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Defect formation during binder removal in ethylene vinyl acetate filled system

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This paper focuses on determining the criteria for defect formation during the early stages of thermal binder removal within an ethylene vinyl acetate (EVA) polymer filled with submicron SiC ceramic powder. The only product of the early stage thermal degradation reaction of EVA within an inert atmosphere is acetic acid. This single component and well characterized organic reaction product has allowed the defect forming criteria to be definitively examined. It will be shown that bloating occurs in the early stages of binder removal as a result of pressure build-up in the specimen resulting from acetic acid formed from the thermal elimination reaction of EVA. The first part of this paper examines defect formation occurring in the pure polymer within a hot-stage optical microscope. Bubble formation is observed in the pure polymer. Next, bloating occurring in the molded system is examined. The affect of mineral oil on bloating is also discussed as well as the effect that molding pressure has on bloating. It was found that molding pressure effects defect formation. Finally, this paper presents binder removal maps that were developed for specimens up to 8 mm thick. These bloating maps indicate the existence of two primary bloating regimes. © *1999 Kluwer Academic Publishers*

1. Introduction

The primary problems encountered in binder removal in filled systems typically occur in the early stages of binder removal [1–6]. It is during this stage when organic species must diffuse through polymer filled pores before they can escape. The escaping species can either be present beforehand or can be products of the degradation reaction(s) taking place. Regardless of there origin, problems such as cracking, bloating or warping may occur during binder removal. The problem of warping or poor tolerances was addressed in a previous paper [7]. This paper specifically addresses the phenomena of cracking or bloating occurring during the early stage of binder removal in an ethylene *co*-vinyl acetate (EVA) copolymer binder system that evolves a single, well known organic species, which is acetic acid. The formation of acetic acid within the system was definitively proven in a previous paper [8]. It was also shown that acetic acid is generated throughout the specimen. The rate of formation of acetic acid was also well characterized in the previous paper while in the presence of the ceramic powder. It is forming from the degradation reaction of EVA at temperatures well above its boiling point of 118 °C.

A paper by Calvert and Cima [1] models a similar process. The case when a polymer decomposes to produce a volatile monomer, in this case PMMA “unzipping” to produce MMA. A bubble is assumed to form when the monomer species concentration is such that the pressure of MMA exceeds atmospheric pressure. The diffusion of the monomer through the liquid polymer is slow, three orders of magnitude slower than diffusion through the gas phase. The decomposition rate of the polymer is causing a concentration build up of monomer within the polymer. The concentration is lowered by diffusion of the monomer out of the specimen. This behavior and the defect forming criteria are similar in nature to the polymer degradation phenomena and defect forming criteria occurring in the present paper.

A group of papers by Edirisinghe *et al.* address the similar case of diffusion of monomer through poly (α-methylstyrene) which decomposed to yield a high percentage of monomer. The decomposed monomer presented in the work of Calvert and Cima and that of Edirisinghe *et al.* diffused through either pores or the liquid polymer. Models were developed which accounted for both types of diffusion [2–6]. The same criteria for bloating was employed in each case: bloating occurs when the monomer concentration is such that the pressure exceeds atmospheric pressure. A model similar in nature was developed for the present system and will be discussed in a separate paper [9, 10].

Renlund and Johnson have patented an injection molding composition which utilizes SiC, EVA and stearic acid [11]. This is similar to the currently utilized system which used EVA to spin filaments. The range of compositions which worked for Renlund *et al.* have been specified in the patent. They have stated that when the vinyl acetate part of the ethylene vinyl acetate copolymer is too low, surface cracks result. They attribute this to too high of a viscosity. However, it may

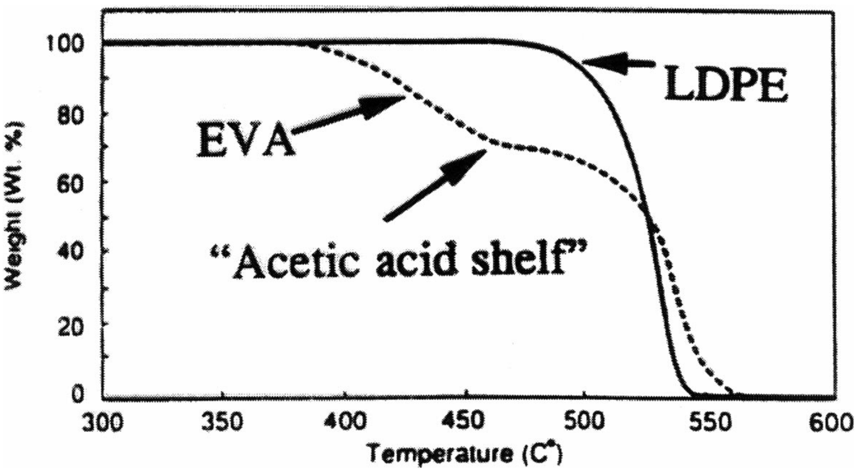
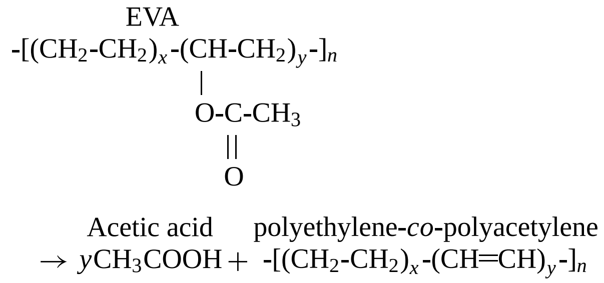


Figure 1 TGA of pure EVA compared to pure polyethylene.

be that the cause of the surface cracks are the result of the increased amount of crystallinity present in the material with less vinyl acetate content. There are large dimensional changes that take place upon crystallization and the higher the crystal content, the larger the dimensional changes as discussed by Hrdina [7, 12].

Renlund also noted that too much vinyl acetate content results in bloating during BBO. Although this was attributed to too low of a viscosity, it seems more likely that the cause of the bloating was the degradation of the EVA. The vinyl acetate initially degrades, as will be discussed shortly, to yield acetic acid. The more vinyl acetate, the more acetic acid formed at a given temperature. Therefore, it is likely that the bloating was simply a result of the increased amount of acetic acid formed as a result of the increased amount of vinyl acetate.

Ethylene Vinyl Acetate has the formula listed below. Upon heating in nitrogen, it first undergoes a side group elimination reaction [13–15], i.e.,



$$\overset{\text{EVA}}{-[(\mathrm{CH_2\text{-}CH_2})_x\text{-}(\underset{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{O\text{-}C\text{-}CH_3}}}{\mathrm{CH}}\text{-}\mathrm{CH_2})_y\text{-}]_n}$$

$$\rightarrow \overset{\text{Acetic acid}}{y\mathrm{CH_3COOH}} + \overset{\text{polyethylene-}co\text{-polyacetylene}}{-[(\mathrm{CH_2\text{-}CH_2})_x\text{-}(\mathrm{CH{=}CH})_y\text{-}]_n}$$

This reaction is one of the primary reasons why this material was chosen for study. It yields a single well known and well characterized product in the first stage of the reaction. It needs to be emphasized that this well characterized reaction eliminates many uncertainties present in previously examined systems. The yield of acetic acid in the presence of the ceramic powder was shown to be almost 100% by gas chromatograph (GC)/mass spectrometry (MS) [8].

This reaction is well characterized and it has been suggested as a method to quantitatively analyzing the vinyl acetate content of EVA [14]. Fig. 1 compares the thermal gravimetric analysis (TGA) degradation behavior of polyethylene to that of EVA [13]. The vinyl acetate is eliminated at a much lower temperature than the temperature at which polyethylene begins to degrade. This results in what will be termed the "acetic acid shelf" in the TGA plot of EVA degradation. The remaining polymer will then be a copolymer of polyethylene co-polyacetylene. Pure vinyl acetate will degrade to leave behind a conjugated polyacetylene structure [13] which is very stable.

Polyethylene, on the other hand, degrades by a random scission process. That is, because all bonds are essentially identical, there is no preferential degradation taking place, so that scission takes place randomly along the polymer chain [13, 16, 17].

2. Experimental

2.1. Composition and processing

The single component moldable ceramic system examined here is composed of a pressureless sintering [18–21] composition of submicron SiC blended with a copolymer of ethylene and also, in some cases, mineral oil, a common industrial paraffinic distillate. The powder is prepared by ball milling, using alumina grinding media, an isopropyl alcohol slurry composed of silicon carbide[1], aluminum oxide[2] and yttrium oxide[3] for 24 h. The powder is next dried and ground to −40 mesh using a mortar and pestle.

Once the powder has been prepared it is then mixed in a heated blender[4] with the polymer or the polymer and mineral oil. The nominal room temperature vol % ratios are 51/49 for the ceramic powder/co-polymer or 54.5/39.5/6 for ceramic powder/co-polymer/mineral oil respectively. Table I lists some of the properties of the pure polymer. The mixing head is first heated to 130 °C, and the EVA copolymer[5] is added. After 1–2 min, the ceramic powder is added which then, because of the high shear, results in an increase in stock temperature to a final mixing temperatures of 150–160 °C. The mineral oil,[6] if used, is then added. The mixing speed is 60 rpm.

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[1] B-Sic, H. C. Starck Grade B 10; SA = 14–17 m^2/g, mps = 0.75 um.

[2] Malakoff Industries, Inc., RC-HP DBM; SA = 7–8 m^2/g, mps = 0.55 um.

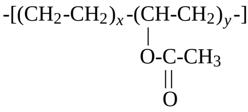
[3] Johnson Matthey, mps = 1–2 um.

[4] C. W. Brabender Instruments, Inc., PL 2000 Plasti-Corder with Roller Blade Mixing Heads.

[5] ELVAX 470, Dupont.

[6] Heavy Mineral Oil, Mallinckrodt, Paraffin Oil, sp. = 0.881.

TABLE I Selective properties of EVA 470

Melt index: 0.7 dg/min	$M_n = 100{,}000$ $M_w = 250{,}000$	$T_g = -20\,^\circ C$ $T_m = 84\,^\circ C$
Density	Formula	Percent
= 0.941 g/cm^3	 $-[(CH_2\text{-}CH_2)_x\text{-}(\underset{\substack{\vert \\ O\text{-}\underset{\substack{\Vert \\ O}}{C}\text{-}CH_3}}{CH}\text{-}CH_2)_y\text{-}]_n$	crystalline = 10% Vinyl acetate (VA) content = 18 wt %

The binder uniformity in a batched material and between batches of material was checked by the random selection of four specimens from two separate batches of material. The percent 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 molding 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 [22, 23]. The batched material was next molded at 27 MPa (4000 psi) in a uniaxial mold. TGA analysis on molded specimens revealed no difference in the binder distribution throughout the specimen indicating that molding did not lead to any preferential binder distribution for this system.

2.2. Thermogravimetric measurements

Two different TGA units were employed. The first TGA,[7] utilized small 10–30 mg samples to study the degradation reaction kinetics of both the pure EVA and the EVA in the presence of the powder. The specimens were placed in a platinum pan and heated at constant heating rate to determine the reaction kinetics. The second TGA[8] utilized larger specimens in which mass transport was considered to be rate limiting.

2.3. Hot-stage microscopy (bubble formation in pure EVA)

Bubble formation in EVA was observed by hot-stage microscopy, similar to previous work by Dong and Bowen [24] in which they examined bubble formation in PMMA mixed with different solvents. Pure EVA 470 was placed between two metal sheets, heated to 125 °C and then molded into a 0.5 mm thick sheet, and cut into 4 mm disks. The EVA disks were sandwiched between two glass disks 6 mm in diameter. The glass disks were cut from 1 mm glass slides and washed with isopropyl alcohol before use. The sandwiched assembly was placed within a controlled atmosphere hot-stage microscope[9] and observed with transmitted light. The specimen was then heated at 2 °C/min in a nitrogen atmosphere to about 350 °C while recording the image with a video camera. In a second experiment, EVA was seeded by mixing approximately 0.05 wt % of 90 wt % SiC, 6 wt % aluminum oxide and 4 wt % yttrium oxide powder. This small amount of powder was not enough to make the system opaque. However, it still provided many particles or possible sites for bubble formation. The particle density was approximated at 2×10^{12} particles/cm^3 based on equivalent spherical diameters. This material was molded into sheets, cut, sandwiched and placed in the microscope in the same manner as the unseeded pure EVA 470 polymer.

It was discovered that in all cases, a bubble which formed grew rapidly and could be seen with the unaided eye within a few seconds of forming. This was recorded as the bubble formation temperature.

2.4. Bloating maps

A number of experiments were run to determine the effect of heating rate and sample size on bloating in the molded specimens. The objective of these experiments was to provide a data base of bloating conditions. The experimental conditions under which bloating takes place is presented here.

Ceramic powder/EVA was compressed in a uniaxial mounting press at 125 °C and 27 MPa. Specimens were 25.4 mm in diameter and varied in thickness between 0.5 and 8 mm. The specimens were in the mold for 15 min at 125 °C temperature to anneal out most of the residual strains reported in another paper [7].

Fig. 2 shows an example of the specimen set-up. The specimens are shown on a setter plate before heating. The upright placement allowed diffusion through both faces of the specimen which approximated planar diffusion. The specimens were then heated at constant heating rates to a specified temperature and furnace cooled to room temperature. Most bloating was readily apparent from the surface. However, all specimens were cut into several pieces to visually inspect for internal cracking or bloating. The minimum bloating temperature was determined to within 20 °C.

3. Results and discussion

3.1. Bubble formation in pure polymer

Bubbles were observed to form in the specimens at temperatures between 286 and 310 °C as shown in Table II. The first bubble that formed grew quickly and appeared typically in proximity to the center region of the disk. As the specimen was heated further, a second or third bubble might form, but always at a relatively large distance (~0.5 mm or more) away from the first bubble. Shown in Fig. 3 is an optical image of a seeded specimen before and after a bubble was observed to form. Seeding did not appear to change the nature of bubble formation. The bubbles formed and grew in the same manner as the pure EVA polymer.

TABLE II Observed temperatures of bubble formation

Specimen	Observed temperatures of bubble formation
Pure EVA	303 ± 3 °C
Seeded EVA	298 ± 12 °C

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[7] TA Instruments Hi-Res TGA 2950.

[8] TGA-171, ATI-CAHN microbalance.

[9] Linkam TH1500.

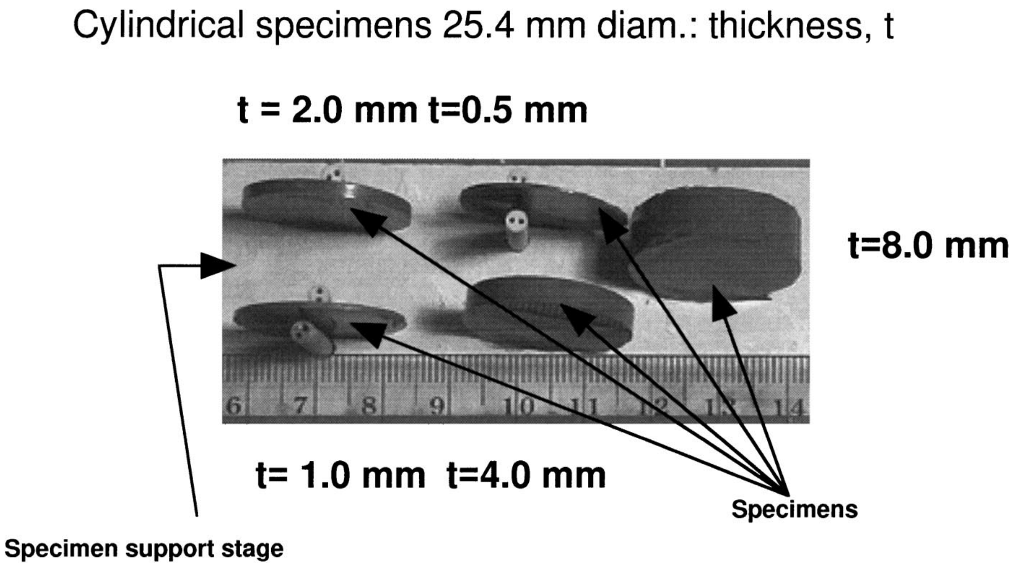


Figure 2 Specimen set-up for mapping bloating conditions.

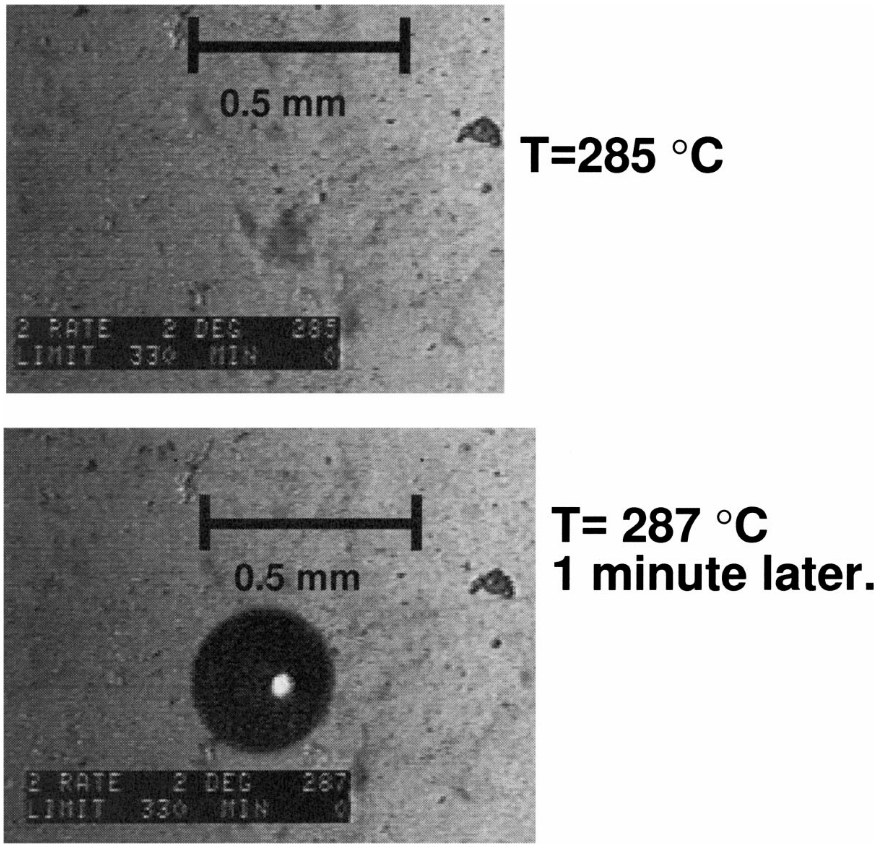


Figure 3 Observed bubble formation in hot-stage optical microscope of seeded EVA sample sandwiched between two glass slides.

Pure acetic acid is a product of the elimination reaction of EVA and is forming during heating throughout the polymer as a dissolve gas (acetic acid boils at 118 °C). A TGA trace of pure EVA at 2 °C/min can be seen in Fig. 4. At 286 °C, only 1.3 wt % of the total organic has decomposed and at 310 °C, 4.5% has decomposed. It is apparent that bubble formation is associated with the beginning of polymer degradation. In a covered slide, generated acetic acid has one escape route, through the polymer to the specimen edge, where it then evaporates. However, if it forms faster then it can escape, a concentration of acetic acid will build up. If the concentration exceeds a critical value, a bubble can form.

It appears that the bubble formation requires a favorable formation site. If this were not true, then bubble formation would always start in the exact center of the specimen, at the point of highest concentration of acetic acid. The distribution in the temperature at which bubbles form also suggests that favorable bubble formation sites are not readily available in the pure polymer. Additionally, the ceramic powder does not appear to act as

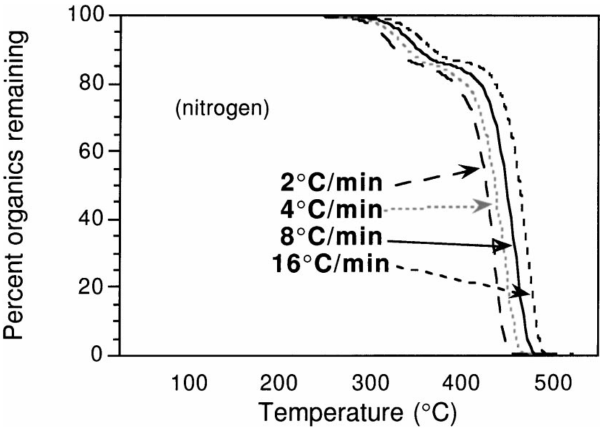


Figure 4 TGA of pure EVA at constant heating rates.

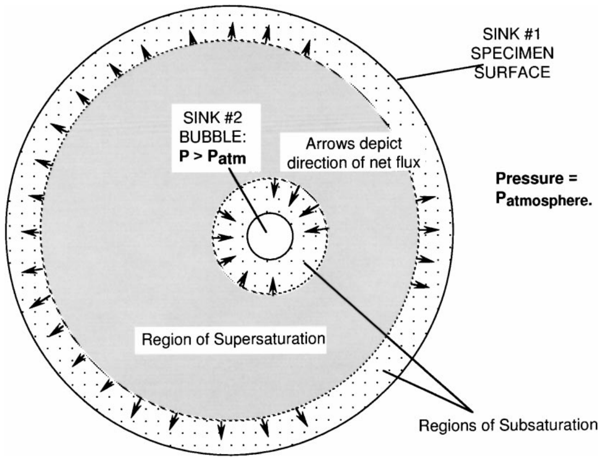


Figure 5 Schematic of diffusing zones during thermal degradation of EVA within hot-stage microscope.

a favorable site for bubble formation because the bubbles still appear to form over a range of temperatures and in a generally central region.

Once a bubble forms, it then appears to act as a sink for diffusing acetic acid species. Others reported similar behavior [25–28]. A schematic of this behavior is presented in Fig. 5. The only sink for the diffusing species is, initially, the surface. It is speculated that acetic acid concentration must build up in the specimen's central region past the point of saturation because favorable bubble formation sites are not available [27]. Once a bubble does form, it then acts as a sink for acetic acid in the surrounding material [26, 27]. Other bubble formation must then take place at distances relatively far away from the two sinks which are the surface and the already present bubbles.

These results indicate that bubbles from within pure EVA and are the result of internal pressure from acetic acid. Acetic acid is the product of the thermal degradation reaction of EVA. The results also indicate that some amount of acetic acid supersaturation is required because of a lack of favorable sites for bubble formation. Therefore, a necessary condition for bubble formation is:

$$a_{\text{acetic acid}} P_0 > P_{\text{atmosphere}} \quad (1)$$

where $a_{\text{acetic acid}}$ is the activity of acetic acid in the polymer, P_0 is the equilibrium vapor pressure of acetic acid over a free surface and $P_{\text{atmosphere}}$ is atmospheric pressure.

No bloating will occur unless this minimum or necessary condition is first met.

3.2. Bubble formation in filled system

The bubble formation in pure EVA appeared to be the result of acetic acid exceeding a critical concentration. This is the primary cause of defects in this moldable system. The primary objective of this section is to confirm that the observed bloating is a result of acetic acid which has exceeded a critical concentration. Two secondary objectives are also examined. First, the effect of mineral oil on bloating in this system is discussed. It is speculated that mineral oil does not contribute to bloating. Finally, it was observed that bloating was effected by molding pressure. A possible explanation for these results will be discussed.

3.2.1. Conditions for bloating

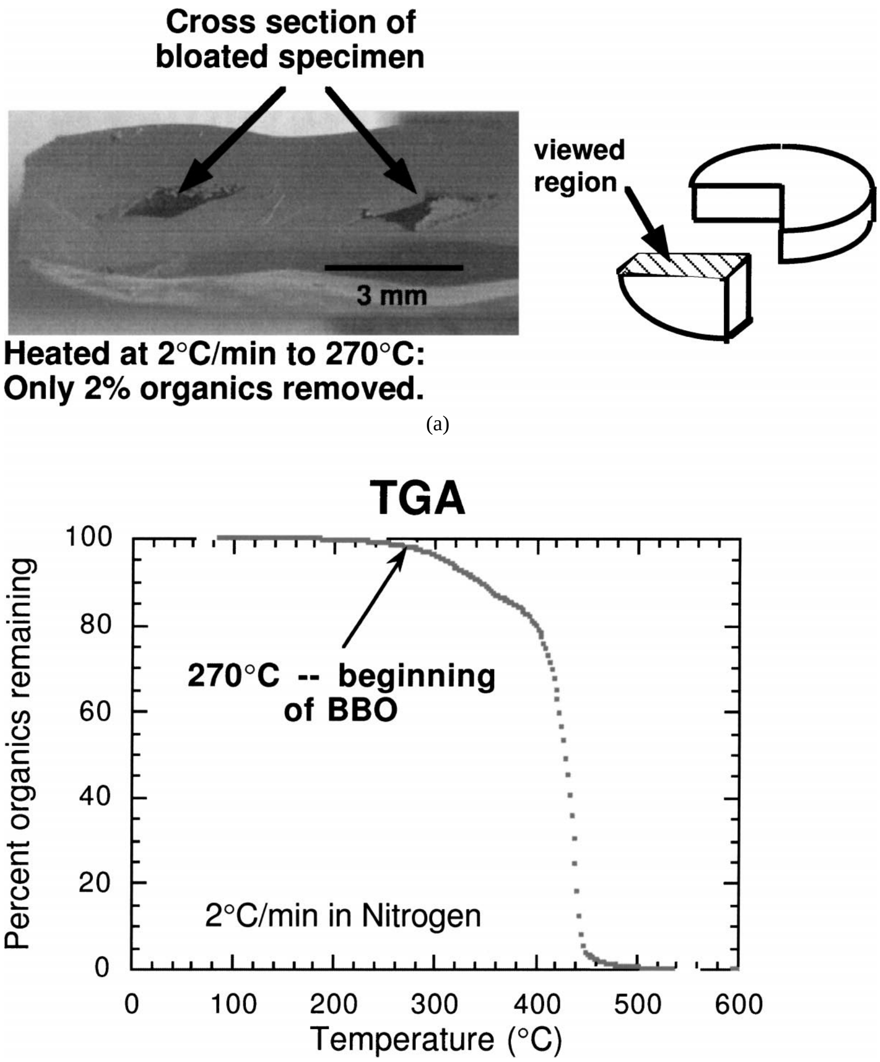
The defects that show up appear to start as an internal crack, and then develop into bloats as a result of the acetic acid exceeding a critical concentration. A typical example of a defect observed in the present system is shown in Fig. 6. This particular specimen is 3 mm thick and was heated at 2 °C/min to 270 °C and cooled. Two rather large bubbles are shown that appear near the center 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 in a previous paper that acetic acid does diffuse through the system to the surface [8]. Therefore, the region of highest concentration is expected to be the specimen center 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 previously in a paper describing the chemistry of degradation in this system [8].

Most bubbles within the filled specimens occur near the center of the specimen, but location varies somewhat from specimen to specimen and from bubble to bubble within a center. This suggests that a minimum supersaturation appears required for formation of a bubble. Large bubbles also suggest that once a bubble forms, it then acts as a sink for diffusing species like in the case of the pure polymer.

Fig. 7a and b are scanning electron micrographs (SEM) of a bloating defect formed in a 2 mm thick specimen that was heated at 2 °C/min to 320 °C and had 4.3% of its binder removed. The crack was not visible from the specimen surface. The specimen had to be cut open to view the crack and like the previous specimen, the crack again appeared in the specimen center. No cracks were observed throughout the rest of the cross section or in the surrounding region.

Similar behavior is found in the filled EVA system as in the filled EVA system with mineral oil. It appears that additions of up to 6% mineral oil (BP = 346 °C) does not affect the acetic acid induced bloating behavior.



(a)

(b)

Figure 6 (a) Defect observed in current system. (b) TGA trace showing defect occurs during initial weight loss.

3.2.2. Demonstration that acetic acid can cause bloating

An experiment was performed in which external acetic acid was added to the specimen, which caused bloating during subsequent heating. A molded 2 mm specimen was soaked in pure liquid acetic acid at room temperature for 9 days. The amount of acetic acid absorbed in the filled specimen was equivalent to about 21% of the polymer's weight. The specimen was heated at 2 °C/min to 150 °C, well below the temperature at which acetic acid forms by the elimination reaction, but well above the boiling point of acetic acid of 118 °C. The results are shown in Fig. 8 for the specimen before and after heating. It is evident that the specimen bloated. Note also that bloating occurs almost precisely in the specimen center.

3.2.3. Effect of molding pressure on bloating

Pieces of 2 mm rods of the SiC/EVA compound were compression molded into rectangular billets. 51 vol % ceramic and 49 vol % EVA was extruded[10] into 2 mm diameter rods. The extrudate was cut into 25 mm lengths and about 20 pieces were placed in a die. Three billets 50 mm × 25 mm × 9 mm were fabricated by pressing at 150 °C at pressures of 1.7, 3.5 and 35 MPa, respectively. The specimens were then placed side by side in a furnace and heated in a nitrogen atmosphere according to the following schedule: 1 °C/min to 145 °C. Then 0.03 °C/min to 250 °C and 0.07 °C/min to 300 °C. Each specimen lost 10% of its organic content. Fig. 9 shows the results of the experiment. The specimen compression molded at 1.7 MPa bloated badly. The specimen molded at 3.5 MPa shows much less bloating. The specimen pressed at 35 MPa did not appear to bloat at all. The only difference between the initial specimen was the molding pressure. It is clear that bloating defects were minimized and or avoided by employing higher molding pressures.

Bloating originates at the weld lines in these samples. The bloated region observed in the specimen pressed at 3.5 MPa in Fig. 9 seems to partially trace the exterior of a 2 mm diameter extruded specimen. This bloat, therefore seems to suggest that bloating is occurring at a weld line. Additionally, breaks in the weld line at the surface of the specimen pressed at 1.7 MPa are clearly seen in Fig. 9 which indicate that the weld lines are regions where fracture occurs.

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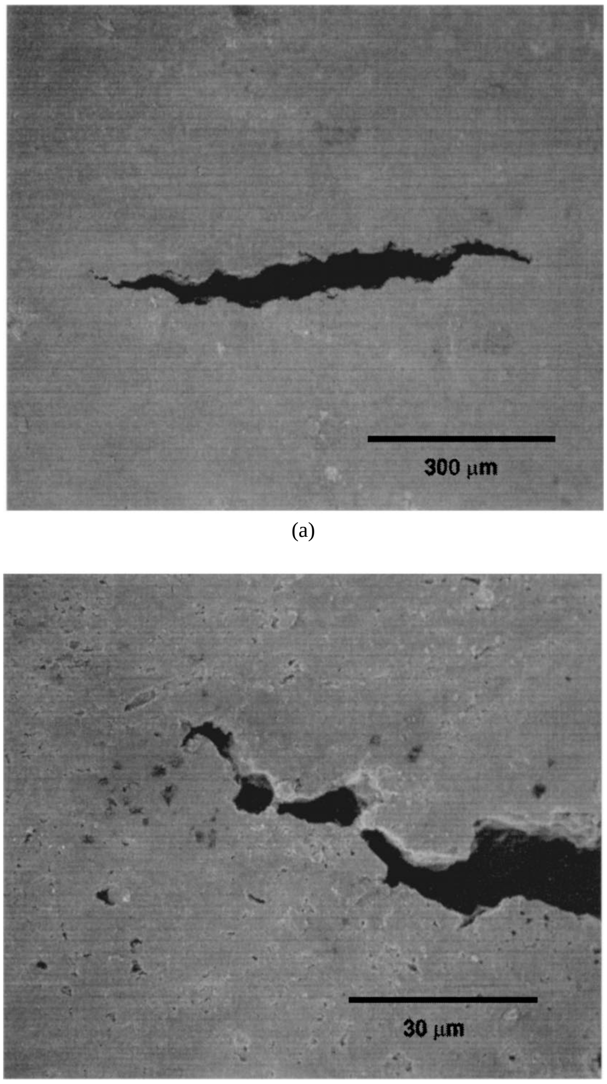
[10] Bradford University Ltd. extruder.



(a)

(b)

Figure 7 SEM of bloated region: (a) low magnification and (b) higher magnification of crack tip.

The strength of weld lines in injection molded parts increases with increasing molding pressure [30]. This is assumed to be the case here as well. It seems plausible, that once the condition of supersaturation was achieved, the weak weld lines in the 1.7 MPa pressed specimen yielded before the weld lines in the other specimens and acted as a sink for further diffusing acetic acid species.

3.3. Bloating maps

"Bloating maps" displaying the temperature at which bloating occurs vs. specimen size and heating rate were prepared. Fig. 10a plots the minimum temperature at which bloating was observed for various size specimens heated at 8 °C/min. Bloating occurs in the region above the curve does not occur in the region below the curve. Fig. 10b summarizes three different heating rates on the same plot. The data in Fig. 10b is plotted for constant heating rates of 0.5, 2 and 8 °C/min. It is apparent that thicker specimens bloat at lower temperatures. It is also apparent that bloating temperature decreases with increasing heating rate.

These data can be combined with the acetic acid generation rate, obtained from TGA traces on small 25 mg samples at the specified temperature and heating rate, with the data of Fig. 10. This is displayed in Fig. 11 as acetic acid generation rate versus sample thickness. It is apparent that the data for all three heating rates appears to collapse into a single curve so that the single line that differentiates the bloating region from the no bloat region could be termed the critical generation rate, G_{critical}. Diffusion is approximated by the generation rate and the diffusion distance, x, is half the specimen thickness. Fig. 11 shows the generation rate versus diffusion distance squared. The results of Fig. 11 suggests the presence of two regimes.

The explanation of the regimes is better illustrated with use of schematic concentration profiles shown in

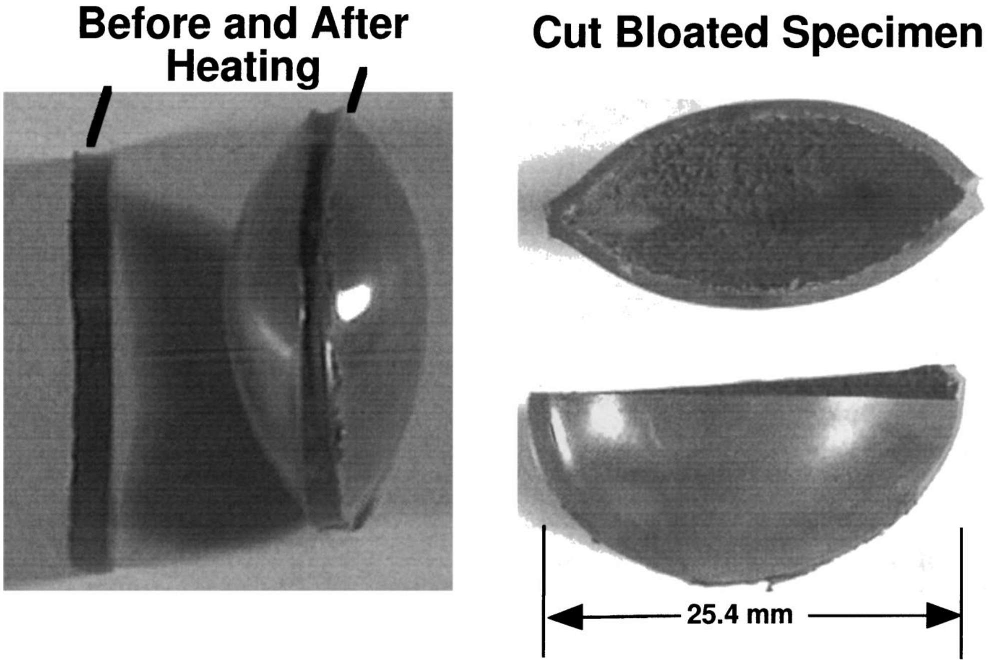


Figure 8 Bloating as a result of external addition of acetic acid.

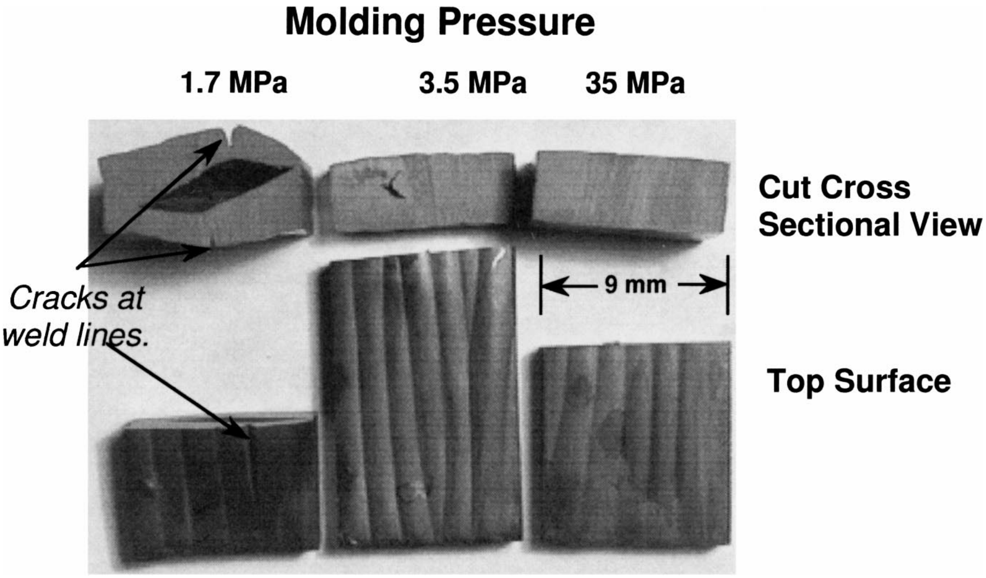
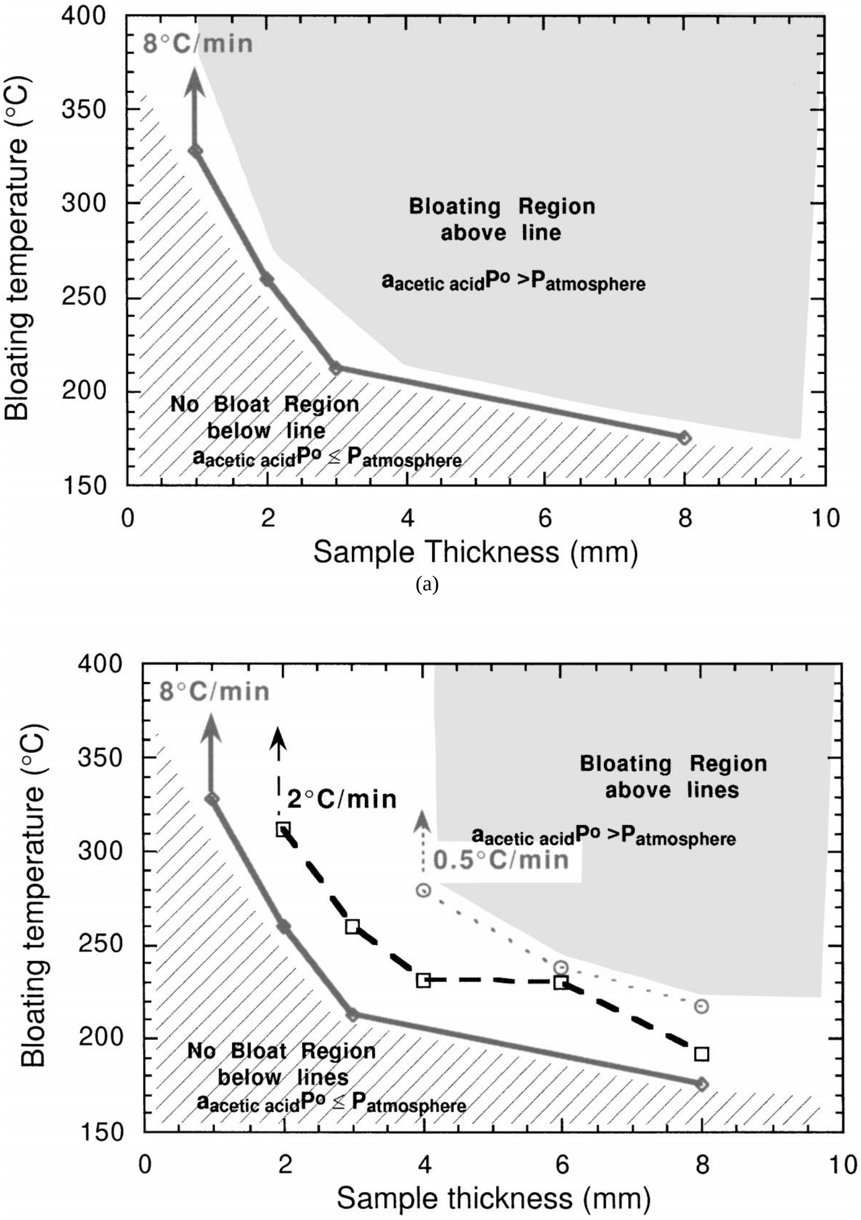


Figure 9 Effect of molding pressure on bloating.



(a)

(b)

Figure 10 Bloating maps: (a) effect of sample size with single heating rate of 8 °C/min and (b) effect of sample size and heating rate with heating rates of 0.5, 2 and 8 °C/min.

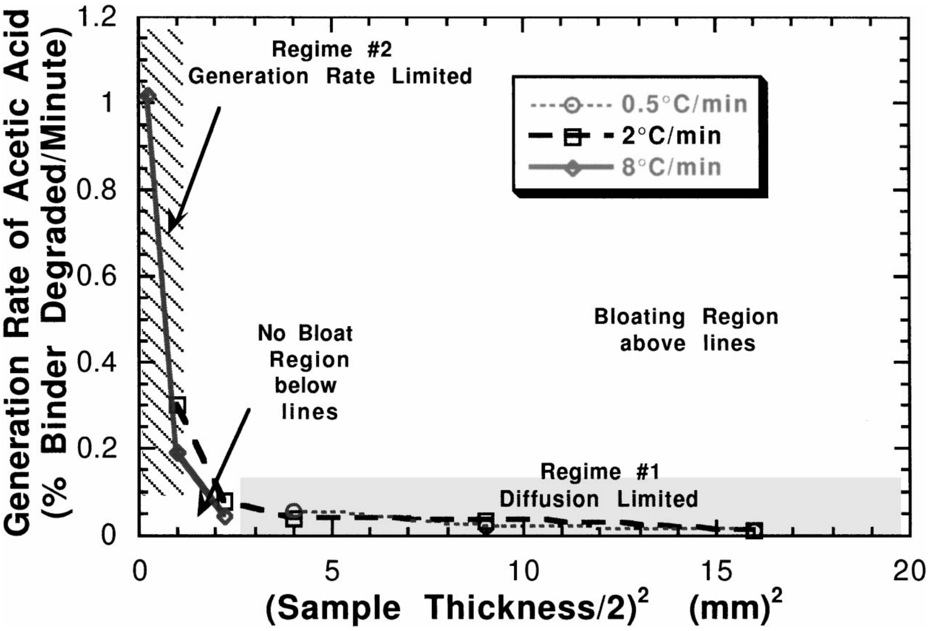


Figure 11 Bloating maps at various heating rates collapse into a single bloating map with two bloating regimes shown.

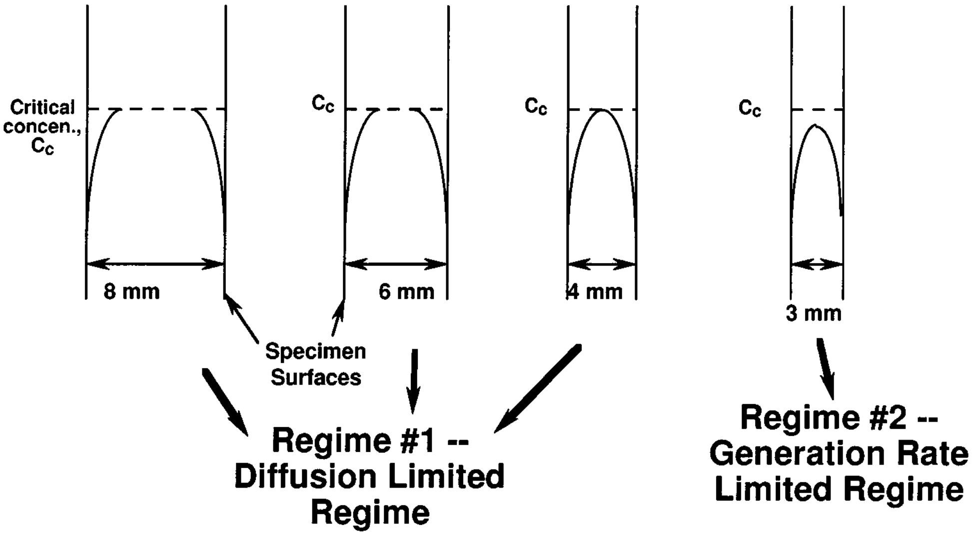


Figure 12 Schematic representation of acetic acid concentration profiles in two bloating regimes.

Fig. 12. Within Regime #1, the specimens appear to all bloat at roughly the same low critical generation rate. Diffusion in these large samples is so low that almost all generated species accumulate in the specimen center in this regime. Bloating then occurs as soon as enough acetic acid is accumulated such that the critical concentration is exceeded. Within Regime #2, the diffusion distance in the thin specimens is small enough so that all that is generated is not accumulated. Bloating in this regime is controlled by a competition between diffusing species leaving the system and generated species added to the system. The rate of generation of acetic acid must exceed the rate at which it diffuses and the distance through which it has to diffuse in order to have accumulation. Bloating occurs when the amount accumulated exceeds the critical concentration. These maps form the data base that will be used in a model presented elsewhere [9, 10].

3.4. Conclusions

Bubble formation during heating was observed in pure EVA. The evidence strongly suggests that bubble formation is from acetic acid exceeding a critical level. The minimum condition for bloating is when the internal pressure exceeds atmospheric pressure such that: $a_{\text{acetic acid}} P_0 > P_{\text{atmosphere}}$. A second but less defined criteria for bloating involved finding a favorable site for bubble formation. Seeding the system with ceramic powder did not appear to change the mechanism for bubble formation. Nor did the powder appear to appreciably alter the likelihood of bubble formation at a specific temperature.

Bloating in filled systems also appears to be the result of acetic acid concentration exceeding a critical value. It was proven that external addition of acetic acid did cause bloating in the filled system in the same manner as in the filled systems which form acetic acid.

Experimental results showed that bloating defects could be minimized or avoided in some cases by employing higher molding pressures. The mechanism by which molding pressure affected defect formation is the subject of future work.

Bloating maps were presented and provide criteria under which defects could be avoided in the present system. The results seem to collapse into a single curve such that a critical rate of generation of acetic acid, G_{critical} is obtained for any specific sample thickness. Bloating occurs if G_{critical} is exceeded. It appears that two bloating regimes exist. The first regime is for large size samples where diffusion is so low that all acetic acid that is generated is accumulated. This is the diffusion controlled regime. The second regime occurs for smaller size specimens where diffusion is fast enough such that generated species are leaving the central region of the specimen at an appreciable rate. Accumulation of species occurs only when the rate of generated species exceeds the rate at which they diffuse away from the specimen. Bloating in this region is controlled by the competition between rate of generation of acetic acid and diffusivity of acetic acid.

Acknowledgement

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