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A study of the microscopic plastic deformation process in poly(methylmethacrylate)/acrylic impact modifier compounds by means of small angle X-ray scattering

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Abstract

A significant improvement of the impact strength for poly(methylmethacrylate) (PMMA) alloy was obtained by using an acrylic rubber modifier containing a small amount of silicone or a butadiene/butylacrylate (Bd/BA) aggregation type of modifier. For the modifier containing silicone, a remarkable small angle X-ray scattering (SAXS) could be observed, and a small sized submicrocracks (SMCs) appeared inside the rubber particle under the deformation. It has been suggested that the small amount of silicone contained in the rubber might play a role in the production of nuclei of SMC origin. Therefore, even if the amount of silicone content was quite small, it was effective enough to generate the SMCs. Thus, the function of the silicone is to improve toughness in view of inducing void formation. The Bd/BA-aggregation type of modifier reaches fracture even under small stress, and followed by jumping suddenly to a cavity far larger than the detection limit of our SAXS apparatus at an early stage of strain. This fracture mechanism is completely different from that of the silicone type. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methylmethacrylate); Izod impact strength; Toughness

1. Introduction

It is well known that the improved toughness of the polymer alloy results from the absorption of impact energy involving plastic deformation due to the following two modes. First is the massive shear yielding of the matrix leading to ductile behavior in the presence of microvoiding (cavitation in the rubber particles or debonding at the modifier/matrix interface). Second is the craze formation.

It has been reported that rubber particles promote massive shear yielding of the matrix, e.g. a pseudoductile polymer such as nylon-6,6, polycarbonate and poly(vinyl chloride) (PVC). Wu asserted that for toughening of nylon-6,6 the shear yielding mechanism becomes dominant when the distance between modifier particles is less than a certain length [1]. With reference to PVC/MBS (methylmethacrylate–butadiene–styrene) rubber alloy, Dompas et al. [2] suggested that a comparable shear yielding effect and toughness can be obtained for both cavitation and debonding mechanisms. In contrast, Ishikawa et al. [3–5] have suggested that the craze formation with recourse to the unstable voids formed due to the rubber modifiers with low elastic modulus is important for the toughening of a PVC polymer alloy. However, the mechanism of the void formation has not been made clear.

On the other hand, Bucknall has explained the mechanism of craze formation in detail for high impact polystyrene (HIPS). A wider width of craze requires a larger deformation of rubber comparable to the craze width, and the width decides the length of the craze that finally develops. Therefore, it is difficult for the small size of rubber particle to efficiently originate the crazes at the interface between the rubber particle and matrix. For uniaxial tension of the polymer alloy containing low-crosslinked elastomer particles, the direct fibrillation of elastomer also contributes to an increase in the amount of crazing owing to large elongation with recourse to the cavitation.

It is well known that poly(methylmethacrylate) (PMMA) tends to have an “intermediate” behavior, crazing and shear yielding [6]. For PMMA alloys, Plummer et al. [7] have reported interesting findings, in terms of the tensile test at a slow deformation, with thin cast film compounds. They have demonstrated that the morphology of a rubber particle influences the deformation modes of crazing and homogeneous shear yielding. Furthermore, it has also been

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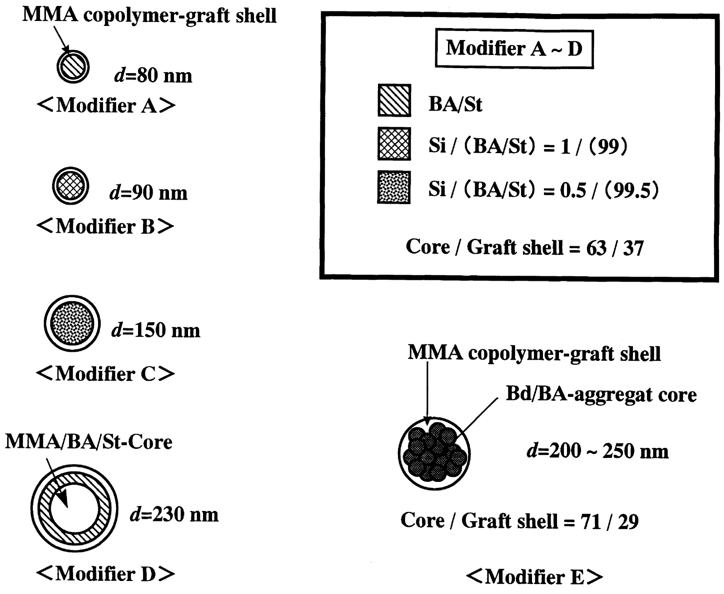

Fig. 1. Characteristics of the acrylic rubber modifiers employed in this study (BA, *n*-butylacrylate; MA, methylacrylate; St, stylen; Si, silicone; MMA, methylmethacrylate; Bd, butadiene).

demonstrated that the range of stress concentration in the immediate vicinity of the small isolated particle is too limited to promote craze nucleation and its development. Also, closely agglomerate rubber particles (cluster of rubber particles) have the ability to cause the widespread crazes appearing in the intervening matrix regions between different clusters (not within the cluster). Still further, within the cluster, they have suggested that the dominant deformation mode is a homogeneous shear banding rather than crazing. However, they go on to say that the stress state in the thin film geometry may be different from that in a bulk compound sample. Mauzac et al. have investigated the deformation modes of bulk samples including different contents of rubber particles, and then reported that there are some complicated crazing modes for PMMA alloys with a low modifier content [8]. However, it has also been indicated that at high modifier content the mechanism of massive shear yielding due to microvoiding of the rubber particle without craze formation existed, and was similar to that of nylon-6,6-toughened polymer alloy.

The deformation mechanism concerning the toughness of PMMA alloys, to our knowledge, seems to be complicated and vary depending primarily on the content and morphology (or physical property) of the rubber modifier. Consequently, we investigated PMMA alloys with some types of acrylic rubber impact modifiers (e.g. aggregation type of rubber modifier, silicone-containing rubber modifier, semi-hard core surrounded by rubber shell type of modifier, etc.) by means of a small angle X-ray scattering (SAXS) measurement and transmission electron microscopy (TEM). In this paper, the impact resistances of the PMMA compounds concerning these modifiers and the microscopic deformation processes of these compounds examined under slow tensile strain are explained. In particular, the marked distinctions concerning these modifiers, thought to be important factors regarding the toughness in high modifier content for the PMMA alloy, are obtained.

2. Experiments

2.1. Preparation of silicone/acrylic composite rubber modifier

Five different types of modifiers are shown in Fig. 1. TEM was used to estimate the morphology and the diameter (*d*) of the rubber particle in each modifier except the graft shell part. Preparation of silicone/acrylic composite rubber modifiers used in this study to modify the impact strength and toughness of PMMA was as follows: a silicone/acrylic composite rubber particle was obtained by seeded emulsion polymerization. A mixture of *n*-butylacrylate (BA), stylen (St) and a crosslinking agent was added a drop at a time to the silicone latex (Si), followed by redox polymerization. Furthermore, it was graft-copolymerized with methylmethacrylate (MMA) copolymer to form a graft shell around the rubber particle. Thus, silicone/acrylic composite rubber modifiers with different silicone contents (Modifier B and C) were finally obtained.

Acrylic rubber modifiers without silicone (Modifier A and D) were likewise produced by the process of conventional emulsion polymerization and the graft-copolymerization mentioned above. Modifier A was a two-layer core-shell, with a crosslinked (BA/St) core and a MMA copolymer shell. Modifier D was a three-layer particle with a semi-hard core (MMA/BA/St), surrounded

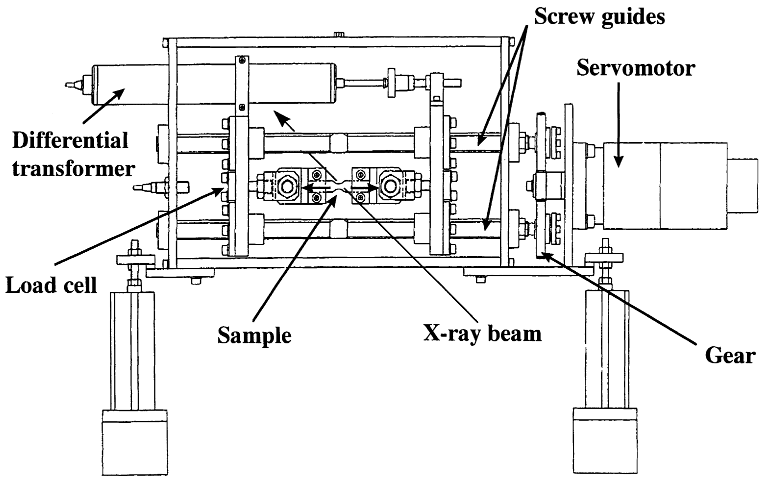

Fig. 2. Apparatus used in performing uniaxial tensile deformation test while measuring SAXS.

by an inner shell of crosslinked BA/St and an outer shell of MMA copolymer. This modifier was designed for the purpose of improving the transparency of the PMMA compound by matching a refractive index of the modifier to that of PMMA matrix.

Modifier E was an aggregation type of modifier, of which the core comprises many aggregate rubber particles of butadiene/*n*-butylacrylate (Bd/BA) copolymer.

2.2. Preparation of PMMA/modifier compound specimen

The PMMA of the matrix polymer was an injection-molding grade with an average molecular weight (M_n) of 60 000. The PMMA beads and modifier were pre-mixed in a mixer and extruded by means of a single-screw extruder with a diameter of 25 mm ϕ at a barrel temperature 230°C, and a 2.2 mm-thickness plate was injection-molded at a molten temperature of 230°C and a molded temperature of 60°C. In this way, molded specimens each containing different types of modifier were prepared. A dumbbell-shaped panel specimen (2.2 mm in thickness, 12 mm in gauge width, 12 mm in gauge length) cut out from the molded specimen was used to carry out SAXS measurements under the uniaxial tensile deformation.

Impact strength was evaluated by means of the Izod impact test using a 0.25 in. U-notched compound specimen.

2.3. Apparatus to draw sample

Fig. 2 shows the apparatus produced by the authors for the purpose of the uniaxial tensile deformation test while measuring SAXS. The apparatus could be precisely driven by feeding electric pulses to the servomotor, which was able to provide the exact drawing speed and displacement. A rotating mechanical power was transmitted from the servomotor to two screw guides by means of gears as illustrated in Fig. 2. CW and CCW screw structures were placed at both sides of the center of the screw guide, which corresponds to the position that the X-rays were applied in the dumbbell-shaped specimen. Two chuck mounts were employed to enable the specimen to slide in opposite directions from each other by rotating the screw guides. Finally, the specimen was stretched toward both sides at the same speed. Therefore, the X-ray incident beam would always penetrate a certain position in the specimen. The deformation rate was 0.24%/min of the slow strain. Drawing displacement and load were monitored by using a differential transformer and a load cell, respectively. Their measurement accuracy was ±0.001 mm and ±0.01 MPa, respectively. All operations of equipment, the data acquisition and the analysis of the stress–strain curve were automatically performed by program control using a personal computer (NEC).

2.4. Small angle X-ray scattering measurement and analysis

SAXS measurement was performed to investigate the microscopic deformation processes of the PMMA and PMMA/modifier compounds under uniaxial tensile stress. A monochromatic CuK$_\alpha$ beam from a rotating anode generator (Rigaku Co.) was used as a source. Three slits (the 1st and 2nd slits were 0.16 and 0.12, the 3rd was a two-dimensional-adjustable slit) were used as a collimating system. An X-ray incident beam, which penetrated through the sample, was captured by means of a metal stopper. The SAXS were detected using a position-sensitive proportional counter (PSPC), which was set so as to obtain information concerning the SAXS profile parallel to the drawing direction. However, the SAXS profile perpendicular to the drawing direction was not measured due to the limitation of our X-ray measuring equipment. A vacuum chamber (1 m in length) was placed in the scattering path from the sample mounted in the drawing equipment to the PSPC detector in order to eliminate any parasitic scattering caused by air.

The SAXS profiles were measured at different strain levels while continuously drawing the sample. The detection time in each frame of measurement was 5 min, therefore,

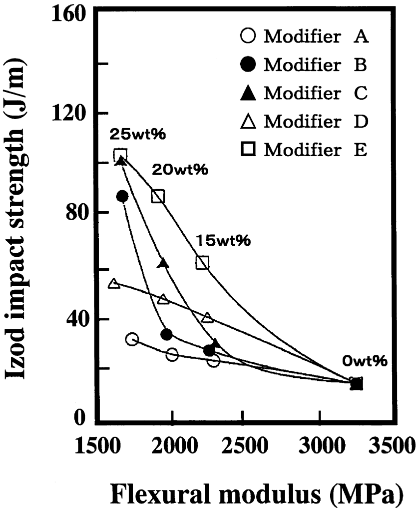

Fig. 3. Relationship between Izod impact strength and flexural modulus of PMMA compound with different modifier contents (15, 20 and 25 wt%) for the modifiers A through E illustrated in Fig. 1.

the SAXS data reflected the average information of the plastic deformation structures existing during a detection time of 5 min (corresponds to 1.2% in strain increment) in the consecutive deformation process.

Size and occupation volume (concentration) of a sub-microcrack (SMC_i), the *i* denotes the index to differentiate different size of SMCs, were analyzed on the assumption that the SAXS profile is given by following Guinier equation:

$$I(\theta) = \sum K_i W_i \exp(-4\pi^2 H_i^2 \theta^2 / 3\lambda^2), \qquad (1)$$

where $I(\theta)$ is the scattering intensity at a scattering angle θ, K_i is the proportional constant related to scattering amplitudes of atoms, W_i corresponds to an occupation volume and/or number of the SMC_i with an inertia diameter H_i which is considered (here) roughly to the size of SMC_i, λ the wavelength of incident X-ray. From the slope of the Guinier plots ($\log I$ vs. θ^2), one can calculate the value of H_i. The intensity at $\theta = 0$, obtained by an extrapolation of a straight line to $\theta = 0$, provides us with the value of $K_i W_i$ from Eq. (1). If K_i is independent of the size of SMC_i, in this case, $K_i W_i = KW_i$, which enables us to obtain the information of the occupation volume of SMC_i. However, SMCs in excess of ca 180 nm in inertia diameter was beyond the detection limit of our SAXS apparatus.

Following are details of the analysis method, here, for the sake of convenience, we define:

$$H_1 < H_2 < H_3 < \cdots < H_i < H_m. \qquad (2)$$

In most case, the Guinier plots in terms of Eq. (1) indicates a nonlinear relationship owing to the superposition of some scattering profiles with different size of SMCs identified by the index *i*. However, since a tail region of the SAXS profile at a scattering range far from $\theta = 0$ is formed by an almost single component of scattering profile $\{I(\theta)_1 = K_1 W_1 \exp(-4\pi^2 H_1^2 \theta^2 / 3\lambda^2)\}$ due to the smallest size of SMC_1, the Guinier plots shows a linear relationship at the scattering range, where one can analyze and estimate H_1 and KW_1 for the smallest size of SMC_1. In order to estimate the H_2 and KW_2 ($i = 2$), Guinier plots analysis is performed in terms of the following equation of analytically modified SAXS profile:

$$I(\theta) - I(\theta)_1 = \sum K_i W_i \exp(-4\pi^2 H_i^2 \theta^2 / 3\lambda^2) - K_1 W_1 \exp(-4\pi^2 H_1^2 \theta^2 / 3\lambda^2), \qquad (3)$$

A tail region of the modified SAXS profile also reflects a single component of scattering profile $\{I(\theta)_2 = K_2 W_2 \exp(-4\pi^2 H_2^2 \theta^2 / 3\lambda^2)\}$ due to the second smallest size of SMC_2, the Guinier plots show a linear relationship at the scattering region. Therefore, one can obtain values of H_2 and KW_2 from these Guinier plots in a similar manner as the analysis for H_1 and KW_1. For the estimation of the H_3 and KW_3 ($i = 3$), a further modified SAXS equation $\{I(\theta) - I(\theta)_1 - I(\theta)_2\}$ is used for Guinier plots analysis. Similar analytical procedures are repeated in numerical order for $i = 4 \sim m$ in order to estimate H_4, KW_4, H_5, $KW_5, \ldots, H_m$, KW_m. Thus different sizes and occupation volumes of SMCs can generally be obtained in each strain level.

2.5. Sample preparation for TEM

Pre-deformed and deformed PMMA/modifier compounds were observed by TEM. The compounds were carefully cut to an ultrathin section of 100 ~ 150 nm in thickness using a microtome, and stained with an aqueous solution of rutheniumoxide (RuO_4) for samples of TEM observation.

3. Results and discussion

3.1. Impact strength of PMMA/modifier compound

Fig. 3 shows the Izod impact strength and flexural modulus of PMMA/modifier (A through E) compounds investigated with different modifier contents of 15, 20 and 25 wt%. The flexural modulus of the compounds decreased as the modifier content increased because of the rubber component with low elastic modulus. The improved results obtained using a modifier containing silicone on the impact strength of PMMA was remarkable. The particle size and morphology of modifier B were almost similar to those of modifier A. However, the Izod impact strength of the compound with modifier B containing a small amount of silicone of 1 wt% at 25 wt% in modifier content, became much larger than that of modifier A without silicone. This experimental finding was a very interesting question. Furthermore, the impact strength

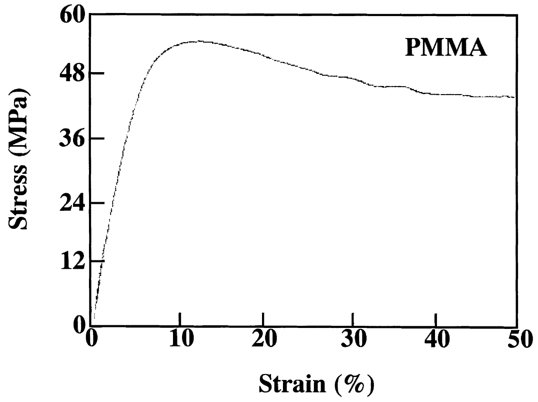

Fig. 4. Strain–stress curve of PMMA under slow tensile deformation rate of 0.24%/min.

could be largely improved with a larger size of the modifier C containing 0.5 wt%-silicone, without a decrease of flexural modulus than that expected from other modifiers. As for modifier D, the effective improvement on the impact strength was not as great in the range of high content in comparison to modifier B and C containing silicone.

Regarding the over all range of content, the aggregation-type modifier E exhibited the most excellent Izod impact strength property among these modifiers tested.

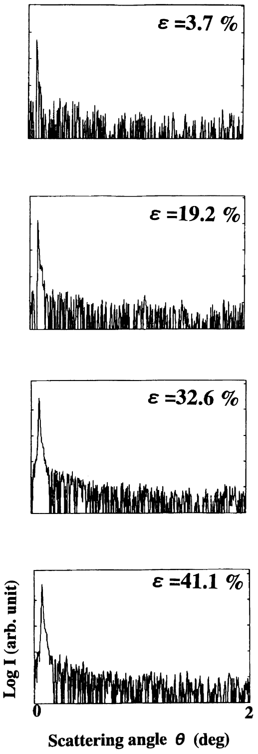

Fig. 5. SAXS profiles of PMMA at different strain levels under slow deformation rate of 0.24%/min: $\log I$ is the logarithm of SAXS intensity I (diffuse scattering corresponding to $10 \sim 20$ nm sizes of SMCs could be observed at large strain levels).

3.2. Ductile behavior in PMMA under slow deformation process

The microscopic deformation process of the PMMA has been investigated in detail by Kuksenko et al. [9], Shichijyo et al. [10,11] and Yamashita et al. [12] by means of SAXS measurement and/or ultrasonic measurement and/or acoustic emission (AE). It has been made clear that the PMMA exhibiting a brittle mode generates a large amount of SMCs, which contribute to the softening of the polymer before originating the crazes. The PMMA specimen usually indicates a brittle mode in deformation, failure point in strain is several percent, and a large number of SMCs that possess lens-like shapes ($20 \sim 80$ nm in thickness to the tensile direction), which causes intensive diffuse scattering over the wider range of scattering angle θ, and can be observed from initial stage (below 2.8% in strain) up to the failure point [10–12]. In this case, it is well known that the size and concentration of SMCs are widely dispersed.

However, for the slow deformation process with 0.24%/min in strain rate, the tensile elongation of the dumbbell-shape specimen of PMMA was as long and larger than 60% in strain as exhibited in Fig. 4. Fig. 5 shows SAXS profiles at different strain levels for the PMMA, and the results of the Guinier plot analysis of them (transition of the diameter and occupation volume (*KW*) of the SMC vs. strain level) is shown in Fig. 6. Existence of SMCs with $80 \sim 100$ nm in diameter, of which diffuse scattering appeared at θ smaller than 0.17°, was observed all over when the strain level was larger than 7%. The occupation volume increased with the increase of strain. However, no estimative diffuse scattering at θ larger than 0.17° could be observed up to around 28%-strain, i.e. SMCs smaller than 80 nm were not observed in this strain range under the slow deformation rate. These

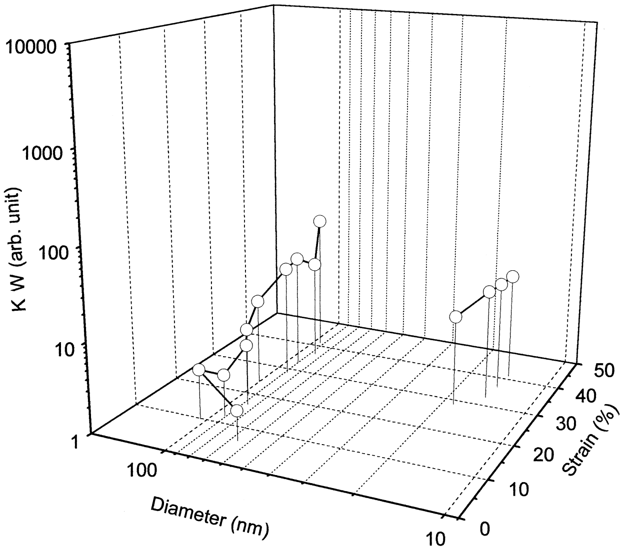

Fig. 6. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA.

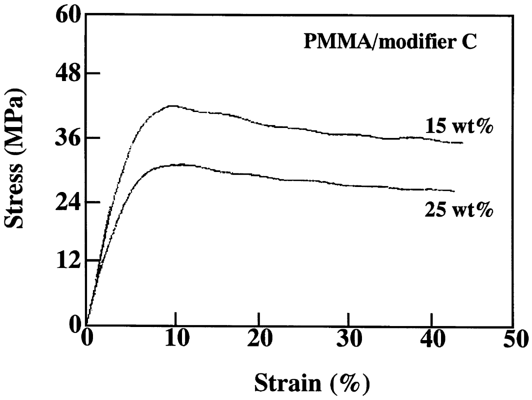

Fig. 7. Strain–stress curves for PMMA/modifier C compounds of 15 and 25 wt%-modifier contents.

experimental findings demonstrated that the PMMA behaves as a ductile amorphous polymer in the slow deformation process and origin of SMCs in the smaller sizes tended to be strongly restrained [13].

On the other hand, with a further increasing strain over 28%, very small sized SMCs (10 ~ 20 nm) emerged with a certain large amount of occupation volumes as shown in Figs. 5 and 6. As these SMCs were confined to a very small size, the origination of the SMC perhaps resulted from the voids formed in crazes and/or their precursor-like structures.

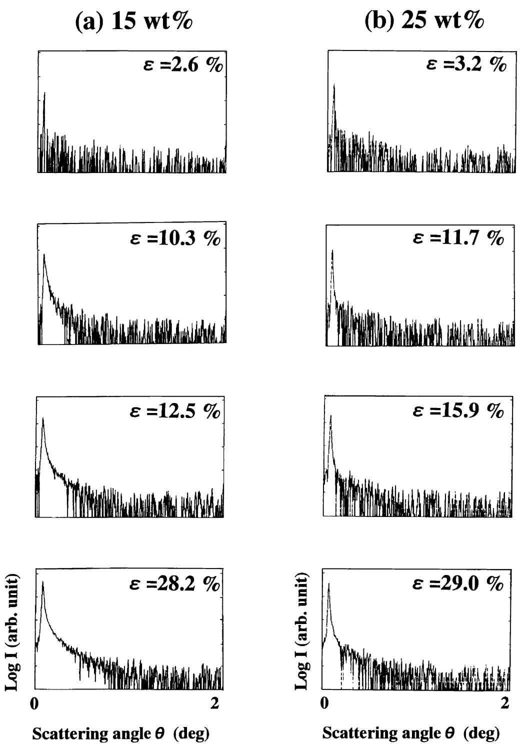

Fig. 8. SAXS profiles for PMMA/modifier C compounds of (a) 15 wt%-modifier content and (b) 25 wt% at different strain levels: log I is the logarithm of SAXS intensity I.

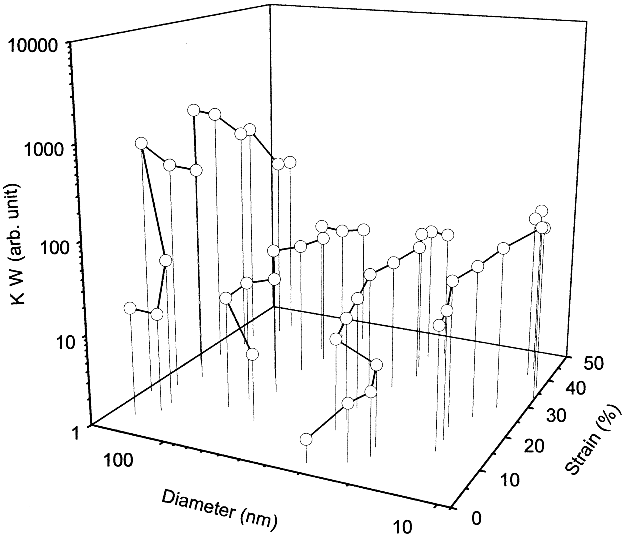

Fig. 9. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA/modifier C compounds of 15 wt%-modifier content.

3.3. Microscopic deformation process for PMMA/modifier compounds

We have investigated the microscopic deformation process for the PMMA/acrylic rubber impact modifier (A through E) compounds in varying combination.

Fig. 7 shows stress–strain curves for the PMMA/modifier C compound with contents of 15 and 25 wt%, respectively. The yield stress of the compound was lowered as the modifier content increased: 54.9 MPa for 0 wt% (PMMA), 42.1 MPa for 15 wt% and 30.9 MPa for 25 wt%-content. The yield point was about 10%-strain. The tendency of the stress–strain curve was also similar for other types of modifiers. No results deserving special mention could be shown among these types of modifiers A through E in the slow deformation rate.

Fig. 8(a) and (b) is SAXS profiles at different strain levels for the PMMA/modifier C compounds of 15 and 25 wt%-modifier contents, respectively. Results obtained from Guinier plot analysis of the SAXS profiles according to Eq. (1) are shown in Fig. 9 (15 wt%-modifier content) and Fig. 10 (25 wt%-modifier content). Remarkable diffuse scattering could be observed especially from around the yield point. Small sized SMCs (20 ~ 40 nm) appeared at the onset stage of tensile strain before the yield point, and a large number of SMCs with various sizes and occupation volumes appeared around the yield point. With further increasing strain, it was obvious that the size distribution of the SMCs dispersed more widely with increasing strain. In particular, the increase in the amount of SMCs with 90 ~ 170 nm for 15 wt% content was extremely prominent. The increase of size and occupation volume was thought to be due to an enlargement and/or the coalescence of pre-existing small sized SMCs. The increase of the occupation volume of SMC with 10 ~ 20 nm can be explained as

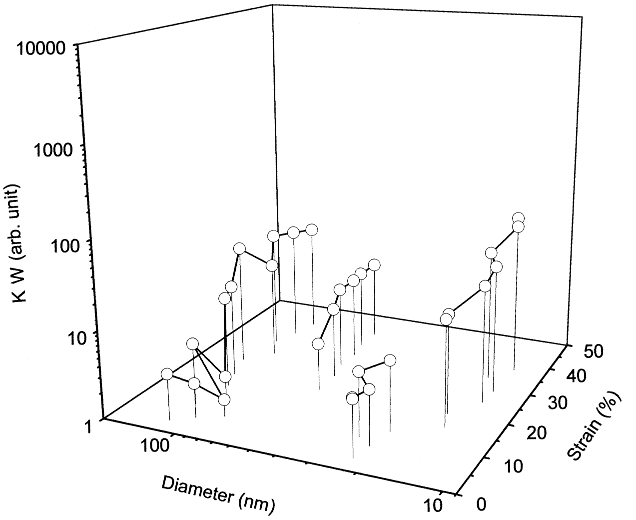

Fig. 10. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA/modifier C compounds of 25 wt%-modifier content.

follows: very small sized SMCs originated at any strain level, but they were not detectable by SAXS measurement because of rather low concentration. That is, after reaching a certain concentration and/or diameter by applying strain, the small sized SMC become detectable for the first time by means of the SAXS measurement. As the strain reached over an yield point, the compound sample was strongly whitened.

For the 25 wt% content, the amount of SMC generation and development were confined to low levels. Especially, those of the SMCs with 90 ~ 170 nm were very small in comparison with those for the 15 wt% content. For the 25 wt% content, judging from the values and changes of occupation volumes for the SMCs with 90 ~ 170 nm, their origin could be suggested to be primarily attributable to the PMMA matrix as mentioned in the previous section. However, the origin mechanism should be completely different from that of 15 wt% content.

Interesting results are shown in Fig. 9 for the 15 wt% content. It can be seen that the occupation volumes for SMCs of 20 ~ 90 nm decreased a little as the strain reached over 36%, and those of 90 ~ 170 nm largely decreased as the strain reached over 24%. These suggest that some of the SMCs collapsed owing to molecular slippage in the large strain region. It is especially likely for the larger sized SMCs to collapse and manifest slippage in the large strain region.

Likewise, the same experimental findings were obtained as the PMMA/modifier B compound was examined in the same manner (Figs. 11 and 12). However, the generation efficiency of SMCs for modifier B was a little inferior to that for modifier C containing a lower content of silicone.

In contrast to modifiers B and C, diffuse scattering was poor all over the strain level up to 60% for modifier D without silicone (Fig. 13). Thus, little SMC generation could be observed for the modifier D, except for the 70 ~ 120 nm sized SMCs which perhaps primarily arise from the PMMA matrix. These tendencies of SMC generation were almost similar for that of modifier A.

It should also be noted that the origin of the very small sized SMCs which seemed to be due to crazes and/or their precursor-like structures in case of the PMMA were

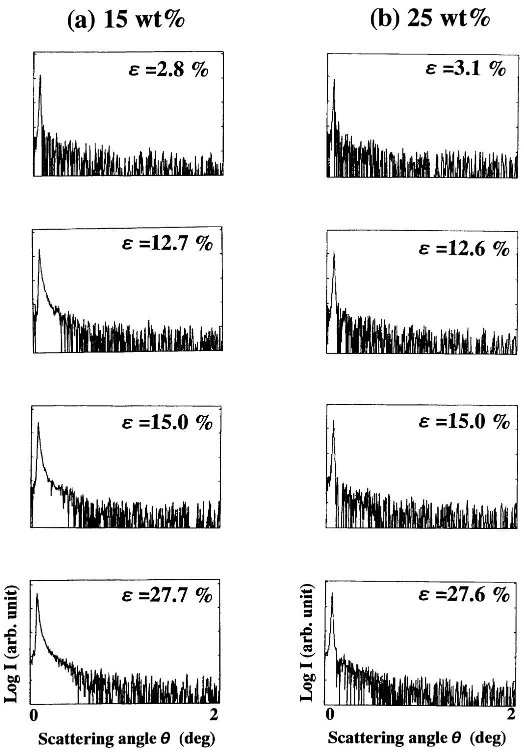

Fig. 11. SAXS profiles for PMMA/modifier B compounds of (a) 15 wt%-modifier content and (b) 25 wt% at different strain levels: log *I* is the logarithm of SAXS intensity *I*.

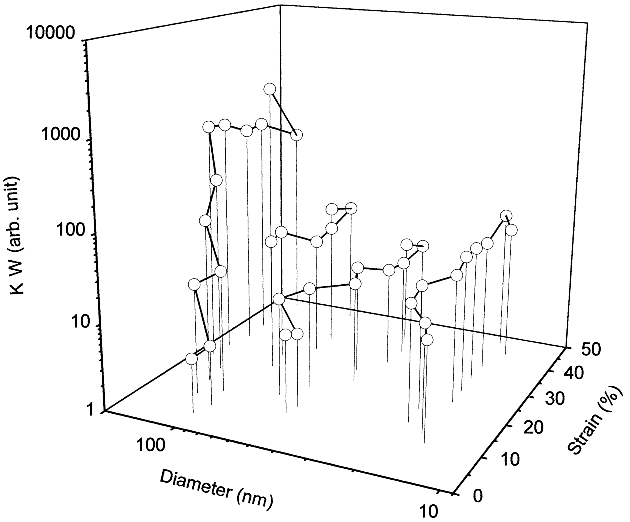

Fig. 12. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA/modifier B compounds of 15 wt%-modifier content.

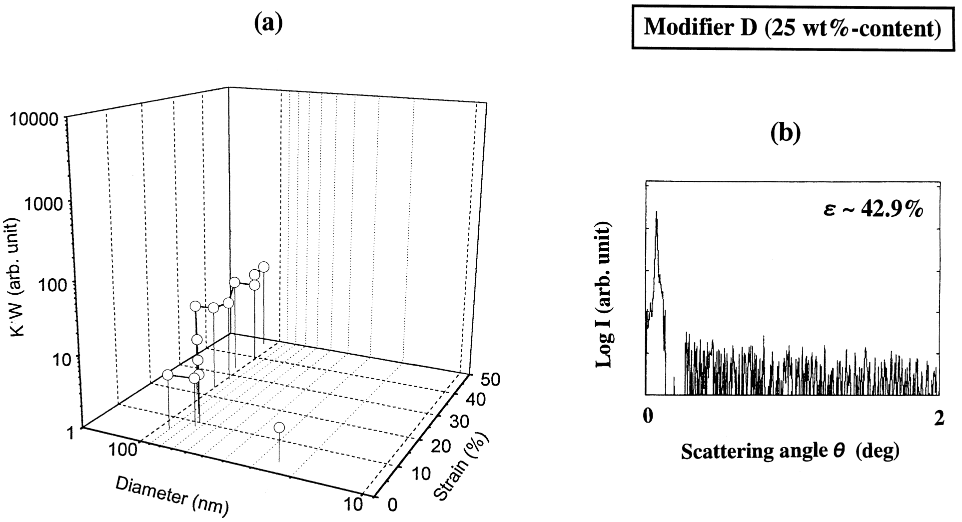

Fig. 13. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA/modifier D (without silicone) compounds of (a) 25 wt%-modifier content, and (b) SAXS profile at strain level of 42.9%; log *I* is the logarithm of SAXS intensity *I* (no diffuse scattering corresponding to 10 ~ 20 nm sizes of SMCs could be observed).

completely restrained at any large strain levels by adding the modifiers (Fig. 13(a)), because an yield stress of the compound decreased. This fact could also be clearly discerned in comparison between the SAXS profiles of Figs. 5 and 13(b).

SAXS intensities in the vicinity of the scattering angle $\theta = 0$, which are considered an index representing the degree of total occupation volume for the microscopic structures such as very small voids and/or dilatant free volume in the specimen (besides the observable SMCs which cause large X-ray diffuse scatterings), were compared for these compounds concerning modifier A through D in Fig. 14 (each modifier content was 15 wt%). The scattering intensity gradually increased with increasing strain. The intensity for modifier D was a little larger than that of modifier A all over the range of strains. For modifiers B and C, of course, the scattering intensity was remarkably larger and beyond that of modifiers A and D.

It is clear to see that the generation of the large amount of SMCs in the PMMA/modifier B or C compounds must be a notable feature concerning the silicone component existing in the rubber particle. Thus, the small amount of silicone in the rubber particle seems to play an important role in the origin of SMCs.

Further, it should be noted that the origin and development of SMCs were predominant at a low modifier content of 15 wt% in comparison with that of 25 wt%. Prior to completely interpreting the findings, it soon become evident where the SMCs originated in the specimen, that is, the mechanism of SMC generation.

3.4. Mechanism of SMC origin and development

Some facts should be taken into account with respect to the prominent origin of SMCs observed for modifiers B and C, e.g. crazes in the PMMA matrix, interface separation between the PMMA matrix and the modifier, and voids formed in the modifier.

It is difficult to attribute the SMC generation to the interface separation, because each modifier A through D has a PMMA graft shell to enhance the bonding strength of interface, which these modifiers had in common. Therefore, if the cause of SMC origin was for the reason above, it would not be confined to the modifiers B and C.

On the other hand, concerning the craze structures, it was likely that the crazes were effectively produced in the matrix, depending on the physical property of the rubber modified by the silicone. However, as demonstrated before, even the PMMA without a modifier no longer indicated

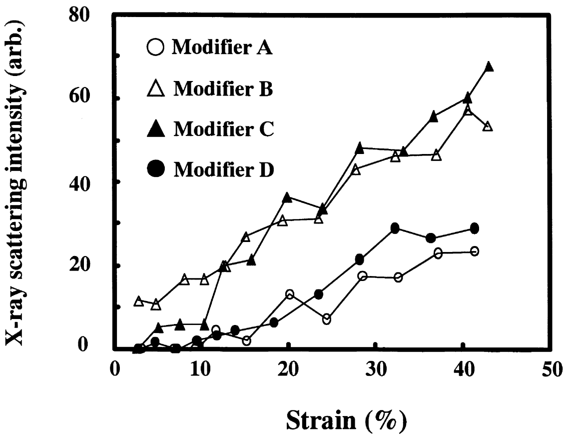

Fig. 14. Comparison of SAXS intensities in the vicinity of scattering angle $\theta = 0$ between PMMA compounds of each modifier A through D (15 wt%-modifier content).

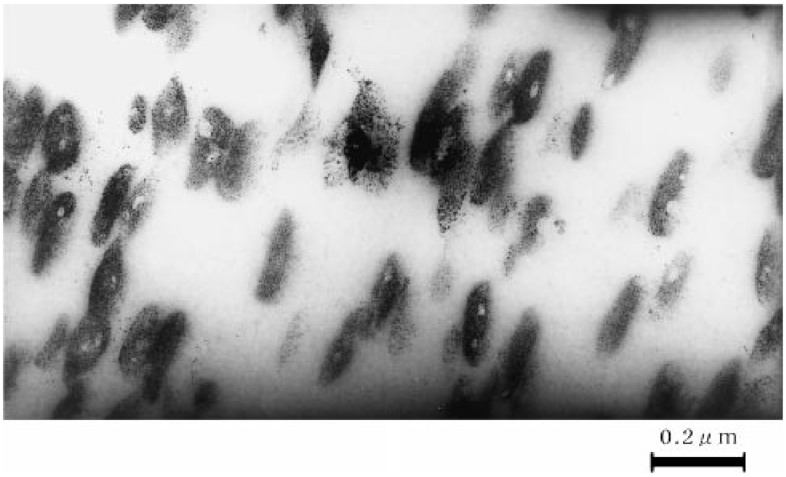

Fig. 15. Transmission electron micrograph of PMMA/modifier C compound of 25 wt%-modifier content after 60%-deformation.

brittle behavior in slow deformation, and the origin of small sized SMCs was restricted. For the PMMA/modifier compound, the tendency would still be to become strengthened. Indeed, the craze formation was completely restricted as shown in Fig. 13. Judging from this information, it was also difficult to attribute the origin of SMCs to the craze formation in the matrix. Fig. 15 shows the TEM for the PMMA/modifier C compounds after deforming them up to 60% strain. The compound strongly whitened. As the results of TEM observation, no craze structures would appear to exist in the matrix of the specimens. The tensile stress had already been taken off in the instance though, if once the craze structures were formed, some traces of them should be left in the electron micrograph.

Finally, we concluded that the SMC originated primarily from inside the modifier in the absence of craze formation. As a certain strain and/or stress is added to the PMMA/modifier compound, the stress concentrated on the rubber particle. Especially at strains around the yield point or larger, the rubber particle tries to greatly deform accompanied by a large plastic deformation of PMMA matrix. The Poisson ratio of the matrix is about 0.37 which enables the matrix to dilate. On the other hand, if the Poisson ratio of the rubber particle is close to 0.5 (the Poisson ratio of an ideal perfect rubber is just 0.5), the dilatation of rubber cannot be accomplished and/or is strongly restricted in contrast to a possible large plastic deformation of the matrix. Therefore, when a certain strain and/or stress is added to the compound specimen, even if it is of slow deformation and uniaxial tensile stress (*x*-direction), the rubber particle tries to contract along the *y* and *z*-directions larger than the matrix does. In this case, a contraction difference exists between the rubber and the matrix, which results in the rubber particle undergoing a strong and triaxial dilatant stress. If a higher Poisson ratio approaches 0.5, a larger dilatant stress is induced, because a further volume change of rubber cannot be allowed and its elastic modulus increases. Hence, the rubber is no longer able to exhibit properties such as entropy elasticity with a low elastic modulus in the case of uniaxial or biaxial deformation as in an isolated rubber. Rather, it becomes rigid as if in a glassy state, and eventually, the rubber would fracture at some point from weakness (weak bonds) inside the rubber and many SMCs would be produced inside. The degree of breakage, i.e. the degree of SMC origin and/or development depends on the Poisson ratio, the strength and elastic modulus of rubber under the triaxial tension.

We concluded that the small amount of silicone contained in the rubber particle became the nuclei of SMC origin and/or fracture such as some weak bonds and/or defects inside the rubber particle. Hence, even if the amount of silicone content was quite small, it was effective enough to generate the SMCs. However, it was very interesting to note that the degree of SMCs origin and development for modifier C was a little dominant compared to that for modifier B, despite the smaller silicone content of modifier C compared to that of modifier B. This suggests that a small amount of silicone plays an important role in the origin of SMCs though, which also depends on the morphology of rubber particle to some extent, because the dilatant stress induced inside the rubber particle and/or its deformation mode maybe changed. The work of the small amount of silicone is thought to be very important in order to improve the toughness of the PMMA compound with a view toward inducing a void formation and releasing the dilatant stress, and then causing stable plastic deformation of the matrix.

SMCs with sizes of 20 ~ 40 nm were observed inside the rubber particles stretched toward the drawing direction as shown in Fig. 15 for the modifier C (60% strain). Because sizes of the SMCs were very small and/or the stress was already released, it was difficult to estimate the origin of small sized SMCs at an early stage and the exact size of SMCs under deformation by observing the TEM after the relaxation of elastomer occurs. However, it is possible to quantitatively evaluate the origin and development of SMCs

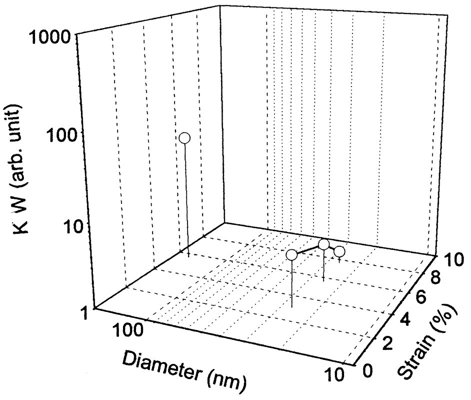

Fig. 16. Diameters and occupation volumes (*KW*) of SMCs at different strain levels for PMMA/modifier E compounds of 25 wt%-modifier content (none of small size SMCs can be observed at strain levels larger than ca 8%).

all over the range of strain level by means of in situ SAXS measurement.

It can be easily deduced from the mechanism of the origin of the SMC mentioned above that the higher dilatant stress load on the rubber particle, the more remarkable the origin of SMCs becomes. Therefore, though the modifier content was low, it seemed reasonable that the generation efficiency of SMCs was predominant for the compound with a modifier content of 15 wt% in comparison with that of 25 wt%, since the compound of 15 wt%-content kept the 42 MPa of stress higher than that of 25 wt% (30 MPa). It may be assumed that both the factors of the higher modifier content and the larger dilatant stress contribute to the higher efficiency of SMC origin and development. However, it should be noted in order to understand the experimental fact for the efficiency in the origin of SMC that the relationship between the two factors above are just the opposite of each other.

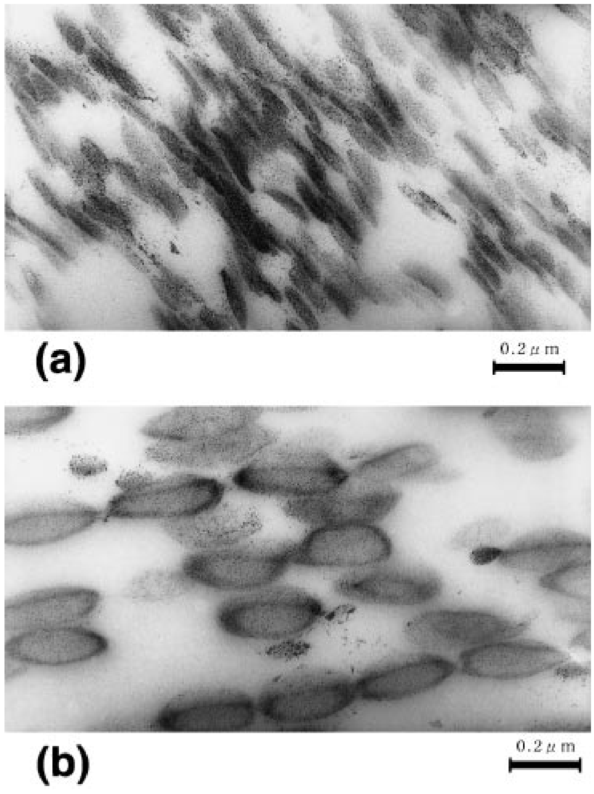

Fig. 17. Transmission electron micrographs for PMMA/modifier compounds of 25 wt%-modifier content after 60%-deformation: (a) for modifier A and (b) for modifier D.

For modifier B and C, it has been already stated that the increase of the occupation volumes of the large sized SMCs (~170 nm) for 15 wt% content was extremely prominent. However, the diameter of SMC was larger than the average one (*d*) of the rubber particle estimated by TEM (see Fig. 1). The reasons for the discrepancy might be interpreted in several ways. First, the large sized SMCs fundamentally originated inside the rubber particle. However, the rubber particle was elongated longer than the initial size. Furthermore, the rubber structure could easily and largely dilate to a greater length toward the stress direction, as the fracture of rubber gradually progressed with the origin of the great number of SMCs. Second, the origin of a great number of small sized SMCs in the rubber particles and their large dilatation and/or the ligament between the deformed rubber particles strongly influenced the plastic deformations of the matrix. Consequently, the larger sized SMCs were formed in the matrix without craze formation as already stated in the previous section concerning the ductile behavior of PMMA.

Thinking in terms of the first reason only, it is difficult to understand that the size of an SMC much larger than 90 nm in diameter of rubber particle for modifier B and the large amount of their occupation volumes exist from ca 22%-strain level. We rather believe the second reason is the explanation of the origin in large sized SMCs. However, there is no clear evidence to support this as yet.

Further, it has been already stated that there was an effect in suppressing the craze formation in the PMMA matrix by adding modifiers. We suppose that a similar effect should be expected by using modifiers B and C. Accordingly it would be more effective if the modifier content increased. However, it was difficult to grasp the effectiveness in terms of the SAXS experiments because such modifiers also gave rise to the large amount of SMCs with 10 ~ 20 nm inside themselves.

3.5. Physical properties of composite rubber and SMC origin

It should be noted that the small sized SMC in the rubber particle containing silicone always originated and developed at any strain level. It can be supposed that the scission of the constrained molecular chain of elastomer progressed gradually as strain increased, and the defects were expanded stepwise. These aspects correspond to the fracture mechanism under triaxial strain for the elastomer with a high crosslink density. On the other hand, for a low

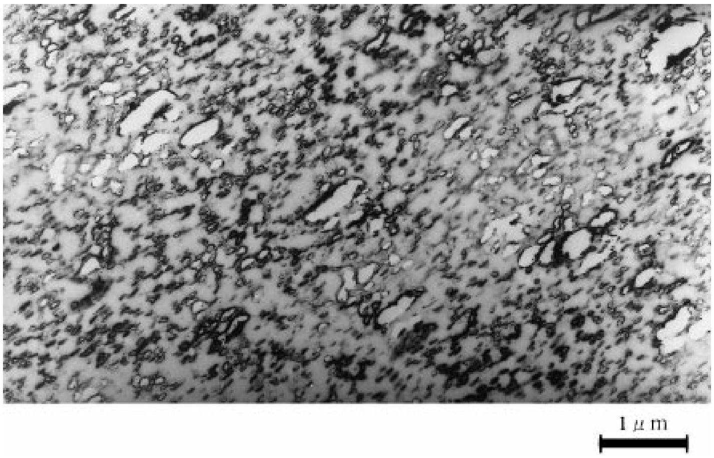

Fig. 18. Transmission electron micrograph for PMMA/modifier E compound of 25 wt%-modifier content after 60%-deformation.

crosslink density, it has been reported by Kawabata [14,15] that the reorientation and/or reconfiguration of the molecular chain occurs accordingly as tension increases so that strain energy becomes minimal, and bundled molecular chains are formed around a small defect. The bundled molecular chains require great strength in order to break themselves, and eventually, interrupt an increasing enlargement of the defect.

Under the fast deformation, furthermore, the rubber particle may behave as an extremely high elastic body. Realistically, the rubber particle used in this study could not have a Poisson ratio of 0.5, so that the dilatation of rubber could be permissible to some extent depending on the degree of Poisson ratio. The deformation mode and void formation for the rubber particle with respect to the physical properties such as the crosslink density, the strength and elastic modulus of the rubber under the dilatant stress may significantly influence the impact resistance. Generally speaking, there are mutual relationships among these physical properties of rubber though, fundamentally, these properties in the composite rubber should be independently taken into account, and can be designed independently, e.g. by introducing silicon into the rubber and employing a peculiar morphology of rubber particle as with modifier E in this study.

For the PMMA/modifier E compound, SMCs with small sizes of 20 ~ 30 nm were observed at the strain range below 8%, however, it was obviously verified that the amount of the SMCs decreased with increasing strain as shown in Fig. 16. Finally, with a further increase in the strain, no SAXS intensity was actually observed over the strain range above 8%. This tendency in SAXS data was completely different from that of the compound concerning modifier A or D. Fig. 17(a) and (b) shows the electron micrographs of the compound deformed up to 60%-strain for the modifiers A and D, respectively, and Fig. 18 for modifier E. In reference to the modifier E, the large cavities with 170 ~ 700 nm in size to the tensile direction and 50 ~ 200 nm in the size perpendicular to the tensile direction could be observed manifestly (there were no cavities for the modifiers A and D). For some extremely large sized cavities, they especially seemed to be formed from collective cavitation due to irregularly combined large clusters of the modifier E. It cannot be completely denied that these large cavities might have been formed from some damage during the preparation of the TEM samples by using a microtome or other utensils. However, judging from these experimental facts, it is certain that the rubber strength was very small in comparison with other modifiers. Furthermore, large cavities and/or SMCs abruptly originated and developed from the small sized SMCs preexisting at around 8%-strain. The sizes of cavities compared to the tensile direction should be far larger than the detection limit of our SAXS apparatus (~180 nm). This was the reason why we were unable to obtain estimative SAXS intensity at around that strain. The SAXS profile corresponding to the very large sized SMCs appeared only at the smaller scattering angle beyond the detectable one, so no SAXS intensity could be detected. This may suggest that the modifier E would reach fracture even with small stress due to the small strength of rubber, and followed by jumping suddenly to the large cavity at an early stage of strain. This fracture mechanism of rubber is completely different from that of the silicone type. This proven weakness of modifier E arose from the segregation of the aggregate Bd/BA rubber particles and/or larger cluster of the aggregate rubber particles.

Provided a proper condition of the deformation rate, so as to give rise to the observable SMCs, is chosen, the information for the deformation mechanism and the ease of void formation and/or strength of rubber particles can be obtained from SAXS measurement and TEM observation.

The modifiers used in this study are put in order of the ease of void formation as follows:

$$\text{modifier E} > \text{modifier C} > \text{modifier B} > \text{modifier D} \sim \text{modifier A} \quad (4)$$

As shown in Fig. 3, the Izod impact strength at 25 wt%

content seemed to be in agreement with this order. However, the Izod impact strength did not obey this order at the range of low modifier content equal to 20 wt% or below. It can be suggested that the ease of void formation in the rubber particle would come to play an important role and be reflected in the absorption of impact energy and improvement of toughness for the PMMA alloy in the range of high modifier content. Plastic deformation mechanism seems to be different between high and low modifier contents with respect to an yield stress level of the compound and the ligament between rubber particles [1,6] depending on the modifier content. However, there would always be competitive contributions of the massive shear yielding mechanism attributed to the microvoiding concerning the rubber particles and the crazing mechanism.

3.6. Fast deformation process and impact resistance

In the range of fast deformation rate, there would appear to be brittle-ductile transition for the PMMA alloy. It would appear that the different modes of plastic deformations, such as massive shear yielding of matrix in the presence of microvoiding and the craze formation, complicatedly affect the fast deformation process of the polymer alloy.

It is very important to clarify how the two modes competitively contribute to the plastic deformation for the PMMA alloy in order to absorb impact energy and improve toughness depending on the modifier content [6], the ligament between rubber particles [1,6] and rubber morphology. It has not been clear yet which is a best method (or both) for taking advantage of two plastic deformation modes mentioned above in order to effectively improve the impact strength of PMMA alloy maintaining an appropriate high flexural modulus in view of industrial applications.

4. Conclusions

It has been made clear regarding the PMMA that the origin of SMCs with 80 ~ 100 nm in diameter occur all over the strain range greater than 7%. On the other hand, the small sized SMCs (10 ~ 80 nm) tend to be largely restrained below 28%-strain, since the PMMA behaves as the ductile polymer under the slow deformation. With a further increasing strain over 28%, very small sized SMCs (10 ~ 20 nm) due to the voids formed in crazes and/or their precursor-like structures emerged with definitely large amounts of occupation volume. However, the structures were completely restrained at any large strain level by adding impact modifiers, because a yield stress decreased.

The large improvement of the impact strength for the PMMA alloy was obtained by using the acrylic rubber modifier containing a small amount of silicone or the Bd/BA-aggregation type of modifier in a high content. Especially, the aggregation type of modifier indicated the most excellent property for the Izod impact strength all over the range of its content among the modifiers used in this study.

For the modifier containing silicone, small sized SMCs (20 ~ 40 nm) appeared inside the rubber particle at an early stage of tensile strain below the yield point. With a further increasing of strain, a remarkable diffuse scattering of SAXS could be observed, and large amounts of SMCs appeared inside the rubber particle and/or the PMMA matrix from around the yield point in the absence of craze formation. Their sizes dispersed more widely (10 ~ 170 nm) with increasing strain. In particular, an increasing number of SMCs with 10 ~ 20 nm was prominently observed. It has been clarified that a great number of small sized SMCs would originate and develop in the modifier at any strain level. The aspect of stepwise fractures corresponds to the fracture mechanism of an elastomer with a high crosslink density. It has been suggested that the small amount of silicone contained in the rubber particle might play a role in the production of nuclei of SMC origin and/or a fracture such as the weak bonds and/or defects inside the rubber particle. Consequently, the weakness would lead the rubber to be fractured even by a small dilatant stress. Therefore, even if the amount of silicone content was a very small, it was effective enough to generate the SMCs. Thus, the function of the silicone is to improve toughness of the PMMA compound with a view to inducing void formation and releasing the dilatant stress. The degree of SMC origin and development depends on the crosslink density, the actual strength and elastic modulus of rubber under the triaxial tension. These factors would be significant regarding the impact resistance.

The Bd/BA-aggregation type of modifier easily reaches fracture even under small stress due to the small strength of the rubber, and followed by jumping suddenly to a cavity far larger than the detection limit of our SAXS apparatus (>180 nm) at an early stage of strain. This fracture mechanism is completely different from that of the silicone type. Proof that such a low strength of the modifier arises from a segregation of the aggregate Bd/BA rubber particles and/or larger cluster of the aggregate rubber particles has been considered.

The Izod impact strength at a high modifier content was in agreement with the ease of void formation. Therefore, this suggests that the void formation would come to play an important role and be reflected in the absorption of impact energy and improvement of the toughness of the PMMA alloy in a high modifier content. Plastic deformation mechanism seems to be different between high and low modifier contents with respect to the ligament between rubber particles. However, there would always be competitive contributions of the massive shear yielding mechanism attributed to the microvoiding concerning the rubber particles and the crazing mechanism. A further detailed investigation will be required.

References

[1] Wu S. Polymer 1985;26:1855.

[2] Dompas D, Groeninckx G, Isogawa M, Hasegawa T, Kadokura M. Polymer 1995;36:437.

[3] Ishikawa M, Yoko S, Yanagase A, Ito M, Yamamoto N. Polymer 1996;37:5583.

[4] Yanagase A, Ito M, Yamamoto N, Ishikawa M. J Appl Polym Sci 1996;60:87.

[5] Yanagase A, Ito M, Yamamoto N, Ishikawa M. J Appl Polym Sci 1996;60:1387.

[6] Wu S. Polym Engng Sci 1990;30:753.

[7] Plummer CJG, Béguelin Ph, Kausch H-H. Polymer 1996;37:7.

[8] Mauzac O, Schirrer R. J Appl Polym Sci 1989;38:2289.

[9] Kuksenko VS, Tamuzs VP. Fracture micromechanism of polymer materials. Hague: Martinus Nijhoff, 1981.

[10] Shichijyo S, Shirouzu S, Taki S, Matsushige K, Takemura T. Jpn J Appl Phys 1983;22:1315.

[11] Shichijyo S, Matsushige K, Takemura T. Jpn J Appl Phys 1984;23:L218.

[12] Yamashita T, Shichijyo S, Takemura T, Matsushige K. Jpn J Appl Phys 1988;27:104.

[13] Shichijyo S, Nishimura K, Shirouzu S, Matsushige K, Takemura T. Jpn J Appl Phys 1983;23:846.

[14] Kawabata S. Koubunshi 1993;42:394.

[15] Kawabata S. J Macromol Sci: Phys B 1973;8:605.