

Control of Coefficient of Thermal Expansion in Elastomers Using Boron Nitride

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ABSTRACT: The thermal expansion properties of three commercial elastomers; Pebax[®], Estane[®] and Hytrel[®] modified with 2.5–10 wt % boron nitride were investigated. The glass transition temperatures of the filled materials were relatively unaffected; however boron nitride did effectively reinforce all the three elastomers as seen by dynamic mechanical analysis and tensile tests. The coefficients of thermal expansion

of the composite materials do not obey the rule of mixtures and show a large decrease without the loss of ductility typically associated with filled elastomers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5153–5161, 2006

Key words: elastomers; composites; thermal properties; mechanical properties

INTRODUCTION

Modification of thermoplastic polymers by the addition of different organic and inorganic fillers is an effective method for generating a nearly limitless array of new materials with unique properties. The fillers used in these systems differ in physical and chemical properties as well as in their size and geometries. Inorganic fillers constitute a significant group of fillers used for reinforcing and toughening of thermoplastic polymers.

It is well-known that the glass transition of high polymers is virtually unaffected by the incorporation of reinforcing fillers at technologically important loadings.¹ In spite of this observation, several authors have proposed that fillers significantly impede segmental motion in the rubbery and transition regions of viscoelastic response.^{2,3} It is postulated that adsorption of polymer molecules on filler surfaces occurs with considerable loss in segmental mobility, affecting a substantial fraction of the total polymer volume and causing a shift in the relaxation spectrum toward higher temperatures. It would seem that such a mechanism would result, if not in an actual increase in the experimentally observed glass transition, then at least in the change in the coefficient of thermal expansion, the latter being related to the free volume of the system and hence to the mobility of the polymeric chain segments.

Fillers generally used for control of coefficient of thermal expansion of elastomers, include mica, chalk, kaolin, lampblack, carbon black, and glass fibers. Voevodskaya and Bartenev have shown that the addition of up to 30 vol % chalk to elastomers resulted in a linear decrease in the coefficient of thermal expansion below the glass transition and a negligible change above the glass transition.⁴ Faehndrich and Boehlke have reported the use of glass fibers in polyurethane coatings to reduce the coefficient of thermal expansion of elastomers.⁵

This study reports the use of boron nitride as a filler to reduce the coefficient of linear thermal expansion (CLTE) of commercial elastomers. Boron nitride possesses a very low coefficient of thermal expansion, which can increase the dimensional stability of elastomers and can also be used as a processing aid due to its unique, sheet-like structure.⁶ Boron nitride is also a high strength material with a bulk modulus of 36 GPa⁷; due to its high strength, it also has the potential to reinforce elastomers. Finally, because of their fine particle size, boron nitride can also improve the surface finish of the composites.

EXPERIMENTAL

Thermoplastic elastomers used for testing included Pebax[®] (a trademark of Arkema, Grade 5533, Arkema, block polyether block amide elastomer), Estane[®] (a trademark of Noveon, Grade 58,810, Noveon Inc, polyether based polyurethane) and Hytrel[®] (a trademark of Dupont, Grade 4556, Dupont, polyether block polyester elastomer). Each material was obtained directly from its manufacturer and used as supplied. The materials were dried at appropriate temperatures (100°C/

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48 h) before processing. Boron nitride was obtained from ZYP coatings with a mean particle size between 4 and 8 μm and was used in this study as a filler to reduce the coefficient of linear thermal expansion of these thermoplastic elastomers.

Samples were first run on a DACA corotating twin screw microextruder (model 20000) at 100 rpm (4 g batch size) to check general processing characteristics, then were scaled up on a Werner and Pfleiderer model ZSK-30, with screw extruder, with a diameter of 30.7 mm and length 880 mm. Corotating screws with two mixing zones were assembled and were operated at 150 rpm, to prepare the composites. The processing conditions of the samples were set as listed in Table I.

The extruded samples were pelletized, re-dried, and injection molded into standard flexural bars of $0.5 \times 5 \times 0.125$ in. (ASTM D-790) dimensions, as part of a two cavity family mold, on a Boy 22-S injection 22 ton molding machine. These molded bars were used to determine the coefficient of linear thermal expansion of the materials.

Characterization

Thermogravimetric analysis (TGA) was performed on the flex bars, on a Mettler-Toledo TGA (Model 851e), to determine the actual weight fraction of boron nitride incorporated into the composites. Thermomechanical properties of the composites were characterized using a Tritec 2000 dynamic mechanical analyzer (Triton Technologies). Tensile tests were carried out on an Instron 5565 universal tester using mechanical grips and a strain rate of 100% per minute. Tensile samples were cut from compression-molded films using a dog bone shaped die according to ASTM D-638. The length of the test area was 10 mm and the width was 3.2 mm. All samples were stretched until break. The coefficients of linear thermal expansion of the samples were measured using the following method: the injection-molded flex bars were initially measured along their length at room temperature, then were placed in an oven at preset temperatures (the temperatures used in this study were 75, 100, and 135°C; the bars were placed in the oven for 2 h under vacuum to minimize degradation) and sample lengths were subsequently remeasured. Samples were imaged using a JEOL JSM 840A scanning electron microscope. The flex bars were imaged along the thickness as well as along the width.

TABLE I
Processing Conditions for Hytrel, Pebax,
and Estane (°C)

Material	Zone 1	Zone 2	Zone 3	Zone 4	Die zone
Hytrel 4556	160	180	210	220	230
Pebax 5533	130	150	180	210	220
Estane 58810	120	140	160	170	180

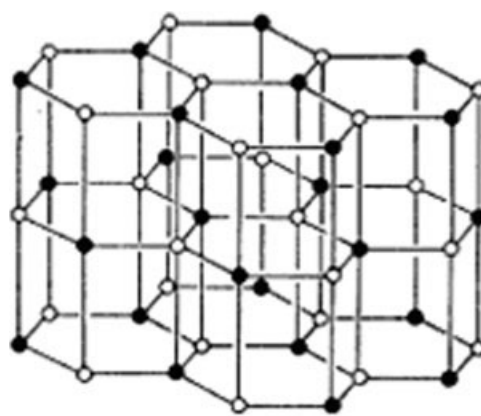


Figure 1 Structure of Boron Nitride. (●) nitrogen and (○) boron.

RESULTS AND DISCUSSION

Processing of boron nitride composites

The boron nitride used in this study has a hexagonal lattice structures similar to that of graphite as shown in Figure 1.⁸ It is available as a fine white powder. Because of its graphitic structure, boron nitride can be cleaved or sheared easily, resulting in good lubricating properties and a low coefficient of friction (0.2–0.7).⁹ Not surprisingly, the lubrication properties of boron nitride translated to lower required extruder torque, compared to unfilled systems, when added to elastomers. The addition of boron nitride also results in white composites with a smooth surface finish. The ability of boron nitride plates to shear easily, along with the ease of processing is an obvious advantage over conventional glass fibers used for reduction of thermal expansion coefficient, which result in a rough surface and are susceptible to breaking during processing. The addition of glass fibers during processing also tends to increase the viscosity of the polymer and makes conventional processing more challenging.

Thermogravimetric analysis

TGA curves for Hytrel, Pebax, and Estane composites with different weight percentages of boron nitride

TABLE II
Char Yields of Elastomer/BN Composites

Blend composition	Char yield % at 600°C	wt % BN
Hytrel	1.61	–
Hytrel 2.5 wt % BN	3.87	2.26
Hytrel 10 wt % BN	10.97	9.36
Pebax	0.90	–
Pebax 2.5 wt % BN	4.49	3.59
Pebax 7.5 wt % BN	7.28	6.38
Estane	7.37	–
Estane 2.5 wt % BN	9.97	2.60
Estane 7.5 wt % BN	14.78	7.41

TABLE III
Composite Densities and Volume Fraction of Matrix and Filler
of Elastomer BN Composites

Blend composition	Matrix volume fraction	Filler volume fraction	Calculated density (g/cc)	Measured density (g/cc)
Hytrel	—	—	—	1.12
Hytrel 2.5 wt % BN	0.989	0.011	1.13	1.14
Hytrel 10 wt % BN	0.952	0.048	1.18	1.18
Pebax	—	—	—	1.01
Pebax 2.5 wt % BN	0.984	0.016	1.03	1.03
Pebax 7.5 wt % BN	0.979	0.021	1.05	1.05
Estane	—	—	—	1.11
Estane 2.5 wt % BN	0.987	0.013	1.12	1.14
Estane 7.5 wt % BN	0.962	0.038	1.15	1.16

were run to determine the exact amount of boron nitride incorporated in the elastomers. The actual weight percentages of boron nitride incorporated into the elastomeric composites were calculated by subtracting the char yield of pure elastomers from the composites. Since boron nitride does not degrade and has a melting point of over 1500°C, the difference in weight indicates the weight percentage of boron nitride in the composites. The char yields for the composites are tabulated in Table II.

In all future theoretical calculations, the experimentally measured values of weight fraction of boron nitride will be used. The weight percentages of the elastomer and boron nitride in the composites were converted into their respective volume fractions using the following formula¹⁰

$$V_f = \frac{\rho_c W_f}{\rho_f} \quad (1)$$

$$V_m = \frac{\rho_c W_m}{\rho_m} \quad (2)$$

where, V_m and V_f are the volume fraction of the matrix and the filler respectively, ρ_m , ρ_f and ρ_c are the densities of the matrix, filler, and composite respectively, and W_m and W_f are the weight fractions of the matrix and filler in the composite respectively. The densities of the composites were directly measured from the weight and the dimensions of the flexural bars. The calculated composite densities along with the volume fraction of the fillers and matrices are listed in Table III. The density of boron nitride was taken as 2.27 g/cc while those of the matrix materials were measured directly from the flexural bars. The calculated and the measured densities are in close agreement with each other, indicating no change in the densities of either elastomer or boron nitride when blended.

Tensile testing

Figure 2 shows the tensile behavior of the Hytrel with varying percentages of boron nitride. The results are

typical of a marginal level of reinforcement accompanied by a small decrease in elongation at break. It was however interesting to note that even with 15 wt % boron nitride in Hytrel, the material still retained significant extensibility. The elongation at break in these systems steadily decreased from about 2200% strain in unfilled Hytrel to about 1000% strain in the 15% boron nitride composite. This decrease in elongation may be caused due to two reasons: (a) flaws created by the filler particles and/or (b) increased interactions between the filler and the matrix which decrease chain mobility.¹¹ Other fillers, such as short glass fibers, result in > 90% reduction in the original elongation at break of elastomeric matrix polymers.¹² Mica and glass fiber fillers also reduce elastomer impact strengths, rendering them brittle. In the present study, all of the composites exhibited significant toughness by visual inspection.

The modulus of an elastomer is usually expressed as a function of strain using the relation,¹³

$$G = \frac{\sigma}{\lambda - 1/\lambda^2} \quad (3)$$

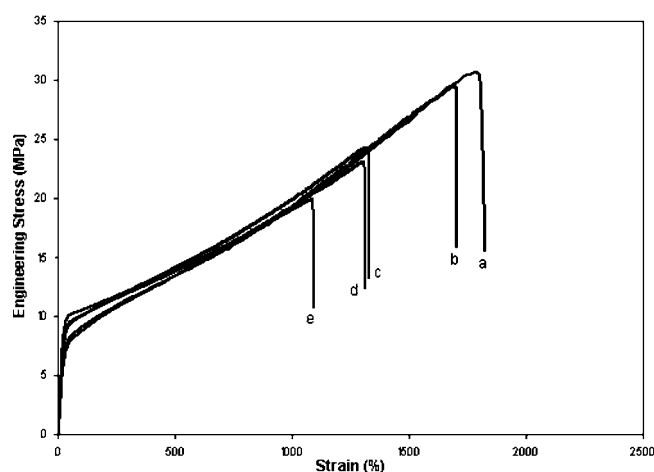


Figure 2 Tensile properties of Hytrel/boron nitride composites. (a) Hytrel, (b) 2.5% BN, (c) 7.5% BN, (d) 10% BN, and (e) 15% BN.

TABLE IV
Tensile Moduli of Elastomer/Boron Nitride Composites

Blend composition	E' (MPa) modulus 100%	% Change
Hytrel	15.4 ± 0.5	—
Hytrel 2.5% BN	15.8 ± 0.4	2.6
Hytrel 7.5% BN	17.6 ± 0.2	14
Hytrel 10% BN	17.6 ± 0.4	14
Hytrel 15% BN	18.5 ± 0.5	20
Pebax	24.9 ± 0.4	—
Pebax 2.5% BN	24.4 ± 0.9	-2
Pebax 7.5% BN	26.4 ± 0.4	6
Estane	8.37 ± 0.3	—
Estane 2.5% BN	11.72 ± 0.5	40
Estane 7.5% BN	13.45 ± 0.9	60

where σ is the stress in MPa, λ is the draw ratio, and G is the shear modulus of the elastomer. The tensile modulus E is then equal to $3G$ and the values of tensile modulus at 100% elongation for the three elastomers are listed in Table IV; there is an increase in the tensile modulus of the material, with increasing in boron nitride content. Averages of five samples along with the standard deviation are reported.

Similar results were obtained with Pebax and Estane composites. Figures 3 and 4 illustrate the tensile responses of Pebax and Estane, respectively, with various loadings of boron nitride. A significant decrease in the elongation at break of Estane was observed with boron nitride addition, while this decrease was smaller in the Pebax system. Sample slippage within the test fixture occurred in each of the Estane control samples (at $\sim 1800\%$ strain); hence, the data plotted does not show the elongation at break for the pure Estane.

Among the three classes of elastomers investigated, Estane composites showed the maximum increase in the tensile modulus and improvements in the yield stress and yield strain among the three elastomers investigated. While Estane is an amorphous elastomeric thermoplastic, Pebax and Hytrel are semicrystalline

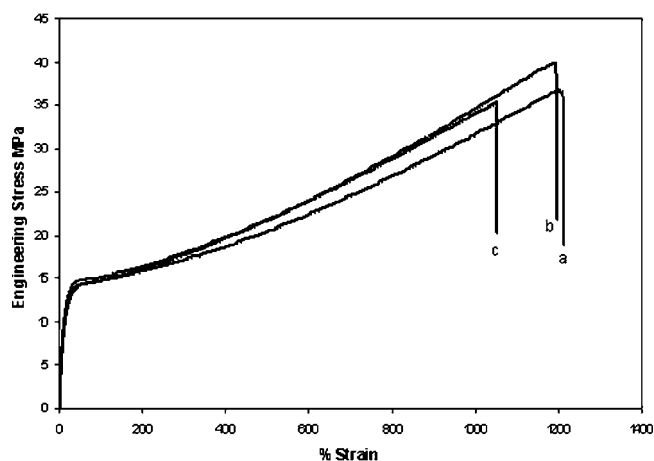


Figure 3 Tensile properties of Pebax/boron nitride composites (a) Pebax, (b) 2.5% BN, and (c) 7.5% BN.

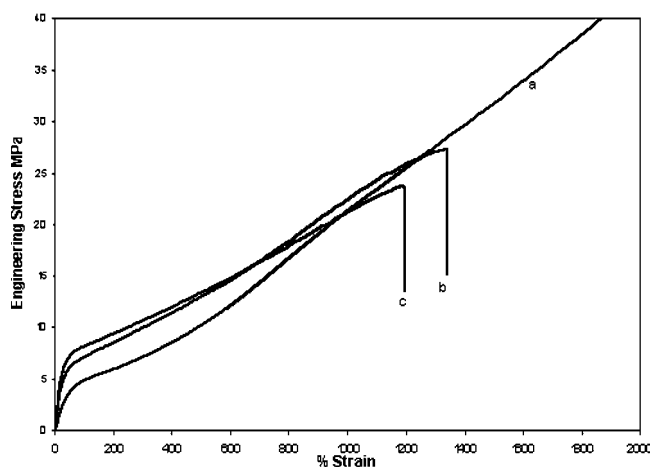


Figure 4 Tensile properties of Estane/boron nitride composites (a) Estane, (b) 2.5% BN, and (c) 7.5% BN.

thermoplastic elastomers. These materials have two glass transition temperatures: one below room temperature for the soft segment and the other for the semicrystalline hard segment—often above room temperature. The presence of these semicrystalline domains may diminish the reinforcing effect of boron nitride. In case of Estane, there are no rigid domains that can act as physical crosslinks and reinforce the soft segments. Hence, boron nitride is more effective in reinforcing Estane compared to the other two elastomers.

In all composites investigated, a high degree of elongation was retained. We believe that this is a result of preferential alignment of the boron nitride platelets, which aids chain slippage and thus helps in retaining high extensibility in these materials. This hypothesis will later be supported by morphological characterization of the composites.

It is also reasonable to assume that during compression molding, majority of the boron nitride plates will be aligned along the plane of the film since the injection-molded bars were compression molded. These bars already have orientation effects as seen by SEM. The results from the tensile measurements and the DMA should therefore compare reasonably with thermal expansion measurements made using the flexural bars.

Scanning electron microscopy

Images of the elastomer/boron nitride composite cross sections are presented in Figures 5–7. Each composition was imaged along the cross section of the width as well as along the thickness of the molded bars. A high degree of filler particle orientation is evident for each of the molded elastomer/boron nitride systems.

The physical properties of injection-molded specimens are known to depend on direction within the specimen relative to the polymer melt flow, which occurs during the molding process.¹⁴ There have been

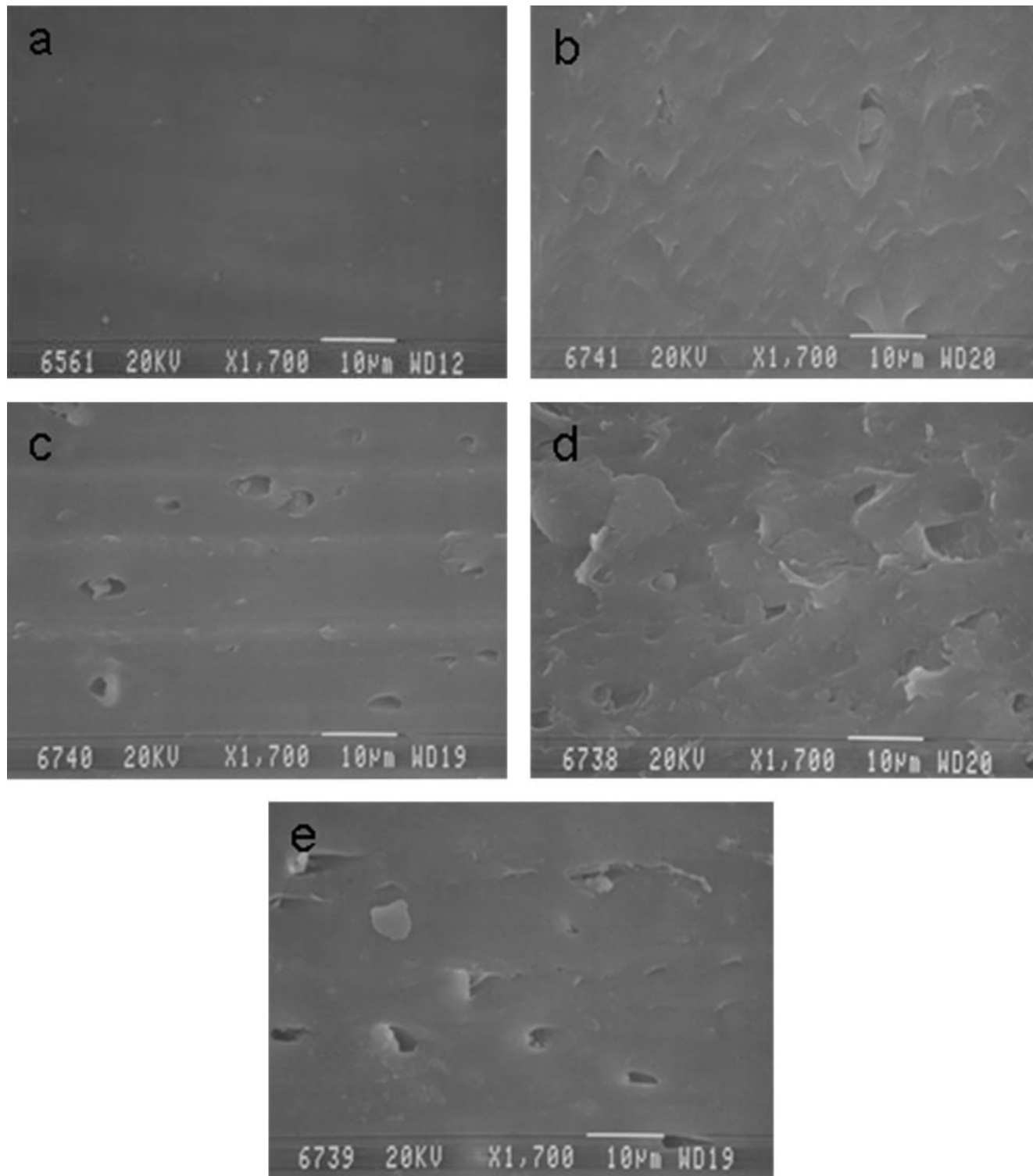


Figure 5 Scanning electron micrographs of Hytrel/boron nitride composites. (a) Hytrel cross section, (b) Hytrel 2.5% BN width cross section, (c) Hytrel 2.5% BN thickness cross section, (d) Hytrel 10% BN width cross section, and (e) Hytrel 10% BN thickness cross section.

many studies carried out which describe how anisotropic particles align during flow.^{15,16} Processing directions are commonly described by an orthogonal coordinate system identified by the flow direction, transverse direction, and normal direction. The properties

of injection-molded polymer nanocomposites are expected to be sensitive to direction, especially when the high aspect ratio particles, such as boron nitride platelets, are dispersed in the polymer. Depending on the flow fields encountered during injection molding,

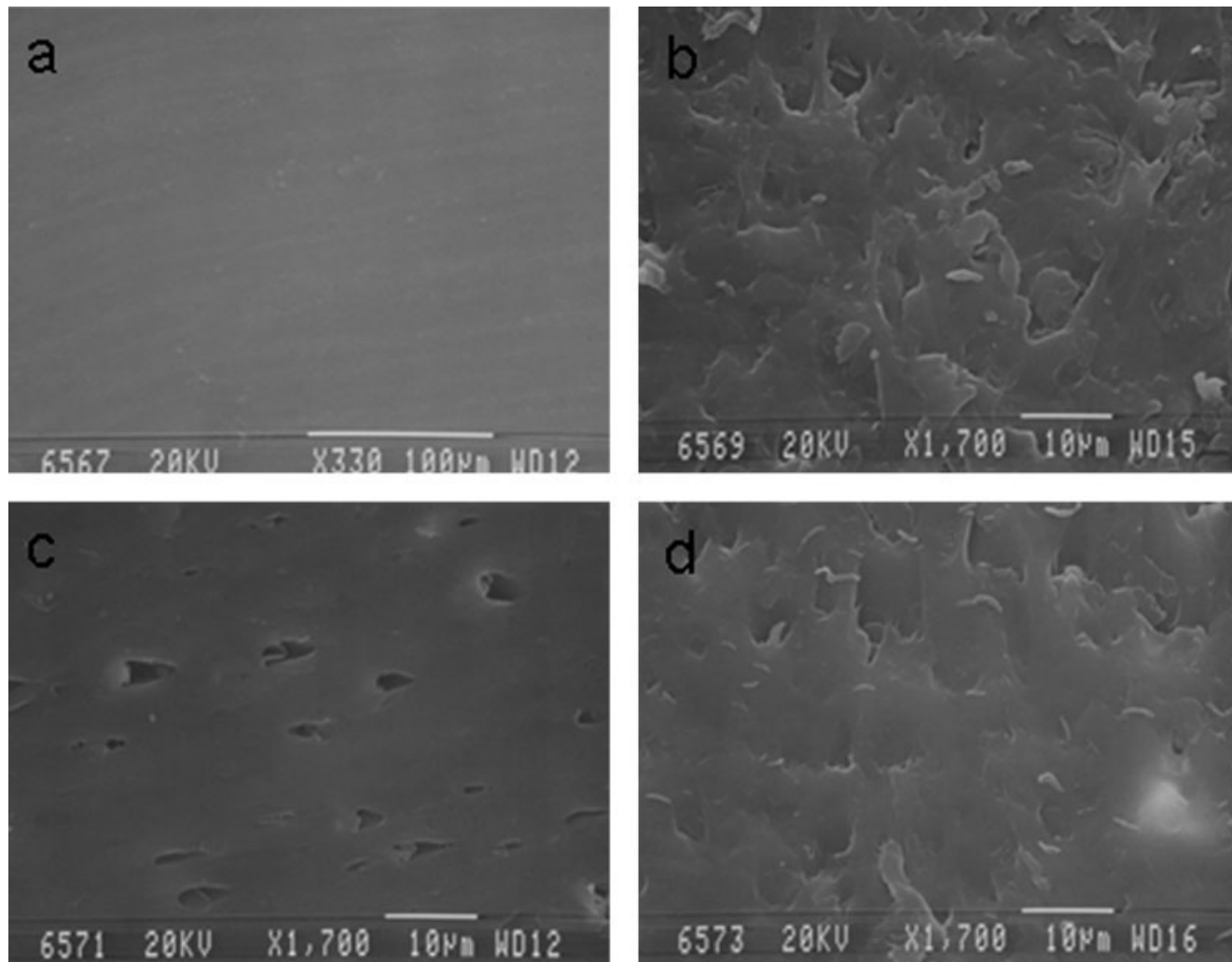


Figure 6 Scanning electron micrographs of Pebax/boron nitride composites. (a) Pebax cross section, (b) Pebax 2.5% BN width cross section, (c) Pebax 2.5% BN thickness cross section, (d) Pebax 7.5% BN width cross section, (e) Pebax 7.5% BN thickness cross section.

these platelets may have a wide range of orientations within the polymer matrix. The thermal expansion of a composite will greatly depend on the average orientation of the platelets, i.e., whether the surfaces of platelets are parallel to flow direction and to transverse direction or to the normal direction. Therefore, the details of platelet orientation must be carefully considered to understand the thermal expansion behavior of nanocomposites.

Glass fibers are commonly added to polymer matrices to reduce the coefficient of thermal expansion of polymers in addition to increasing stiffness. Layered silicates seem attractive for this purpose owing to their high modulus, high aspect ratio, and low coefficient of thermal expansion; in addition, they are likely to be less detrimental to surface finish and ductility than conventional fillers. For the same reason mentioned with silicates, boron nitride was used in the present study to improve the surface finish of the composite material, while at the same time improving the

dimensional stability and mechanical performance of elastomers.

Since boron nitride has a high aspect ratio, and a very low coefficient of thermal expansion along the platelet direction, a considerable reduction in the CLTE of elastomer/BN composites could be expected in the injection molded specimens when the platelets are oriented. The SEM images clearly reveal that there is significant orientation of the boron nitride platelets along the direction of flow, resulting in greater dimensional stability in these systems.

Coefficient of thermal expansion

The rule of mixtures can be used as a first approximation for theoretically estimating the coefficient of linear thermal expansion of the composites,¹⁷ which states:

$$\alpha_c = (1 - \phi)\alpha_m + \phi\alpha_p \quad (4)$$

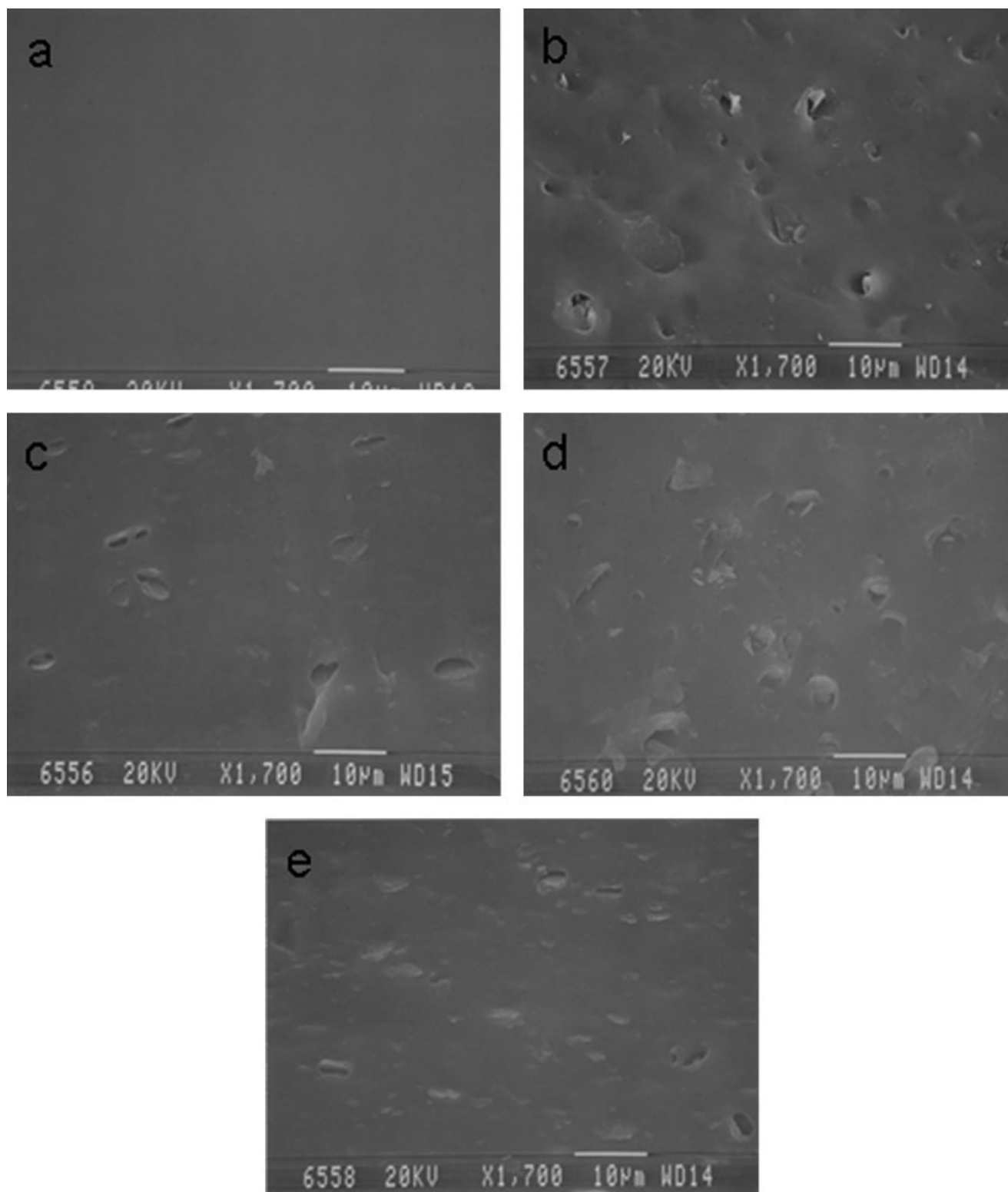


Figure 7 Scanning electron micrographs of Estane/boron nitride composites (a–e). (a) Estane cross section, (b) Estane 2.5% BN width cross section, (c) Estane 2.5% BN thickness cross section, (d) Estane 7.5% BN width cross section, (e) Estane 7.5% BN thickness cross section.

where α_c , α_m , and α_p represent the CLTE values of the composite, the matrix, and the particle (filler), respectively, and ϕ is the volume fraction of the fil-

ler. The CLTE of boron nitride is reported as $38 \times 10^{-6}/^{\circ}\text{C}$ parallel to the platelet direction and $-2.7 \times 10^{-6}/^{\circ}\text{C}$ in the perpendicular direction.⁶ Thermal

TABLE V
Literature Values for CLTE of Hytrel, Pebax, and Estane

Polymer	Coefficient of thermal expansion ($^{\circ}\text{C}$)
Hytrel 4556	1.72×10^{-4} (Ref. 18)
Pebax 5533	1.70×10^{-4} (Ref. 19)
Estane 58810	1.20×10^{-4} (Ref. 20)

expansion coefficients of the three elastomers obtained from literature are listed in Table V. These values differ significantly from those obtained by our experiments (Table VI). The values obtained from the literature are generic values of the elastomers whereas the material being processed is of a specific grade material used, which could be one of the reasons for the different values of coefficient of thermal expansion obtained in our experiments.

The rule of mixtures model was modified by Turner et al. to take into account the mechanical interactions between different materials within a composite.²¹ Based on the assumption that all phases in the composite have the same dimensional changes with temperature, he derived a relationship that is expressed as

$$\alpha_c = \frac{(1 - \phi)E_m\alpha_m + \phi E_p\alpha_p}{(1 - \phi)E_m + \phi E_p} \quad (5)$$

where E_p and E_m are the elastic modulus of the particle and matrix respectively. Inserting the measured values of CLTE and elastic modulus (obtained from dynamic mechanical testing; Table VII) of the pure materials, the CLTE of the composites can be calculated and these results are also tabulated in Table VI.

Figure 8 and Table VI present the experimentally measured values of the reduction in CLTE as a function of filler content in the elastomer composites. These values were calculated using the following procedure; an average of at least three samples was measured at each temperature. The change in length of the specimens with respect to change in temperature (reference

temperature being room temperature) were plotted and the slope of the line was taken as the thermal expansion coefficient of the elastomers. A significant, linear reduction in the CLTE of elastomers as a function of boron nitride loading was observed. As can be seen from the table, the values recorded experimentally compare reasonably with calculated values using the Turner equation, indicating a modest degree of interaction between boron nitride filler particles and the elastomers.

Dynamic mechanical analysis

Dynamic mechanical analysis was used to obtain the elastic modulus of the elastomers as well as to see the affect of boron nitride on the thermomechanical properties of the composites. The elastic modulus values obtained for the pure elastomers are listed in Table VII and were used to calculate the CLTEs of the composite materials using the Turner equation.

Addition of boron nitride results in small improvements in the thermomechanical properties of the composites. The elastic modulus of the composites in the glassy and the rubbery plateau was marginally higher than the unmodified elastomers. There is however no increase in the glass transition temperatures of these elastomers with addition of boron nitride. This would lead to the conclusion that boron nitride does not decrease chain mobility or reduce the free volume of the elastomers. The observed behavior of increase in elastic modulus with increase in weight fraction of boron nitride is also consistent with the theory of increase in the interfacial area between boron nitride and the elastomer.

Boron nitride is known to be an excellent thermal sink due to its high thermal conductivity.²² We believe that when these elastomeric composites are heated, a significant amount of heat is absorbed by boron nitride, thus reducing the heat intake by the polymer. This would explain the decrease in the thermal expansion of the composites, even though there is no decrease in the glass transition temperatures.

TABLE VI
Measured and Calculated CLTE Values for Elastomer/Boron Nitride Composites

Blend composition	Rule of mixtures	Turner equation measured	CTE ($^{\circ}\text{C}^{-1}$)	% Change in CTE
Hytrel Control			1.17E-04	0.00
Hytrel 2.5% BN	1.16E-04	1.07E-04	1.01E-04	-13.6
Hytrel 10% BN	1.13E-04	8.66E-05	9.15E-05	-21.7
Pebax Control			1.36E-04	0.00
Pebax 2.5% BN	1.34E-04	1.19E-04	1.06E-04	-22.0
Pebax 7.5% BN	1.34E-04	1.15E-04	9.65E-05	-29.0
Estane Control			1.36E-04	0.00
Estane 2.5% BN	1.35E-04	1.23E-04	1.12E-04	-17.6
Estane 7.5% BN	1.32E-04	1.05E-04	1.00E-04	-26.4

TABLE VII
Measured Elastic Modulus Values of Elastomers

Material	Elastic modulus (GPa)
Hytrel 4556	2.9
Pebax 5533	2.9
Estane 58810	3.1

CONCLUSIONS

Boron nitride elastomeric composites show significant reductions in coefficients of linear thermal expansion as compared pure elastomers. The reduction in the CLTE is a result of lower thermal conductivity of boron nitride, favorable interactions between matrix and filler and the ability of boron nitride to act as a thermal sink. Tensile modulus of the elastomers increases significantly with the addition of boron nitride with the highest effect seen in Estane. Boron nitride particles also preferentially align along the direction of flow

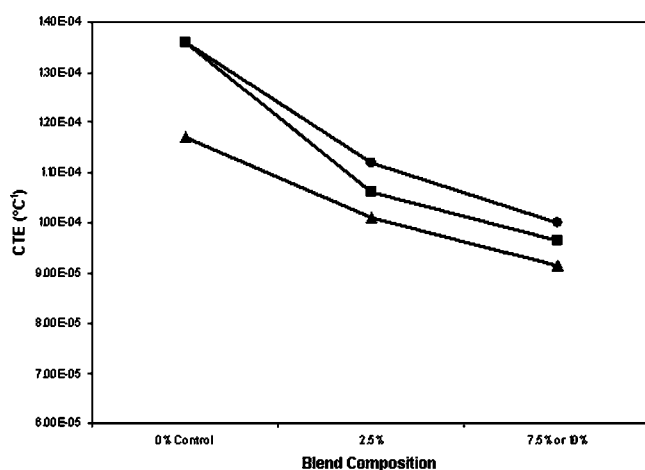


Figure 8 CLTE versus wt % BN for elastomer/boron nitride composites (▲) Hytrel, (■) Pebax, and (●) Estane.

during injection molding, as demonstrated by scanning electron microscopy.

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