Micrographs of Fractured Vinyl Ester Composites

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Abstract: This paper reports the difference in impact strength between microwave cured vinyl ester particulate composites and those cured under ambient conditions by examining the micrographs of the fractured specimens. Drop weight impact test had been used to fracture the samples. The original contribution of this paper is to tell the fracture behaviour of the samples as well as the relative toughness of the specimens by viewing their micrographs. The results show that the difference in the impact strength between optimally (lower power and longer exposure duration) microwave cured samples and those cured under ambient conditions is minimal. However, if the specimens were cured using higher power, the resulting toughness of the samples would be lower as many voids would form in the samples due to the initial expansion of the composite.

Introduction

Composite components made from vinyl ester resins suffer considerable shrinkage during cross-linking. This shrinkage is particularly serious if the fiber composite components are large. It can be more than ten percent in volume, which is much higher than claimed by some researchers and resins' manufacturers [1, 2]. The main drawback of this shrinkage in a composite component is to have stresses set up internally. These stresses in plane are usually tensile in the core of the component and compressive on the surface [3]. When these stresses act together with the applied loads during service they may cause premature failure of the composite components. A method to reduce the shrinkage is to cure the composites using microwave power [4-7]. In the previous study, the difference in average energy required to fracture or initiate the crack between specimens cured under microwave conditions and those in

ambient conditions were found to be very small. The more powderised appearance in the crushed zone in the microwave cured samples may be due to higher impact resistance.

In addition, quite a number of specimens that were cured with microwaves tended not to fracture when they were impacted from a drop height of 400mm; whereas most of the specimen cured under ambient condition tended to fail at a drop height of 400mm [8, 9]. This research is to try higher level of microwave powers with shorter duration of exposure to increase processing efficiency but at the same time maintain the quality of the samples. The same composite, thirty three (33%) by weight of fly ash particulate reinforced vinyl ester resins [VE/FLYASH (33%)], is used.

The impact strength of a material is the energy required to initiate and propagate a crack through the material. The impact energy of a material is the amount of energy required to fracture a given volume of the material. The crack propagation energy is related to the toughness of the material and the length of that crack tip that must travel in order to fracture a component [10].

The Composite samples and the test

In this study, Hetron 922 PAW (vinyl ester resin used in winter) was used. The resin catalyst (MEKP) ratio used in the experiment was 98% resin by volume and 2% catalyst by volume [11]. The reinforcement was fly ash (ceramic hollow spheres) particulate and they were made 33 % by weight in the cured vinyl ester composite [VE/FLYASH (33%)]. Thirty three percent by weight of fly ash in the composite is

considered optimum because the composite will have a reasonable fluidity for casting combined with a good tensile strength in service.

The resin, a colourless liquid, is first mixed with the colourless accelerator. After that the fly ash is added to the mixture and they are then mixed to give the uncured composite. As the raw materials of the composites are liquid and ceramic hollow spheres (E-spheres SLG with a mean diameter of 130 µm), the short bar specimens were cast to shape. The uncured composite was poured into the moulds of PVC tubes (Figure 1) for curing in ambient or microwaved conditions [6].

The preference for drop weight impact test over the more conventional methods, e.g., Charpy and Izod tests, is due to the limitations that are experienced while trying to perform impact testing on composite materials. Another main advantage of using drop weight impact test over other standard tests is its ability to reproduce conditions under which real life component would be subject to impact loading. This means that if a material specimen or an actual item was tested, replication of the testing arrangement should be possible, provided enough testing samples should be produced.

The method of using the drop weight impact includes the use of a falling weight which impacts the specimen. The drop weight impact test set-up is shown in Figure 2. The impact striker is known as a tup which falls through a vertical guide tube that directs it to the centre of a specimen. The guide tube must be perpendicular to the impact surface as stated in the American testing standards. In testing composite materials, the constant weight and varying height method has to be used because composite material is strain rate sensitive [10, 12]. Instrumentation is incorporated to

reduce the number of samples required and increase accuracy. The required items are accelerometer, charge amplifier, A/D converter and data acquisition equipment.

Microwaves and sample size

The material properties of greatest importance in microwave processing of a dielectric are the complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and the loss tangent, $\tan \delta = \dfrac{\varepsilon''}{\varepsilon'}$ [13].

The real part of the permittivity, ε', sometimes called the dielectric constant, mostly determines how much of the incident energy is reflected at the air-sample interface, and how much enters the sample. The most important property in microwave processing is the loss tangent, $\tan \delta$ or dielectric loss, which predicts the ability of the material to convert the incoming energy into heat. For optimum microwave energy coupling, a moderate value of ε', to enable adequate penetration, should be combined with high values of ε'' and $\tan \delta$, to convert microwave energy into thermal energy. The microwave facility used in this project is shown in Figure 3.

Latin Square is used to establish the required sample size for each type of microwave treatment and the sample size chosen was the same as in the previous study [8, 9, 14]. In this project, in addition to exposing samples to 10, 15 and 20 seconds respectively to microwave power of 540 W, the composite was also exposed to microwave irradiation of 180 and 360 W. The duration of exposure for both power levels was 30, 35 and 40 seconds respectively as in the previous study.

Energy consumed in breaking the samples

Comparison of average energy used to initiate the crack can provide good indication on the initial failure of the specimens among these groups. Table 1 shows the results of average energy used to initiate the crack between the specimens cured under microwave conditions with a power level of 540 Watts. Samples cured with microwaves for 10 seconds tended to require less energy to initiate the crack. It requires 0.57 joules of energy less than those cured under ambient condition (Table 2) [8]. In addition, the spread of this group was largest as compared with others. From specimens cured with microwaves for 15 seconds, the average energy required to initiate the crack was 0.36 joules less than those cured for 10 seconds. The amount of energy required to initiate crack for specimens cured with microwaves for 20 seconds was very low. It was 4.56 joules less than those cured for 10 seconds. This may be due to a lot of pores inside the samples. From Table 2, it can be found that the energy required to initiate crack for samples exposed to microwaves of 30 and 35 seconds were higher than that cured under ambient conditions. By investigating Table 3, it can be argued that the samples cured by microwave power of 360 W were the toughest. In order to study the fracture behavior of the specimens, some samples were carefully investigated with the aid of scanning electron microscope (SEM).

Scanning electron microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages in using the SEM instead of a

light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. SEM requires conductive samples and Figure 4 shows the Scanning Electron Microscope (SEM). The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.   The sputter coater is used to coat non-metallic samples with a thin layer of gold and it is shown in the Figure 5. Since the composite samples were non-conductive, it was necessary for them to be coated with a thin layer of gold. Figure 6 illustrates that a sample is being coated with a thin layer of gold. The surface will look like Figure 7 after being coated with a thin layer of gold. This makes them conductive and ready to be viewed under SEM.

When the electron beam strikes the sample, both proton and electron signals are emitted. Figure 8 shows the electron and specimen interaction. While all these signals are present in the SEM, not all of them are detected and used for gathering images. The signals most commonly used are the secondary electrons, the backscattered electrons and X-rays.   When an SEM is used, the column must always be at a vacuum. There are many reasons for this. If the sample is in a gas filled environment, an electron beam cannot be generated or maintained because of a high instability in the beam. Gases could react with the electron source, causing it to burn out, or cause electrons in the beam to ionize, which produces random discharges and leads to instability in the beam. The transmission of the beam through the electron optic column would also be hindered by the presence of other molecules. Those other molecules, which could come from the sample or the microscope itself, could form

compounds and condense on the sample. This would lower the contrast and obscure detail in the image. A vacuum environment is also necessary in part of the sample preparation. One such example is the sputter coater. If the chamber is not at vacuum before the sample is coated, gas molecules would get in the way of the argon and gold. This could lead to uneven coating, or no coating at all. Figure 9 illustrates a prepared sample mounted on a specimen stub and placed on the stage.

Results and Discussions

Figure 10 shows the 5 points chosen to be investigated on specimens cured under microwave conditions with a power level 180 Watts, exposure time of 40 seconds. Figure 11 shows the 5 points chosen to be investigated on specimens cured under microwave conditions with power level 540 Watts and exposure time of 10 seconds. Figures 12 and 13 show the five locations studied under SEM for ambient cured and microwave cured (180 W and 35 seconds) samples respectively. The reason for choosing these 5 points was because these points showed the crushed zone and fracture propagation zone of these four specimens.

Figure 14 illustrates area 1 of Figure 10 (microwave cured, power = 180 W and time = 40 seconds); it shows a big crushed on the top surface (curving area) of the specimen. Figure 15 depicts area 2 of Figure 10; it illustrates the start of the fractured surface; a small hole was also found when the magnification was increased to 300 times. Figure 16 shows area 3 of Figure 10; it illustrates 50 % of the crushed zone; 50 % of fractured propagation zone was also found. Figure 17 shows area 4 of Figure

10; it also shows secondary cracking; 90 % of fractured propagation zone and 10 % of crushed zone were found. Figure 18 illustrates area 5 of Figure 10; it shows small pieces of debris on the cracked surface; the direction of crack growth was towards the left. Figure 19 also illustrates area 5 of Figure 10. The magnification was 5,000 times and brittle fractured surface was found.

Figure 20 illustrates area 1 of Figure 11 (microwave cured, power = 540 W and time = 10 seconds); it shows a big crushed on the top surface. Figure 21 depicts area 2 of Figure 11; it illustrates longer fractured surface. Figure 22 shows area 3 of Figure 11; it depicts 70 % of crushed zone and 30 % of fractured propagation zone. Figure 23 also shows area 3 of Figure 11 but with a magnification of 2,500 times; small pieces of debris were found on the cracked surface. Figure 24 shows area 4 of Figure 11; it shows small pieces of debris and brittle fracture; in addition, crack was also found propagating through fly ash particle. Figure 25 illustrates area 5 of Figure 11; it shows much of the brittle fracture was on crack propagation zone.

Figures 12 and 13 show the five locations studied under SEM for ambient cured and microwave cured (180 W and 35 seconds) samples respectively. Figures 26 and 27 illustrate area 1 of ambient cured and microwave cured (180 W, 35 s) samples respectively. The magnification for both locations is 1000 times. It is observed that there is more powder in the crushed zone of sample cured under microwave conditions. Otherwise, the difference between the two figures was not much. Figures 28 and 29 illustrate area 2 of ambient cured and microwave cured samples respectively. More powder was also found in the crushed zone of microwave cured sample. Similar phenomenon were observed with three other areas, 3, 4 and 5 as

shown in Figures 30 through 35 for ambient cured and microwave cured samples respectively.

Figures 36 and 37 illustrate area 1 of ambient cured and microwave cured samples respectively. The magnification for both locations is 16,000 times. Flake of powder can be found in Figure 37 but not in Figure 36. By and large, under the magnification of 1000 times (Figures 30 through 35), the results obtained for specimens cured under microwave conditions showed not much difference with those cured under ambient condition.

From Table 1, it was found that the energy required to initiate crack for sample of 540 W and 10 seconds was 8.27 joules. Table 3 shows that the energy required to initiate crack for samples of 180 W and 40 seconds and of 180 W and 35 seconds were 8.66 and 8.81 joules respectively. This means that sample of 540 W and 10 seconds was the most brittle specimen and followed by sample of 180 W and 40 seconds. Figures 25 (540 W, 10s), 18 (180 W, 40s) and 35 (180 W, 35 s) were the micrographs of the above 3 samples respectively. Figure 18 shows the most severe brittle fracture and is followed by Figure 25. Figure 35 is the most ductile as no brittle cleavage appearance can be identified. From Table 2, it can be found that the energy required to initiate crack in this group of samples were higher than those found in Tables 1 and 2. It seems that the micrographs of the samples in Table 2 would show more eminent ductile failure than their counterparts. In general, the displacements at peak force for samples in Table 2 were also higher than the other groups in Tables 1 and 3. From the above discussions, it can be argued that by studying the micrographs of the

fractured composite, it is possible to predict whether the composite samples are tough or not.

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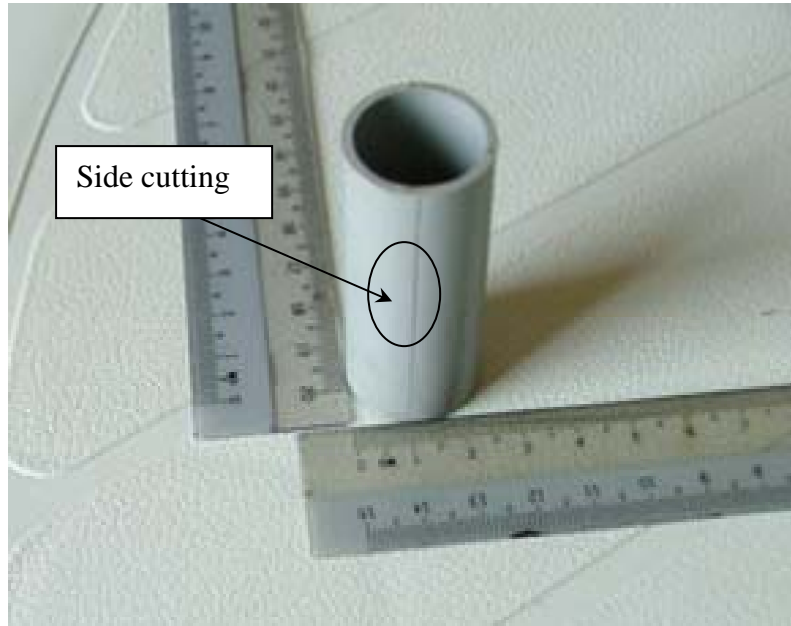
Figure 1: The mould
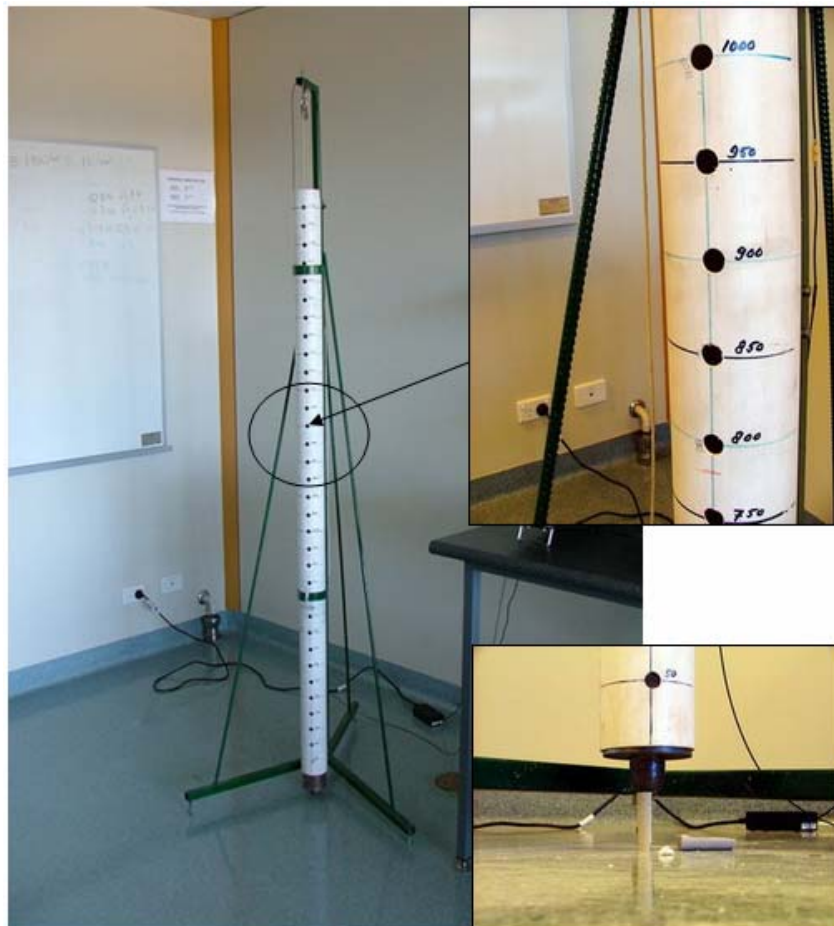
Figure 2: The drop weight tower
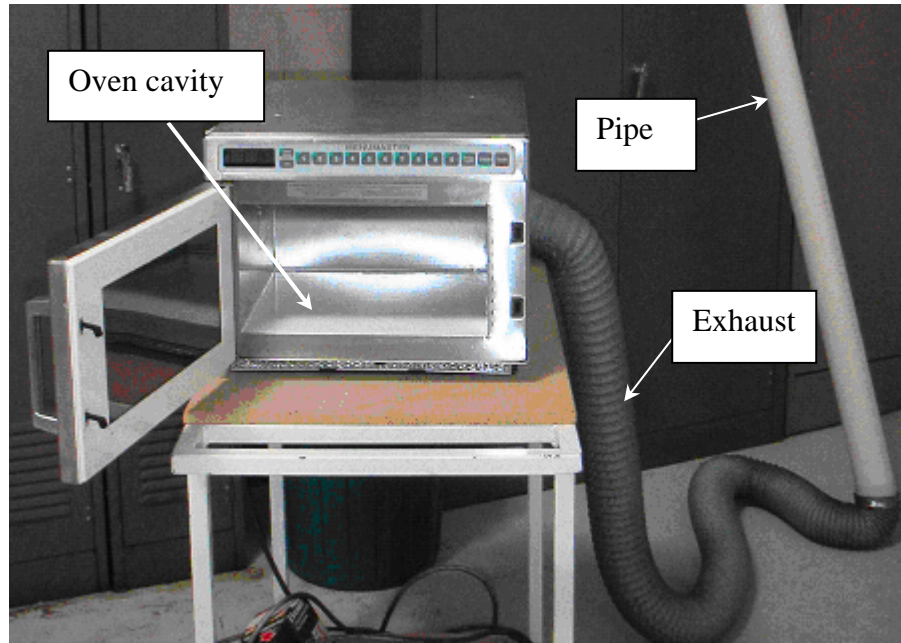
Figure 3: The microwave facility

Figure 4: Scanning Electron Microscope (SEM)

Figure 5: The sputter coater

Figure 6: The sputter coaster is coating a thin layer of gold on the specimen's surface

Figure 7: The specimen after being coated with a thin layer of gold
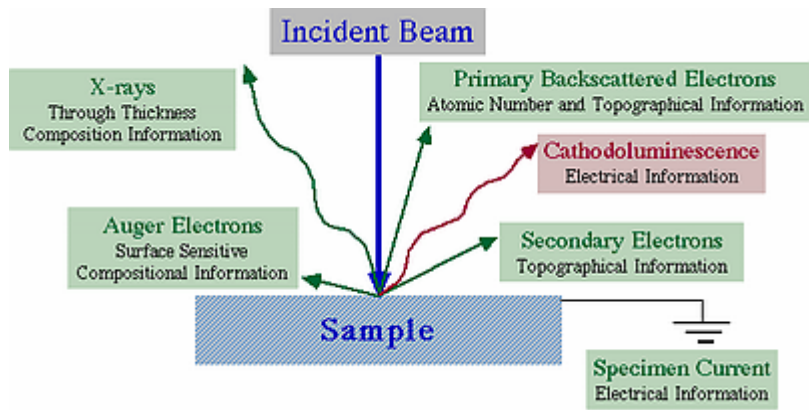
Figure 8: Electron and Specimen Interaction
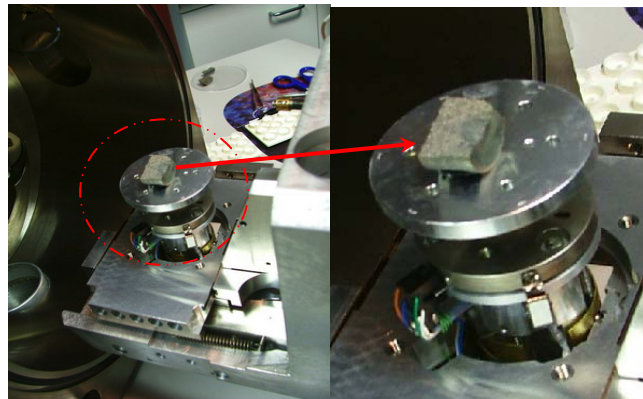
Figure 9: Specimen stub
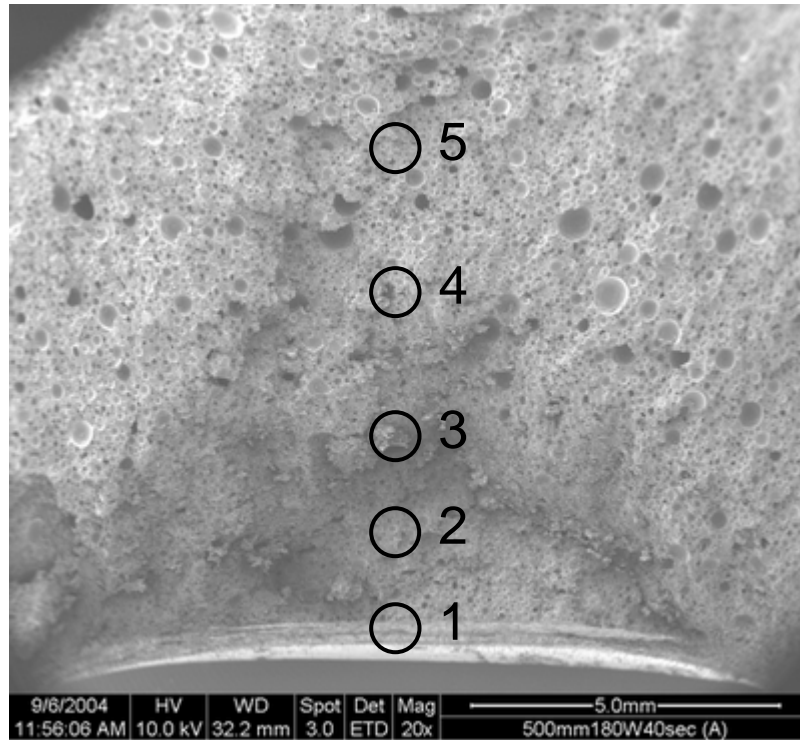
Figure 10: Microwave conditions with 180W and expose time of 40 seconds
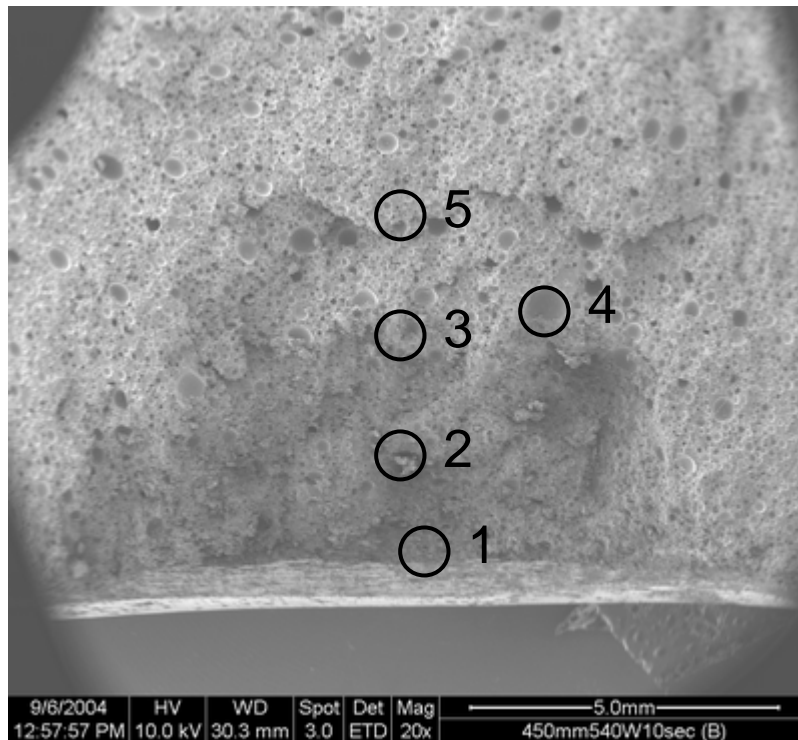
Figure 11: Microwave conditions with 540W and expose time of 10 seconds
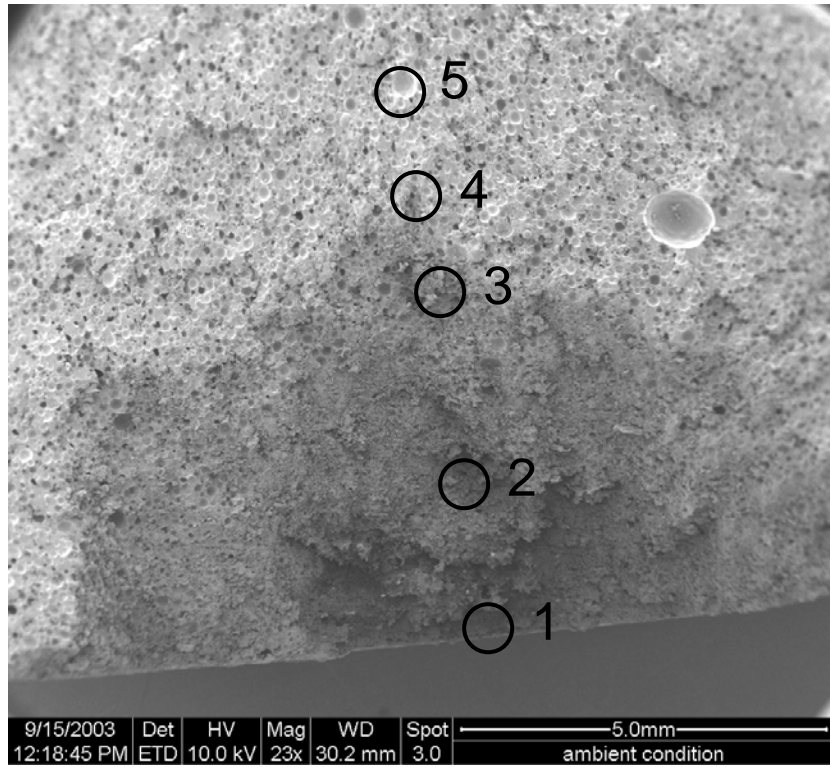
Figure 12: Five points chosen to be investigated with specimens cured under ambient condition
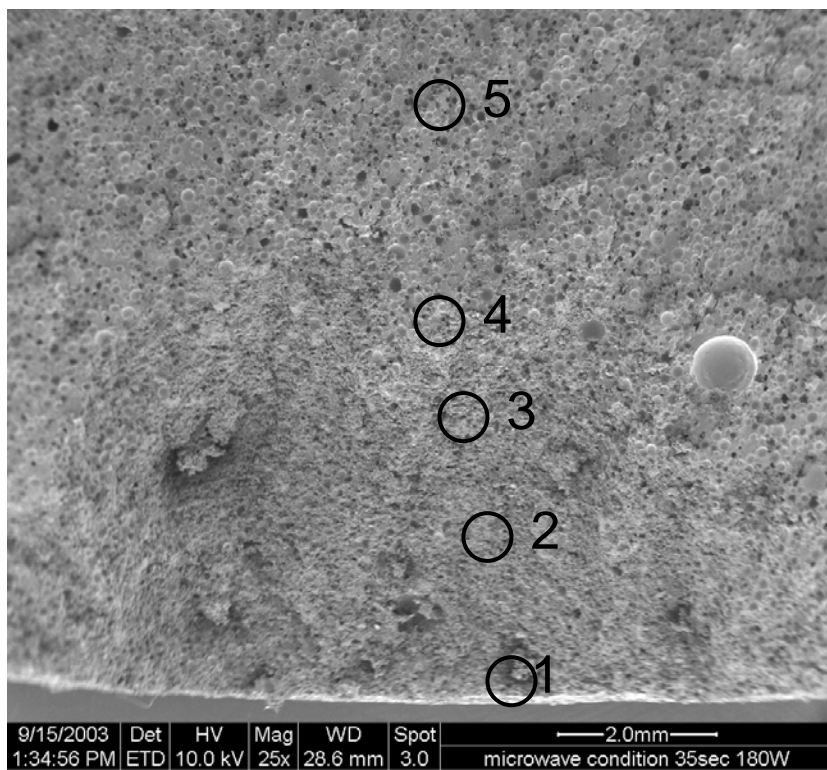
**Figure 13: Five points chosen to be investigated with specimens
cured with microwaves of 180 W for 35 seconds**

First fractured surface

9/6/2004	HV	WD	Spot	Det	Mag	
12:10:48 PM	10.0 kV	35.0 mm	3.0	ETD	80x	⊢——1.0mm——⊣
						500mm180W40sec (A)
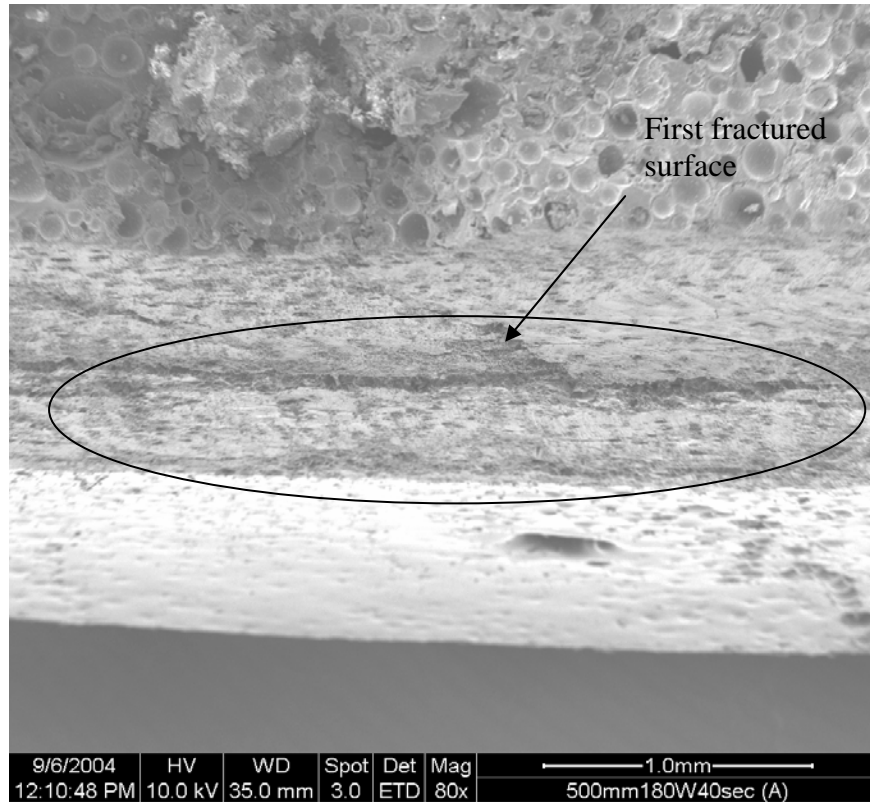
Figure 14: Area 1, 180 W & 40 s, magnified by 80 times, first fractured surface

Empty hole

9/6/2004	HV	WD	Spot	Det	Mag	
12:29:48 PM	10.0 kV	32.6 mm	3.0	ETD	300x	⊢——300.0µm——⊣
						500mm180W40sec (A)
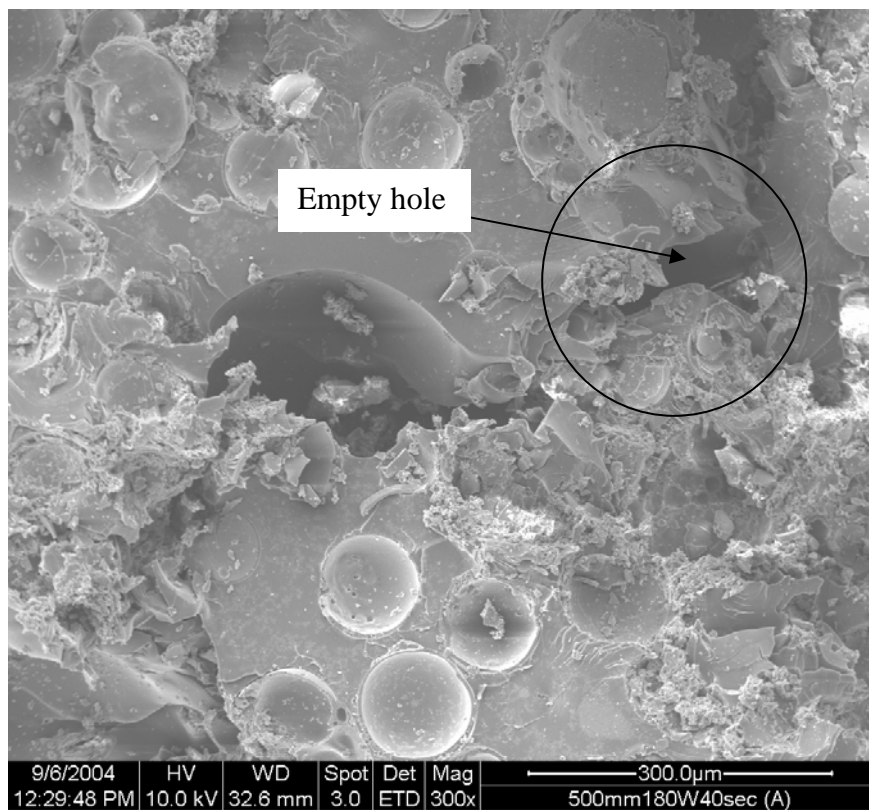
Figure 15: Area 2, 180W& 40s, magnified by 300 times, second fractured surface
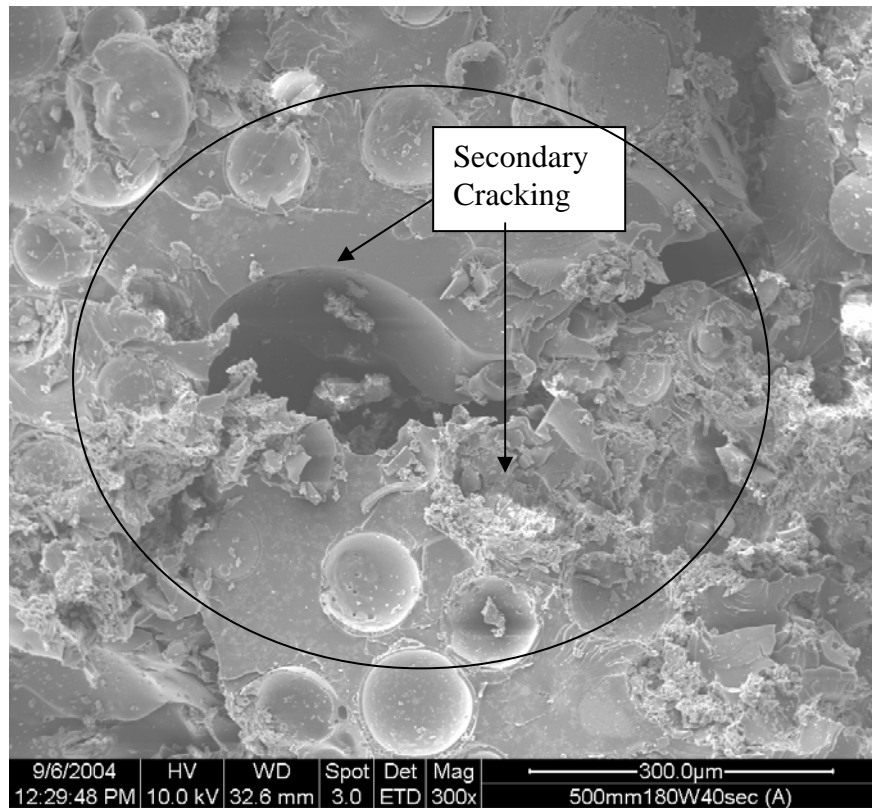
Figure 16: Area 3 180 W & 40s, magnified by 300 times, secondary cracking
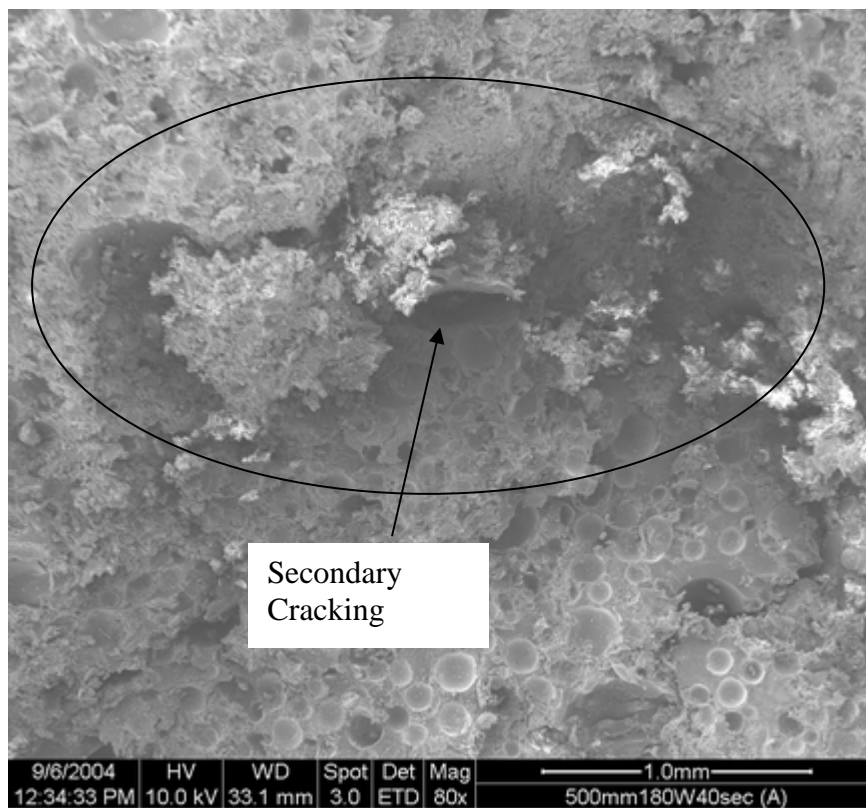
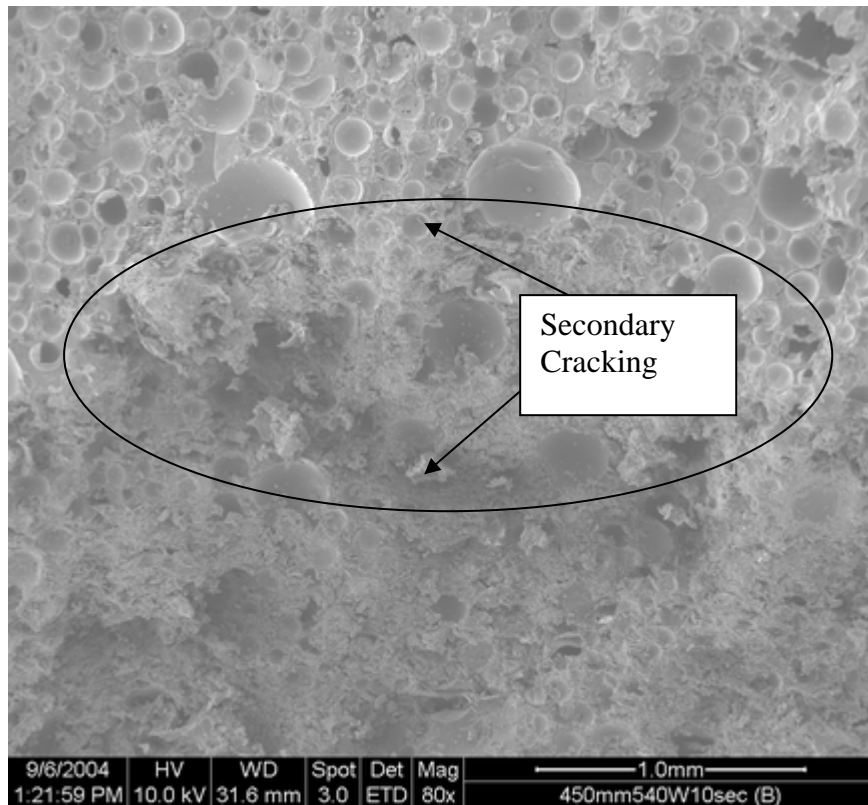**Figure 17: Area 4, 180 W & 40 s, magnified by 80 times, secondary cracking**
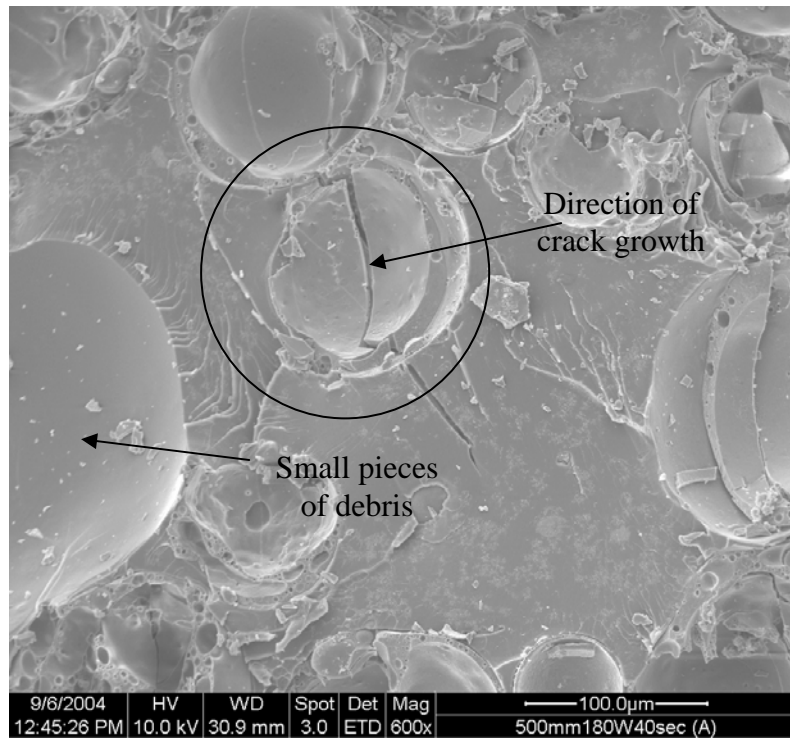
Figure 18: Area 5, 180 W & 40s, magnified by 600 times, direction of crack
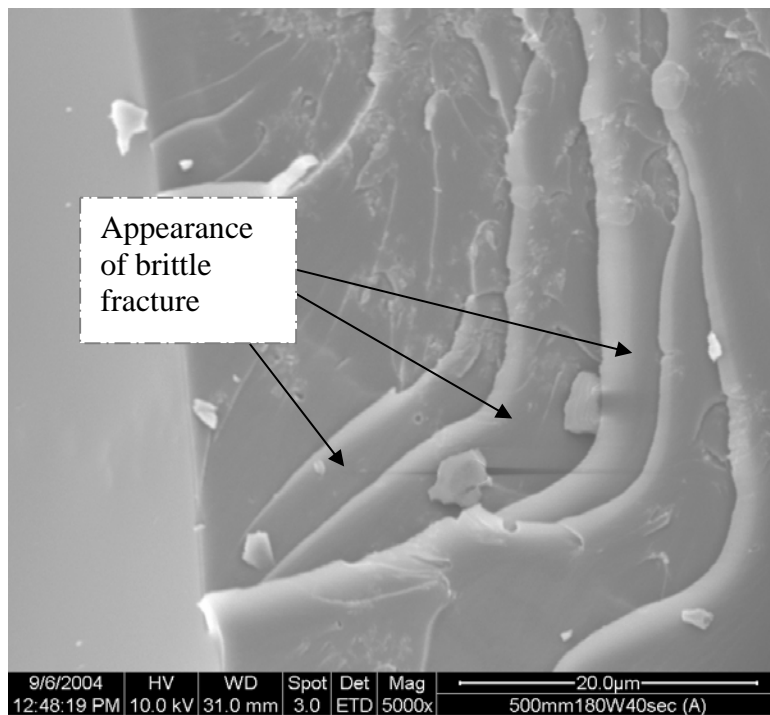
Figure19: Area 5, 180 W & 40s, magnified by 5000 times, brittle fracture

First fracture surface
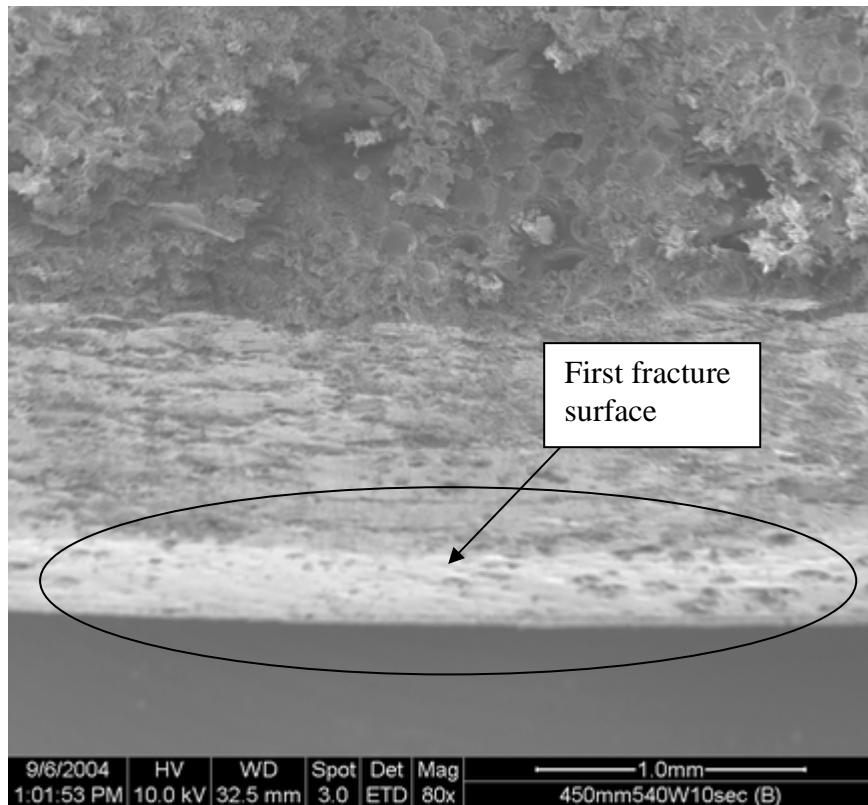
Figure 20: Area 1, 540 W & 10 s, magnified by 80 times, brittle fracture

Longer fracture surface
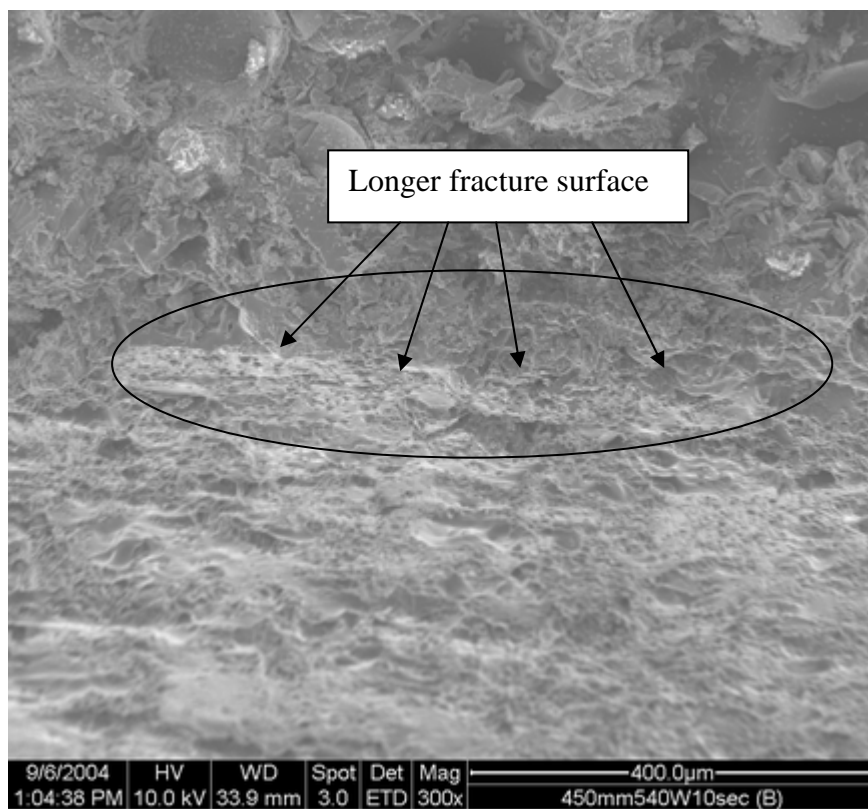
Figure 21: Area 2, 540 W & 10 s, magnified by 300 times, longer fractured surface
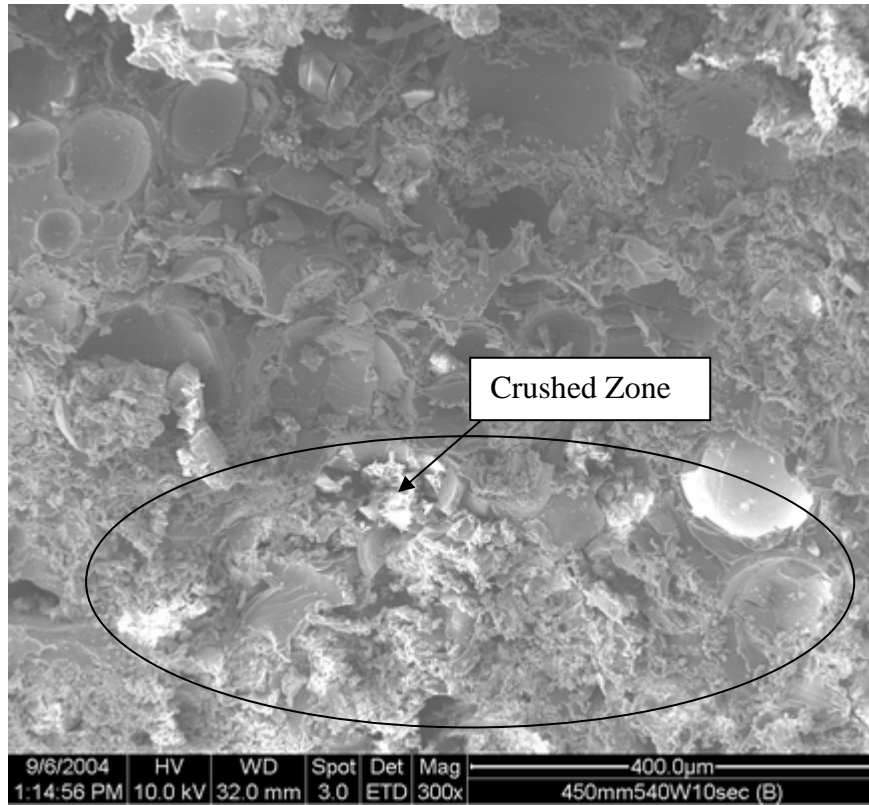
Figure 22: Area 3, 540 W & 10 s, magnified by 300 times, crushed zone
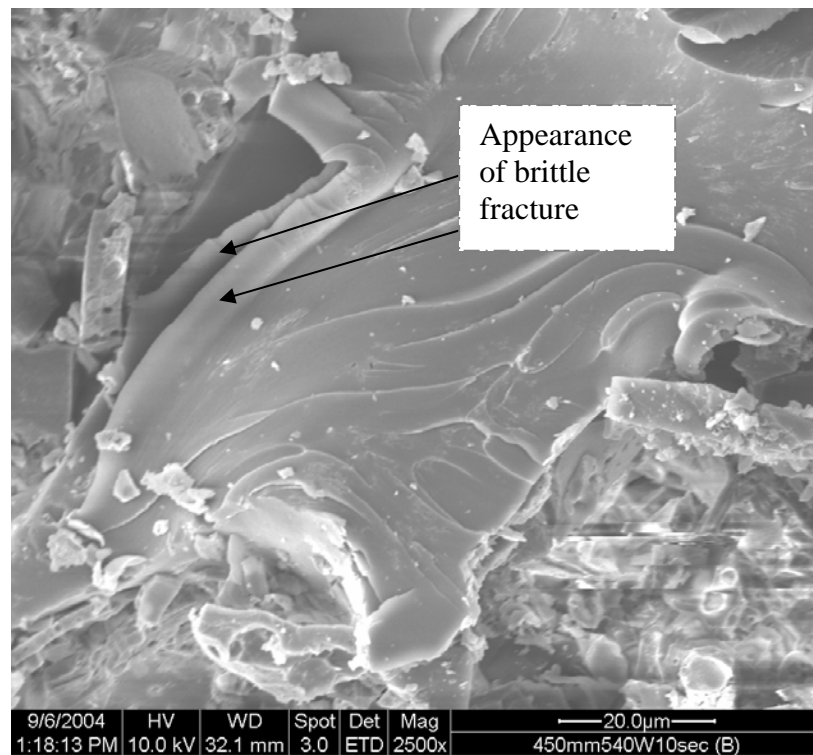
Figure 23: Area 3, 540 W & 10 s, magnified by 2500 times, brittle fracture

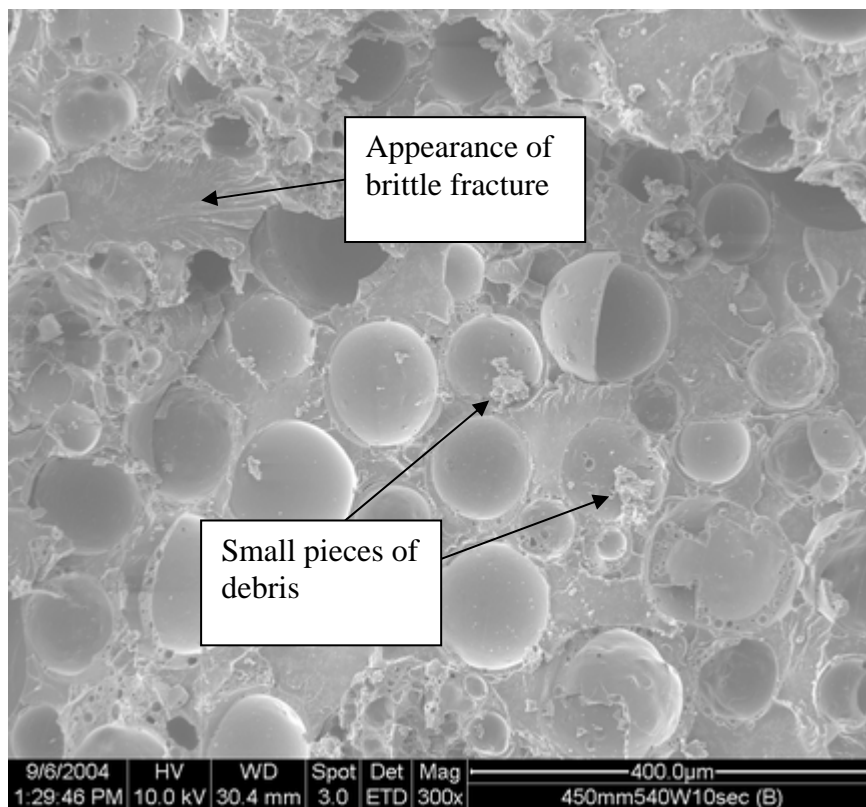**Figure 24: Area 4, 540 W & 10 s, magnified by 80 times, secondary cracking**

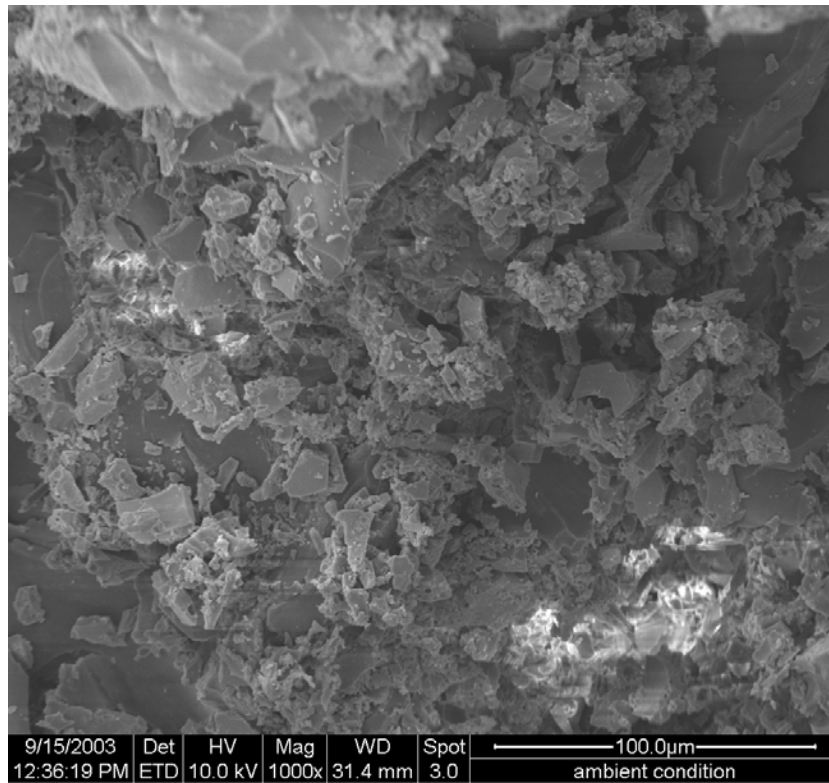**Figure 25: Area 5, 540 W & 10 s, magnified by 300 times, brittle fracture**

9/15/2003 | Det | HV | Mag | WD | Spot | ————100.0μm————
12:36:19 PM | ETD | 10.0 kV | 1000x | 31.4 mm | 3.0 | ambient condition

Figure 26: Area 1, ambient cured, magnified by 1,000 times

9/15/2003 | Det | HV | Mag | WD | Spot | ————100.0μm————
1:42:01 PM | ETD | 10.0 kV | 1000x | 32.4 mm | 3.0 | microwave condition 35sec 180W
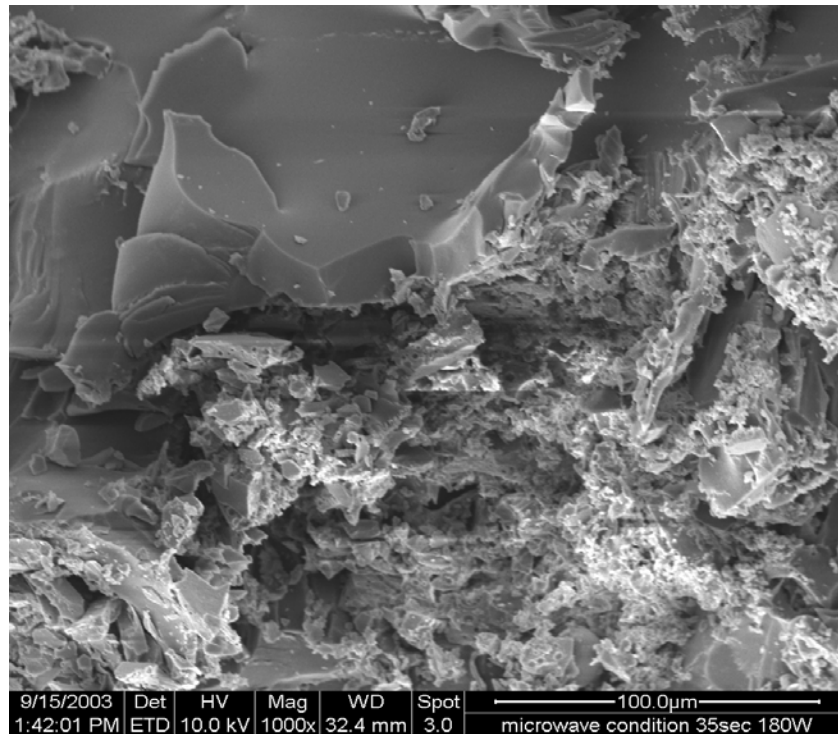
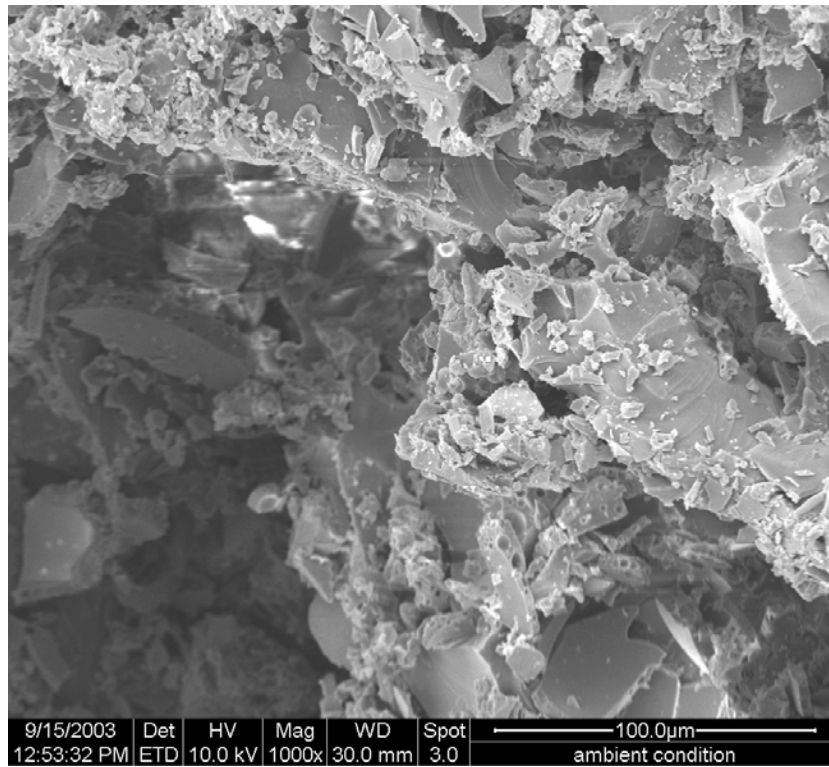**Figure 27: Area 1, microwave cured (180 W for 35 seconds), magnified by 1,000 times**

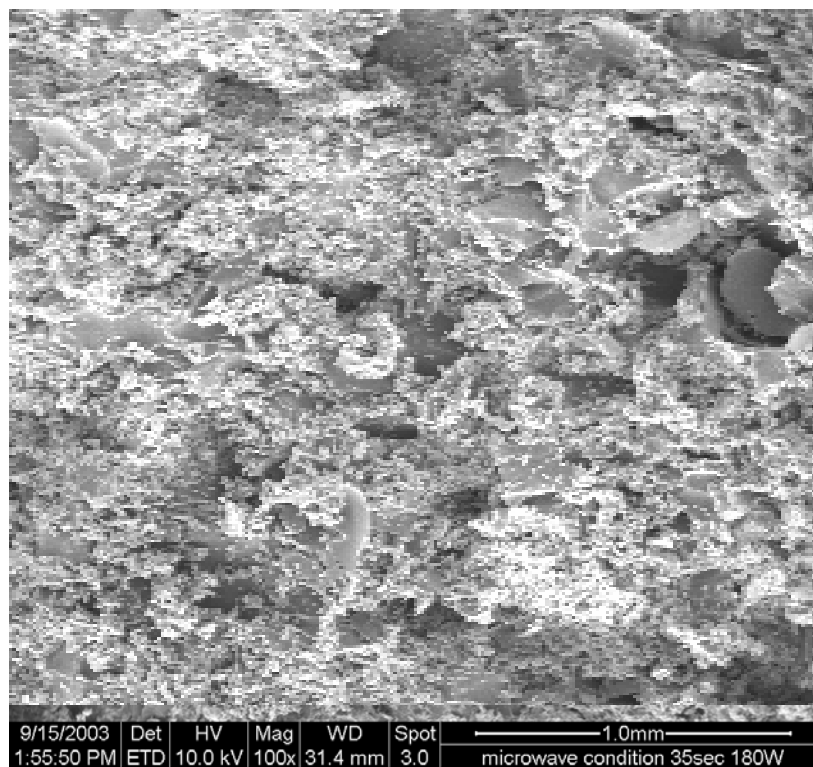**Figure 28: Area 2, ambient cured, magnified by 1,000 times**

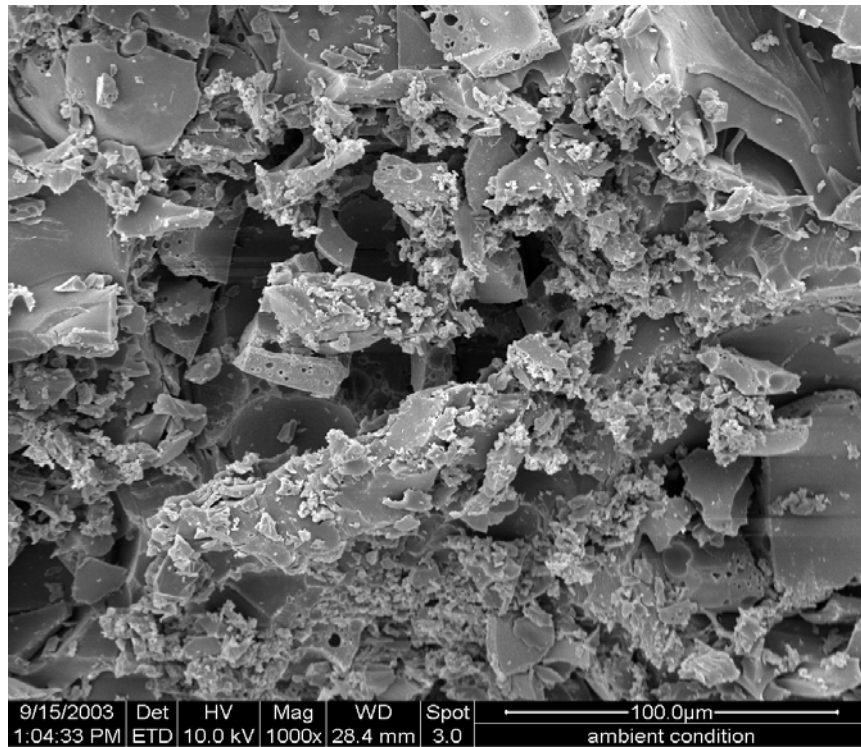**Figure 29: Area 2, microwave cured (180 W for 35 seconds), magnified by 100 times**

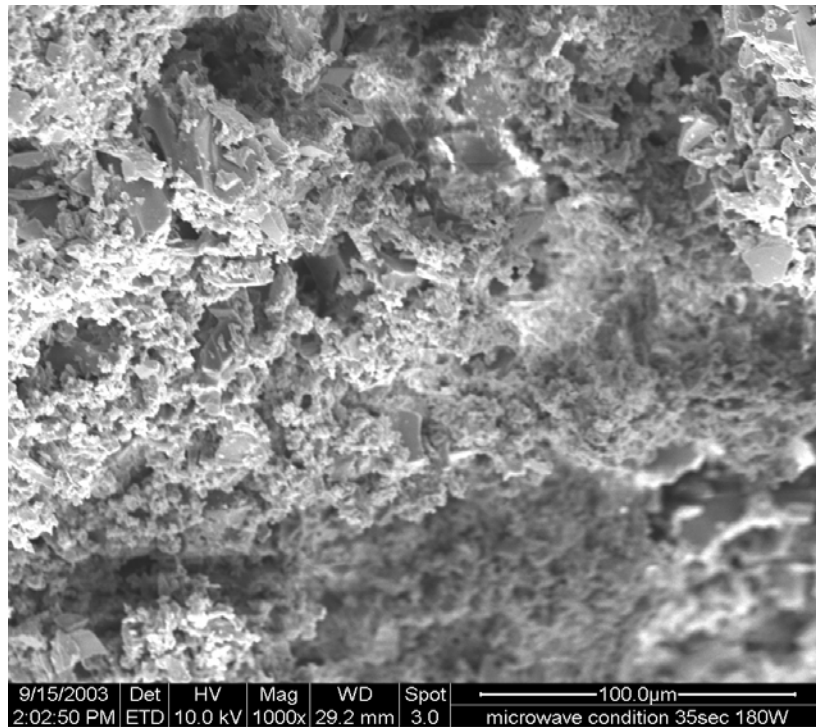**Figure 30: Area 3, ambient cured, magnified by 1,000 times**

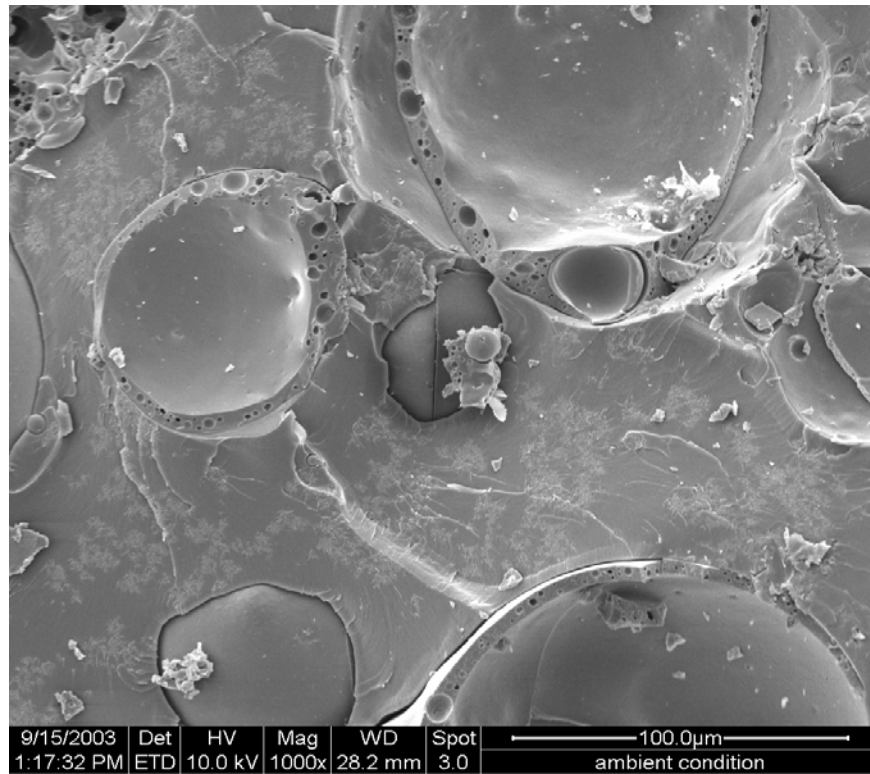**Figure 31: Area 3, microwave cured (180 W for 35 seconds), magnified by 1,000 times**

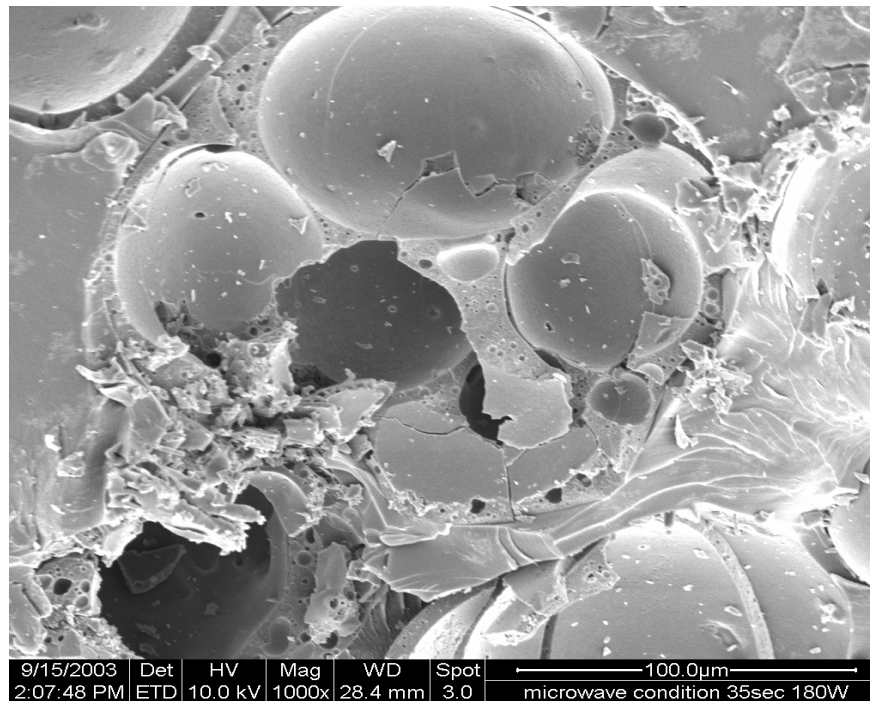**Figure 32: Area 4, ambient cured, magnified by 1,000 times**

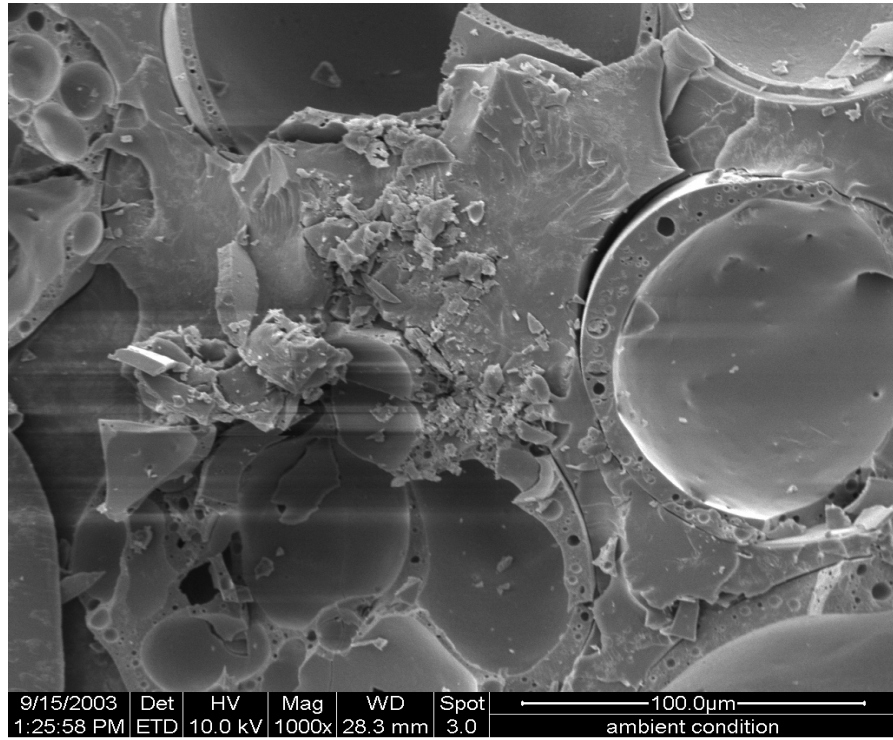**Figure 33: Area 4, microwave cured (180 W for 35 seconds), magnified by 1,000 times**

9/15/2003	Det	HV	Mag	WD	Spot	⊢————100.0µm————⊣
1:25:58 PM	ETD	10.0 kV	1000x	28.3 mm	3.0	ambient condition

Figure 34: Area 5, ambient cured, magnified by 1,000 times

9/15/2003	Det	HV	Mag	WD	Spot	⊢————100.0µm————⊣
2:12:28 PM	ETD	10.0 kV	1000x	28.0 mm	3.0	microwave condition 35sec 180W
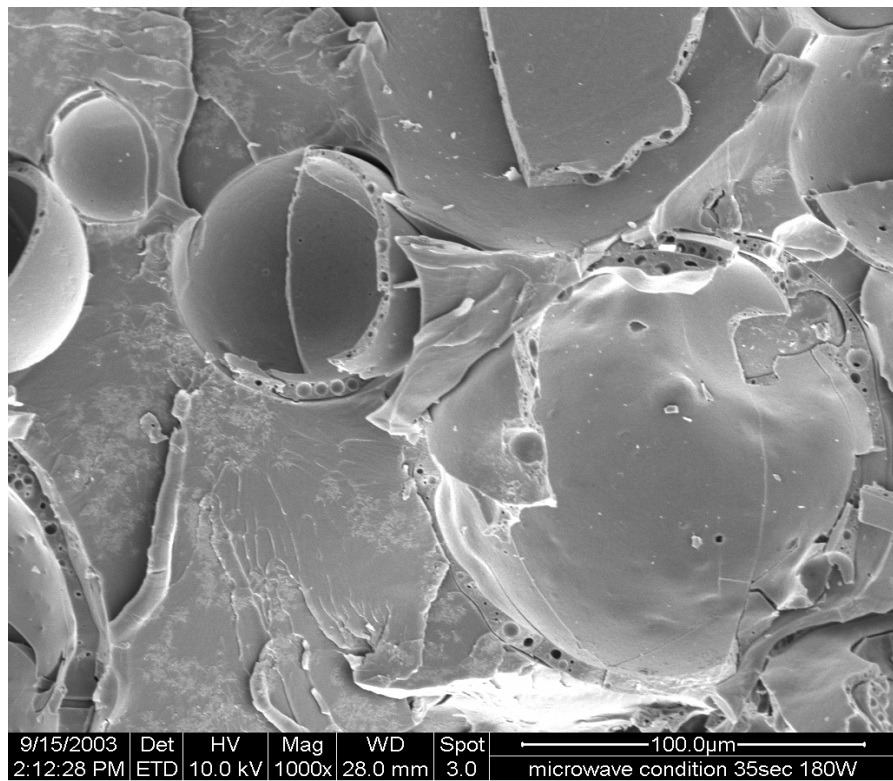
Figure 35: Area 5, microwave cured (180 W for 35 seconds), magnified by 1,000 times

9/15/2003 | Det | HV | Mag | WD | Spot | ⊢——————5.0µm——————⊣
12:42:35 PM | ETD | 10.0 kV | 16000x | 31.2 mm | 3.0 | ambient condition
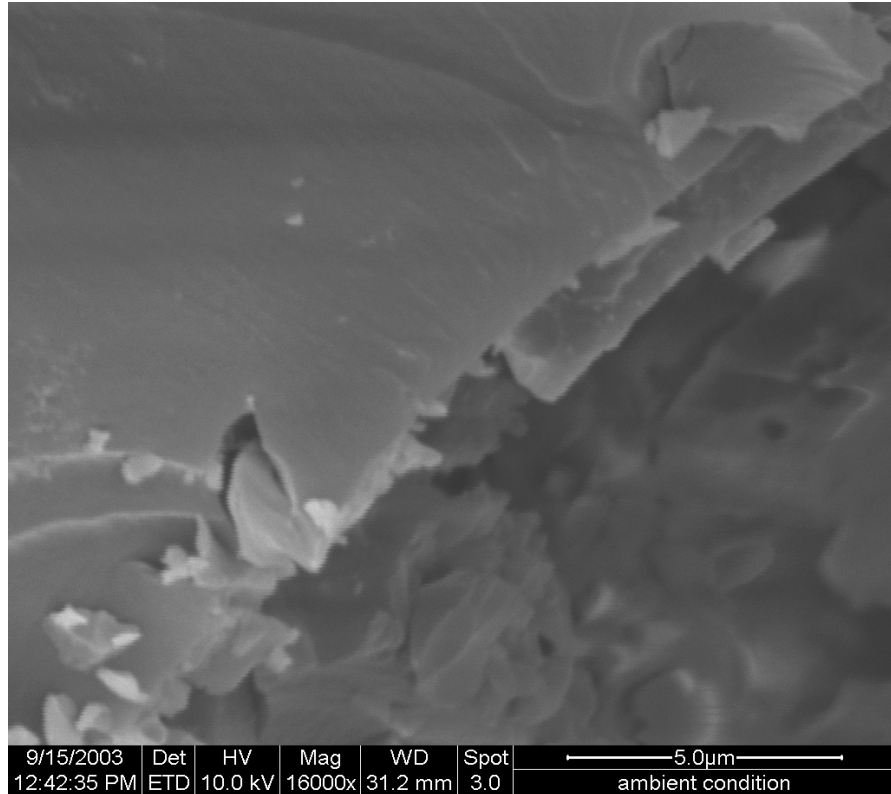
Figure 36: Area 1, ambient cured, magnified by 16,000 times

9/15/2003 | Det | HV | Mag | WD | Spot | ⊢——————5.0µm——————⊣
1:52:19 PM | ETD | 10.0 kV | 16000x | 32.4 mm | 3.0 | microwave condition 35sec 180W

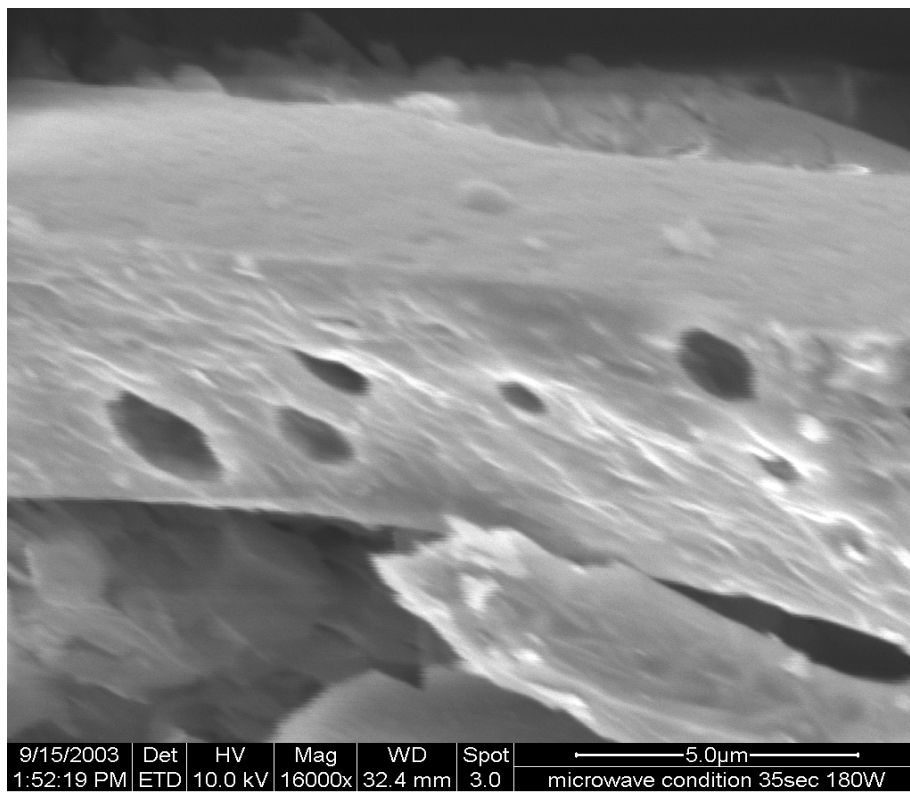**Figure 37: Area 1, microwave cured (180 W for 35 seconds), magnified by 16,000 times**

Table 1: Average energy required to fracture specimens cured with a power level 540 Watts

Curing Condition	Power Level of 540 Watts		
Exposure time	10 seconds	15 seconds	20 seconds
Energy used to initiate the crack	8.27 joules	7.91 joules	3.71 joules
Energy used to propagate the crack	1.83 joules	-2.77 joules	0.507 joules
Total Energy Dissipated	10.1 joules	7.91 joules	4.217 joules
Displacement at peak force	0.0018 m	0.0017 m	0.0015 m

Table 2: Average energy required to fracture specimens cured with a power level 360 Watts

Curing Condition	Microwave with power level of 360 Watts			
Specimens Type	Fractured Specimens			
Specimens Materials	VE/FLYASH (33%)			
Exposure time	Ambient Condition (0 second)	30 seconds	35 seconds	40 seconds
Energy used to initiate the crack	8.84 *joules*	9.45 *joules*	9.02 *joules*	8.50 *joules*
Energy used to propagate the crack	2.16 *joules*	1.03 *joules*	2.12 *joules*	2.53 *joules*
Total energy dissipated	11.00 *joules*	10.84 *joules*	11.14 *joules*	11.03 *joules*
Displacement at peak force	0.0018 *m*	0.0017 *m*	0.0018 *m*	0.0017 *m*

Table 3: Average energy required to fracture specimens cured with a power level 180 Watts

Curing Condition	Power Level of 180 Watts		
Exposure time	30 seconds	35 seconds	40 seconds
Energy used to initiate the crack	8.22 joules	8.81 joules	8.66 joules
Energy used to propagate the crack	2.62 joules	2.16 joules	2.16 joules
Total Energy Dissipated	10.84 joules	11.97 joules	10.82 joules
Displacement at peak force	0.0017 m	0.0018 m	0.0017 m