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Characterization of toughness variation due to intrinsic defects in high-thermal-resistant poly(acrylonitrile-butadiene-styrene) (ABS)

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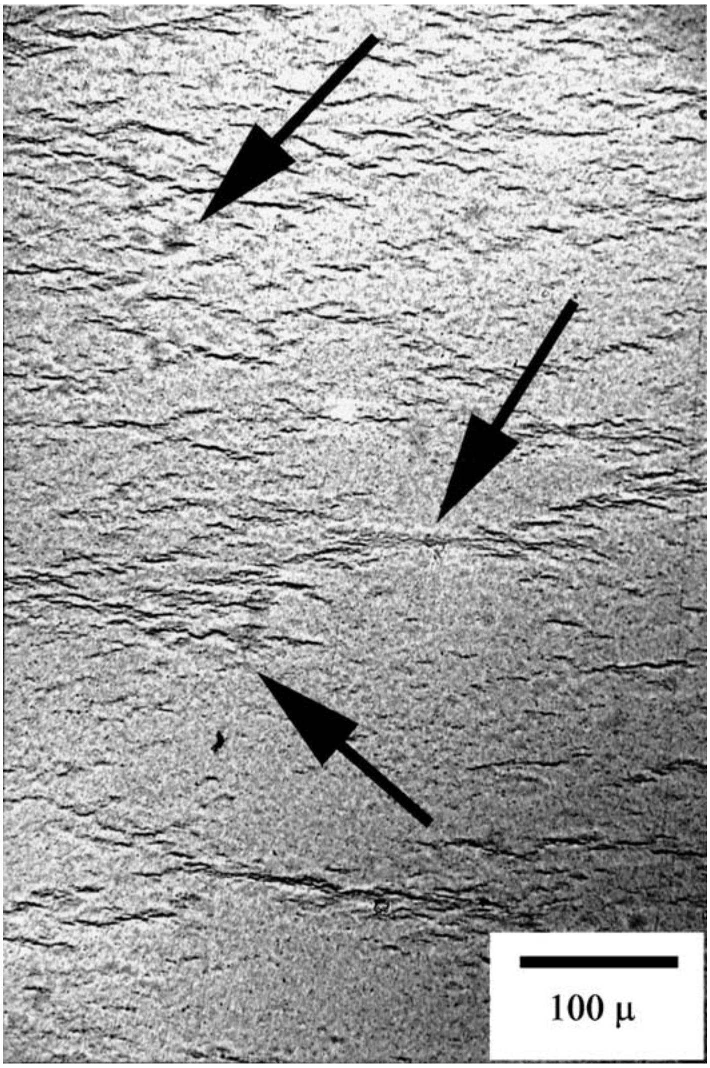
A mechanical testing method, named TACL test, is proposed to characterize the effect of gel-like particles on mechanical properties of high-thermal-resistant poly(acrylonitrile-butadiene-styrene) (ABS). The TACL test introduces cracks in the vicinity of gel-like particles by cyclic loading. Mechanical properties are then measured using the cyclically loaded specimens under monotonic tension. Preliminary results show that the mechanical properties, especially the maximum elongation and the total absorbed energy, are very sensitive to the cyclic loading. The study suggests that the TACL test can serve as a means to "semi-quantitatively" characterize number and distribution of the gel-like particles, which is useful for monitoring batch-dependent toughness variation of the ABS.

1. Introduction

Gel-like particles of arbitrary shape with dimensions around 100 μm were identified to cause crack initiation in emulsion-polymerized, high-thermal-resistant poly(acrylonitrile-butadiene-styrene) (ABS), due to poor bonding of the gel-like particles with the surrounding matrix. The number of gel-like particles is known to be small, but their existence severely affects the toughness of the ABS. In our recent experience, the gel-like particles are probably the cause of more than 50% of the toughness variation between two batches of high-thermal-resistant ABS that were otherwise identical [1]. Since the gel-like particles have similar composition to the surrounding ABS, based on recent infrared analysis [2], we believe that the particles are produced during the blending process, initiated by residual rubber gel that acts as a precursor for their formation. Because the gel-like particles are not an external contaminant, they are named "intrinsic" defect, which implies that the particles are unlikely to be completely removed from the material. As a result, it is important to understand how the gel-like particles affect mechanical toughness of the ABS.

Effect of the gel-like particles on deformation and fracture behaviour of the high-thermal-resistant ABS are demonstrated in Fig. 1. Fig. 1a is a transmission optical micrograph from a stress-whitening region of a tensile-fractured high-thermal-resistant ABS specimen. Due to low contrast with the surrounding matrix, arrows are used in Fig. 1a to indicate locations where some of the gel-like particles have been identified under the microscope. The micrograph suggests that existence of the gel-like particles has affected the crack growth path, which limits the extent of deformation and reduces the energy absorption capability of the specimen. Fig. 1b shows a scanning electron micrograph, taken from the fracture surface of a tensile specimen, in which a gel-like particle is located in the centre and has clearly acted as an initiator for fracture. Since no method is available to characterize the size and distribution of the gel-like particles, their effect on mechanical toughness is not known. Nevertheless, variation of the particle's quantity among batches is believed to be the main cause of batch-dependent toughness variation of the ABS.

This paper is part of a study that is aimed at developing a means to characterize the effect of the gel-like particles on mechanical properties of the high-thermal-resistant ABS. An early attempt was to use microscopic techniques, such as optical microscopy and scanning electron microscopy, to characterize the size of the gel-like particles and their distribution. However, we soon realized that these techniques require a large number of micrographs to ensure statistically accurate characterization of the gel-like particles, due to their irregular 3-dimensional shape and small number in each



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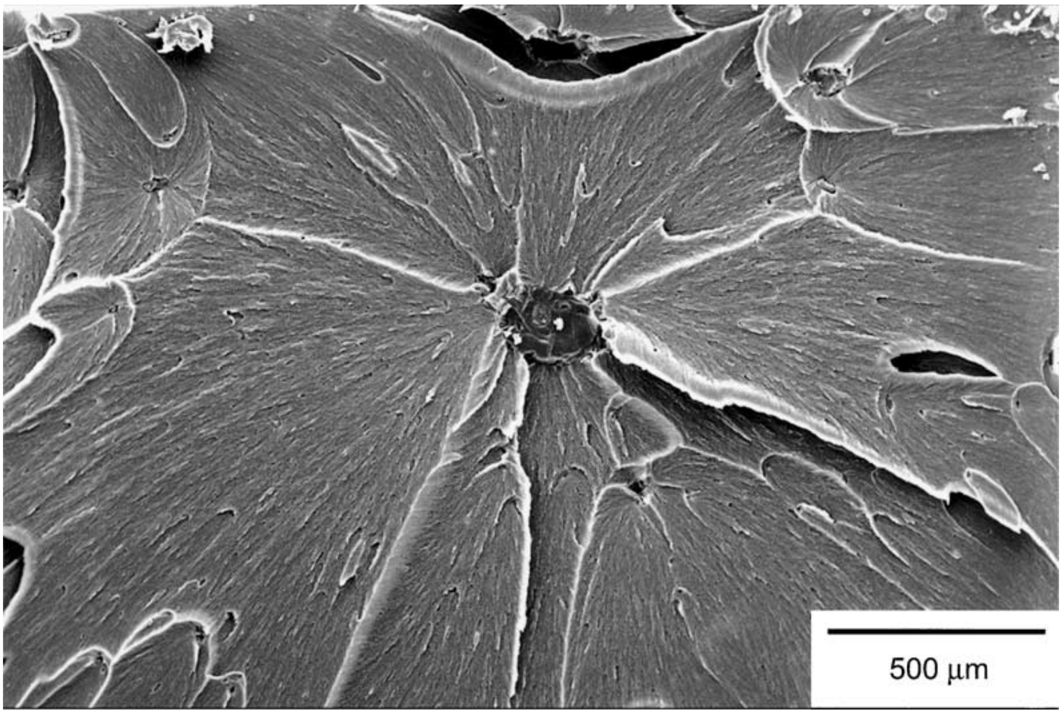


(b)

Figure 1 Tensile-fractured specimens: (a) transmission optical micrograph of a thin section in the stress-whitening zone, showing the damage pattern, and (b) SEM micrograph for one of the fracture initiation regions on the fracture surface. Arrows in (a) indicate some of the gel-like particles, and central part of (b) is a gel-like particle that initiated the fracture.

micrograph. As a result, the first step of the study was focused on characterizing the effect of the gel-like particles on mechanical properties.

This paper reports a mechanical testing method that can "semi-quantitatively" characterize the effect of gel-like particles on the mechanical properties of the ABS. The method combines cyclic loading and monotonic tensile loading, named tensile-after-cyclic-loading (TACL) test, to produce a characteristic curve that reflects the effect of the number and distribution of the gel-like particles on the toughness variation of the ABS. The paper details the testing methodology, with some preliminary results showing the reduction of tensile properties caused by the cyclic loading. The trend of property reduction can serve as an indicator for the number and distribution of the gel-like particles. This paper also compares deformation and fracture introduced by the cyclic loading with that caused by monotonic tensile loading.

2. Materials and test specimens

The high-thermal-resistant ABS used in the study contains (i) 20 wt% poly(styrene-N-phenyl-male-imide) (SMI) that has a monomer weight ratio of 45 : 55 for styrene to phenyl-male-imide, (ii) 44 wt% poly(styrene-co-acrylonitrile) (named "SAN_{add}") with a monomer weight ratio of 72 : 28 for styrene to acrylonitrile, and (iii) 36 wt% regular ABS that has a weight ratio of 50 : 50 for butadiene to poly(styrene-co-acrylonitrile) (named "SAN_{ABS}"). The weight ratio of the constituent monomers in the SAN_{ABS} is 77 : 23 for styrene to acrylonitrile, which is slightly different from that of the SAN_{add} (72 : 28). The weight-average molecular weights of the constituent polymers are 171,000 for SMI, 120,000 for the SAN_{add} and 89,000 for the SAN_{ABS}. The three constituents (SMI, SAN_{add} and SAN_{ABS}) are known to be fully miscible with each other at all mixing ratios [3]. Therefore, the high-thermal-resistant ABS has a uniform, single-phase matrix that is a blend of SMI and two SANs. Due to SMI's high glass transition temperature (196°C [4]), the glass transition temperature of the high-thermal-resistant ABS has been reported to be at least 10°C higher than that of the regular ABS [5].

Dumb-bell specimens used in the study were injection moulded from high-thermal-resistant ABS pellets that were formed by blending three constituent polymers in a twin-screw extruder. The barrel temperature of the injection-moulding machine was set at 260°C, and that of the extruder at 280°C. The mould temperature for injection moulding the dumb-bell specimens was set at 60°C. The dumb-bell specimens have a gauge section of 65 mm in length and $3 \times 12.3\ \text{mm}^2$ in cross section.

3. Tensile-after-cyclic-loading test (TACL test)

A schematic diagram of the TACL test is shown in Fig. 2. It contains two steps. The first step is cyclic loading with a fixed stress range, of which the purpose is to generate damage around the gel-like particles, not to fracture the specimen. After the cyclic loading, the specimens were then tested in tension to record tensile strength, maximum elongation and total absorbed energy (defined as the area under the force-displacement curve). The tensile test properties were then plotted versus the number of cyclic loadings, which is used to characterize the effect of the gel-like particles on mechanical properties of the ABS.

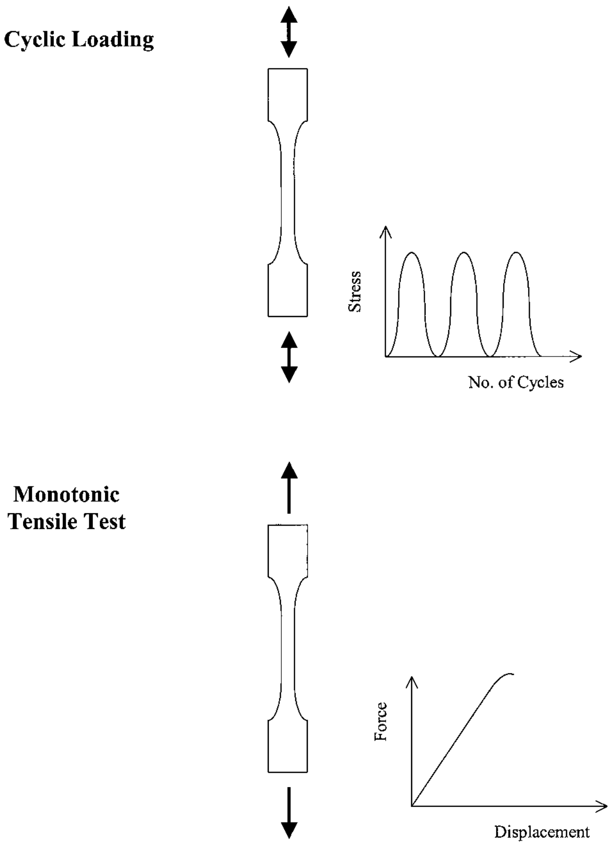


Figure 2 A schematic diagram of the TACL test.

All tests reported in this paper were conducted using an Instron 4505 universal testing machine that is equipped with the capability of low-frequency cyclic loading. The cyclic loading was applied under force control with a sinusoidal wave function, and the monotonic tensile loading was under a crosshead speed of 5 mm/min. Since the results were highly reproducible, only two specimens were used for each loading condition, the results of which were averaged and presented in "Results and Discussion."

The cyclic loading used in this study has a stress range of 0 MPa to 32 MPa, and loading frequency of 0.1 Hz. The maximum stress of 32 MPa, which is equivalent to 67% of static tensile strength of the high-thermal-resistant ABS, was selected based on two requirements: (i) The stress has to be low enough so that damage is only initiated from the gel-like particles, not from the regular rubber particles in ABS, and (ii) The stress has to be high enough so that a small number of cyclic loadings is sufficient to generate noticeable damage to affect the tensile properties of the specimen. As to be shown in the results, the maximum stress of 32 MPa met both requirements, with 1000 being the maximum number of loading cycles used. The loading frequency of 0.1 Hz was selected to provide sufficient time to dissipate heat generated from the cyclic loading, in order to minimize complications that may arise from the temperature effect.

It is believed that when material processing conditions are kept the same, the number of the gel-like particles is relatively constant among specimens of the same batch. Therefore, by increasing the number of loading cycles, the crack size generated from the gel-like particles is enlarged and the number of cracks increases, which is equivalent to decreasing the distance between the adjacent cracks. As a result, the mechanical properties measured under tension are expected to decrease.

The crack growth mechanism under monotonic tension of the cyclically loaded specimens is expected to be coalescence of existing cracks, which once started, will continue until the specimen fractures. By monitoring the variation of the tensile mechanical properties with the number of cyclic loadings, we obtain characteristic information about crack evolvement around the gel-like particles. Although the information does not directly characterize the number and distribution of the gel-like particles, it serves the purpose of comparing their effect on mechanical properties of ABS of different batches, thus being regarded as a "semi-quantitative" method.

4. Microscopic observation

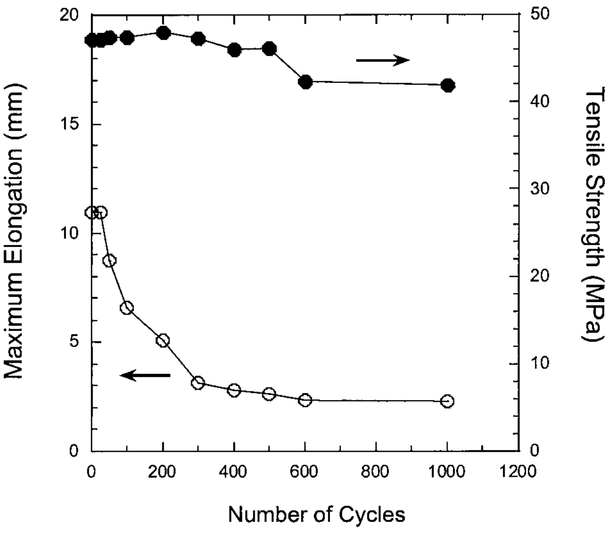
A scanning electron microscope (SEM, Cambridge S360) and a transmission electron microscope (TEM, Hitachi H7100) were used to examine deformation and fracture behaviour of the specimens. Details of the procedure for TEM sample preparation are described in [6].

5. Results and discussion

Fig. 3 summarizes the tensile test results as functions of the number of cyclic loadings. A clear contrast between tensile strength and maximum elongation is shown in Fig. 3a. While the tensile strength only decreases slightly (~12%) after 1000 cyclic loadings, the maximum elongation drops significantly, to a level that is less than 25% of the original value. The significant drop in maximum elongation occurred during the first 300 cycles of loading, beyond which the maximum elongation remains relatively constant. Decrease of the tensile strength, on the other hand, shows a transition from 500 cycles to 600 cycles in Fig. 3a, though the transition is not as obvious as that for the maximum elongation.

The total absorbed energy (a combined effect of tensile strength and maximum elongation) is shown in Fig. 3b, which has the same trend as that of the maximum elongation, apparently due to the significant variation of the maximum elongation with the number of cycles.

SEM examination of fracture surfaces from tensile tests is summarized in Figs 4 and 5. Fig. 4 shows a comparison of overall fracture surface topography of specimens after 50, 200, 400 or 1000 cyclic loadings. A cluster of grey, circular spots is visible in the lower half of the micrographs with 400 and 1000 cyclic loadings, but not in those with 50 or 200 cyclic loadings. The latter only show sporadic circular spots of which the size is relatively small but within the size distribution of the former. Apparently, by increasing the number of cyclic loadings, the number of the circular spots increases much faster than the size of each spot.



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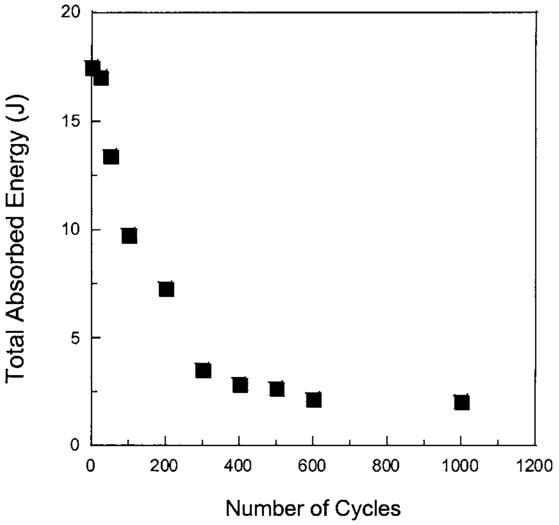


(b)

Figure 3 Plots of tensile test results as functions of the number of cyclic loadings: (a) tensile strength and maximum elongation, and (b) total absorbed energy.

A close look at one of the grey, circular spots is shown in Fig. 5a that was taken from a specimen with 1000 cyclic loadings. A gel-like particle is located at the centre of the figure, which indicates that the circular spots in Fig. 4 represent the annular areas surrounding each of the gel-like particles. Fig. 5a also indicates that the tensile fracture process was initiated from these annular areas that were most likely formed during the cyclic loading, due to stress concentration generated by the gel-like particles.

Micrographs at high magnification, taken within or outside the annular area of Fig. 5a, are shown in Figs. 5b and c, respectively. The two micrographs show very different surface topography. The former consists of large circular regions, with diameters slightly less than 1 μm, surrounded by numerous, much smaller circular spots; while the latter mainly consists of large circular regions that are also slightly less than 1 μm in diameter, surrounded by relatively homogeneous matrix with no distinctive spots. The large circular regions in the two micrographs are different in that the former are filled up to a level slightly lower than the circular perimeter, while the latter are circular craters.

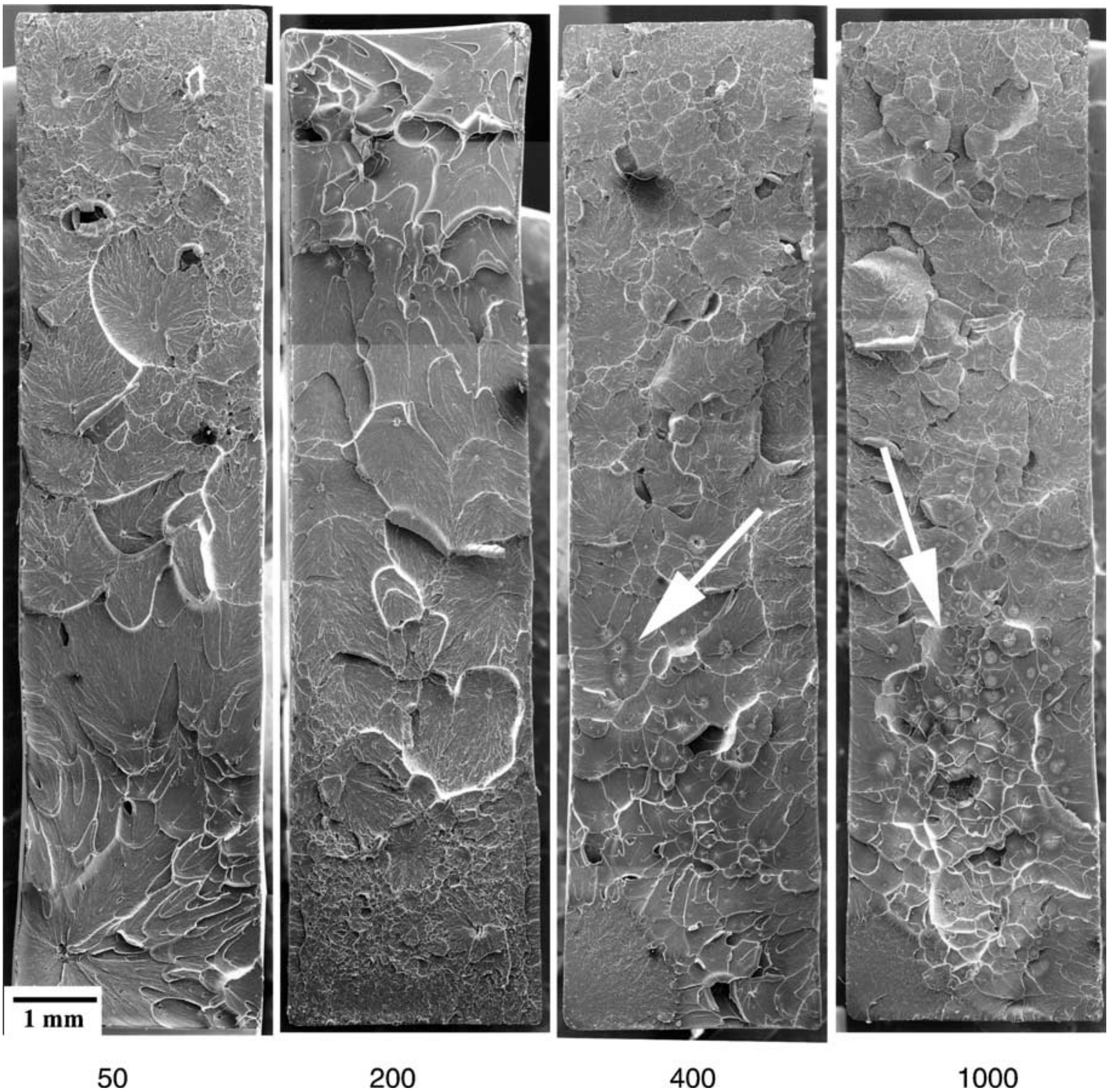


Figure 4 SEM micrographs of fracture surfaces from tensile fractured specimens, after being subjected to cyclic loading. The number under each micrograph indicates the number of cyclic loadings prior to conduct of the tensile test. The white arrows indicate locations of clusters of the grey, circular spots.

The high-thermal-resistant ABS used in the study is known to have rubber particles of bi-modal size distribution, with average diameters of around 1 μm and 0.1 μm, respectively [7]. Therefore, the large circular regions in Figs 5b and c are believed to be where the large rubber particles were, and the tiny spots in Fig. 5b are the small rubber particles. The two micrographs suggest that the large rubber particles fractured in a cleavage manner under the cyclic loading; but under the monotonic tension, fracture of the rubber particles proceeds with cavitation. The matrix of the ABS also fractured in a relatively brittle manner under the cyclic loading, which enabled us to identify the small rubber particles that separated from the matrix during the fracture process, possibly through debonding. Under monotonic tension, on the other hand, ductile deformation of the matrix has made it difficult to identify the small particles.

The deformation behaviour shown in Fig. 5c was further investigated using TEM. A TEM micrograph taken in a region outside but very close to one of the annular areas is shown in Fig. 6a, which is from a tensile-fractured specimen with 1000 cyclic loadings. The micrograph clearly shows the involvement of crazing and rubber particle cavitation in the deformation process, similar to that reported previously under tensile fracture [alloy #1 in ref. 7]. However, the shape of the rubber particles in Fig. 6a remains fairly circular, in contrast to the elliptical shape previously observed. In addition, the over-all tensile deformation of the specimen after being subjected to 1000 cyclic loadings was fairly brittle, with no stress-whitening and the maximum elongation of only around 2.5 mm, as shown in Fig. 3a. This is different from specimens subjected to only monotonic tensile loading, which showed an extensive stress-whitening zone. It should be noted that subjected to only monotonic tensile loading, the maximum elongation for the high-thermal-resistant ABS used in the current study is 11 mm, as shown in Fig. 3a, but 8 mm in the previous study [7] (30% reduction in

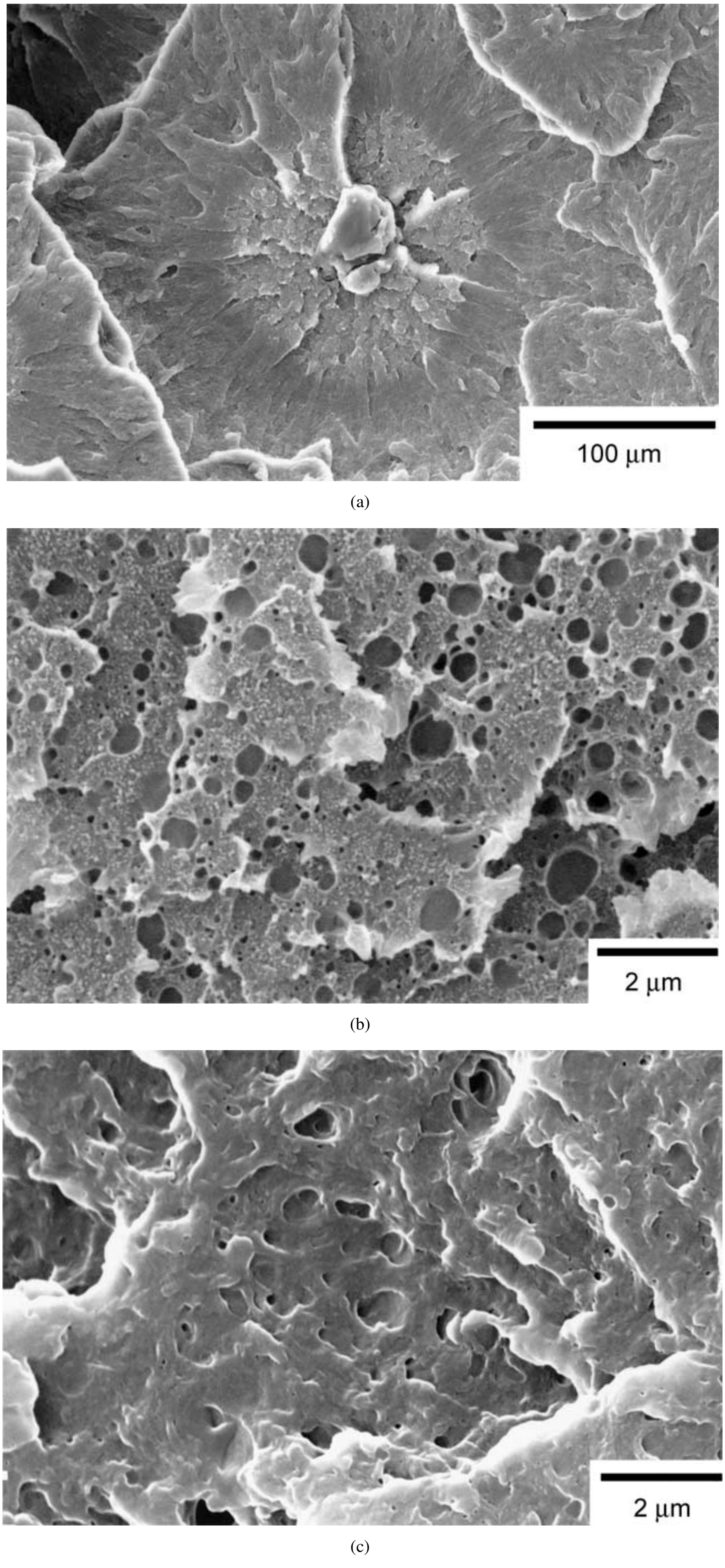
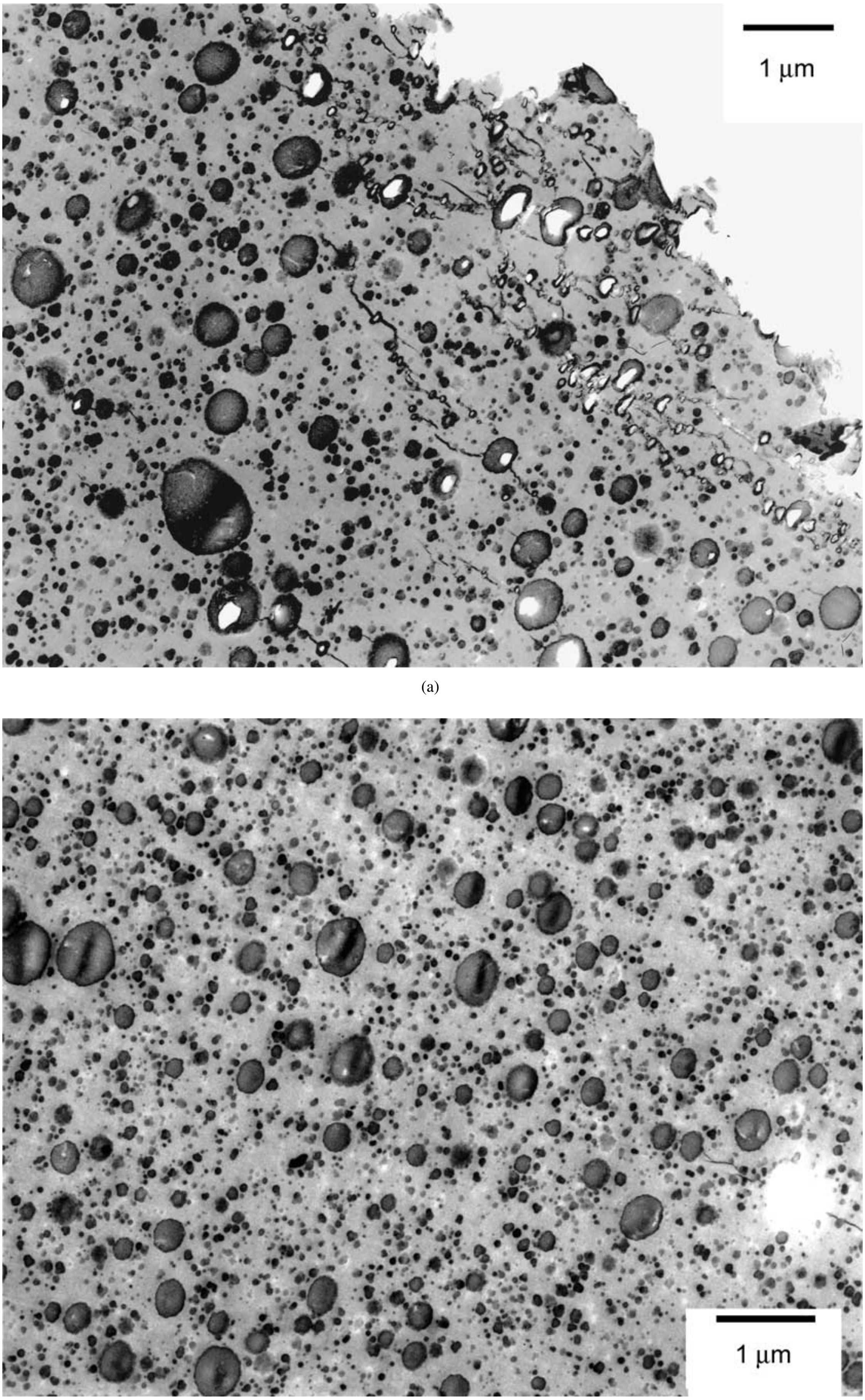


Figure 5 SEM micrographs of a tensile-fractured surface after 1000 cyclic loadings: (a) low magnification showing the cyclic-loading-generated damage zone and the surrounding area, (b) high magnification within the cyclic-loading-generated damage zone, and (c) high magnification in the surrounding fracture surface that was generated during monotonic tensile loading.



(a)

(b)

Figure 6 TEM micrographs from one of the ABS specimens after 1000 cyclic loadings: (a) from a region immediately beneath the fracture surface, outside but close to the annular grey region, and (b) from the gauge section that is more than 5 mm away from the fracture surface.

ductility), despite that the two ABS samples had identical material characteristics and were tested under the same conditions. The inconsistent tensile ductility is possibly due to the different amount of gel-like particles contained in the two batches of ABS.

A TEM micrograph taken from the same specimen as that for Fig. 6a, but in a gauge section of more than 5 mm away from the fracture surface, is shown in Fig. 6b. Very few crazes or particle cavitations were found in the micrograph, suggesting that the maximum stress used in the cyclic loadings did not cause particle cavitation, only generating cracks in the vicinity of the gel-like particles. The particle size variation in Fig. 6b confirms its bi-modal distribution that was suggested in Fig. 5, with average diameter of the large particles being around 1 μm and that of the small particles around 0.1 μm.

Fig. 6b shows some agglomeration of small particles, but the distribution is much more uniform than that reported by Bernal *et al.* [8].

6. Conclusions

Gel-like particles were found to be responsible for batch-dependent variation of mechanical properties for high-thermal-resistant ABS. A testing method, named TACL test, is suggested to characterize the effect of the gel-like particles on ABS's mechanical properties. The proposed testing method uses cyclic loading to generate cracks around the gel-like particles, and then a tensile test to monitor the corresponding change in mechanical properties. The number of the cracks, and to a lesser extent, their size was found to increase with increasing the number of the cyclic loadings. Since cracks are only generated around the gel-like particles, the change of the mechanical properties under tension is expected to reflect the number and distribution of the gel-like particles. By monitoring the change of mechanical properties with respect to the number of the cyclic loadings, we can characterize the effect of number and distribution of the gel-like particles on mechanical properties of the high-thermal-resistant ABS.

The results also show that deformation behaviour under cyclic loading is very different from that under monotonic tensile loading. This raises a question on validity of applying toughness measured from a monotonic tensile test to the design of ABS-based products that are subjected to cyclic loading. Further study on this aspect is currently being conducted in our laboratory.

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