition of 5 vol %. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 215–226, 2012

Key words: polycarbonates; thermal expansion; composites; inorganic materials; morphology; mechanical properties; flow

INTRODUCTION

A major challenge for polymers in engineering applications is to reduce their thermal expansion coefficients to achieve dimensional stability with temperature fluctuations more analogous to metals. Polymers with low coefficient of thermal expansion (CTE) are highly desirable particularly in electronics and optical precision devices where thermal gradients and temperature fluctuations at operating environment could cause substantial change in dimensions leading to distortion in shape accuracy.[1,2] Moreover, several end-use applications, such as automotive parts, enclosure assemblies of electronic, and electrical devices etc., demand polymers to reside in close contact with metal parts. Now, inorganic materials typically possess much lower CTE compared to that of organic polymers.[3] CTE of polymers are approximately an order of magnitude higher than mineral fillers or metals.[4] The differential expansion and contraction of polymers and metals in intimate contact (insert molding or over-molding situations, in particular) can cause internal stress or distortion or even microcracking with change in temperature.[5] Strategies of reducing CTE of polymers typically involve incorporation of inorganic fillers into the matrix.[5] Several studies have already carried out on the influence of shape, size, and volume fraction of the inorganic fillers on the thermal expansion of the polymers.[6–8] Polymer composites with long fibers possessing significantly lower thermal expansion coefficients are reported.[9] However, the fibers in polymer matrix have a tendency to preferentially align along the direction of flow and hence the CTE along the flow direction is much lower than the transverse directions leading to significant anisotropicity.[10,11] Use of particulate fillers to reduce CTE of polymer composites is also documented. However, it is challenging to decrease the CTE of polymers to a desired level with lower proportion of particulate fillers (10–30 vol %).[12,13] Viscosity issues during melt processing of polymer composites prevent incorporation of particulate fillers in their higher volume (>50 vol %) fractions. Moreover, incorporation of particulate fillers, especially without any surface treatment, often found to be detrimental for certain critical performances of polymers such as flow, ductility, surface esthetics, etc.[5]

TABLE I
Ingredients Used in Formulations

Ingredients	Details	pH	Source
	POLYMER		
Polycarbonate (PC)	BPA polycarbonate resin prepared by interfacial polymerization. MVR [300°C/1.2 kg] 17–21 g cm^{-3}10 min; $M_w \sim 50$ k, Density 1.19 g cm^{-3}	–	SABIC Innovative Plastics
	FILLERS		
Mica	Muscovite, $K_2Al_4(Al_2Si_6O_{20})(OH)_4$, Suzorite® 200HK Density 2.7 g cm^{-3}, CTE $\sim$ 8–15 μm m^{-1} °C^{-1}	9.6	Surzite Mica Products Inc.
Boron nitride	BN, PolarTherm® PT 360 Density 2.29 g cm^{-3}, CTE $\sim$ 3–12 μm m^{-1} °C^{-1}	9.6	Momentive Performance Materials
Talc	$3MgO.4SiO_2 .H_2O$, Jetfine® Density 2.71 g cm^{-3}, CTE $\sim$ 8–15 μm m^{-1} °C^{-1}	9.9	Luzenac, Europe
Wollastonite	$CaSiO_3$, NYGLOS® M30. Density 2.9 g cm^{-3}, CTE $\sim$ 6–7 μm m^{-1} °C^{-1}	11.1	Nyco Minerals
Calcium carbonate	$CaCO_3$; Powder, Density 2.9 g cm^{-3}, CTE $\sim$ 9–10 μm m^{-1} °C^{-1}	9.8	Alfa Aesar
Barium sulphate	$BaSO_4$, Blanc Fixe® F, Density 4.5 g cm^{-3}, CTE $\sim$ 10–12 μm m^{-1} °C^{-1}	9.0	Sachtleben Chemie
Zinc oxide	ZnO, Powder, Density 5.6 g cm^{-3}, CTE $\sim$ 3–6.5 μm m^{-1} °C^{-1}	9.9	Alfa Aesar
Zinc sulfide	ZnS, Sachtolith®, Density 4.1 g cm^{-3}, CTE $\sim$ 6.4–7.9 μm m^{-1} °C^{-1}	7.9	Sachtleben Chemie
Titanium dioxide	Rutile TiO_2; Ti-Pur® R104, Density 4.2 g cm^{-3}, CTE 3–9 μm m^{-1} °C^{-1}	5.0	DuPont
Alumina	Al_2O_3; Martoxide®, Density 3.5 g cm^{-3}, CTE $\sim$ 4–8 μm m^{-1} °C^{-1}	9.0	Martinswerk GmbH
	ADDITIVES		
Irganox® 108 (F 542)	Phosphite-based antioxidant used as a stabilizer	–	Ciba

The pH values of fillers were measured in their 10% slurry in water. CTE and density values at room temperature are gathered from open literature.

Bis-phenol A (BPA) polycarbonate (PC) represents one of the most widely used engineering thermoplastics owing to its unique performances such as transparency, impact, mechanical properties, and thermal stability. Typically BPA-PC has CTE value in the range of $\sim$ 70–80 μm m^{-1} °C^{-1}, which is significantly higher than that of metals, for example steel has CTE in the range of $\sim$ 11.0–13.0 μm m^{-1} °C^{-1}.[3] Usages of fibers to reduce coefficient of thermal expansion of polycarbonate is documented.[14] There are only a few published reports available in the public domain illustrating the effects of micro-sized fillers on the dimensional stability and certain other performances (primarily mechanical and rheological properties) of polycarbonate and its blends.[15–18] Most of the literatures concerning polycarbonate-based composites deal with nano-fillers such as nanoclay[19] nanosilica,[20] nano-calcium carbonate,[21] and carbon nanotubes.[22] To the best of our knowledge there is no published literature available illustrating in details the influence of naturally occurring inorganic particulate micro-fillers of varied shape and size on coefficient of thermal expansions as well as other key performance parameters of bisphenol A polycarbonate (BPA-PC). The current research initiative is primarily targeted to evaluate the influence of a few

naturally occurring inorganic particulate fillers in polycarbonate composition to reduce CTE values and in turn increase the dimensional stability. The influence of fillers on mechanical properties, flow and impact were also investigated to assess their reinforcement capabilities as well as performance trade-offs in BPA-PC-based compositions.

EXPERIMENTAL

Materials

The details of the ingredients used for current research are displayed in Table I. The inorganic fillers were used here as received without prior modification. The densities and coefficient of thermal expansion values of the fillers, mentioned in Table I, are gathered from open literatures. The pH values of the respective fillers measured in their 10 wt % aqueous dispersions (slurry) are also given in Table I.

Sample preparation and molding

The BPA-polycarbonate (will be simply designated subsequently in the test as polycarbonate) composites were prepared using different types of fillers at their identical loading of 5 vol %. Since the fillers possess different densities, therefore for the sake of

TABLE II
Formulations Used with Fillers

	Unfilled	1	2	3	4	5	6	7	8	9	10
PC (wt %)	100	89.3	88.6	88.6	83.4	90.8	80.1	84.6	84.3	86.6	89.3
Irgaphos- 168 (phr)	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Mica (wt %)		10.7									
Wollastonite (wt %)			11.4								
CaCO3 (wt %)				11.4							
BaSO4 (wt %)					16.6						
Boron Nitride (wt %)						9.2					
ZnO (wt %)							19.9				
ZnS (wt %)								15.4			
TiO2 (wt %)									15.7		
Alumina (wt %)										13.4	
Talc (wt %)											10.7

comparison, they were evaluated with respect to their equivalent volumes rather than equal weights. To compensate the different amounts fillers in the formulations, the amount of polycarbonate was varied. Table II displays the actual formulations used to prepare different composites in wt %. The relationship used between volume fraction of fillers, V_f, to their weight fraction, W_f is:

$$V_f = \frac{W_f}{\left[W_f + (1 - W_f) \times \left(\frac{\rho_f}{\rho_m} \right) \right]} \qquad (1)$$

where ρ_f and ρ_m are densities of the filler and the polymer, respectively.

All composites in the form of pellets were prepared through melt extrusion process using a Twin Screw Extruder (Krupp Werner and Pfleiderer Model #ZSK 25) with six-barrel setup at temperature range of 280–290°C. The screw speed was set at 300 rpm. The feed rate was maintained at 15–17 kg h^{-1}. Injection molding of the predried pellets [at 100°C for 2–3 h] was done using an L and T Demag 60T machine. The melt temperature was set at 290°C and mold temperature was at 80°C.

Characterizations

Particle sizes of the fillers as well as morphology of the resultant composites were evaluated through scanning electron microscopes (SEM) (JEOL FE-SEM and QUANTA 400 FE-SEM). For the determination of particle sizes, the fillers were dispersed in methanol and sonicated for 90 min. A drop of the dispersion was placed on SEM stub and allowed to dry in air for few minutes and subsequently sputter coated with gold. For morphological evaluations of polymer composites, the specimens were prepared by fracturing the tensile bars after exposing them into cryogenic conditions for 10–15 min. Specimens were mounted on a SEM stub using double-sided

tape and subsequently sputter coated with gold. Micrographs of fillers and composites at various magnifications ranging from 100× to 10,000× were taken at 30-kV acceleration voltage, with 12 μA of emission current and with 9 μA of probe current. Digital image acquisition was done using a side mounted Gatan model 794 camera. Coefficients of thermal expansion were determined according to ASTM E 381-06 using a Perkin–Elmer thermomechanical analyzer (TMA-7). Rectangular specimens (with approximate dimensions of 10 mm × 10 mm × 4 mm) were prepared by milling the central part of injection-molded ISO tensile bars. To investigate the directional dependencies of thermal expansion, measurements were carried out in flow directions and cross-flow (normal) direction in the same specimen over temperature range from −20 to 120°C at a heating rate of 5°C per minute in nitrogen atmosphere using an expansion probe with pressure set to 0.05N. An illustration of the directions in which the CTE measurements were made is shown in Figure 1. The relationship for thermal expansion of a solid is,
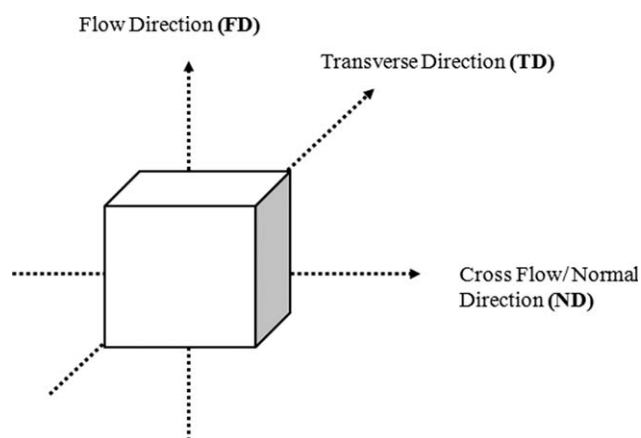

Figure 1 Illustration of specimen geometry and directions of measurement of thermal expansion. The transverse direction represents the thickness direction of the specimens.

TABLE III
Shapes and Sizes of Particulate Fillers Used

Filler	Shape	Size (μm) Mean	Size (μm) Standard dev.
Mica	Platy; Diameter	81	30
	Thickness	1	0.1
Boron nitride (BN)	Platy; Diameter	9	3
	Thickness	0.8	0.2
Talc	Platy; Diameter	47	21
	Thickness	1	0.1
Barium sulfate (BaSO$_4$)	Granular; Length	2	0.5
	Diameter	0.8	0.1
Wollastonite	Acicular; Length	8	1
	Diameter	2.1	0.7
Zinc oxide (ZnO)	Granular	237	105
Zinc sulfide (ZnS)	Granular	176	42
Titanium dioxide (TiO$_2$)	Loosely agglomerated. Primary particle almost spherical	184	45
Alumina (Al$_2$O$_3$)	Granular	5	2
Calcium carbonate (CaCO$_3$)	Granular	57	12

$$\Delta L = \alpha \times L \times \Delta T \qquad (2)$$

where α represents the coefficient of thermal expansion, L is the length of the specimen, ΔL is the change in length, and ΔT is the change in temperature. eq. (2) indicates a liner relationship between ΔL and ΔT with α. The coefficient of thermal expansion (α) in the range of 0–100°C was determined from the slope of the plot of relative dimensional change ($\Delta L/L$) versus temperatures (T), using TMA-7 standard data analysis software. The CTE was measured in at least two specimens from the same composition and average value was reported within a standard error of $\sim$ 4%. The mold shrinkage measurement was carried out in flow directions as well as cross flow directions of the molded plaques (of 1/8 in. thickness) of the selected samples in accordance to standard D955-000. The percentage of mold shrinkage was calculated using the following equation:

$$MS = \left(\frac{DC - DS}{DC}\right) \times 100 \qquad (3)$$

where MS is the percent mold shrinkage observed, DC is the dimension of the mold cavity in millimeter and DS is the dimension of the specimens. A minimum of 10 samples were tested and the average value and standard deviations were reported. Tensile measurements were carried out following ISO 527 protocol using an Instron universal testing machine (model 5500) at room temperature (23°C) at a crosshead speed of 50 mm min^{-1}. Prior to the testing, the samples were conditioned for 48 h at 23°C and 50% relative humidity. At least five specimens were tested for each set of composition. Notched Izod impact (NII) measurements were done at room temperature according to ISO 180 standards. Flow

characteristics of the blends in terms of melt volume rate (MVR) were evaluated at 300°C with 1.2 kg of load and residence time of 6 min following ISO 1133 protocol. Gel Permeation Chromatography (GPC, Shimadzu) equipped with an auto sampler was used for the purpose of measuring the molecular weights of the extruded pellets and molded specimens in accordance to ASTM D5296-97 after solvent extraction of the polycarbonate from the filled composites. The commercially available polystyrene standards with narrow molecular weight distribution were used as standard, as is common practice.[23] Every sample was run at least twice and the average values reported here with a standard error in the measurement as ±5%. Glass transition temperature (T_g) of the selected composites were measured on compounded granules (pellets) and molded specimens using differential scanning calorimeter, (DSC, model 2920, TA Instruments) in the second heating run in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Most of the performances of polymer composites are governed by the particle size, shape, and the subsequent distribution of fillers in the polymer substrate.[24] Therefore prior to using fillers in the composites, their particle sizes were determined. Table III displays the shapes and average sizes of the particulate fillers as observed through SEM studies. Mica, talc, and boron nitride are plate-like fillers with the platelet thickness of about 1 μm. Wollastonite is an elongated needle-shaped (acicular) filler, but with relatively lower aspect ratio than conventional fibrous fillers. Moreover, since they are softer, there is a possibility that they can be cleaved further under extrusion conditions.[25] The rest of the
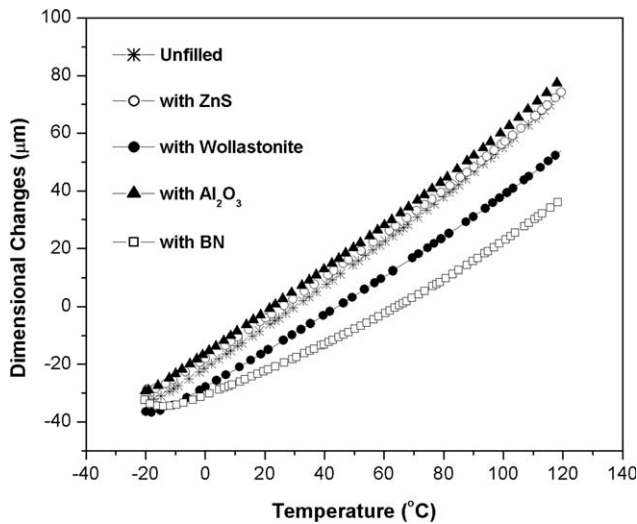
Figure 2 Dimensional changes measured in flow direction of unfilled polycarbonate and its composites with different fillers at 5 vol % loading.

mineral fillers used here are all granular and rather irregular in shape.

The performance of polycarbonate based composites with mineral particulate fillers were evaluated and subsequently compared to unfilled counterpart, used here as benchmark.

Influence of fillers on thermal expansion of composites

Figure 2 provides a representative and comparative assessment of the dimensional changes within the temperature range of −20 to 120°C for composites with 5 vol % of some of the mineral fillers vis-a-vis unfilled compositions. It is apparent that with

boron nitride the dimensional changes are not only less compared to unfilled specimen but also lower with respect to filled composites with zinc sulfide (ZnS), wollastonite, and alumina.

The CTE values of the composites containing 5 vol % of fillers are determined and reported here. Figure 3 captures the CTE values of the composites upon addition of different fillers measured along the flow direction. It is apparent from Figure 3 that mica, wollastonite, and boron nitride are effective in appreciably reducing the CTE of the composites compared to unfilled version in the flow direction. The CTE of unfilled composition (72.5 $\mu m\ m^{-1}\ °C^{-1}$) has been reduced to ~ 51, ~ 63, and $\sim 58\ \mu m\ m^{-1}\ °C^{-1}$ with addition of 5 vol % of boron nitride wollastonite and mica, respectively. Calcium carbonate ($CaCO_3$), titanium dioxide (TiO_2), and talc, on the other hand, can reduce the CTE only marginally. Fillers such as barium sulfate ($BaSO_4$), zinc oxide (ZnO), zinc sulfide (ZnS), and alumina do not contribute to reduce CTE at all. In their presence, in fact, the CTE value of polycarbonate has increased to some extent.

Figure 4 displays the influence of different fillers on the CTE values of the composites in comparison to unfilled system, measured in cross-flow direction. It has been observed that most of the fillers assessed here are not effective in reducing the CTE of polycarbonate in the cross-flow direction at all. With mica and boron nitride, the CTE have been reduced only marginally with respect to that of unfilled composition, changing from 70.4 to 68 $\mu m\ m^{-1}\ °C^{-1}$ and 68.9 $\mu m\ m^{-1}\ °C^{-1}$, respectively. With titanium dioxide the change in CTE was also very marginal. With other fillers, CTE values of the composites in fact showed an increase with respect to unfilled
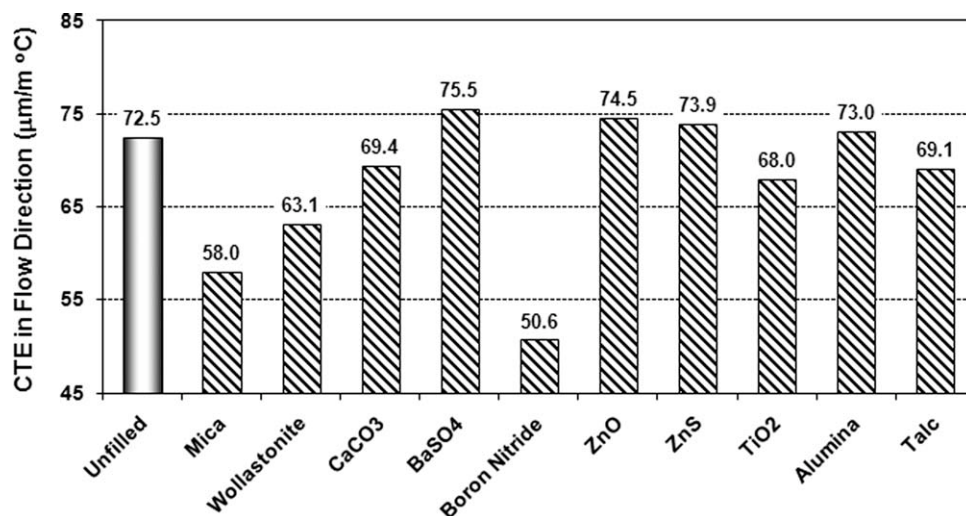

Figure 3 Coefficient of thermal expansions of composites measured in flow direction with different fillers at equivalent loading of 5 vol % compared to unfilled.
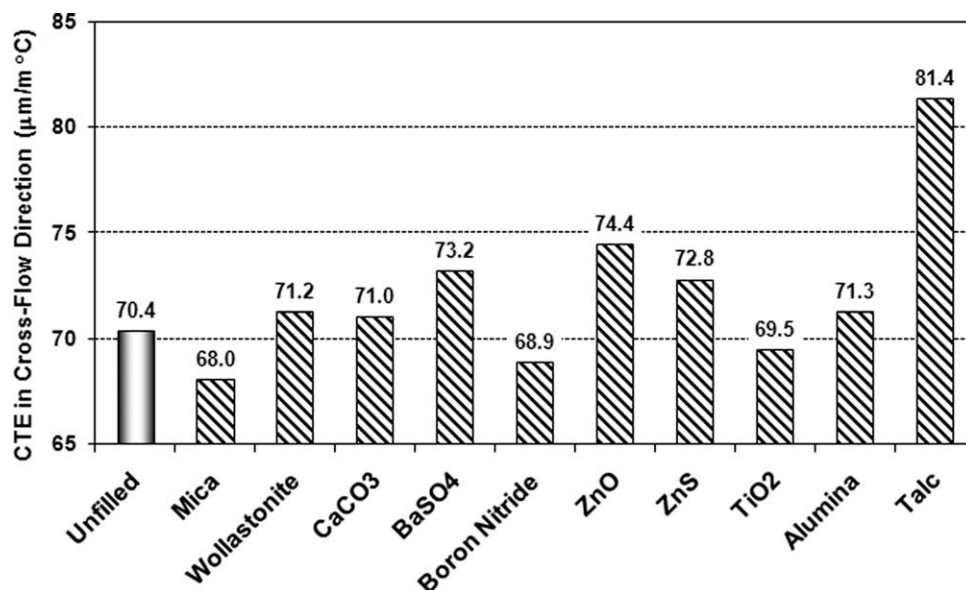
Figure 4 Coefficient of thermal expansions of composites measured in cross-flow direction with different fillers at equivalent loading of 5 vol % compared to unfilled.

composition. Maximum increase in CTE (worst scenario) has been evidenced with talc as filler. With talc the CTE of the polycarbonate composite was found to be 81.4 μm m^{-1} °C^{-1}.

Application of rule of mixtures to the CTE of composites comprising of inorganic fillers results into:

$$\alpha_c = \alpha_p \phi + \alpha_f (1 - \phi) \qquad (4)$$

where α_c is the CTE of resultant composites α_p and α_f are the CTE vales of polymer and filler, respectively, and ϕ is the volume fraction of the filler. Since the inorganic fillers possess much lower CTE compared to polycarbonate (Table I), it is expected from eq. (2) that incorporation of inorganic fillers in the polymer matrix would bring down CTE values of the composites at least to some extent. However, in reality it has been seen that only a few fillers are effective in reducing CTE. Upon incorporation of most of the fillers the CTE values remained unchanged or increased to some extent. To understand as to why some of the fillers evaluated here are more effective in lowering the CTE compared to others, an effort has been taken to assess the morphology of the filled composites. It is known that polymer–filler interaction plays an important role in controlling the CTE of the composites.[5] A better dispersion of fillers in the polymer matrix ensures better polymer filler interaction and hence would contribute more in lowering the CTE. The primary objective for the morphological evaluation is, therefore, targeted to investigate the dispersion of fillers in the polymer matrix.

It can be highlighted here that with boron nitride and mica, the CTE values have found to be depend-

ent on direction of the measurement: CTE in flow direction being substantially low compared to that in cross-flow. To get an insight into the anisotroposity of the CTE values of the composites filled with mica and boron nitride, morphological observations may also be proved to be effective.

Influence of fillers on morphology of the composites

Figure 5 displays the microstructures of the fractured surfaces of the composites with different fillers, as observed through SEM. It can be seen that mica [Fig. 5(a)], boron nitride [Fig. 5(b)], talc [Fig. 5(c)], wollastonite [Fig. 5(d)], and barium sulfate [Fig. 5(e)] are embedded and dispersed over the matrix without any apparent agglomeration. The primary particle sizes of these fillers do not change appreciable after forming composites. It can be observed however that zinc oxide [Fig. 5(f)], zinc sulfide [Fig. 5(g)], titanium dioxide [Fig. 5(h)], and alumina [Fig. 5(i)] all demonstrate significant agglomerations. Because of the formation of agglomeration of irregular shapes and subsequent phase separation, ZnO, ZnS, TiO$_2$, and alumina probably did not contribute to lowering the CTE. Calcium carbonate [Fig. 5(j)] does not show appreciable agglomeration in the polycarbonate matrix; however, it seemed to be phase separated out completely, presumably because of its angular and sharp edges and lack of sufficient interaction with the matrix. Therefore, based on the morphological observations it can be inferred that the efficient dispersion of mica, boron nitride and wollastonite in polymer matrix ensures improved polymer-filler interaction
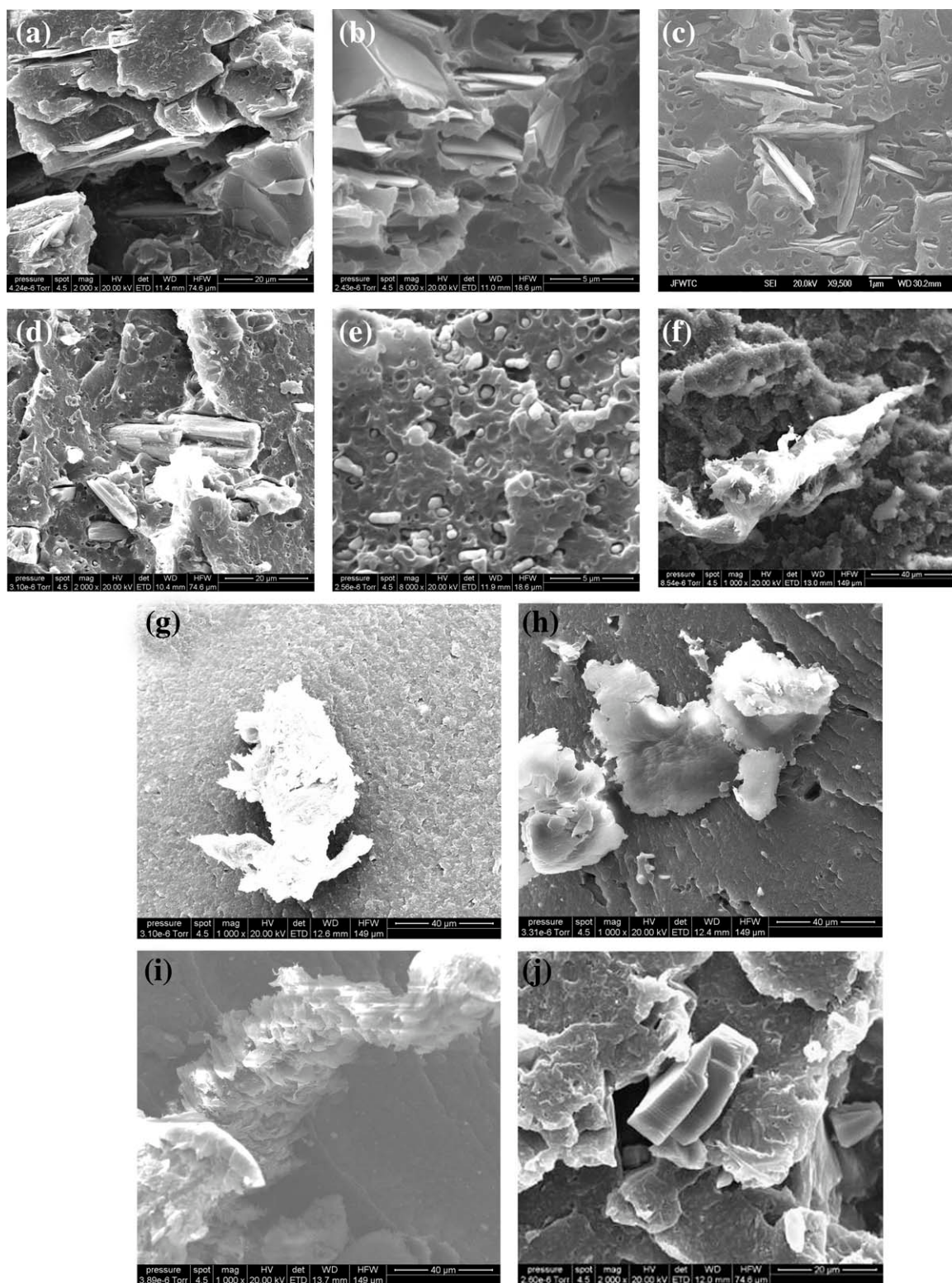
Figure 5 SEM micrographs of cryo-fractured surfaces of polycarbonate composites with different fillers (a) with mica (magnification: 2k), (b) with boron nitride (magnification: 8k), (c) With talc (magnification: 9.5k), (d) with wollastonite (magnification: 2k), (e) with barium sulfate (magnification: 8k), (f) with zinc oxide (magnification: 1k), (g) with zinc sulfide (magnification: 1k), (h) with titanium dioxide (magnification: 1k), (i) with alumina (magnification: 1k), (j) with calcium carbonate (magnification: 2k).
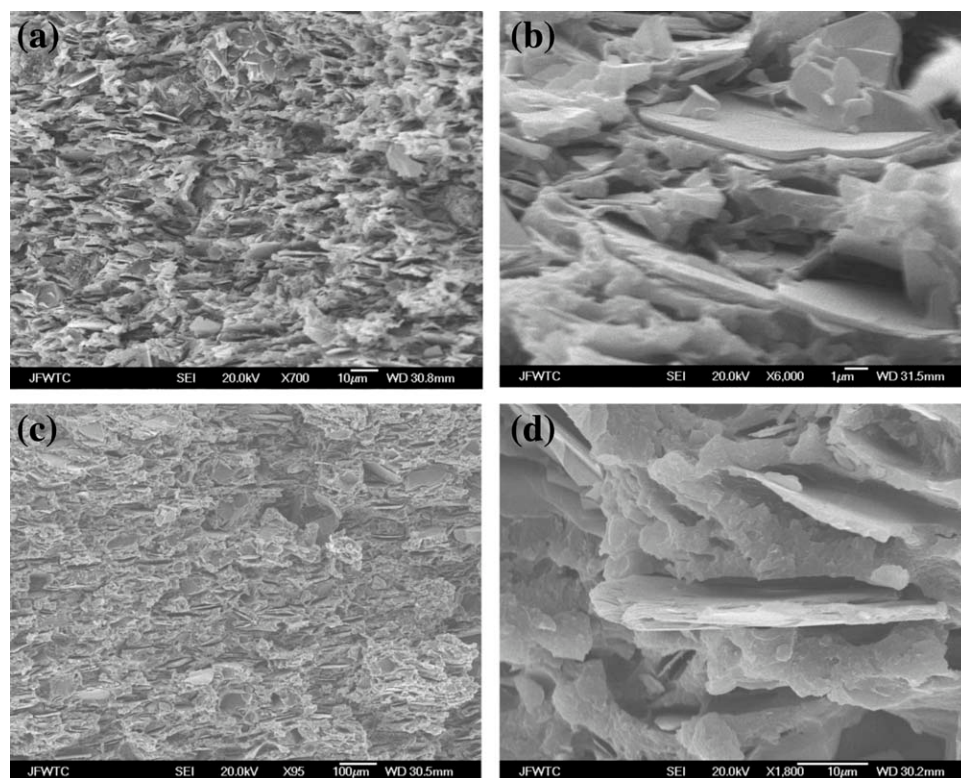
Figure 6 SEM micrographs of cryo-fractured surfaces of polycarbonate composites with boron nitride and mica (a) with boron nitride (magnification: 700), (b) with boron nitride (magnification: 6000), 6(c) with mica (magnification: 95), 6(d) with mica (magnification: 1800).

and hence contributing for reduction of CTE values. The platelet structure of mica and boron nitride additionally provides larger surface areas for favorable polymer–filler interactions. Poor packing of the fillers results into micro-cracks in the composites, which in turn provided slippage planes causing the CTE values remaining unaltered to even increases considerably than the expected values.

To explain the anisotropicity or directional dependencies of the CTE values of the composites with boron nitride and mica, SEM micrographs are taken and the results are provided in Figure 6(a–d). It needs to be emphasized here that the SEM samples are prepared through cryo-fracturing the molded bars along the direction of flow. It is apparent from Figure 6(a–d) that both mica and boron nitride preferentially orient themselves along the direction of flow. It is known that boron nitride and mica are platy fillers with thickness ~ 1 μm and width of ~ 10–50 μm. Therefore, along the direction of flow the specimens with boron nitride or mica experience much higher resistance for thermal expansion compared to that measured in cross-flow direction. As a result the CTE values measured in flow direction came out to be much smaller compared to that in cross-flow. Moreover, much finer distribution of boron nitride [Fig. 6(a,b)] over polycarbonate matrix compared to that of mica [Fig.

6(c,d)] explains higher efficiency of boron nitride to reduce CTE of polycarbonate over mica.

Influence of fillers on mold shrinkage of the composites

The dimensional stability of a few of polycarbonate composites was determined in terms of the mold shrinkages and the results are displayed in Table IV. It can be seen from Table IV that virgin polycarbonate shows mold shrinkage is $\sim 0.7\%$ in both flow and cross-flow directions. Upon incorporation of 5 vol % of mica as well as boron nitride the mold shrinkage gets reduced to become $\sim 0.5\%$. However, with talc, wollastonite, and calcium carbonate the mold shrinkage values do not show substantial

TABLE IV
Influence of Fillers on Mold Shrinkage

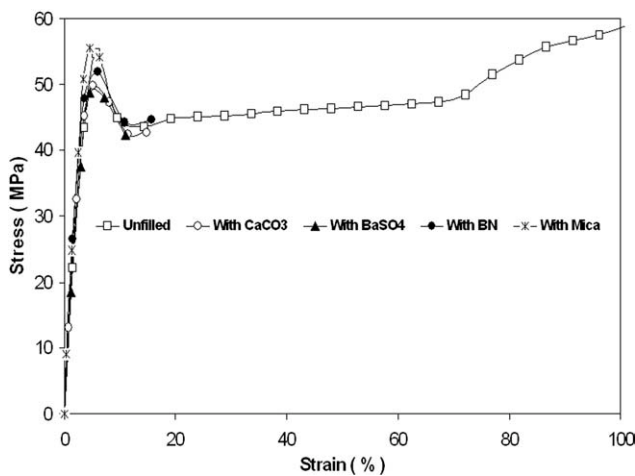| Fillers	Mold shrinkage (%)	
	Flow	Cross-flow
No filler	0.72 ± 0.02	0.74 ± 0.04
Mica	0.52 ± 0.02	0.57 ± 0.02
Boron nitride	0.48 ± 0.01	0.54 ± 0.02
Talc	0.69 ± 0.03	0.73 ± 0.01
Wollastonite	0.67 ± 0.04	0.79 ± 0.03
Calcium carbonate	0.71 ± 0.03	0.78 ± 0.04

Figure 7 Stress–stain curves of unfilled polycarbonate and its composites with calcium carbonate (CaCO$_3$), barium sulfate (BaSO$_4$), boron nitride (BN), and mica.

changes as compared to that of the unfilled. The mold shrinkage data, therefore, corroborates to our observation of alteration of CTE with addition of fillers where we evidenced maximum drop in CTE with mica and boron nitride.

Influence of fillers on tensile performances of composites

Figure 7 demonstrates the representative tensile stress–strain curves of unfilled system and composites with some of the fillers. It is apparent that the tensile behavior of the composites differs depending on the type of fillers used. In general, for all composites, elongation at break decreases substantially as compared to the unfilled. Figure 8 shows the changes in tensile modulus upon addition of different fillers with their identical loading of 5 vol % with respect to the unfilled composition. With almost all the fillers except alumina, the elastic modulus values of polycarbonate composites increases
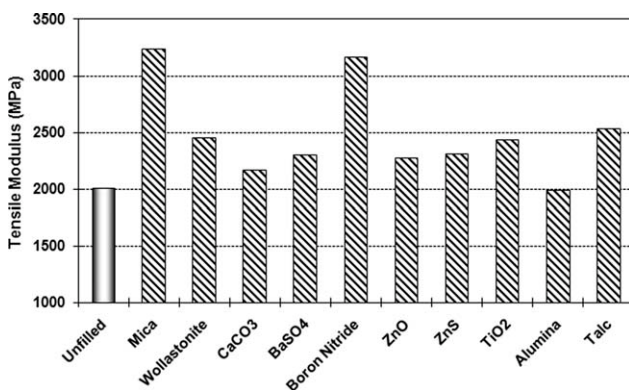

Figure 8 Influence of different fillers (with 5 vol % loading) on tensile modulus of the composites compared to unfilled.
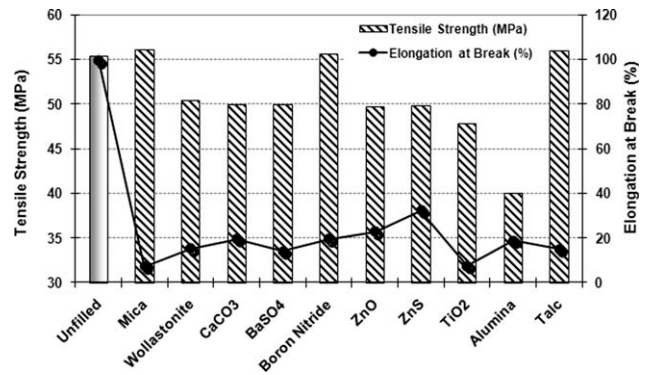

Figure 9 Influence of different fillers (with 5 vol % loading) on tensile strength and elongation at break values of the composites.

upon incorporation of fillers. Unfilled polycarbonate has tensile modulus of $\sim$ 2 GPa. The inorganic fillers evaluated here as such possess much higher modulus than polycarbonate. For example, boron nitride and mica has bulk modulus of $\sim$ 36 and $\sim$ 17.2 GPa, respectively.[5] Calcium carbonate as such possess bulk modulus of $\sim$ 35 GPa. It can be noted that even though modulus of calcium carbonate and boron nitride are comparable, however, their influence on the modulus of the composites are exceedingly different. With 5 vol % of calcium carbonate the modulus of the composite is $\sim$ 2.2 GPa, only marginally ($\sim$ 8%) higher than the unfilled polymer. On the other hand, upon incorporation of 5 vol % of boron nitride, the increment of elastic modulus was substantial. The composite with boron nitride showed modulus of $\sim$ 3.2 GPa: an increment of $\sim$ 60% with respect to the unfilled counterpart. Composites based on mica also demonstrated much higher tensile modulus value of 3.2 GPa, even though mica itself possesses relatively less modulus as compared to calcium carbonate and alumina.[3] Significant increment of modulus with mica and boron nitride can be explained by considering their improved dispersion and better polymer–filler interaction. It has been seen earlier through morphological observations that mica and boron nitride remain embedded and well-dispersed in polymer matrix resulting in enhanced polymer–filler interaction. The platy structures of those fillers also contribute to larger surface areas leading to better interactions with polycarbonate, resulting into substantial improvement in modulus of the composites.

Influence of fillers on tensile strength values of composites vis-à-vis unfilled counter part is displayed in Figure 9. As observed in Figure 9, tensile strength values with mica, boron nitride, and talc remained analogous compared to unfilled specimens. With rest of the fillers evaluated here, the tensile strength values of the composites decrease
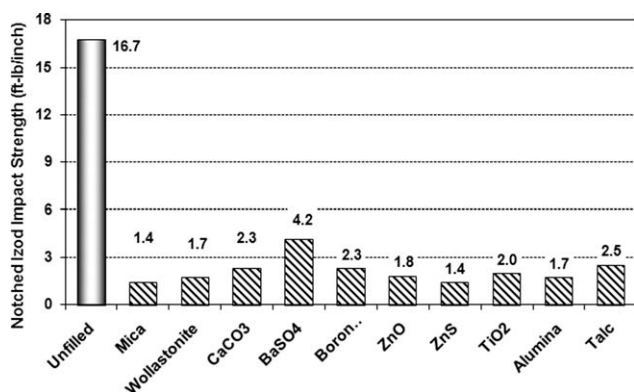
Figure 10 Influence of different fillers with equivalent loading of 5 vol % on notched Izod impact strength of the composites.

upon their incorporation. In polymer composites, the distributions of micro-fillers often become nonhomogeneous during extrusion and molding due to the differences in flow or prevalent filler–filler interaction over limited/no polymer matrix–filler interactions. The uneven distributions of fillers at weld lines in particular, create weak points and cause failure. Consequently the tensile strength reduces. Morphological evaluations clearly indicates that there remains significant inhomogeneity in distributions of most of the fillers evaluated here, which corroborates tensile results of decreasing strength upon incorporation of fillers. For ZnO, ZnS, TiO_2, and alumina with their significant agglomeration in composites [Figure 5(f–i)] cause significant drop in tensile strength. In addition, if there exists any substantial drop in molecular weight caused by degradation, the tensile strength also may reduce. The influence of fillers on molecular weight will be discussed later in this article.

The influence of different fillers on elongation at break values is monitored and the results are provided in Figure 9. It has been noticed that the elongation of break values decrease substantially upon addition of fillers. The elongation at break values were reduced by 60–90% with all the fillers used here as compare to unfilled polycarbonate.

Influence of fillers on notched Izod impact performance of composites

The influence of the fillers on notched izod impact (NII) performance of the composites upon addition of different fillers with respect to unfilled compositions were checked at room temperature and the results are shown in Figure 10. It has been found that the impact performance significantly diminishes upon addition of fillers. It has been established and reported earlier that inorganic particulate fillers with high modulus

typically act as stress concentration and hence their inclusion in polymer matrix cause reduction in impact performance.[26]

Influence of fillers on flow of composites

Figure 11 displays the melt volume rate (MVR) values of the composites with different fillers vis-à-vis the unfilled specimen. It has been found that with most of the fillers evaluated, the flow increases to a significant extent except for boron nitride. Unfilled specimens demonstrated MVR of 9.9 cm^3/10 min whereas the composite sample with 5 vol % [∼ 9 wt %] of boron nitride showed MVR of 8.4 cm^3/10 min: a reduction of ∼ 20%. With rest of the fillers, MVR increases significantly. For example with 5 vol % of mica, MVR values have changed from 9.9 cm^3/10 min (unfilled) to 32.4 cm^3/10 min leading to an increment of ∼ 200%. The increase in flow with mica can be explained by considering its plasticization effect, owing to its platy geometry. The possibility of decrease in molecular weight of polycarbonate and subsequent increase in flow in presence of mica cannot also be ruled out. It has been seen from Figure 11 that the flow (MVR) increases tremendously, as high as 600–800% with ZnO, ZnS, TiO_2, and alumina. This massive increase in flow poses an obvious doubt about the stability of the polycarbonate matrix upon incorporation of those fillers. It is known that polymers can undergo mechano-chemical degradations at elevated temperatures.[27] Untreated inorganic fillers can further promote the degradation through catalyzing depolymerization of polycarbonate, particularly at elevated temperatures.[28] It can be emphasized here that during extrusion, the polymer components are subjected to heat exposure only for 15–20 s. In molding stage, the time of heat exposure increases up to a minute. During MVR measurement, the
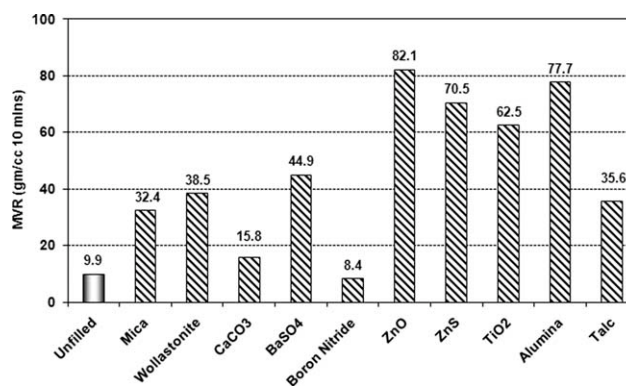

Figure 11 Influence of different fillers (with 5 vol % loading) on flow performance (melt volume rate) of the composites compared to unfilled.

TABLE V
Influence of Fillers on Molecular Weight

Fillers		Specimens	
		Pellets	Molded bars
No filler	M_n	19,351	18,967
	M_w	50,616	49,576
Mica	M_n	18,064	17,297
	M_w	48,848	47,146
Boron nitride	M_n	19,480	18,752
	M_w	50,934	49,515
Talc	M_n	15,429	14,043
	M_w	42,942	37,605
Wollastonite	M_n	15,096	14,201
	M_w	45,073	41,002
Calcium carbonate	M_n	18,064	17,297
	M_w	48,848	47,146
Barium sulphate	M_n	16,444	14,395
	M_w	44,764	40,488
Zinc oxide	M_n	15,317	14,161
	M_w	41,867	35,792
Zinc sulfide	M_n	14,908	13,270
	M_w	41,200	36,533
Titanium dioxide	M_n	15,223	14,653
	M_w	34,953	31,660
Alumina	M_n	15,406	15,340
	M_w	40,413	35,668

specimens are subject to 300°C for more than 6 min under load. Therefore, the probability of degradation of molecular weight at high temperature becomes reasonably high during MVR test.

Influence of fillers on molecular weights

The number average (M_n) and weight average molecular weights (M_w) of polycarbonate in the composites upon addition of fillers are checked as the extruded pellets as well as in molded bar and are reported in Table V. For comparison, the molecular weight data for unfilled specimens are also provided. It can be seen that the M_w of unfilled polycarbonate is $\sim$ 50,000, which remains almost unaltered before and after molding. Molecular weight of extruded pellets of composites with zinc oxide, zinc sulfide, $BaSO_4$, and alumina are all showing significantly less ($\geq$20%) molecular weights compared to the unfilled specimens. When considered the molecular weight of the extruded pellets as such, with TiO_2 in the formulations, the maximum reduction ($\sim$ 36%) in polycarbonate molecular weight with respect to unfilled composition. For those fillers the M_w showed further plunge after molding. The reduction in molecular weight of polycarbonates in presence of $BaSO_4$, ZnO, ZnS, TiO_2, and Alumina corroborates to the unusually high flow of their composites shown earlier in Figure 11. In presence of untreated zinc oxide and TiO_2, the reduction in molecular weight of polycar-

bonate is documented earlier[28] in literature. With mica, wollastonite, and calcium carbonate the changes in molecular weight are less than or equal to 10%, while measured in pellets. After molding, the molecular weights for these composites have reduced to some extent. With boron nitride as fillers no appreciable change in M_w has been monitored in pellets as well as in molded bars as compared to those of unfilled specimens.

Influence of fillers on glass transition temperatures

The effect of fillers on the glass transition temperature (T_g) of the composites is shown in Table VI. The T_g of the composites were measured in extruded pellets as well as in molded bars. The unfilled polycarbonate showed T_g of 151.8°C in pellets and 151.4°C in molded bars. With mica, boron nitride, and calcium carbonate as fillers, the T_g values remain comparable to that of unfilled, within a maximum reduction of $\sim$ 1°C when measured in pellets and $\sim$ 2°C, when the measurement was carried out in molded bars. With boron nitride, the T_g values were found to be closest to the unfilled. With rest of the fillers such as talc, wollastonite, zinc oxide, zinc sulfide, $BaSO_4$, and alumina, the glass transition temperature of polycarbonate reduced significantly. The maximum reduction in glass transition temperature was observed with zinc sulfide. In the pellets, the T_g value was reduced to about 6°C in presence of zinc sulfide and in molded bars the reduction was about 9°C as compared to unfilled. The drop in glass transition temperature further substantiates our observation of reduction in molecular weight of polycarbonate in presence of certain fillers. The dependency of T_g to molecular weight is typically expressed mathematically by Fox-Flory equation[4] as,

$$T_g = T_g^\infty - K \times M^{-1} \qquad (5)$$

TABLE VI
Influence of Fillers on Glass Transition Temperature

Fillers	T_g (°C)	
	Pellets	Molded bars
No filler	151.8	151.4
Mica	150.4	149.5
Boron nitride	152.1	151.2
Talc	146.8	144.4
Wollastonite	146.3	144.7
Calcium carbonate	150.4	149.5
Barium sulphate	148.4	145.0
Zinc oxide	146.6	144.5
Zinc sulfide	146.0	142.8
Titanium dioxide	146.5	145.5
Alumina	146.8	146.6

where T_g is the glass transition temperature of the polymer with molecular weight M, T_g^∞ is the limiting glass transition temperature at infinite molecular weight and K is a constant.

CONCLUSIONS

The following conclusions can be drawn from the experimental results:

- Boron nitride and mica can reduce the CTE in both flow and cross-flow directions in polycarbonate. The reduction in CTE along the direction of flow is by far more pronounced than that measured normal to flow (cross-flow).
- The homogeneous distributions of mica and boron nitride over polycarbonate matrix contribute to their capabilities in reducing CTE.
- Most of the particulate fillers evaluated here contribute in increasing tensile modulus of the composites, however, at the expense of ductility.
- With most of the fillers evaluated here, flow increases substantially upon their addition, primarily associated to a significant decrease in molecular weight. For fillers such as mica, the increment in flow of the composites can also be due to its plasticization effect.

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