JOURNAL OF MATERIALS SCIENCE 33 (1998) 2795–2803

Chemistry of removal of ethylene vinyl acetate binders

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The research presented herein has focused on debinding of an ethylene copolymer from a SiC based moulded ceramic green body within an inert atmosphere. Upon heating, the pure polymer undergoes a two-stage thermal degradation process. In the first stage, acetic acid is the only degradation product formed. The effect of the introduction of high surface area powder on the chemistry and kinetics of this first stage reaction was examined. The effluents were captured and analysed in a gas chromatograph/mass spectrometer. The product of the reaction was not altered by introduction of the ceramic powder. However, the kinetics of the reaction were altered. The kinetics of the reaction were determined with the use of thermogravimetric analysis (TGA). The mechanism of mass transport during binder removal was determined by monitoring dimensional changes during binder removal. It was found that one unit volume of shrinkage corresponded with one unit volume of binder removed, indicating that no porosity developed. The escaping acetic acid effluents must diffuse through the liquid polymer filled pores to escape. Bloating was observed in certain conditions and was attributed to the concentration of acetic acid exceeding a critical value, resulting in bubbling. © *1998 Kluwer Academic Publishers*

1. Introduction

The process of binder removal from mouldable ceramic materials is quite complicated. Most systems contain multicomponent species which themselves may degrade during thermal decomposition to additional species. Often it is not clear which species are involved and at what rate they are being generated and removed. This paper examines binder removal in a simplified system which contains submicronate SiC powder and an ethylene vinyl acetate (EVA) copolymer. The initial product of EVA degradation is exclusively acetic acid, a single component and well known organic species with an atmospheric boiling point of 118 °C. EVA is not only a model system, but also a practical binder for moulded components [1–3].

Others have noted that the presence of high surface area ceramic powder alters the reactions taking place in other binder systems [4–6]. This paper specifically investigates the effect that high surface area ceramic powder has on the chemistry and kinetics of the first stage degradation reaction of EVA. It is during the initial stages of binder removal, when organic species must diffuse through the polymer filled pores, that most binder burnout problems arise [7–12]. This is the region which is studied in this paper.

Large dimensional changes were also observed to occur during the thermal degradation process of this filled system. These dimensional changes, which can lead to warping, creeping and cracking in the system, were extensively reported in another paper [13]. A third paper examines in detail the type of defects observed in the present system within the initial stages of binder removal [14]. Finally, the initial stages of binder removal are modelled for the present system in another set of papers [15, 16].

Ethylene vinyl acetate is a random copolymer of ethylene and vinyl acetate. Upon heating in nitrogen, it first undergoes a side group elimination reaction [17] which generates acetic acid and leaves a double bond in the polymer chain, so the remaining polymer can be considered polyethylene co-polyacetylene. This process can be represented by:

$$\underset{\text{EVA}}{-[(CH_2\text{–}CH_2)_x\text{–}(\underset{\substack{|\\ O\text{–}\underset{\substack{\|\\ O}}{C}\text{–}CH_3}}{CH}\text{–}CH_2)_y\text{–}]_n} \longrightarrow y\,\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{polyethylene co-polyacetylene}}{-[(CH_2\text{–}CH_2)_x\text{–}(CH=CH)_y\text{–}]_n} \qquad (1)$$

This reaction is well characterized by thermogravimetric analysis (TGA), and can be used to quantitatively analyse the vinyl acetate content of EVA [18, 19]. Fig. 1 compares the TGA degradation behaviour of polyethylene to that of EVA [18]. The vinyl acetate is eliminated at a much lower temperature than the temperature at which polyethylene begins to degrade. This results in what was termed the "acetic acid shelf" in the TGA plot of EVA degradation. At this stage, the remaining polymer is a copolymer of polyethylene *co*-polyacetylene. The second stage degradation reaction was not studied in depth, but the stability of the remaining polymer up to temperatures of around 400 °C (depending on heating rate) was noted.

The critical stage of binder removal in this, as well as other filled polymer systems [20, 21], is during initial weight loss. It is at this time, in the current system, that bloating is often observed. Therefore, the primary focus of this paper is on this first stage of binder removal that occurs during the acetic acid elimination reaction. In the present system, the copolymer has 18 wt % vinyl acetate content, which, upon initial polymer degradation, will result in 12.5% of the copolymer's weight converting to acetic acid. Note that the degradation reactions take place at temperatures above the boiling point of acetic acid. The amount converted assumes that the reaction is unaltered by the presence of the ceramic powder. A large portion of this paper explores the effect of the ceramic powder on the degradation process. This includes how the presence of the powder has altered the reaction rate and also examines if the ceramic powder has altered the product of the reaction. To do this, effluents were collected and then analysed within a gas chromatograph (GC) and mass spectrometer (MS).

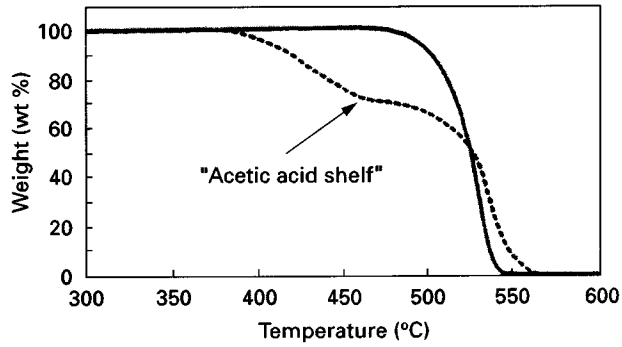

Figure 1 Degradation of ethylene vinyl acetate (EVA) (– – –) compared with low density polyethylene (LDPE) (—) from [17].

TABLE I Selected properties of EVA 470

Melt index: 0.7 dg min^{-1}	M_n = 100 000 M_w = 250 000	T_g = − 20 °C T_m = 84 °C
Density = 0.941 g cm^{-3}	Formula $-[(CH_2-CH_2)_x-(CH-CH_2)_y-]_n$ O–C–CH_3 O	Per cent crystalline = 10% Vinyl acetate (VA) content = 18 wt %

2. Experimental procedures

2.1. Composition and processing

The polymer-ceramic powder composition is reported as a nominal room temperature vol %, based on the room temperature densities of the components. The compositions are 51 vol % ceramic powder + 49 vol % copolymer for the ceramic/EVA system, or 54.5 vol % ceramic + 39.5 vol % EVA + 6 vol % mineral oil for the systems containing mineral oil. The EVA copolymer* has 18 wt % vinyl acetate content. Table I lists some of the properties of the EVA polymer. The ceramic powder was prepared by ball milling using alumina grinding media, an isopropyl alcohol slurry composed of silicon carbide†, 6 wt % aluminium oxide‡ and 4 wt % yttrium oxide§ for 24 h. The alumina/yttria ratio used is a eutectic composition (mp = 1760 °C) which facilitates liquid phase sintering of SiC [22–25]. The ceramic powders were mixed by ball milling in isopropanol for 24 h, using alumina grinding media, followed by drying. Blending of the powder with the resin was carried out in a heated shear mixer¶ with roller blades. The EVA resin was added first and melted under shear at 130 °C at a constant speed of 60 r.p.m. The ceramic powder was added in small increments of mixing for 1–2 min. The increased shear, upon adding the powder, increased mixing temperatures to 150–160 °C. The mineral oil** if used, was added next.

The binder uniformity within a batched material and between batches of material was checked by the random selection of four specimens from two separate batches of material. The per cent of binder in each material was determined by TGA analysis. These results indicate no significant differences between binder content within a batch of material or between batches. The moulding process may lead to preferential binder distribution if the polymer phase preferentially flows or is extruded away from high pressure regions leaving behind a powder rich phase [26, 27]. The disc-shaped specimens were compression moulded at 27 MPa (4000 p.s.i.) and 120 °C in a uniaxial mould. TGA analysis on moulded specimens revealed no difference in the binder distribution throughout the specimen indicating that moulding did not lead to any preferential binder distribution for this system.

* ELVAX 470, DuPont.
† β-SiC, H.C. Starck grade B 10; SA = 14–17 m^2 g^{-1}, mps = 0.75 μm.
‡ Malakoff Industries, Inc., RC-HP DBM; SA = 7–8 m^2 g^{-1}, mps = 0.55 μm.
§ Johnson Matthey, mps = 1–2 μm.
¶ C.W. Brabender Instruments, Inc., PL 2000 Plasti-Corder with roller blade mixing heads.
** Heavy mineral oil, Mallinckrodt, paraffin oil, sp. = 0.881.

2.2. Displacement and GC/MS measurements

Dimensional changes were measured in a thermomechanical analyser (TMA) built specifically for studying the binder removal process from mouldable green ware [13]. The same instrument was modified to collect effluents during thermal degradation of the binder system. A schematic of the instrument is shown in Fig. 2. The specimen rests on a platform at the bottom of an inner fused silica tube which is vertically oriented. A fused silica rod, rests on top of a porous fused silica plate which in turn, rests on the specimen. The porous fused silica glass with pore sizes of 90–150 μm was used to distribute the load that the rod places on the specimen and still allowed unimpeded binder removal. A typical nominal pressure of 1.4 kPa rested on the specimen during each test. The linear variable differential transformer (LVDT) core and bore reside on a fused silica support above the furnace. Elaborate cooling means were used to thermally isolate the specimen from the LVDT core system to localize all dimensional changes to that of the specimen alone. A ± 1 μm change was noted during heating a blank from room temperature to 500 °C.

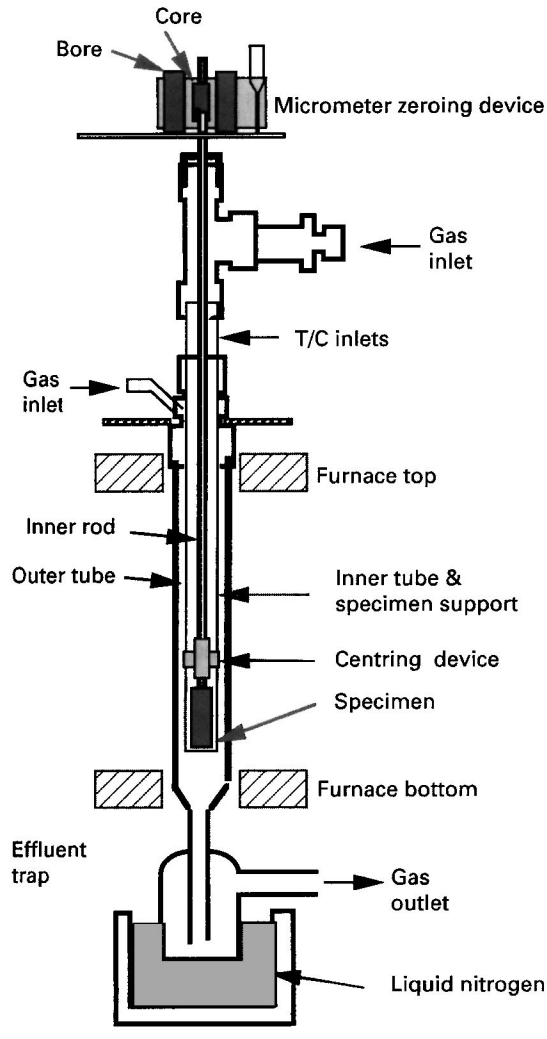

Figure 2 Schematic of thermomechanical analyser (TMA) modified to collect effluents for gas chromatograph (GC)/mass spectrometry (MS).

Normal displacement measurements were made with nitrogen gas flowing through the inner tube down to the specimen and then up through the annulus between the inner and outer tube to the exhaust port. Alternatively, gas effluents were collected during binder removal through the modification of the existing TMA instrument. In this instrument, a 4.5 g polymer filled specimen (51/49 ceramic/EVA) was placed on a platform at the bottom of an inner fused silica tube which is vertically oriented. The specimen was next heated at 2 °C min^{-1} to 315 °C with helium gas flowing past the specimen and into a liquid nitrogen cooled condensing chamber. The condensed effluents were later analysed in a GC/MS*. Helium gas was used to minimize reactions in the gas phase and as a carrier gas through the liquid nitrogen trap. Once the sample had been collected, the liquid nitrogen trap containing the condensed effluents was removed and allowed to warm to room temperature while sealed with parafilm® to reduce contamination. GC/MS micro-litre samples were then taken from the condensed liquid in the container and injected into the GC/MS port.

Differential thermal analysis (DTA)† was utilized to examine the endothermic/exothermic nature of the degradation reactions. The specimens were heated at 10 °C min^{-1} under a flowing nitrogen atmosphere and used an alumina reference. An 8 mg sample was used for the neat EVA and an 18 mg sample was used for the 51/49 ceramic powder/EVA specimen.

A moulded specimen 9 mm × 25 mm × 50 mm was heated in a nitrogen atmosphere to a temperature of 315 °C for the purpose of partially removing the binder and then furnace cooled to room temperature. The specimen was heated according to a schedule used by a collaborating company that was found to produce defect-free parts. The specimen was heated from room temperature to 145 °C at 1 °C min^{-1}, from 145 °C to 250 °C at 0.033 °C min^{-1}, and finally, from 250 °C to 315 °C at 0.067 °C min^{-1}. The partially burned out specimen was sectioned using a slow speed saw‡. The binder distribution was then determined with a TGA§.

2.3. Kinetic measurements

Two different thermogravimetric analysis (TGA) instruments were employed. The first TGA¶, utilized small (10–30 mg) samples to study the degradation reaction kinetics of both the neat EVA and the EVA in the presence of the powder. The specimens were placed in a platinum pan and heated at a constant

*Hewlett Packard 5890.
†TA Instruments 1600 DTA.
‡Buehler Isomet.
§TA Instruments.
¶TA Instruments Hi-Res TGA 2950.

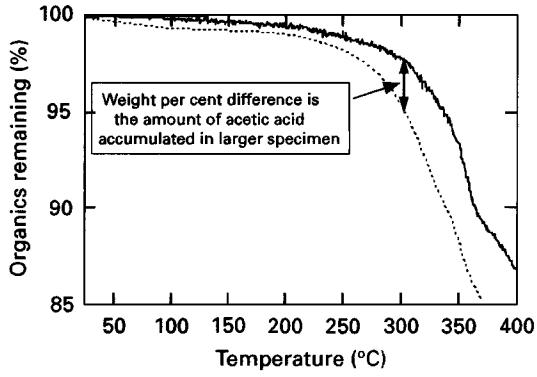

Figure 3 Fraction of organics remaining in sample, from thermogravimetric analysis for small 25 mg (---) and large 2 g (—) samples, 2 °C min^{-1} heating in nitrogen, SiC/EVA = 51/49.

heating rate to determine the reaction kinetics. The second TGA* utilized larger specimens in which mass transport was rate limiting.

Directly measuring the EVA elimination reaction while in the presence of the ceramic is desirable. However, no direct observations were readily accessible. An estimate of the generation rate of acetic acid within the filled system was obtained by TGA weight loss data on small 25 mg size samples at constant heating rates of 1, 2, 4, 8, and 16 °C min^{-1}. In this study, kinetics were determined with the assumption that the rate of weight loss as measured by the TGA on small 25 mg specimens was equal to the rate of generation of acetic acid. This assumes that no storage or accumulation of the formed acetic acid takes place within the small 25 mg specimens. Additionally, the small 25 mg samples were cut into smaller size pieces to further reduce the transport path.

It was further assumed that the rate of acetic acid generation in the 25 mg samples corresponded with the rate at which the elimination reaction proceeded in the larger 0.5 g to 8 g specimens. Fig. 3 elaborates on this point. For example, the 25 mg sample shown in Fig. 3 was found to lose 4% of the organics weight at 300 °C. The bulky 2 g sample was found to lose only 2.5% of its organics at 300 °C. The rest of the acetic acid formed from the remaining 1.5% organic conversion was accumulated or stored within the sample.

3. Results and discussion

3.1. Reaction products

The specimen that was placed in the TMA for effluent collection had lost 5% (0.05 g) of the organic content while heating to 315 °C and then cooling. This region is clearly in regime I, the regime where only acetic acid should be formed. This is also under the 12.5% expected if total acetic acid elimination was to occur. The GC and MS results of the effluents collected are shown in Fig. 4a and b, respectively. The GC results show one major peak. This indicates that only one reaction product is being formed. The mass

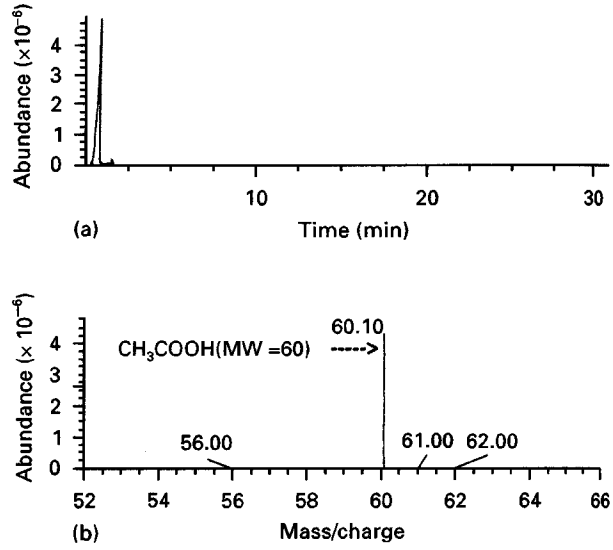

Figure 4 (a) GC, and (b) MS data.

spectrometer results shown in Fig. 4b reveal that the molecular weight of this peak is 60, which is the molecular weight of acetic acid. It appears, therefore, that the ceramic powder has not altered the product of this first stage elimination reaction. Acetic acid is still the only product of the initial stage degradation reaction.

3.2. Reaction kinetics

3.2.1. TGA and DTA

The combined TGA and DTA results for the neat and filled polymer are shown in Fig. 5a and b, respectively. A comparison of the TGA results for neat versus filled EVA shown in Fig. 5 reveals a difference in the first stage reaction rate for the two specimens. Neat EVA shows a clear acetic acid shelf and the filled polymer shows a more gradual weight loss process during the initial stage degradation behaviour. It appears that the reaction process has been slightly altered. Section 3.2.2. will examine the kinetics in more detail.

The character of the DTA traces of the neat and filled EVA polymer shown in Fig. 5a and b, are similar. In each case, three distinct endothermic peaks are seen. The endothermic peaks at 88 °C and 86 °C for the neat and filled polymer respectively correspond to the melting of the polymer crystals. DSC measurements were previously reported and quantitatively identified the area of the neat polymer at 29.5 J g^{-1} polymer and that of the filled polymer at 19.5 J g^{-1} polymer [13, 28].

The endothermic peaks at 349 °C and 375 °C for the neat and filled polymer, respectively, correspond to the first stage elimination reaction. The peak for the neat polymer is more defined in shape while that of the filled polymer appears as a shallow trough. The high surface area ceramic filler has extended the region over which the first stage reaction proceeds so that the

*TGA-171, ATI-CAHN microbalance.

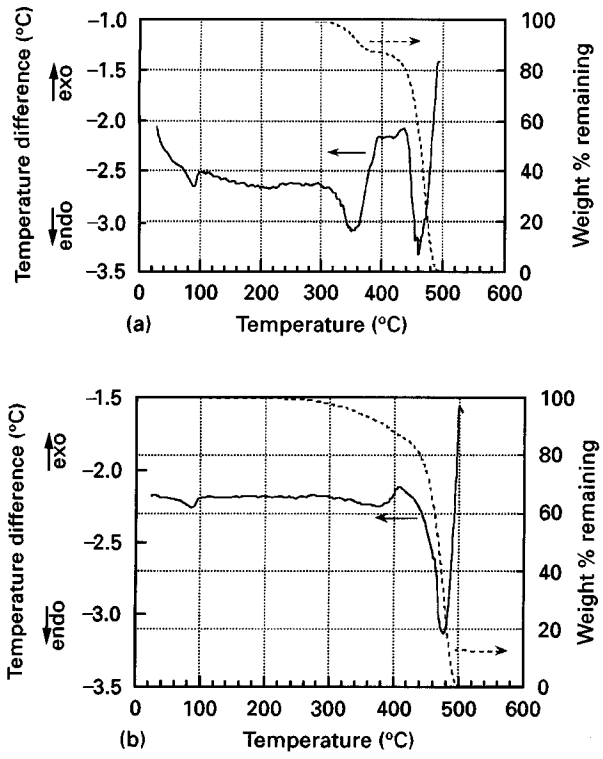

Figure 5 (a) DTA/TGA of unfilled polymer (EVA 470), (b) DTA/TGA of filled polymer (51/49 Ceramic/EVA).

clearly defined acetic acid shelf in the neat polymer is not clear for this filled specimen.

The second region of weight loss, i.e. the region in which the last 88% of the binder is removed, begins with predominantly endothermic reactions and ends with predominantly exothermic reactions. For both neat and filled EVA, the last endothermic reactions increase up to the point at which only 30 to 40% of the polymer is remaining. This is attributed to chain scission and evaporation. Then, heat evolution appears to occur and accelerate until all the mass is gone. This might be evidence of carbon–carbon bond or cyclic ring formation occurring along with chain scission [29]. However, no carbon residue was measured or noted in the case of the neat polymer which might have substantiated carbon–carbon bond formation.

3.2.2. Altered kinetics

Several methods of kinetic analysis that use TGA weight loss data are presented in the literature. These methods include the isothermal temperature method [30–32], the variable heating rate method [31, 33], and the method used in this study, the constant heating rate method [31, 34]. In the case of EVA degradation, the following kinetic equation is applied [31, 33]:

$$d\alpha/dt = Ag(\alpha)\exp(-E/kT) \qquad (2)$$

where: α = mass fraction remaining, t = time, A = pre-exponent (frequency factor), E = activation energy, $g(\alpha)(1-\alpha)^n$ for EVA system, and n = reaction order.

TABLE II Literature values for kinetics of neat EVA [33]

Region	Log (A)	Reaction order, n	Activation energy, E (kJ mole^{-1})
I	13.2	0.9–1.2	163–186
II	18.2–19.0	0.6–0.9	248–270

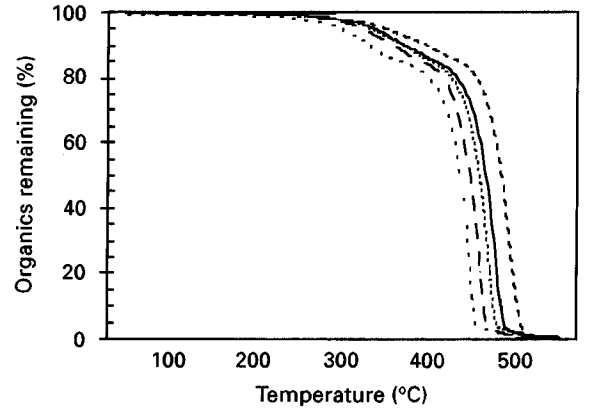

Figure 6 TGA of filled EVA in nitrogen at constant heating rates of (·-·) 1, (–-) 2, (----) 4, (—) 8 and (–––) 16 °C min^{-1}.

Table II lists results from the literature for application of this equation for regions I and II for the neat polymer only. Equation 2 provides a good description of the experimental behaviour for neat EVA.

The kinetics for decomposition in region II were not of interest in this paper other than for the observation that the rate of decomposition in the neat and filled specimens appeared to be the same for region II. However, it should be noted that within the literature, Equation 2 was also applied to region II and found to fit. The actual physical interpretation of the fit becomes unclear since many decomposition reactants and products are taking place in region II instead of one elimination reaction process.

The TGA results are summarized for the various heating rates in Fig. 6 for the filled EVA polymer. Faster heating rates shift the weight loss to higher temperatures.

3.2.2.1. Activation energy. The Flynn–Wall method was used for the determination of activation energy at various percentage levels of conversion for both the neat and filled EVA systems [31]. This is accomplished by application of the natural log of both sides of Equation 2 such that:

$$\ln(d\alpha/dt)\alpha = \ln(A) + \ln[g(\alpha)] - E/kT \qquad (3)$$

A plot of $\ln(d\alpha/dt)$ versus $1/T$ for various constant levels of conversion should then yield a straight line with slope of $-E/k$.

Within the present system, the wt % of organics that converts to acetic acid is calculated to be 12.5%. Therefore, the activation energy for the region I reaction should be the same from 0 to close to 12% conversion. Fig. 7a [31] and b compares the data of

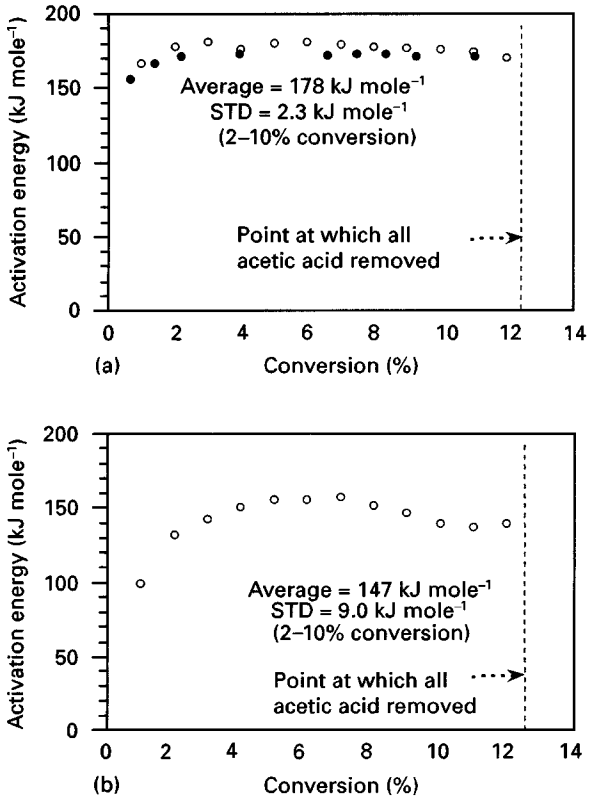

Figure 7 Activation energy as function of conversion for the Flynn–Wall method applied to a) unfilled EVA (open circles – this work: filled circles – [31]), b) filled EVA.

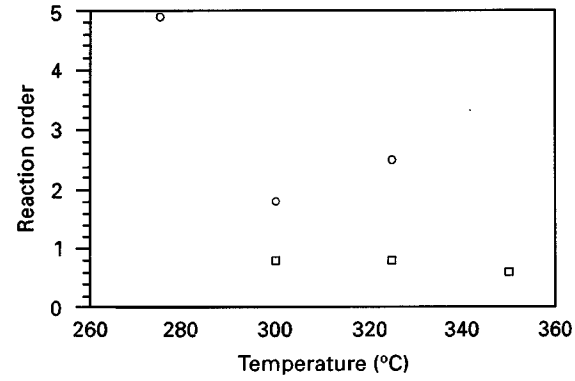

Figure 8 Reaction order as a function of temperature for the Day *et al.* method applied to EVA. The unfilled EVA (□) follows first order kinetics. The filled EVA (○) does not follow this same type of kinetic behaviour.

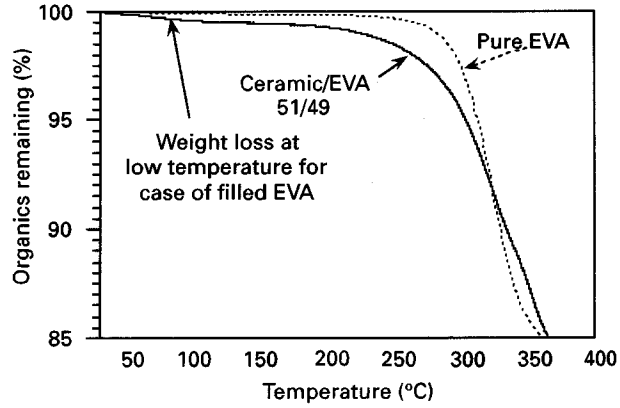

Figure 9 TGA traces showing initial weight loss in nitrogen at temperatures for filled systems at 2 °C min^{-1} heating.

Nam and Seferis [31] to the presently utilized neat EVA system. Note that the EVA used by Nam and Seferis had 30% acetic acid compared to 12.5% for our system. Note also that the activation energy is constant with the per cent conversion in each case, indicating an activated reaction process. Note also that the activation energy of 178 kJ mole^{-1} obtained in the present system matches the 163–186 kJ mole^{-1} activation energy in the literature.

The same Flynn–Wall plot for the filled system appears in Fig. 7b. The activation energy is still constant with the per cent conversion indicating that the reaction still follows an activated process. However, the powder appears to have lowered the activation energy from 178 kJ mole^{-1} for the neat polymer to 150 kJ mole^{-1} for the filled polymer. The reason for this change is not known at this time.

3.2.2.2. Reaction order. A method used by Day *et al.* [32] was used for determination of the reaction order according to Equation 2 with $g(\alpha) = (1 - \alpha)^n$. This was done at various temperatures for the region I reaction. For this method, the natural log of Equation 2 is taken such that:

$$\ln(d\alpha/dt)_T = \ln(A) + n\ln(1 - \alpha)_T - E/kT \quad (4)$$

Plots of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ at constant temperatures result in straight lines whose slopes are the reaction orders. The resultant reaction orders at various temperatures are plotted in Fig. 8 for both the neat and the filled polymer. The reaction order for the neat polymer appears constant with temperature indicating that Equation 2 with $g(\alpha) = (1 - \alpha)^n$ appears to describe the reaction. The reaction order of 0.8 for the neat polymer is not much different from the reaction order of 0.9–1.2 from the literature [33]. The reason for this small difference is considered to be within experimental variations.

As seen in Fig. 8, the reaction order for the filled system is not constant with temperature so that $g(\alpha)$ does not equal $(1 - \alpha)^n$ in this case. The ceramic powder has appeared to alter the kinetics so that the reaction cannot be simply described since $g(\alpha) \neq (1 - \alpha)^n$. The more detailed kinetic analysis required to better describe the kinetics was beyond the scope of this research and is the subject of future investigation.

3.2.2.3. Powder adsorbates and pre-existing degradation products. The presence of the ceramic powder has not only appeared to alter the kinetics of the degradation reaction, but also has another characteristic that differentiates it from the neat polymer. Fig. 9 is an example of this distinct region at a heating rate of 2 °C min^{-1}. This figure shows that weight loss on the order of 0.7% of the total organic content is observed at temperatures of about 100 °C for the filled system. As will be shown in other papers [15, 16, 28], this low

temperature region is partially responsible for some of the bloating behaviour.

Further investigation indicated that some, but not all, may be attributed to adsorbates on the ceramic powder. For detailed results, see Hrdina [28]. However, it is noted that the kinetics of the filled system, even with correction for adsorbents, are still different from those of the neat EVA. The altered kinetics are not from adsorbents on the powder. The reason for the altered kinetics was not identified. Catalytic effects in which the reaction process is speeded up might explain the weight loss at lower temperatures in the ceramic filled system. However, it does not explain why the final stages of the region I reaction are not also accelerated, but are delayed.

The altered kinetics might be explained by another possibility. Perhaps, some decomposition of the EVA polymer took place during prior shear mixing in the plasticorder. The mixing in the plasticorder is at high shear rates and at temperatures close to the decomposition temperature of neat EVA (150 °C to 170 °C). It is suspected that the mechanical and thermal energy input may have been enough to cause some partial decomposition of EVA which resulted in some "precharging" of the filled polymer with acetic acid. The kinetics may have been altered as a result of the presence of pre-existing acetic acid.

It should also be noted that the polymer used in this study contains 0.02 to 0.1 wt % BHT (butylated hydroxytoluene) which is an antioxidant added by the manufacturer with a boiling point of 265 °C [35]. This quantity of material does not account for the 0.7% organic weight change observed.

3.3. Mechanism of mass transport

The mechanism for binder removal presented in this paper is based on the premise that molecular species originate from throughout the specimen and then diffuse through the liquid polymer to the surface where they then evaporate. These two conditions must be met by the system. The first, that the diffusing species originate from throughout the specimen, is dealt with here. The second condition, that the species are diffusing through the liquid polymer, is examined in the following section.

The molecular species leaving the filled EVA system is acetic acid generated from the vinyl acetate portion of the copolymer. A sectioning experiment was undertaken to infer if the degradation was occurring uniformly through the thickness of the material. A specimen was heated to 300 °C, which would result in approximately 10 wt % removal. The sample was sectioned into 0.5 mm slices, as shown in Fig. 10, and the amount of polymer in each slice was determined by TGA. The TGA data indicated that each slice had experienced an average of 10.8 wt % loss, uniformly through the thickness.

It should also be noted that the uniform distribution of binder seen in Fig. 10 leads to the conclusion that acetic acid has not appreciably accumulated within the sample. The transport of acetic acid out of the sample was apparently fast enough to remove

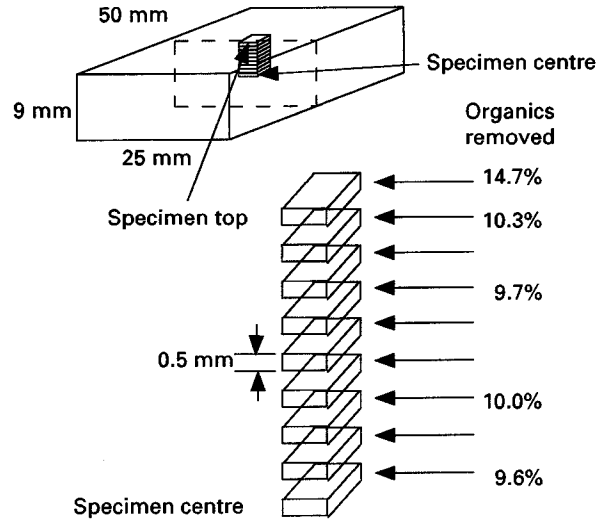

Figure 10 Binder distribution in partially burned out specimen showing evidence that the binder is removed from throughout the specimen.

the generated acetic acid from the sample for this particular heating schedule.

We infer that the acetic acid is transported by diffusion through the liquid polymer during the early stages of the binder removal because there is no open porosity in the samples until more than 30 wt % of the binder has been removed. We report elsewhere [13] that these samples undergo 6% linear shrinkage and remain fully saturated as the first 30% of the binder is removed. Generation of volatile species takes place within the entire system as a result of thermal decomposition of the polymer. The generated species then diffuse through the liquid polymer phase to the surface of the specimen where they are removed by evaporation. Samples containing mineral oil have the same mechanism of mass transport in this filled polymer system.

3.4. Phenomena of bloating

The predominant defects that show up in this system appear to start as an internal crack, and then develop into bloats. They are a result of the acetic acid exceeding a critical concentration. A typical example of a defect observed in the present system is shown in Fig. 11. This particular specimen is 3 mm thick and was heated at 2 °C min^{-1} to 270 °C and cooled. Two rather large bubbles are shown that appear near the centre of the specimen. Duplicate specimens heated to 250 °C at the same rate did not bloat.

It should be remembered that acetic acid is forming everywhere in the material during heating. It was also shown that acetic acid diffuses through the system to the surface. Therefore, the region of highest concentration is expected to be the specimen centre which has the longest diffusion path. This is also the primary region where bloating is observed. The bloating is also associated with the initial region of weight loss. Acetic acid was found to be the overwhelming product of the reaction in this region as was reported in Section 3.1.

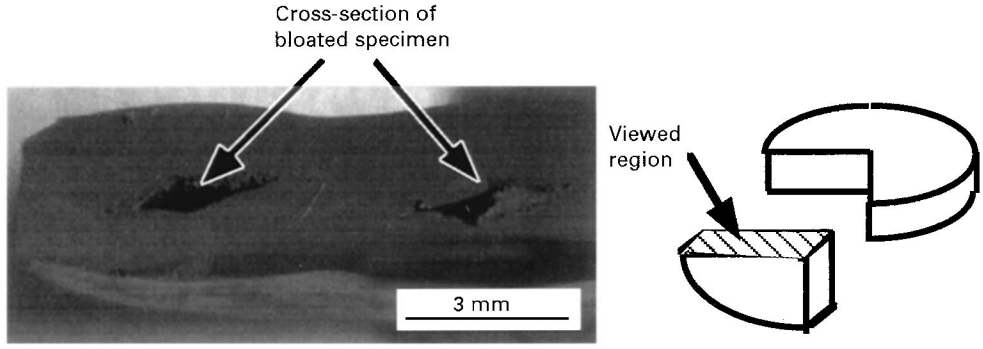

Figure 11 Typical bloating defect observed in present system.

Most bubbles within the filled specimens occur near the centre of the specimen, but location varies somewhat from specimen to specimen and from bubble to bubble within a centre. This suggests that a minimum supersaturation appears to be required for formation of a bubble. A more detailed examination of bubble formation is reported in [15, 16].

4. Conclusions

The EVA copolymer degradation process can be broken into two distinct regions. In the first region, EVA undergoes an elimination reaction that results in the evolution of acetic acid. TGA and DTA results show that the ceramic powder has altered the reaction rate. However, GC/MS results show that the ceramic powder has not altered the reaction product. Acetic acid is still the primary product. The second stage reaction loses weight in a manner similar to the degradation behaviour of polyethylene.

The kinetics of degradation for neat EVA in the first region of decomposition where acetic acid is formed follows first order kinetics with an activation energy of 178 kJ mole^{-1}. The addition of the ceramic powder altered the kinetics of the reaction so that they no longer appear to follow any reaction order. The reason for the altered kinetics is not known, but "precharging" may contribute to the apparent alteration in the kinetics.

The escaping species from the filled system was shown to originate throughout the specimen. No porosity develops during the initial stages of binder removal. Therefore, it is concluded that during the initial stages of binder removal, the escaping species, which in this case is acetic acid, must be diffusing through the liquid polymer filled pores to the specimen surface where it then evaporates.

Finally, bubble or crack formation occurs during heating from the acetic acid concentration exceeding a critical level.

Acknowledgement

This research was supported by the Defense Advanced Research Projects Agency and the Office of Naval Research through grant N00014-94-1-0278.

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Received 30 July 1997
and accepted 13 February 1998