

# Binder Removal from Ceramic-Filled Thermoplastic Blends

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**Thermogravimetric analysis is used to examine the degradation of a multicomponent polymer binder consisting of a blend of a polyethylene co-ethyl acrylate with a polyisobutylmethacrylate polymer. In the polymer blends without ceramic powder, the methacrylate component degrades at a temperature lower than the ethylene copolymer. Minor additives polyethylene glycol, stearic acid, and paraffinic mineral oil are also considered. The thermal degradation of a five-component blend is only approximately as expected from the individual components, with retardation of the methacrylate degradation. Oxide ceramic powder significantly alters polymer degradation, retarding degradation in the early stages but accelerating degradation in the later exothermic stages. Polymer–polymer interactions and oxide–polymer interactions make the degradation behavior of blends difficult to predict from single component behavior.**

## I. Introduction

CERAMICS can be produced by forming a composite of ceramic particles and polymer binders. The polymer binder imparts plasticity during formation, but must be eliminated before sintering, which is often difficult and time consuming. Binder removal methods include solvent extraction, wicking, and thermal debinding.<sup>1,2</sup> Wicking can be effective for relatively coarse particles with binders that melt into fluid liquids, such as waxes. High-molecular-weight binders, such as thermoplastic polymers, are too viscous to flow upon melting, and are removed by thermal degradation or “binder burnout.” Pyrolysis reactions degrade the polymer to form more fluid liquid or gaseous products, which can be transported to the surface where evaporation ensues.

The binder system is typically a multicomponent polymer blend, often with one or more plasticizers or other additives. Thermoplastic binders offer the advantage of multiple materials and intricate features and this may be fabricated by the coextrusion process.<sup>3,4</sup> The focus of this paper is on the thermal debinding of thermoplastic blends. Both neat organics and multicomponent binder systems will be analyzed in inert and oxidative atmospheres in an effort to determine degradation behavior during binder removal.

Organic product removal is typically accomplished with thermogravimetric analysis (TGA), to identify temperature regions of rapid mass loss, with gas chromatography, mass spectroscopy, and Fourier transform infrared analysis used to identify the volatile species.<sup>5,6</sup> Thermomechanical analysis can be used to examine dimensional changes during these processes, which can be significant with thermoplastic binders.<sup>7</sup> Binder removal schedules consist of a series of heating steps and multiple dwell times. Careful control of heating rates, isothermal dwell times, and appropriate debinding atmospheres is necessary to

avoid defect formation such as warping, bloating, and cracks in the green body during the binder removal operation.<sup>8–12</sup>

## II. Background of Binder Degradation

Basic thermal mechanisms of binder removal from ceramic green bodies are thermal degradation (by chain scission, unzipping, or free radical attack), oxidative degradation, and evaporation.<sup>1,9</sup> Thermal degradation occurs by free radical reactions when no oxygen is present in the atmosphere. Degradation in combusive atmospheres often occurs at lower temperatures of decomposition, as oxygen acts as a reactant with autocatalytic processes. Polymer degradation mechanisms during pyrolysis include depolymerization, random scission, and side group elimination. Low-molecular-weight products from degradation migrate to the surface–atmosphere interface where they are removed by evaporation.

Gas-phase transport and diffusion are the mechanisms by which volatile species and degradation products are removed from the green body. If the diffusion of degradation products from the center of the body outward to the surface is rate limited, gases accumulate within the body. Moreover, if this vapor pressure exceeds the ambient, bloating and cracking result. Defects due to the boiling of the organics coupled with rate-limited diffusion are considered to be the greatest problem of thermal removal of binders.<sup>11</sup> Additional effects complicating the process are degradation products participating in side reactions such as cyclization and cross-linking, creating carbonaceous residues requiring higher temperatures for pyrolysis. Interactions of the ceramic surface with polymer degradation products can catalyze decomposition to smaller molecules and isomerization reactions as well as promote cross-linking during pyrolysis. Oxide surfaces are known to have a catalytic effect on binder removal.<sup>13</sup>

## III. Experimental Procedure

The thermoplastic binder system is one used previously for thermoplastic processing of ceramics by coextrusion<sup>3</sup> and green machining.<sup>14</sup> The binder system has five components based on a blend of poly(ethylene-co-ethyl acrylate) (EEA) and poly(isobutyl methacrylate) (PiBMA). The EEA copolymer provides melt strength, excellent processability 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 ( $T_g = 65^\circ\text{C}$ ). Poly(ethylene glycol) (PEG), stearic acid, and mineral oil are used as processing aids during the shear mixing of the thermoplastic composite.

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). The specific surface area is  $4.8\text{ m}^2/\text{g}$ . 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. Thermoplastic MFCX processing of this powder has been used to fabricate antenna substrates.<sup>15,16</sup> The powders were ball milled using alumina balls for 24 h, and then dried at  $85^\circ\text{C}$  for more than 24 h.

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

Component	Density (g/cm <sup>3</sup> )	Wt%	Vol%	Binder (wt%)
BBNT	5.862	86.8	52.0	—
EEA	0.93	7.9	29.8	59.85
PiBMA	1.03	3.7	12.8	28.0
Stearic acid	0.845	0.2	1.0	1.52
HMO	0.875	0.1	0.5	0.76
PEG 1000	1.10	1.3	4.0	9.85

EEA, ethylene co-ethyl acrylate; PiBMA, poly(isobutyl methacrylate); HMO, heavy mineral oil; PEG1000, poly(ethylene glycol).

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 three head mixing unit was 105°C. Pellets of ethylene-ethylacrylate (EEA 6182, Union Carbide, Danbury, CT) and PiBMA resin (Acryloid B67, Rohm and Haas, Philadelphia, PA) were melted and blended in the shear mixer at a rate of 30 rpm. The ceramic powder was added in gradual increments and mixed for 2–3 min. Adding the ceramic increased the shear values and mixing temperatures to 120°–130°C. PEG (Acros, MW1000, Fisher Scientific, Pittsburgh, PA), stearic acid, and mineral oil (Heavy Mineral Oil, Witco, Petrolia, PA) were added throughout the mixing process as needed. Compositions of the thermoplastic compounds are listed in Table I.

A Bradford Small Scale Extrusion Unit (Bradford University Research Ltd., West Yorkshire, U.K.) was used for extrusion of the thermoplastic compounds; detailed descriptions of the primary feedrod fabrication are listed elsewhere.<sup>3,4</sup> Extrusion was performed at 120°–130°C at rates of 2–3 mm/min using an 8:1 square reduction die.

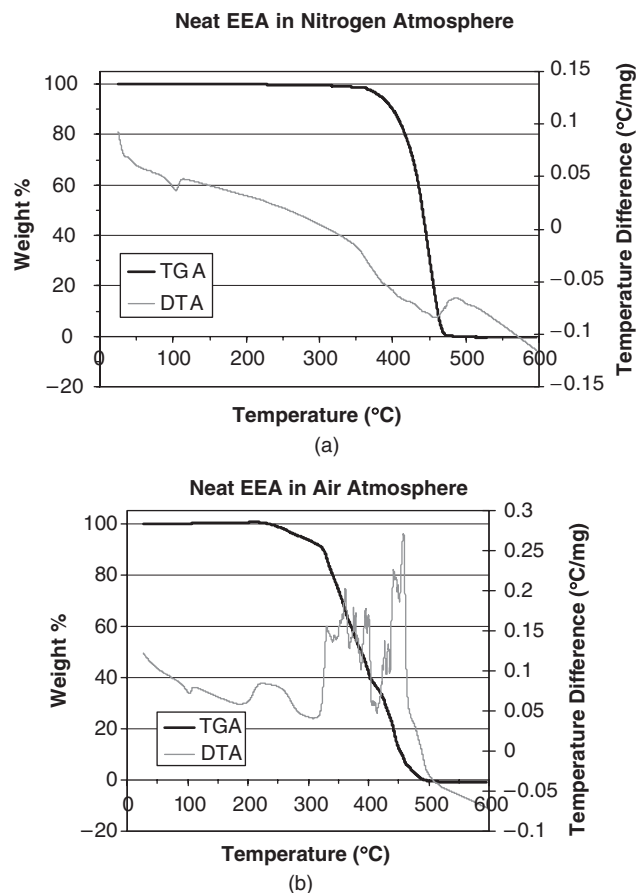
Samples of 10–40 mg placed in alumina pans were subjected to TGA in an SDT2960 TA simultaneous TGA-DTA (differential thermal analysis) instrument. Simultaneous recording of the TGA-DTA data allows for observation of the temperatures corresponding to the maximum rate of mass loss. The heating rate consisted of 3°C/min to 600°C in atmospheres of dynamic nitrogen or air.

#### IV. Results and Discussion

The thermal degradation of each individual constituent was examined separately, followed by blends of the components, and ultimately blends containing ceramic powder. We compare TGA weight loss in air and in inert nitrogen, used to prevent the onset of thermal oxidation. It should be noted that these experimental DTA traces have a significant endothermic baseline drift. Thermal events are compared with a drifting baseline, with exothermic events distinguished by positive temperature deviations, and endothermic events by negative temperature deviations.

##### (1) EEA

The thermal degradation behavior of EEA has been reported by McNeill and Mohammed.<sup>17</sup> Our TGA data for EEA in nitrogen and air atmospheres are shown in Figs. 1(a) and (b). In dynamic nitrogen, mass loss occurs nearly as a single event from 365° to 475°C. Two endotherms observed are attributed to melting at 105°C and endothermic decomposition with a maximum rate of mass loss at 465°C. Based on McNeill's results, the major products being generated during degradation should be unsaturated and saturated alkanes, esters of ethyl acetate, acrylate, and butanoate, and CO<sub>2</sub>. These results are consistent with McNeill and Mohammed in terms of degradation start and maximum weight loss temperatures.



**Fig. 1.** Poly(ethylene-co-ethyl acrylate) (EEA) degradation (a) in N<sub>2</sub> atmosphere, (b) in air. For differential thermal analysis (DTA) exothermics appear as upward events, endotherms downward.

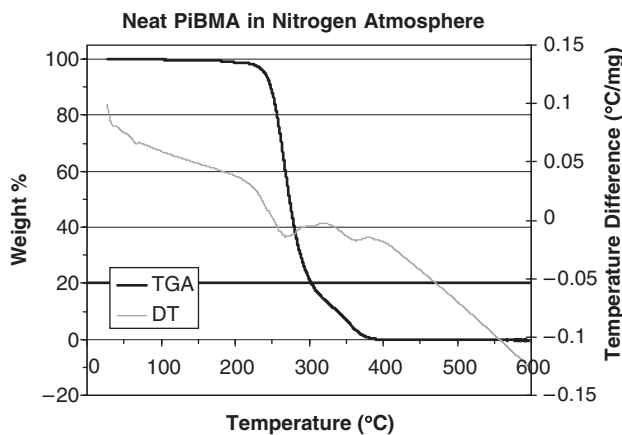
In an air atmosphere, two stages of mass loss occur: the first 10% of mass loss occurs from 200° to 320°C as an endothermic reaction, perhaps associated with the loss of acrylate side groups. The remaining pyrolysis takes place during a more complicated second stage from 325° to 500°C with several exothermic reactions due to combustion. These exothermic events are probably the oxidation of the alkanes. These results are consistent with McNeill, who observed that TG curves obtained in dynamic nitrogen show weight loss occurring in a single step, while a complex degradation pattern occurs in the air atmosphere.

##### (2) PiBMA

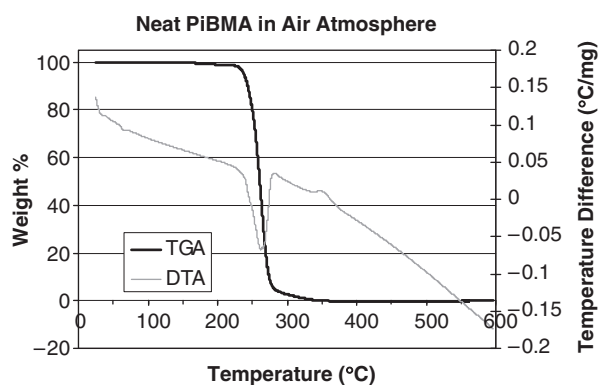
Most polymethacrylates thermally degrade by depolymerization (unzipping). Novaković *et al.*<sup>18</sup> investigated the thermal degradation of PiBMA by examining the polymer residue as a function of time and temperature, and determined that random chain scission occurs initiating depolymerization. Figure 2 shows that in both nitrogen and air, the region of mass loss for PiBMA begins at 240°C. Nearly a single-step reaction occurs in the air atmosphere, with complete mass loss occurring at 355°C. However in the N<sub>2</sub> atmosphere, a second event is required to pyrolyze the remaining 15 wt% of mass from 325° to 400°C. It appears that PiBMA depolymerizes to isobutyl methacrylate vapor (bp 155°C). Unzipping occurs faster in the air atmosphere, but in the absence of exothermic events, oxidation does not occur.

##### (3) PEG

For polyethylene glycol in both nitrogen and air, mass loss occurs in three events (Fig. 3). In N<sub>2</sub>, the first 4% of mass loss occurs over a wide range of temperature from 40° to 285°C. The



(a)



(b)

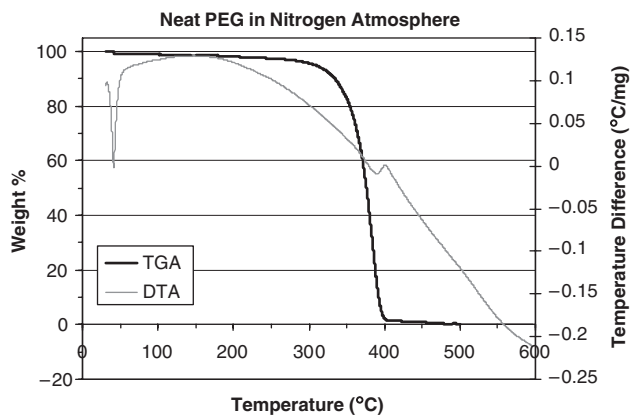
**Fig. 2.** Poly(isobutyl methacrylate) (PiBMA) degradation (a) in  $N_2$  atmosphere, (b) in air. For differential thermal analysis (DTA) exothermics appear as upward events, endotherms downward.

majority of the mass loss occurs in the second event from 285° to 410°C, with the remaining 1.5 wt% organic material pyrolyzed from 415° to 500°C. A sharp endotherm at 40°C occurs at a temperature where melting is expected. The large mass decline between 350° and 400°C is not accompanied by large thermal events. The small thermal event close to 400°C occurs after most of the mass is lost. In this inert atmosphere, evaporation is predominant. In air, 1 wt% of highly volatile material is lost between 40° and 140°C, with the majority of mass loss occurring as a single event from 145° to 335°C. The last 5 wt% mass is removed from 335° to 455°C. Several exotherms are present due to oxidative degradation at 225° and 260°C. A dramatic difference in degradation behavior is evident between these atmospheres.

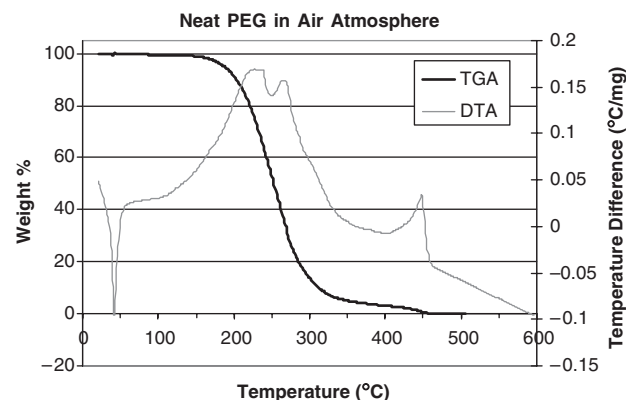
Voorhees *et al.*<sup>19</sup> have investigated PEG degradation in both nitrogen and air atmospheres. Using gas chromatography–mass spectrometry (GC–MS) and Fourier-transform infrared spectrometry (FTIR), five oligomeric series of glycol and ether fragments (MW  $\approx$  300) were identified in both atmospheres. Degradation of PEG occurs by homolytic cleavage at either the C–O or C–C bonds. In the  $N_2$  atmosphere, disproportionation and intramolecular reactions give a large product distribution containing the five oligomeric end series. Oxidation in air atmosphere prevailed over the disproportionation, hydrogen abstraction, or other inter- and intramolecular reactions to reduce the range of degradation products.

#### (4) Heavy Mineral Oil (HMO)

HMO is a paraffinic petroleum distillate. Figure 4(a) shows that it degrades or evaporates in almost a single event in  $N_2$  from 175° to 310°C. A single endotherm at 295°C is attributed to the highest rate of mass loss. Evaporation occurs during the single event, followed by residual pyrolysis from 310° to 390°C. In an



(a)



(b)

**Fig. 3.** Poly(ethylene glycol) (PEG) degradation (a) in  $N_2$  atmosphere, (b) in air. For differential thermal analysis (DTA) exothermics appear as upward events, endotherms downward.

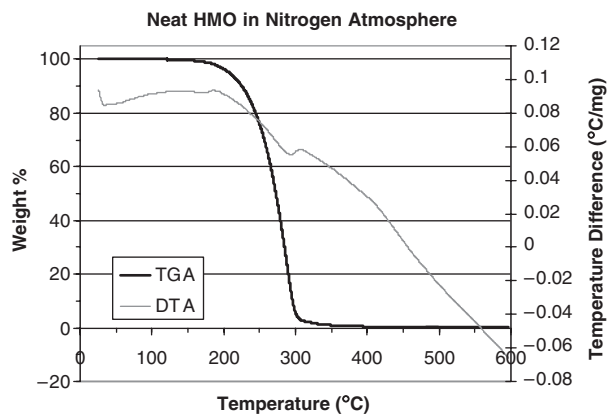
air atmosphere, 90 wt% of material is lost between 200° and 365°C, with the remaining 10 wt% lost from 380° to 510°C (Fig. 4(b)). Several exothermic peaks exist due to the oxidation of material in air.

#### (5) Stearic Acid

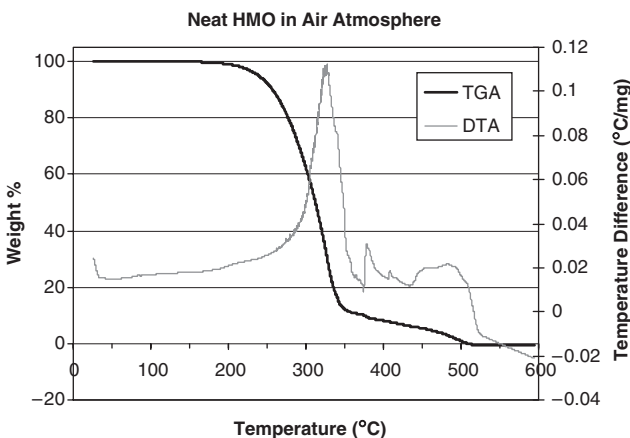
In dynamic nitrogen (Fig. 5(a)), mass loss from stearic acid occurs as a single event from 175° to 275°C due to the evaporation of the material (bp = 198°C). Two endotherms observed can be attributed to the melting at 70°C and the highest rate of mass loss at 265°C. In air, two stages of mass loss occur (Fig. 5(b)). The first 80% of mass loss occurs from 175° to 315°C with an exothermic event; the remaining pyrolysis takes place during a more complicated second stage from 315° to 500°C with several exothermic reactions.

#### (6) Single Components Compared with Polymer Blend

Comparative TGA plots for each neat component are shown in Fig. 6 for both nitrogen and air. All neat organic binders are removed below 500°C for either atmosphere. In both atmospheres, the PiBMA methacrylate is removed at much lower temperatures than the EEA ethylene copolymer. For the minor components, the stearic acid is removed at lower temperatures. Notice the reversal in order for the PEG glycol and the paraffinic HMO, where in nitrogen, HMO is removed below 300°C and PEG remains up to 400°C, while PEG is removed at quite low temperatures in air, while HMO remains up to 350°C. These individual thermograms can be used to predict the behavior of the blend. Figure 7 presents the TGA data for the five-component polymer blend in air, comparing the actual thermogram with a “calculated” behavior based on a weighted sum of each neat thermogram. The calculated weight loss at each tempera-



(a)



(b)

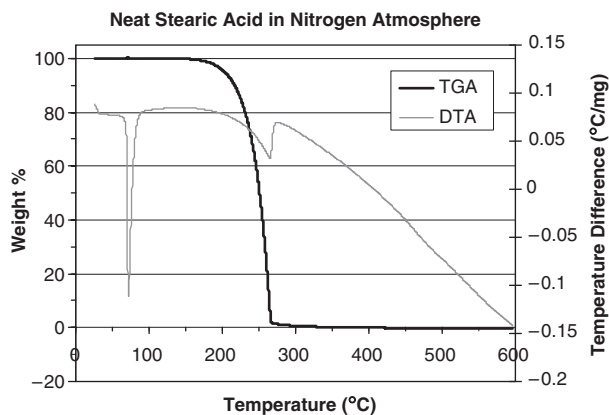
**Fig. 4.** Heavy mineral oil (HMO) degradation (a) in N<sub>2</sub>, (b) in air. For differential thermal analysis (DTA) exothermics appear as upward events, endotherms downward.

ture is 60% of the EEA weight loss, plus 28% of the PiBMA weight loss, plus 10% of the PEG, 1.5% of stearic acid, and 0.8% of HMO. Notice that it is dominated by the major components EEA and PiBMA.

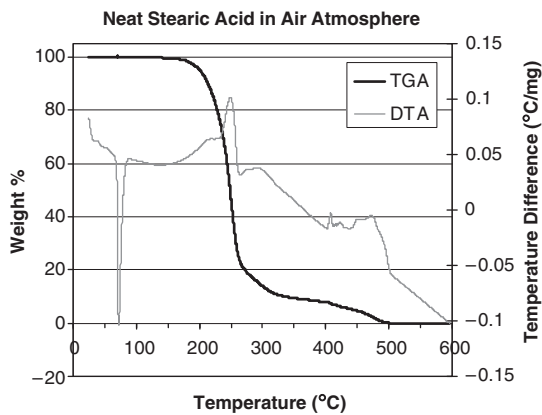
Weighted-sum behavior would be expected for the case where the components in a blend do not interact.<sup>20</sup> As the two curves differ significantly between 250° and 325°C, it appears that the materials are interacting enough to underestimate significantly the early stage behavior. At 225°C, the blend experiences about 6% weight loss, but only about 2% is expected from the single components (mostly PEG and the beginning of PiBMA). At 500°C, the observed and calculated weight loss for the blend are the same at about 10%, but the calculated thermogram has a steep slope reflecting the loss of most of the methacrylate in this temperature range. The experimental thermogram has a more gradual slope, suggesting that thermal degradation of the methacrylate is retarded when it is blended with the ethylene copolymer. Almost all of the weight is lost from neat methacrylate by 275°C, but it seems to persist up to about 340°C in the blend. Beyond 350°C, the experimental thermogram is reflecting the loss of residuals from EEA, and is about as expected, although displaced by about 20°C.

**(7) Polymers with Ceramic Powder**

We first examine mixtures containing only EEA and ceramic powder to examine ceramic interaction effects on degradation. Figure 8 shows the TGA for a 50 vol% EEA: 50 vol% BBNT composite heated in air. As BBNT ( $\rho = 5.9 \text{ g/cm}^3$ ) has a significantly greater density than EEA ( $\rho = 0.9 \text{ g/cm}^3$ ), only 15 wt% of material is to be removed. Mass removal occurs in three events, the first of which occurs from 220° to 360°C, removing 2

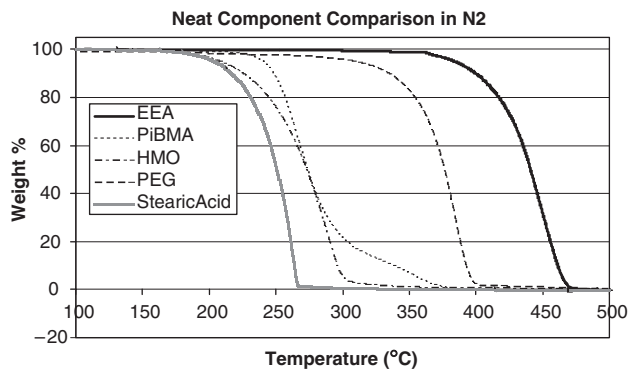


(a)

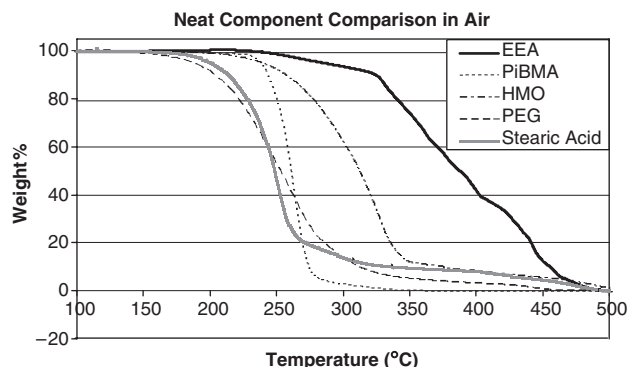


(b)

**Fig. 5.** Stearic acid degradation (a) in N<sub>2</sub>, (b) in air. For differential thermal analysis (DTA) exothermics appear as upward events, endotherms downward.



(a)



(b)

**Fig. 6.** Neat component comparisons, (a) thermogravimetric analysis (TGA) in N<sub>2</sub>, (b) TGA in air.

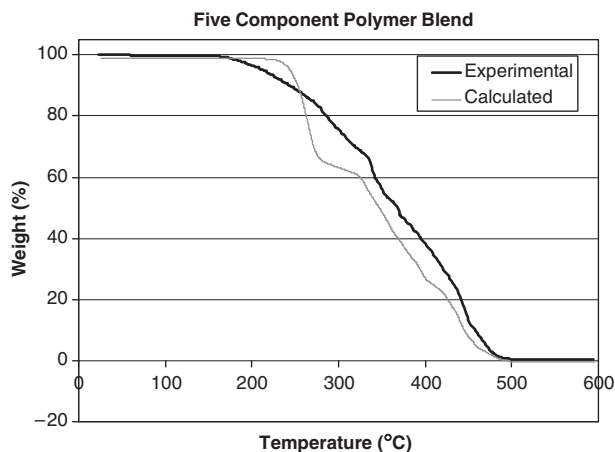


Fig. 7. Thermogravimetric (TGA) analysis of polymer blend.

wt% of material, the second event from 360° to 440°C, removing 5 wt% of material, and the last event from 440° to 485°C, removing the final 8 wt%. The final event is exothermic, with the heat output peaking sharply at the very end of the process. It is tempting to attribute the 360°–440°C weight loss to the first stage seen in neat EEA at lower temperatures, which perhaps were acrylate group removal (250°–325°C). If that is the case, then the ceramic powder has retarded this process and delayed it by almost 100°C.

Figure 9 compares TGA results of the polymers and ceramic blends, with the weight loss shown as a fractional polymer weight loss only (i.e., the mass of the ceramic residue has been normalized out). When only the EEA is present, it is apparent that the ceramic powder retards degradation, with weight loss delayed by about 50°C, until the final stage when the oxide accelerates the loss of the last 10% of the polymer. Thus, the thermogram of the neat EEA is a rather poor predictor of the behavior of the EEA–ceramic blend. Also, in Fig. 9, we compare the thermograms with and without ceramic powder for the five-component polymer blend, which has the ethylene copolymer with the methacrylate and minor additives. Mass loss begins at a lower temperature because of the methacrylate and light additive. Note that the blend loaded with ceramic powder has weight loss retarded in the early stages, when methacrylate degradation is expected to dominate. However, the blends and the blend loaded with powder both have the same midpoint temperature  $T_{50}$ , at 365°C. At higher temperatures, the ceramic powder accelerates weight loss, so that binder removal is complete at 430°C in the presence of powder, while some residue of the blend remains up to 500°C. It is also notable that the polymer blend has all been removed at 430°C, while the simple EEA–ceramic mix still has 60% residual binder. Clearly, the residue of a blend of 60% EEA–28% methacrylate blend, above the temperature where the methacrylate is presumed to be gone, is still quite

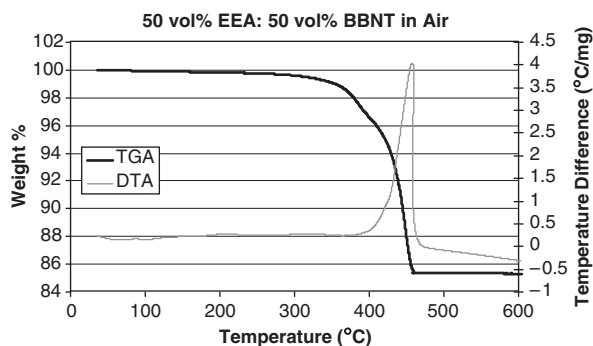


Fig. 8. Thermogravimetric analysis (TGA) of 50 vol% poly(ethylene-co-ethyl acrylate) (EEA): 50 vol% BBNT in an air atmosphere.

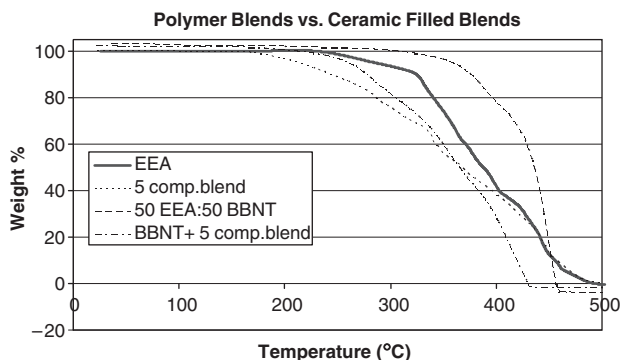


Fig. 9. Thermogravimetric analysis (TGA) comparison plots of neat poly(ethylene-co-ethyl acrylate) (EEA), five-component polymer blend, 50 vol% EEA: 50 vol% BBNT, and ceramic-filled thermoplastic composite in an air atmosphere. Note: 50 vol% EEA: 50 vol% BBNT and the ceramic-filled composite have been normalized to compare with EEA.

different than the residue of the ethylene copolymer itself. This is more evidence that the behavior of a blend is difficult to predict from the behaviors of the individual components.

## V. Conclusions

The individual components of a thermoplastic binder system based on EEA and PiBMA have significantly different degradation behavior in nitrogen and in air, with exothermic oxidative reactions dominating in the later stages in air.

The degradation behavior of blends of these polymers can only be approximately related to the individual behaviors, as methacrylate decomposition is retarded when blended with the ethylene copolymer.

Oxide ceramic powder significantly alters polymer degradation, retarding degradation in the early stages but accelerating degradation in the later exothermic stages.

Polymer–polymer interactions and oxide–polymer interactions make the degradation behavior of blends difficult to predict from single component behavior.

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