

# Characterization of Thermoplastic Blends as Binders for Ceramics

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**Molded ceramics with simple poly(ethylene–ethylacrylate) thermoplastic binders suffer severe distortion during heating associated with relaxation of polymer conformations, but blends of poly(ethylene–ethylacrylate) containing poly(isobutyl methacrylate) resins and polyethylene glycol and mineral additives do not suffer distortions. The polymer blends are characterized using polarized light microscopy and thermal analysis. Crystallinity and spherulite size of the binder are reduced by blending and by the addition of ceramic powder. Plasticizer additives polyethylene glycol and mineral oil phase separate in poly(ethylene–ethylacrylate), but are compatibilized by additions of poly(isobutyl methacrylate). The compatibilized plasticizers are able to relax the polymer conformations after molding, avoiding distortion on subsequent heating.**

## I. Introduction

**B**INDERS play a key role in ceramic processing, and there is an extensive literature on polymers as binders.<sup>1–3</sup> Most literature is concerned with binder removal from the green body<sup>4–6</sup> usually emphasizing transport phenomena,<sup>6,7</sup> degradation reactions,<sup>8,9</sup> or, rarely, dimensional changes.<sup>10,11</sup> Despite their importance, there is little ceramic literature on the characterization of the polymer binders themselves. This is surprising, as a ceramic green body is nothing more than a highly filled polymer matrix composite, with the matrix being typically a multicomponent polymer blend. How can we characterize the binder as a polymer blend? How do the properties of the solid polymer (crystalline fraction, microstructure, residual stresses, preferred chain orientation) affect behavior before and during binder removal? How are the polymer thermal properties (melting point, glass transition temperature) affected by the composition of the blend and the interaction of the polymer with the ceramic powder?

This paper was motivated by an attempt to understand the behavior of a multicomponent thermoplastic ceramic binder<sup>12</sup> used in extrusion,<sup>13</sup> based on poly(ethylene co-ethylacrylate) (EEA). A simplified “model binder system” was prepared consisting only of the primary ethylene copolymer resin EEA. We were surprised that objects formed from a 50 vol% ceramic-filled EEA underwent severe distortions during the early stages of heating. These distortions occurred before any significant weight loss. This was not expected as a multicomponent binder system based on EEA has no measurable distortions. Hrdina and Halloran<sup>10</sup> had previously observed this with a similar one-component ethylene copolymer system, which was attributed to relaxation of non-equilibrium chain orientation in the polymer as it was heated. Hrdina used thermomechanical analysis to show that, on the first heating cycle after molding, the object expanded in the direction of the compression direction of the prior molding, and contracted in the perpendicular direction.

The previous deformation history of the polymer–ceramic compound left polymer chains aligned in the deformation direction, resulting in a conformational “memory.” This phenomenon was irreversible, and did not occur upon subsequent heating cycles. Hrdina also investigated a multicomponent binder system that displayed no distortions. Apparently, the additives in the multicomponent thermoplastic systems ameliorate the conformational memory that causes these distortions. This paper characterizes such multicomponent EEA-based blends to attempt to explain these observations.

## II. Experimental Procedure

The thermoplastic binder system is one used previously for thermoplastic processing of ceramics by coextrusion<sup>13</sup> and green machining.<sup>14</sup> The binder system has five components based on a blend of poly(ethylene-co-ethyl acrylate) (an EEA copolymer with 19% acrylate, EEA 6182, Union Carbide, Danbury, CT) and poly(isobutyl methacrylate) (PiBMA) (Acryloid B67, Rohm and Haas, Philadelphia, PA). The EEA copolymer provides melt strength and is flexible at room temperature due to its low glass transition temperature ( $T_g = -80^\circ\text{C}$ ). The flexibility of EEA is modified by blending with PiBMA, which has a high glass transition temperature ( $T_g = 65^\circ\text{C}$ ). Polyethylene glycol (Acros, MW1000, Fisher Scientific, Fairlawn, NJ) and heavy mineral oil (Heavy Mineral Oil, Witco, Petrolia, PA) are used as processing aids during the shear mixing of the thermoplastic composite, and serve as plasticizers for the polymers. Stearic acid (Fisher Scientific) is added as a lubricant.

The ceramic powder used in this case is a commercial dielectric based on bismuth barium neodymium titanate composition (ULF 101, Ferro Corporation, Penn Yan, NY), which we previously investigated with thermoplastic processing.<sup>14</sup> The specific surface area was 4.8 m<sup>2</sup>/g. Sedimentation analysis (Horiba CAPA 100, Horiba Ltd., Kyoto, Japan) showed a median particle size of 800 nm, with a 90% tile of 1300 nm and 10% tile of 500 nm. The powders were ball milled using alumina balls for 24 h, and then dried at 85°C for more than 24 h.

Ceramic-filled thermoplastic composites were compounded using a heated shear mixer with roller blades (Plasti-Corder PL 2100 Electronic Torque Rheometer, C. W. Brabender, South Hackensack, NJ). The initial temperature of the mixing unit was 105°C. Pellets of EEA and PiBMA resin were melted and blended in the shear mixer. The ceramic powder was added in gradual increments. Adding the ceramic increased the torque and mixing temperatures to 120–130°C. Polyethylene glycol, stearic acid, and mineral oil were added throughout the mixing process. The compositions are listed in Table I.

Compounds with simpler polymer blends were prepared as model systems. This included 50 vol% EEA–50 vol% bismuth barium neodymium titanate ceramic powder (BBNT) (86.3 wt% BBNT powder in 13.7 wt% EEA) and 35 vol% EEA–15 vol% PiBMA–50 vol% BBNT (85.93 wt% BBNT powder in 9.54 wt% EEA and 4.53 wt% PiBMA). We also prepared 50 vol% EEA–50 vol% compounds with a basic powder (alumina  $\text{pH}_{\text{IEP}} = 9$ ), acidic (titania  $\text{pH}_{\text{IEP}} = 5$ ), and more acidic powder (silica  $\text{pH}_{\text{IEP}} = 3$ –5). We used an alumina with a specific surface area of 8.6 m<sup>2</sup>/g (Alcoa A16 SG, Pittsburgh, PA), a titania with a specific surface area of 5 m<sup>2</sup>/g (Ferro Electronic Materials,

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**Table I. Composition of Ceramic-Filled Thermoplastic Compounds**

Component	Density (g/cm <sup>3</sup> )	Weight (g)	Compound		
			Wt%	Vol%	Resin (Wt%)
BBNT	5.862	128.03	86.8	52.0	—
EEA	0.93	11.62	7.9	29.8	59.8
IBMA	1.03	5.52	3.7	12.8	28.0
Stearic Acid	0.845	0.35	0.2	1.0	1.5
HMO	0.875	0.18	0.1	0.5	0.8
PEG 1000	1.10	1.85	1.3	4.0	9.8

BBNT, bismuth barium neodymium titanate ceramic powder; EEA, ethylene co-ethyl acrylate; IBMA, Poly(isobutyl methacrylate); HMO, heavy mineral oil; PEG1000, poly(ethylene glycol).

Penn Yan, NY, Code 203-4), and a non-porous fumed silica (Aerosil OX50, Degussa, Frankfurt, DE) with a surface area of 50 m<sup>2</sup>/g.

After mixing, the compounds were removed from the hot mixer by reversing the rotation of the roller blades, which forced the taffy-like compound out of a 12 mm × 50 mm slot, like an extrudate. After cooling to room temperature, the rigid solid compound was cut into small pieces 0.1–3 cm<sup>3</sup> in volume. These pieces were loaded into a 25.4 mm brass die and molded into a solid rod at 125°C, with a uniaxial pressure of 27 MPa held for 15 min. After cooling under pressure, the solid rod was cut into 3 mm slices. The weld lines between the melted pieces of compound were visible with most samples. For some samples, a trace of carbon black was dusted on the pieces to mark the weld lines more clearly for photography.

The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), and glass transition temperature ( $T_g$ ) were determined with differential scanning calorimetry (DSC), conducted in flowing nitrogen with a TA Instruments Model 2910 DSC (TA Instruments, New Castle, DE) with 3–20 mg samples sealed between an aluminum pan and lid. The heating rate was 10°C/min to 150°C, with cooling at 5°C/min. Transition enthalpies were obtained from the DSC traces using commercial software. The

fractional crystallinity of the EEA was calculated from the enthalpy, using a value of 287 J/g for the melting transition of 100% crystalline polyethylene, so that percent crystallinity of EEA =  $(\delta H_f \text{ DSC} / \Delta H_f \text{ 100\% crystalline PE})$ . We report crystallinity as the average from DSC experiments on two samples.

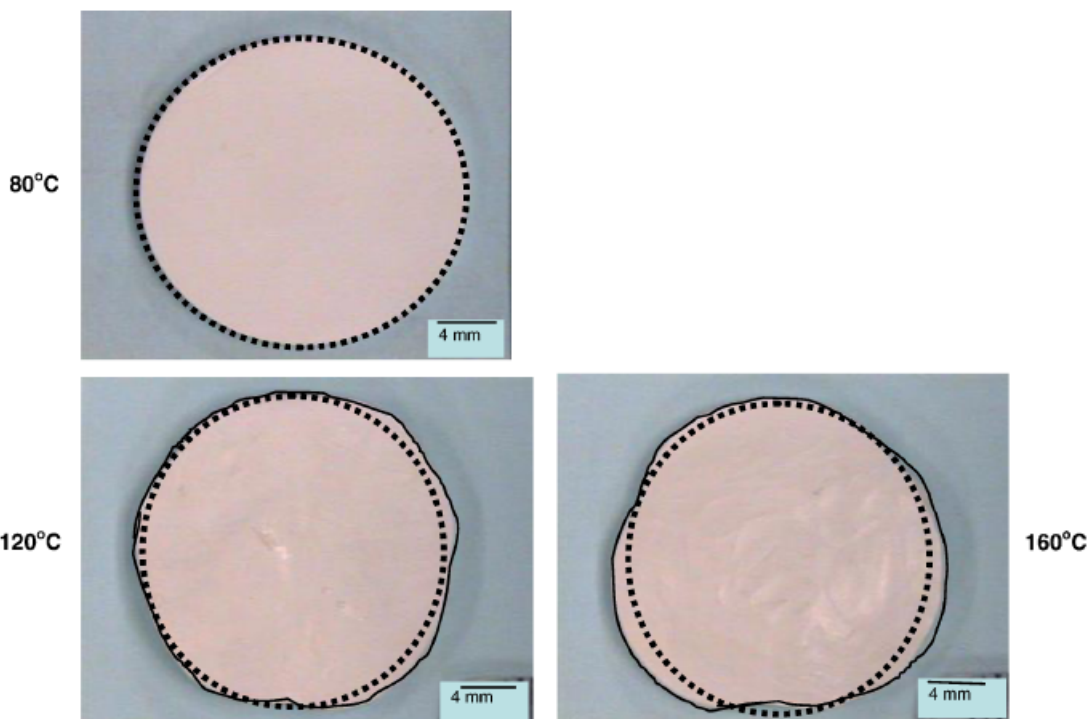
Samples for polarized light optical microscopy (PLOM) were prepared as thin films by melting a small sample of polymer between glass slides. They were annealed at 110°C to complete melting, and then annealed at 85°C for 2 h to grow the spherulites to be large enough to distinguish using a Nikon Optiphot2-Pol optical microscope (Nikon USA, Melville, NY).

### III. Results and Discussion

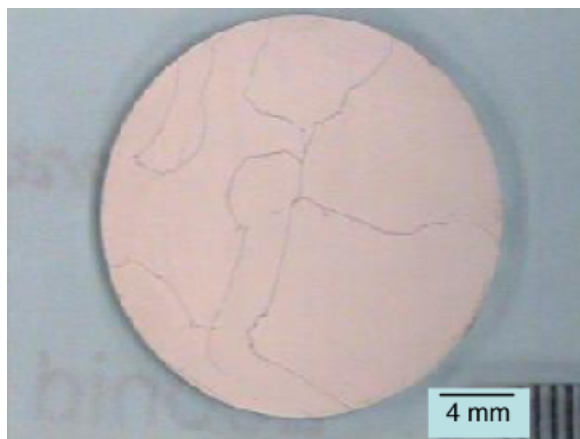
#### (1) Distortion of Molded Ceramic-EEA

The photographs in Fig. 1 illustrate the distortion along the diameter in three representative disks molded from 50 vol% EEA–50 vol% BBNT ceramic powder. The disks maintain their shape after being heated at 80°C. However, when the temperature reached 120°C, close to the molding temperature, significant distortions become obvious. Another disk heated to 160°C suffered even more distortion. This is well above the molding and mixing temperatures, but well below the temperature where measurable weight loss occurs.<sup>12</sup> Other samples behaved in a similar fashion, although of course the details of the warping and distortion differed from one disk to another. Attempts were made to collect quantitative statistics on diametral distortions from disk to disk, and with location within a single disk, but these data were not informative. While not quantitative, extensive observations<sup>15</sup> related these distortions to relaxations of the polymer in the as-mixed EEA–ceramic compound, from which these disks were molded. Figure 2 shows a photograph of an as-molded disk where the individual melted pieces can be distinguished by their weld lines. Subsequent heating of the disk would create patterns of distortions reflecting the domains defined by the weld lines.

Additives to the EEA suppressed these distortions. This was indicated from warping of disks upon heating. The severity of warping was quantified by the camber,  $C$ , as defined by the



**Fig. 1.** Distortion of discs molded from poly(ethylene co-ethylene acrylate) loaded with 50 vol% ceramic powder upon initial heating. Distortions occur before measurable weight loss.



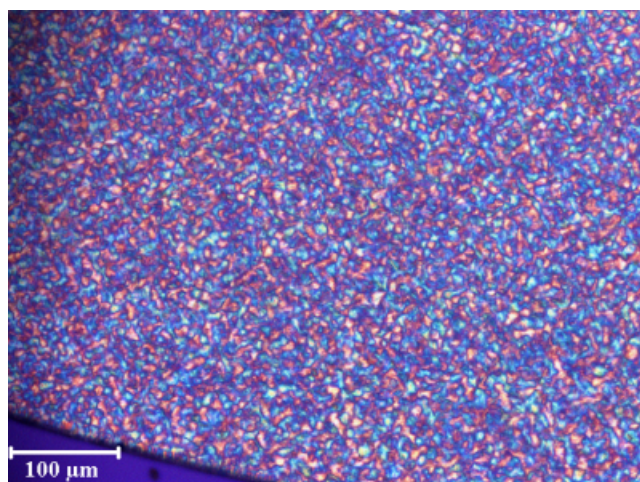
**Fig. 2.** Observations of weld lines between various ceramic filled thermoplastic pieces used to fabricate discs.

maximum distance between the top and bottom of a warped disk, as measured from photographs, divided by the original thickness of the disk. The aforementioned EEA–ceramic disks had a camber that varied between 2 and 2.5. Replacing the EEA with a blend of 75 vol% EEA+25 vol% PiBMA reduced the camber to about 1.3. Disks molded from the five-component blend had camber that was less than 1.05. Clearly, the addition of 28% PiBMA methacrylate resin, 9.8% polyethylene glycol, as well as mineral oil and stearic acid suppressed the polymer relaxations that caused the distortions. We characterized the physical state of the polymer blend in an attempt to understand why the blend was able to relax, while the simple EEA–ceramic mixture did not. The characterization involved thermal analysis of the blend and blend with the ceramic, and the microstructure of the blend without ceramic powder.

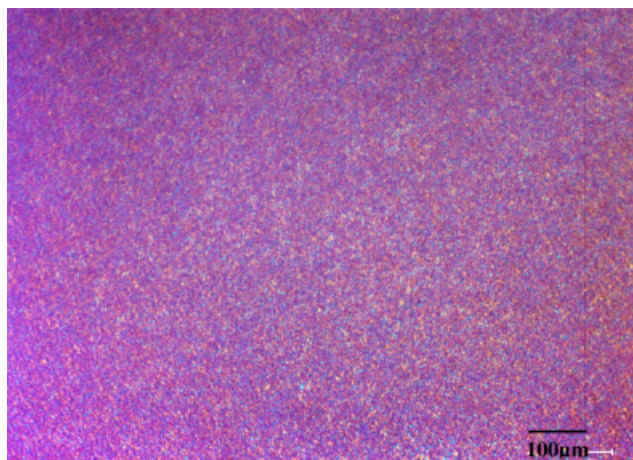
### (2) Microstructure of the Polymer Blend

The microstructure of semicrystalline polymer such as EEA can be examined with PLOM in the transmission mode to image the crystalline spherulites and observe phase separation in blends,<sup>16,17</sup> at least when the relevant domains are large enough for optical imaging. The ceramic-filled green bodies are opaque, and so cannot be studied with transmitted PLOM. As a substitute, we examined ceramic-free blends in a thin section.

Figure 3 shows a thin section of the EEA resin in crossed polarized light, where 10–15  $\mu\text{m}$  features are visible. These features are randomly oriented crystalline spherulites, as expected



**Fig. 3.** Neat ethylene co-ethylacrylate as viewed with polarized light using a colored filter. Random orientations are identified by the different colors of each crystal, each color representing a set of angles at which the crystal is oriented.



**Fig. 4.** The 75 vol% ethylene co-ethylacrylate: 25 vol% poly(isobutyl methacrylate) blend viewed with polarized light.

for EEA, which is 14% crystalline. Blending EEA with 25 vol% PiBMA (an amorphous polymer) reduces the spherulite size to about 2  $\mu\text{m}$ , as shown in Fig. 4. Apparently, the presence of the methacrylate, likely separated in domains too small to resolve optically, has retarded the growth of the polyethylene spherulites.

The addition of low-molecular-weight (1000 Da) polyethylene glycol does not result in a homogenous blend. Figure 5 indicates that the EEA–5% poly(ethylene glycol) PEG mixture is phase separated, with 5–50  $\mu\text{m}$  globules, most likely PEG. The imaging conditions for Fig. 5 do not reveal the spherulites in the EEA. A ternary mixture of 75% EEA–20% PiBMA–5% PEG, however, has no phase separation visible by optical microscopy. Figure 6 shows that the EEA–PiBMA–PEG blend has a fine spherulitic structure (similar to EEA–PiBMA) with no evidence of PEG phase separation. Apparently the PEG has been compatibilized by the PiBMA, and is likely present as a fine-scale segregant at the interfaces between the EEA–PiBMA domains. The behavior of the mineral oil is similar to PEG. A binary mixture of 75% EEA–25% heavy mineral oil (HMO) shows evidence for phase separation in PLOM, quite similar to the images for PEG. Stearic acid, however, behaves quite differently, separating macroscopically to the surfaces of the thin section to form a distinct second layer. The complete five-component blend appears in Fig. 7. Note that it has no obvious phase separation, as the PEO, HMO, and even stearic acid appear to have been compatibilized in the EEA–methacrylate blend. Like the binary EEA–PiBMA blend, the five-component mixture has spherulites in the 2–3  $\mu\text{m}$  size range.

### (3) Thermal Analysis of Blends and Compounds

The state of polymer blends can be revealed using thermal analysis, as shifts in the melting temperatures and enthalpies indicate the extent of interaction of the components.<sup>18,19</sup> We used DSC to determine the glass transition ( $T_g$ ), melting ( $T_m$ ), and crystallization ( $T_c$ ) temperatures of the neat polymers. Changes in the DSC transitions for the polymer blends indicate interactions between the components in terms of miscibility of the blend. Miscible blends contain a single phase and produce properties that may follow the rule of mixtures, i.e., a single  $T_g$  that depends on the composition of the blend. Immiscible blends are classified as compatible or incompatible based upon the interfacial interaction between the components.<sup>18,19</sup> Compatible blends have attractions between the components that are of an order similar to the attractions within each of the polymers, whereas incompatible blends have weak interactions between the components. DSC plots of incompatible blends exhibit the endotherm curves of each individual component as each component exists as a separate phase in the blend. Immiscible but

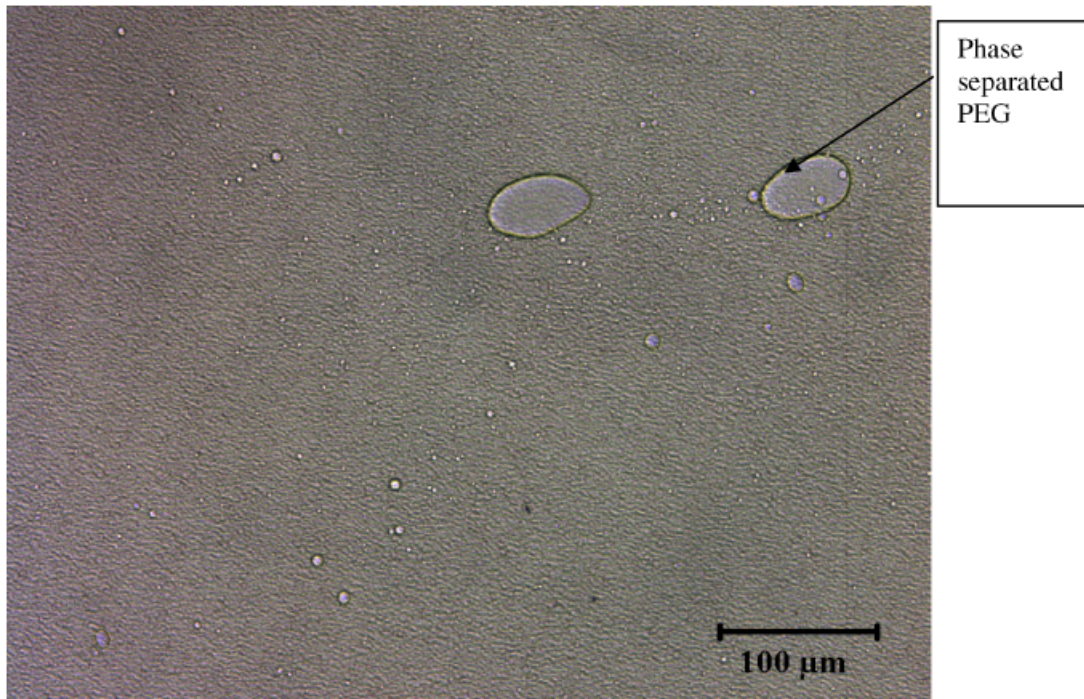


Fig. 5. Optical micrograph of 95 vol% ethylene co-ethylacrylate-5 vol% poly(ethylene glycol) using polarized light; phase separation evident.

compatible blends likewise display the endotherms of each component but the positions of the parameters may be shifted from the corresponding neat polymers due to the interactions between the polymers in the blend.

Table II summarizes the results of the neat EEA and corresponding blends tested. Experiments were conducted on two samples of each material to determine the average percent crystallinity of EEA; however, only one DSC plot is presented in the results below. Figure 8 shows a DSC plot of neat EEA revealing two endotherms at 51° and 102°C. The endotherm at 102°C is consistent with the  $T_m$  literature value of EEA of 99°C, while the endotherm at 51°C is related to the Vicat softening temperature.<sup>20</sup> The enthalpy of the cooling exotherm suggests that the crystallinity of the co-polymer is  $14.2\% \pm 1.2\%$ , which is consistent with a copolymer with this acrylate content.<sup>20</sup>

The glass transition temperature for PiBMA is characteristically around 50°C. The DSC for this material, shown in Fig. 9, has an endotherm at 69°C, which is the  $T_g$  of this commercial material. The higher  $T_g$  is attributed to processing additives in

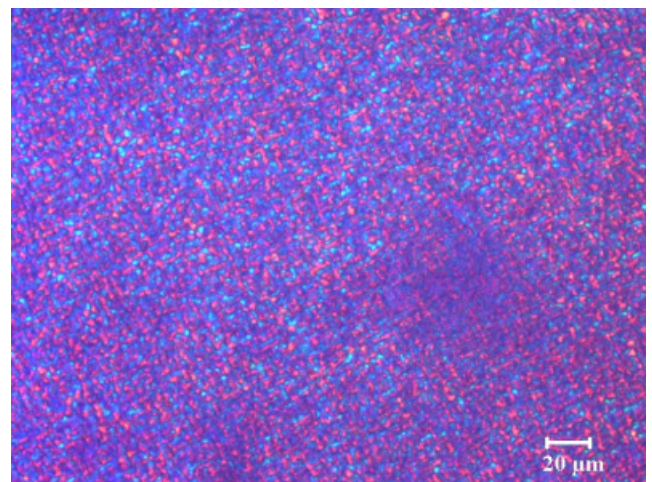


Fig. 7. Five-component polymer blend viewed with polarized light using a colored filter.

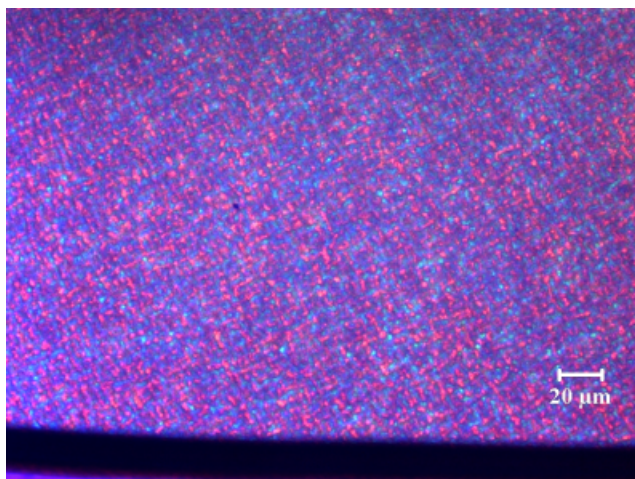


Fig. 6. The 75 vol% ethylene co-ethylacrylate-20 vol% poly(isobutyl methacrylate):5 vol% poly(ethylene glycol) blend viewed with polarized light using a colored filter. No phase separation is apparent.

Table II. Transition Temperatures and Crystallinity of EEA-Based Blends

Polymer composition (vol%)	$T_m$ (°C) melting	$T_c$ (°C) crystallization	% of EEA crystallinity
100 EEA	102–104	87	$14.2 \pm 1.2$
75 EEA:25 PiBMA	103	89	$12.0 \pm 0.1$
75 EEA:25 HMO	99–100	86	$12.2 \pm 0.8$
75 EEA:25 SA	102	88	$11.4 \pm 0.1$
75 EEA:20PiBMA: 5 PEG	104	89	$12.3 \pm 0.3$
95 EEA:5 PEG	105	89	$12.1 \pm 1.1$
Full polymer blend	103	89	$10.4 \pm 1.8$
Full composite blend with BBNT	102	88	$8.6 \pm 1.8$

BBNT, bismuth barium neodymium titanate ceramic powder; EEA, ethylene co-ethyl acrylate; HMO, heavy mineral oil; PEG, poly(ethylene glycol); PiBMA, poly(isobutyl methacrylate).

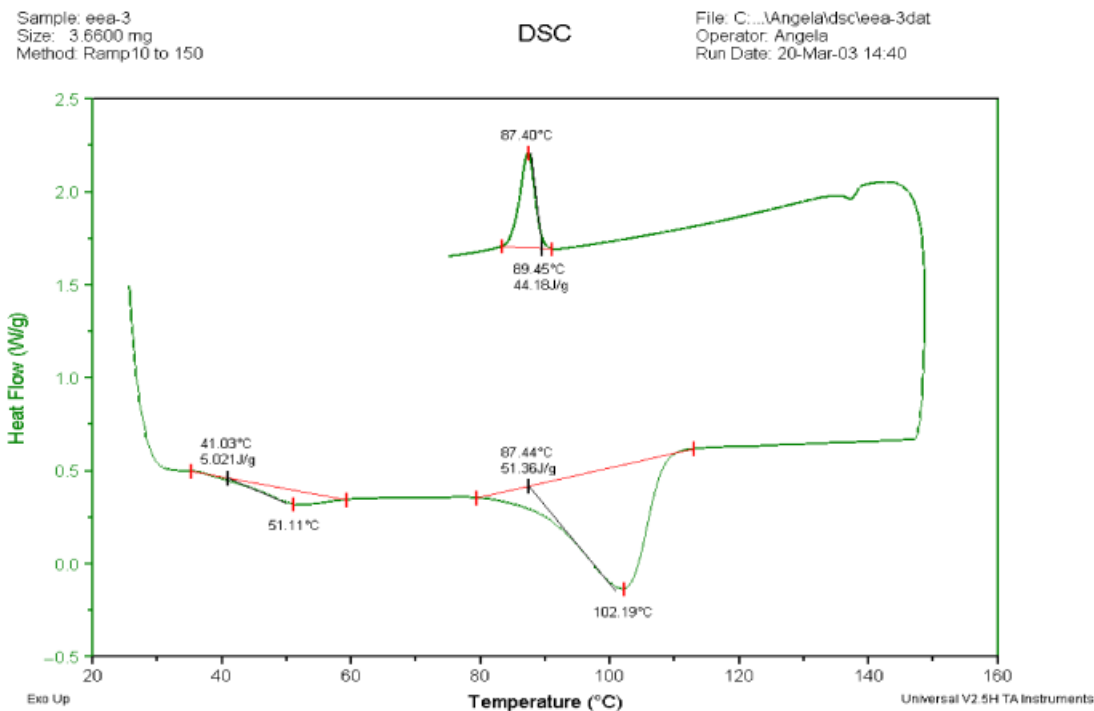


Fig. 8. Differential scanning calorimetry of neat poly(ethylene co-ethylacrylate).

the commercial product. There is no melting temperature ( $T_m$ ); this material is an amorphous methacrylate.

A 75 vol% EEA: 25 vol% PiBMA blend showed three endothermic reactions at 50°, 68°, and 103°C, which are determined to be the softening of EEA,  $T_g$  of PiBMA, and  $T_m$  of EEA, respectively (Fig. 10). The heat of fusion of each endotherm is significantly reduced from its corresponding neat components. Observation of the PiBMA  $T_g$  event is consistent with examples of an amorphous material added to a crystalline material to yield

an immiscible polymer blend. The  $T_g$  of PiBMA and  $T_m$  of EEA events occur at temperatures slightly shifted from the properties of their respective neat components determining this blend to be immiscible and compatible. The percent crystallinity of EEA was reduced to  $12.0\% \pm 0.1\%$  in this blend (from 14.2% for neat EEA), corresponding to the reduced heat of fusion in the DSC endotherms.

A DSC plot of the volume ratio of 75 EEA:25 HMO reveals endotherms at 39° and 99°C, determined to be the softening and

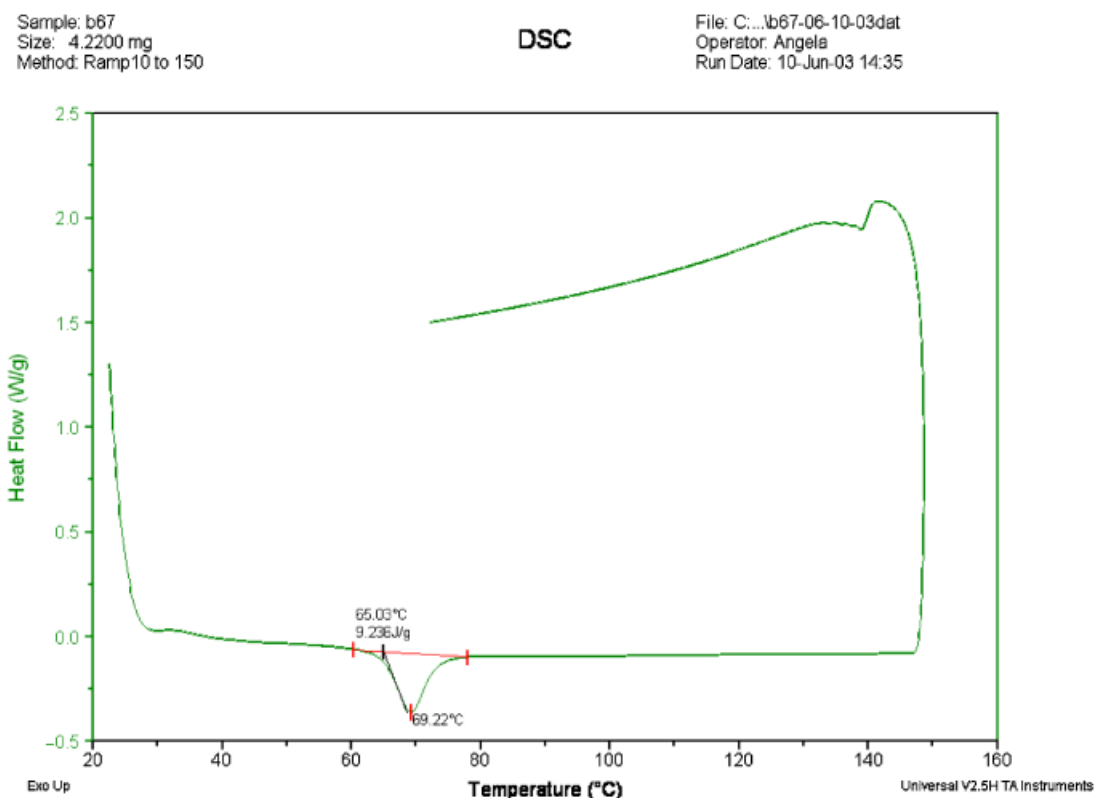


Fig. 9. Differential scanning calorimetry of neat poly(isobutyl methacrylate).

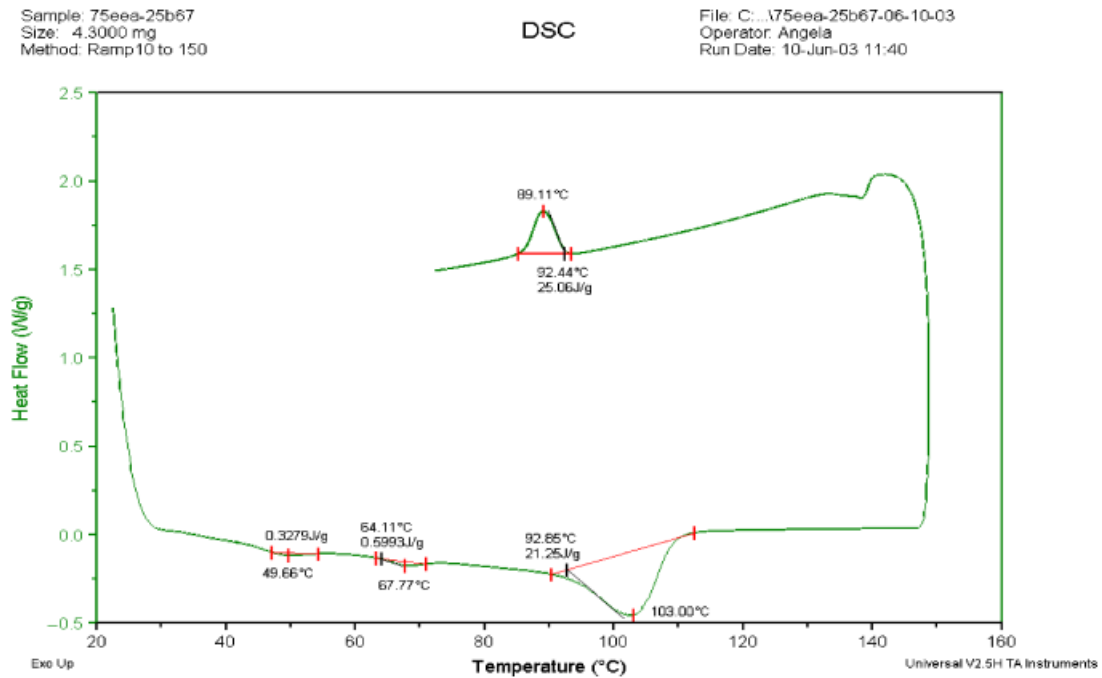


Fig. 10. Differential scanning calorimetry of a blend of 75 vol% poly(ethylene co-ethylacrylate) and 25 vol% poly(isobutyl methacrylate).

$T_m$  of EEA, respectively (Fig. 11); again, both endotherms are reduced compared with neat EEA. According to the definitions of polymeric blends, this system is immiscible and compatible although polarized light revealed phase-separated regions in several areas of the blend (Fig. 5). The percent crystallinity of EEA is reduced to  $12.2\% \pm 0.8\%$ .

The 95 EEA:5 PEG DSC plot displays endotherms at  $45^\circ$  and  $105^\circ\text{C}$  (Fig. 12). The  $T_m$  of PEG is  $35^\circ\text{--}40^\circ\text{C}$ ; this event is not discernible and is considered to be overlapping with the EEA softening event. The percent crystallinity of EEA was reduced to  $12.1\% \pm 1.1\%$  in this blend. While DSC results indicate that this

polymer blend is immiscible and compatible, observations with polarized light showed a clear phase separation (Fig. 5).

After investigating the interaction of each additive with EEA, more complex blends were then studied. DSC of a 75 EEA:20 PiBMA:5 PEG polymer blend displayed endotherms at  $42^\circ$  and  $104^\circ\text{C}$  (Fig. 13), and is consistent with the events of the 95 EEA:5 PEG blend discussed above; the PiBMA  $T_g$  event is indiscernible. Whereas the 95 EEA:5 PEG blend showed distinct phase separation in the optical micrographs, it is interesting to note that no phase separation occurs in this three-component blend (Fig. 6). It is therefore determined that PiBMA is serving

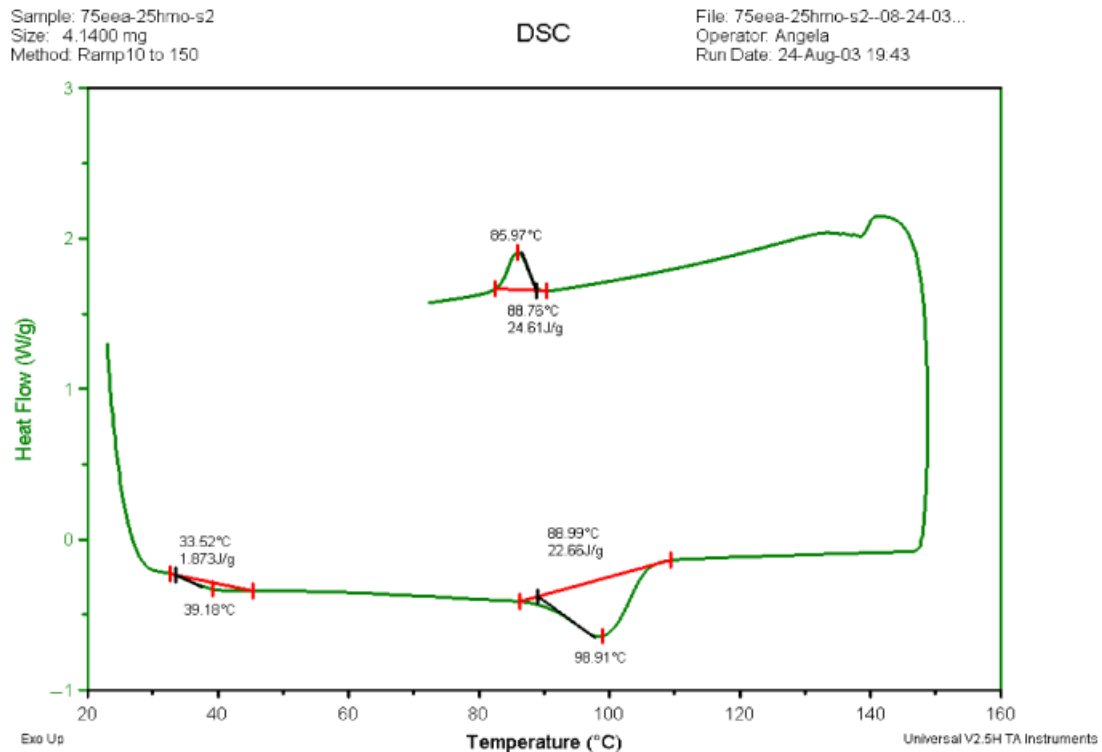


Fig. 11. Differential scanning calorimetry of a blend of 75 vol% poly(ethylene co-ethylacrylate) and 25 vol% mineral oil.

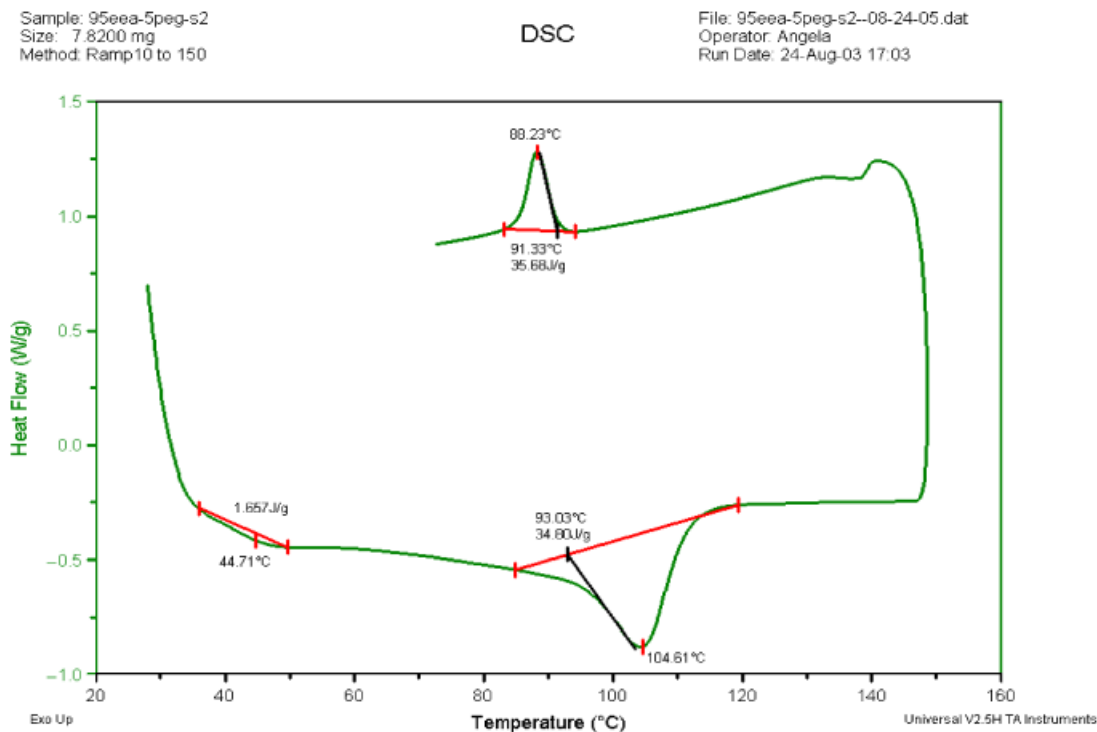


Fig. 12. Differential scanning calorimetry of a blend of 95 vol% poly(ethylene co-ethylacrylate) and 5 vol% poly(ethylene glycol).

as a compatibilizer for the PEG and EEA polymers, allowing this blend to be immiscible and compatible. The EEA spherulite size seems to be slightly reduced while the percent crystallinity of EEA is  $13.4\% \pm 0.8\%$  in this blend.

A blend containing each of the five polymeric components was next investigated with the volume percent ratios of 68.3 EEA:29.3 iBMA:1.0 stearic acid:0.5 HMO:1.0 PEG. The DSC plot of this blend had endotherms at  $103^\circ\text{C}$  (Fig. 14) for the  $T_m$  of EEA and a smaller event at  $61^\circ\text{C}$ . As the  $T_m$  of EEA is nearly unchanged and only one other endotherm is present, this five-component blend is also considered immiscible and compatible.

To compare how the ceramic filler affects the polymer matrix, a 50 EEA:50 BBNT thermoplastic compound was analyzed by DSC. From the plot, the EEA softening temperature is not readily discernible and  $T_m$  is  $101^\circ\text{C}$  (Fig. 15). The lowering of the  $T_m$  is indicative of a reduced growth rate of the polymer crystals due to presence of the filler. Moreover, the crystallinity is reduced to  $9.0\% \pm 0.1\%$ . Fillers are known to increase or decrease crystallinity in the polymer matrix depending on the interfacial reaction of the polymer with the filler surface. Reduction of crystallinity indicates that “strong” interactions are occurring between the ceramic filler and the co-polymer, which

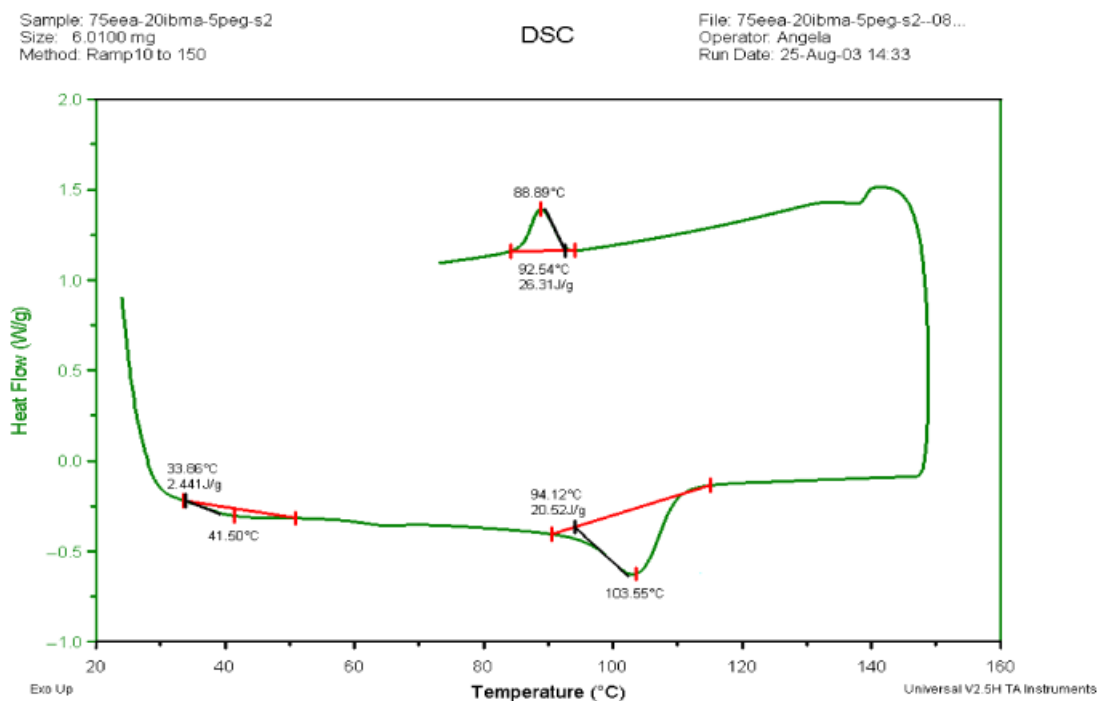


Fig. 13. Differential scanning calorimetry of a blend of 75 vol% poly(ethylene co-ethylacrylate)-20 vol% poly(isobutyl methacrylate)-5 vol% poly(ethylene glycol).

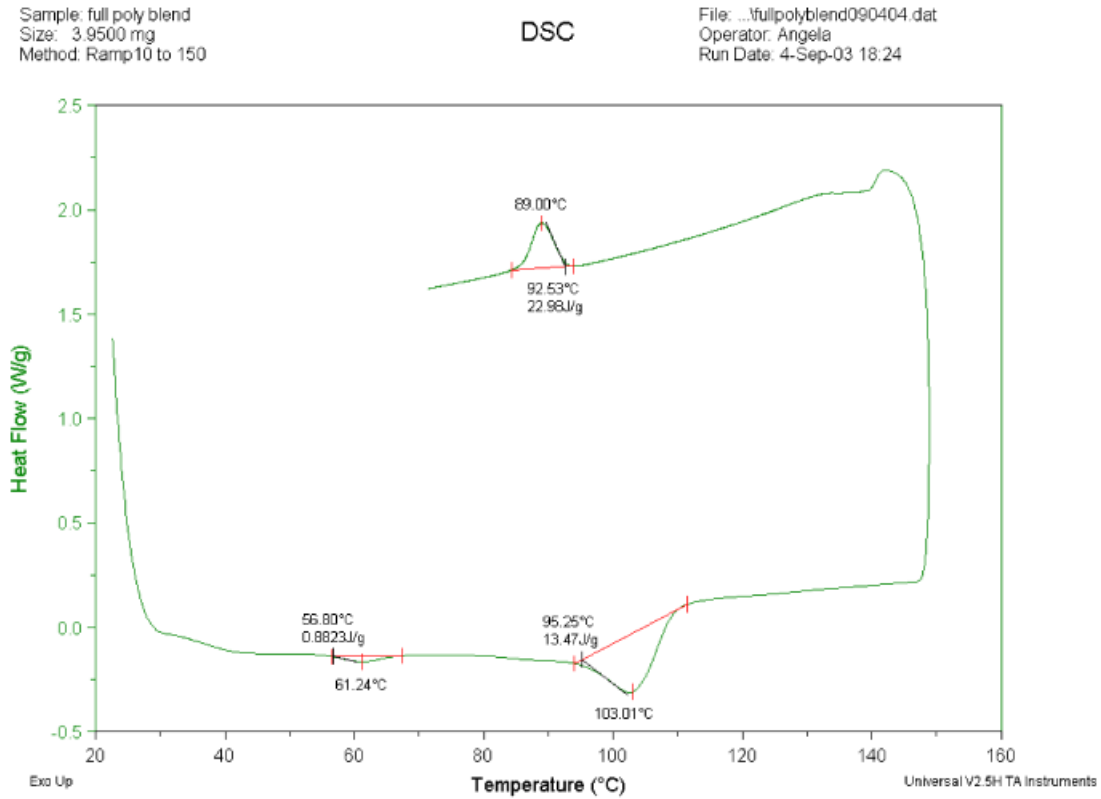


Fig. 14. Differential scanning calorimetry plot of the five-component polymer blend.

is inhibiting the crystallization.<sup>17,21</sup> These results are consistent with the findings of Hrdina, that the SiC–Al<sub>2</sub>O<sub>3</sub>–Y<sub>2</sub>O<sub>3</sub> ceramic filler significantly impacted and reduced the crystallinity percent of EVA.<sup>22</sup> Polymers loaded with 50 vol% of ceramic are

opaque; optical microscopy to reveal details of the polymer microstructure was not possible.

The effect of several other ceramic fillers on the EEA crystallinity was briefly examined. We chose three materials with

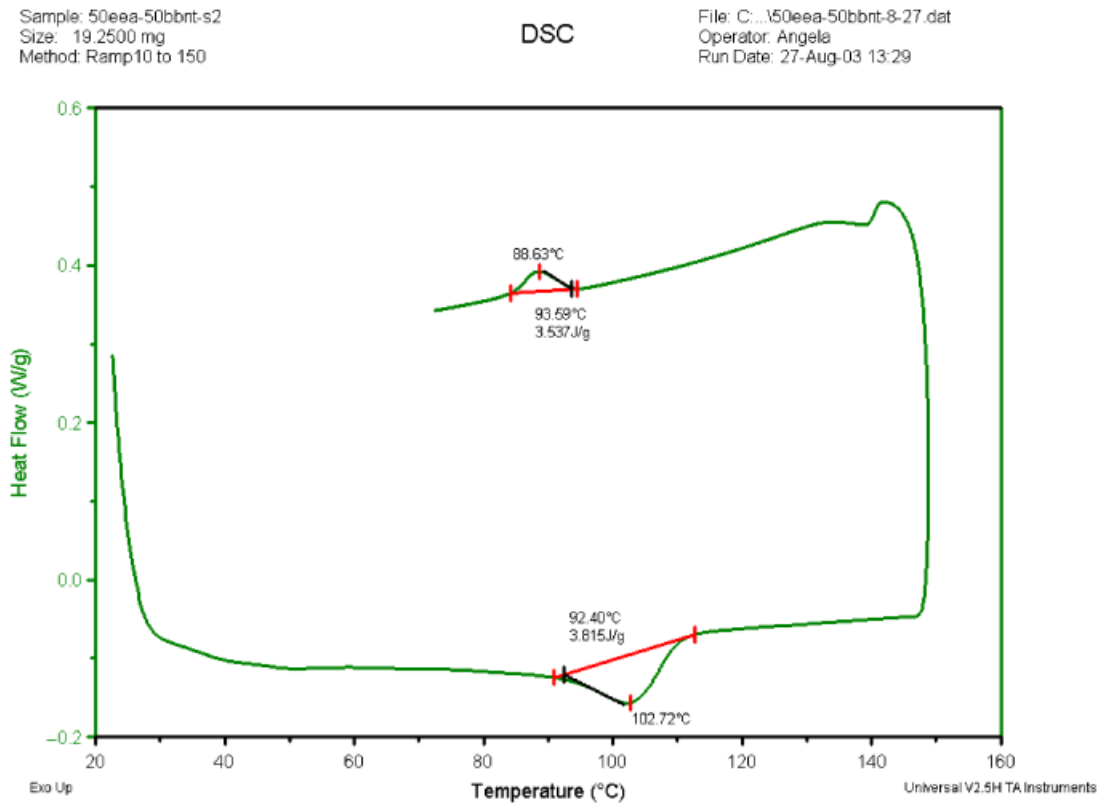


Fig. 15. Differential scanning calorimetry plot of 50 vol% poly(ethylene co-ethylacrylate)-50 vol% bismuth barium neodymium titanate ceramic powder ceramic powder.



**Table III. Transition Temperatures and Crystallinity of EEA with Ceramic**

Polymer composition (vol%)	$T_m$ (°C) melting	$T_c$ (°C) crystallization	% of EEA crystallinity
100 EEA	102–104	87	14.2 ± 1.2
50 EEA:50 BBNT	101–103	89	9.0 ± 0.1
50 EEA:50 Al <sub>2</sub> O <sub>3</sub>	103	90	9.8 ± 0.7
50 EEA:50 TiO <sub>2</sub>	103	89	5.9 ± 0.4
50 EEA:50 SiO <sub>2</sub>	103	88	11.0 ± 0.3

BBNT, bismuth barium neodymium titanate ceramic powder; EEA, ethylene co-ethyl acrylate.

quite different surface acidity, as indicated by their aqueous isoelectric point. These were TiO<sub>2</sub> (pH<sub>IEP</sub> = 6), Al<sub>2</sub>O<sub>3</sub> (pH<sub>IEP</sub> = 9–10), and SiO<sub>2</sub> (pH<sub>IEP</sub> = 3.8–4.8). The transition temperatures are reported in Table III. A softening endotherm was not apparent in DSC plots with these ceramic-EEA blends. While the EEA  $T_m$  is approximately 103°C for the TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> fillers, it is 104°C for the SiO<sub>2</sub> filler. Also, the percent crystallinity varies widely as a function of the ceramic used. In the SiO<sub>2</sub> composite, the crystallinity is 11.0% while the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> composite, are 10.5% and 5.9%, respectively. It appears that EEA is adsorbing strongly to the ceramic filler in a manner not simply related to the pH<sub>IEP</sub> of the ceramic powder.

Lastly, the five-component thermoplastic composite blend with BBNT ceramic powder was investigated. DSC analysis identifies only the  $T_m$  endotherm at 102°C; thus, this is inconclusive as the characterization of this blend. The five-component polymer blend is immiscible and compatible, and the 50 EEA:50 BBNT endotherm shifted the EEA  $T_m$  to a lower temperature. Therefore, it is plausible that the full composite blend is immiscible and compatible as well.

From examination of Table III, it is evident that each polymer additive reduces the EEA crystallinity by 15–20%; however, the five-component blend reduces the crystallinity by nearly 30%. It is interesting to note that the BBNT ceramic powder reduces the crystallinity by 40% in both the 50 EEA:50 BBNT and the thermoplastic composite used for fabricating the 2D textured substrate.

The EEA percent crystallinity is nearly identical for these ceramic-filled composites; it is worthwhile to reconsider the distortions observed in the disks with these same compositions. It was previously discussed that large dimensional changes occurred in ceramic-polymer composite disks when the temperature was increased above the polymer  $T_m$ . While both the 50 EEA:50 BBNT and the thermoplastic composite have the same percent crystallinity, the thermoplastic-blend composite did not suffer distortions. As these two compositions with the same percent crystallinity, these distortions are unlikely to be related to melting transitions.

Distortions occurred most probably due to “memory” of the molecular conformations in the polymer imposed by the shear as the compound flows out of the mixer. Warping due to molecular orientation is a well-known phenomenon in plastics,<sup>23</sup> occurring when a previously molded piece is heated close to the molding temperature. The molecular conformations can be relaxed by effective plasticizers. We suggest that in the five-component binder system, the PEG and HMO are more effective plasticizers because they are compatibilized in the EEA–PiBMA blend. The molecular conformations are more thoroughly relaxed during formation, and cause less distortion during subsequent heating.

#### IV. Conclusions

Molded ceramics with simple poly(ethylene-ethylacrylate) thermoplastic binders suffer severe distortion during early stage heating, before the onset of degradation. These distortions are associated with relaxation of non-equilibrium polymer

conformations from molding. Binders made from ethylene-ethylacrylate blends containing poly(isobutyl methacrylate) resins and polyethylene glycol and mineral additives do not suffer distortions.

Microstructure and DSC analysis show the poly(ethylene-ethylacrylate) resin to be semicrystalline with 14% crystallinity in 10–15 μm spherulites. Blending with 25% poly(isobutyl methacrylate) reduces the crystallinity to 12% with 2 μm spherulites. Addition of 50 vol% ceramic powder reduces the crystallinity significantly to about 9%, depending on the nature of the powder.

The plasticizing additives polyethylene glycol and mineral oil phase separate when mixed in poly(ethylene-ethylacrylate), but are compatibilized by additions of poly(isobutyl methacrylate), forming an immiscible but compatible polymer blend. The compatibilized plasticizers are able to relax the polymer conformations after molding, reducing the tendency to cause distortions during subsequent heating.

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