

High ductility in poly(methyl methacrylate) induced by absorption and desorption of an acetonitrile aqueous solution

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Tension tests were conducted in air at room temperature on PMMA sheet specimens which had been previously soaked in a 40 vol % acetonitrile aqueous solution at 20 °C for 24 h and then dried in air at room temperature for 480 h. In contrast with an untreated specimen which fractured at a stress of 84 MPa and a strain of 9%, shear yielding clearly took place at 42 MPa and the elongational fracture strain increased to about 148%. No crazes were observed on the specimen surface and as a result the transparency of the PMMA was thoroughly maintained until fracture. Thus this soaking treatment may change PMMA to a completely ductile polymer without a crazing mechanism. The results of the dynamic viscoelastic measurements at 1 Hz show that the glass transition temperature was lowered to about 80 °C (as compared to about 110 °C), and the β relaxation became much sharper with a higher peak value of 20 °C (as compared to a broad curve with a peak at 50 °C). This clear β relaxation at room temperature may contribute to shear yielding and large plastic elongation of the treated PMMA.

1. Introduction

Poly(methyl methacrylate) (PMMA) behaves as a brittle material under tension in usual environments, e.g., in air at room temperature. In order to enhance its toughness, defined in this case as the total energy for fracture per unit volume of the specimen, attempts to mix or blend PMMA with a rubber [1-3] or a ductile polymer [4-6] have been reported. In these cases a phase-separated structure (sea-island structure) is generally obtained. The toughness is brought about by both the large capability of the rubber or ductile polymer to be heavily deformed up to fracture and also by crazing at the interface between different polymer phases. The latter mechanism is, however, not always beneficial. It is well known that a craze plays dual role, acting both as a source of plastic strain contributing to toughness and also as a precursor of cracks leading to fracture. A good example of the problems associated with crazes is a potential decrease in the fatigue lifetime in the rubber modified polymer. Sauer and Chen [7] pointed out that the fatigue lifetime of an unnotched specimen of high impact polystyrene (HIPS) is less than that of homo polystyrene (PS). In addition, a number of crazes that were nucleated around the particles causing large deformation will obviate the optical transparency of PMMA,

which is the specific characteristic of this polymer of interest for engineering applications. A high ductility can also be obtained by introducing suitable smaller molecule plasticizers. However, this may be accompanied by a large reduction in the elastic moduli as the polymer of rubbery state is formed.

Thus it is of interest to find other ways of producing a high ductility or toughness in PMMA that does not produce crazing and thus maintains the PMMA transparency and its moduli. In this paper we describe a novel and more convenient way to obtain ductile PMMA by applying absorption and desorption phenomena of acetonitrile aqueous solutions.

2. Experimental procedure

The material used is a commercially available PMMA sheet of 1 mm thickness (Mitsubishi Rayon Co., $M_w = 6.16 \times 10^5$, $M_w/M_n = 4.60$) from which rectangular specimens 82 mm long by 17 mm wide were prepared for the absorption and desorption tests. The cut sides were polished with No. 1000 abrasive paper. In addition dumb-bell shaped specimens with a gauge length of 40 mm and a width of 17 mm were machined from the sheet. All the specimens were annealed at

90 °C for 2 h and slowly cooled to room temperature in a forced-air oven.

The rectangular specimens were immersed in a 40 vol % acetonitrile (CH₃CN) aqueous solution at 20 °C for 72 h and then dried in air at room temperature. The weight of the specimens were measured at appropriate time intervals using an electronic balance (Mettler, AE 240). The components of the acetonitrile resident in a specimen that had been soaked for 24 h and then dried for 200 h were analysed by means of a Fourier-transform infrared (FT-IR) microspectrometer with a HgCdTe detector (Japan Spectroscopic Co., FTIR 8900 μ). To enable comparisons thin films 10 μm thick were prepared from the dried specimen and the as-received one by using a microtome (Erma Inc., Type 08-200). A square region of 60 × 60 μm² was analysed by the FT-IR in transmission mode. In all some 50 scans of 4 cm⁻¹ resolution were recorded.

The dynamic viscoelastic measurements were performed on rectangular specimens, whose dimensions and preparation method were the same as those for the weight measurement. The as-received specimen and the treated one which had been previously immersed in the reagent for 24 h and then dried for 480 h were tested to measure the storage modulus and the loss tangent at 1 Hz at a constant heating rate of 5 °C per min by means of a dynamic viscoelastic apparatus (Orientec Co., VFA-1KNA).

The dumb-bell-shaped specimens were also immersed in the solution at 20 °C for 6, 12, 18, and 24 h, and subsequently dried in air at room temperature for 480 h. They were then used in the tension tests made in air at room temperature using an Instron testing machine (Shimazu Co., AGE-50KN). The nominal strain rate was 12.5 % per min.

The tensile fracture surfaces were observed in a scanning electron microscope (SEM) with a field emission gun (Hitachi Co., S-4000). Before observation in the SEM, the fracture surfaces were sputter-coated with a thin layer of gold.

3. Results and discussion

The results of the absorption and the desorption experiments of the reagent are shown in Fig. 1(a) and (b), respectively. An equilibrium solubility of about 32 wt % was achieved after about a 30 h immersion. The type of diffusion operating in this system is case II diffusion [8], since the weight gain increase is proportional to the immersion time. This conclusion is also supported by the fracture surface observation for the specimen presoaked for 6 h, as is shown in Fig. 7, which shows a clear surface swollen layer which is one of the peculiarities of case II diffusion. The weight reduction during drying takes place rapidly in contrast with the absorption process. It is noted that the weight reduction effectively ceases after a drying time of 200 h and that about 5.5 wt % of the penetrant stably remains in the specimen.

Fig. 2 shows the infrared spectra for the specimen presoaked in the solution for 24 h and then dried and also for the as-received one. In the treated specimen

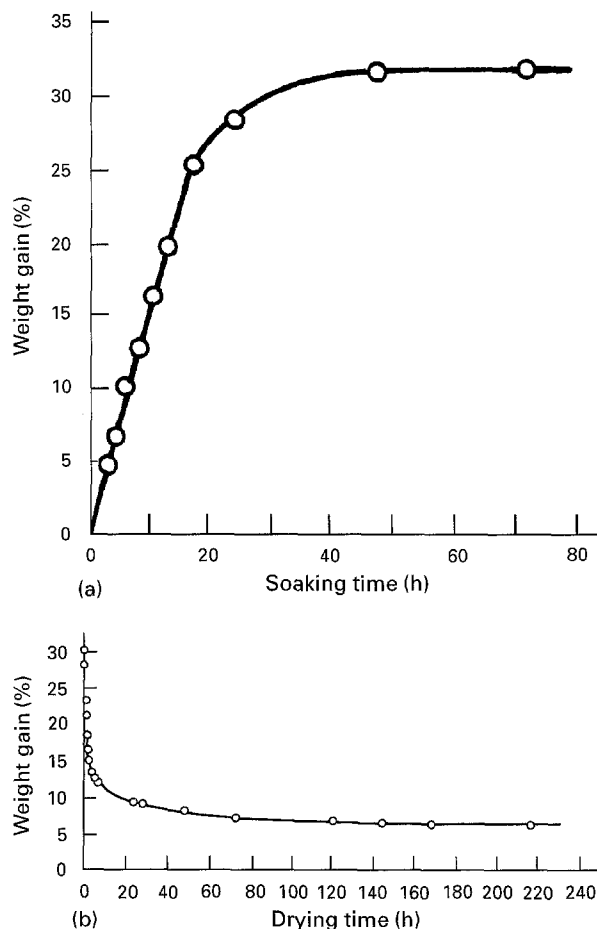


Figure 1 Absorption and desorption of 40 vol % acetonitrile aqueous solution by a PMMA sheet of 1 mm thickness: (a) absorption curve at 20 °C, (b) desorption in air at room temperature.

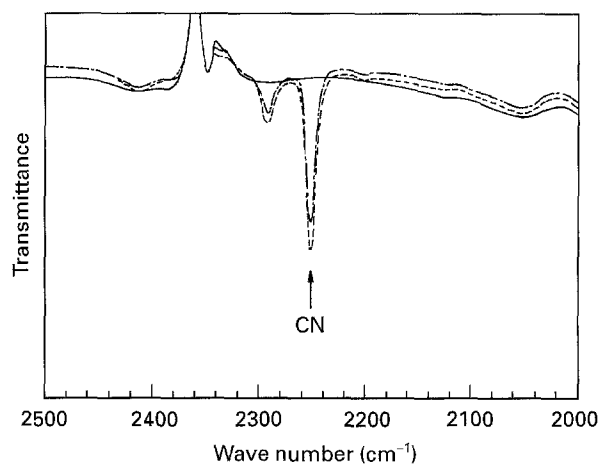


Figure 2 Infrared spectra for the specimen soaked in the reagent for 24 h and then dried for 200 h, and for the as-received one: (·····) inner region of treated specimen, (---) outer region of treated specimen, (—) as-received specimen.

clear absorption is observed at the wavenumber of 2255 cm⁻¹ which is thought to arise from the stretching vibration of the nitrile (C≡N) group. No peak is observed at this wavenumber for the as-received specimen. The intensity of absorption is stronger in the inner region than in the outer region of the specimen. Therefore, as expected, acetonitrile may be confirmed to exist in the residue in the dried sample. On the other hand, accurate information on water, which is also

expected to remain, was not obtained by the present analysis, since some signals were detected in the region of $3450\text{--}3650\text{ cm}^{-1}$ corresponding to the hydroxyl group even in the cut film from the as-received specimen. They imply the existence of water in the as-received specimen. We have investigated the effects of environmental alcohol on the fracture behaviour of PMMA [9]. From FT-IR spectroscopy on a surface scratch as produced in several alcohols, it was inferred that at a region of stress concentration the alcohol molecules with a smaller volume such as ethanol and 1-butanol can easily penetrate. These molecules are chemically adsorbed onto the polymer chains by forming hydrogen bonding between the hydroxyl hydrogen atom of alcohol and the carbonyl oxygen atom of the ester group of the PMMA side chain. A similar "mechano-chemical" mechanism may operate between a water molecule and a PMMA side chain during the microtome sectioning in air. Thus at the present stage it is difficult to imagine the structure and state of the residue comprising acetonitrile and water.

The changes in the dynamic viscoelastic properties produced by the presoaking treatment and subsequent drying are shown in Fig. 3. The storage modulus, E' , in the treated specimen is considerably reduced with increasing temperature, and as a result the α relaxation (glass transition), which originally occurs at about 110°C , now takes place at about 80°C . However the value of E' at 20°C is still about 82 % of that of the untreated specimen. It is of interest that the energy loss, $\tan \delta$, is always greater, and moreover the β relaxation becomes much sharper with

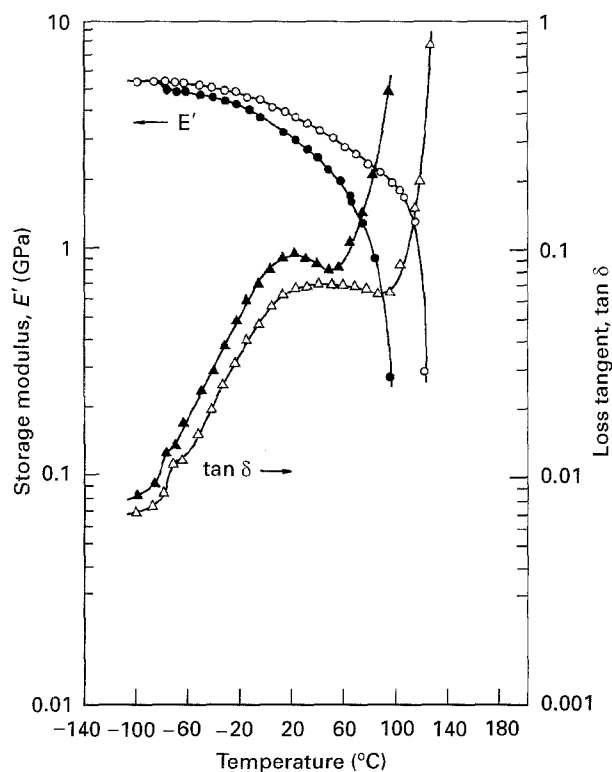


Figure 3 Variations in E' and $\tan \delta$ measured at 1 Hz for the specimens as-received and presoaked in the reagent for 24 h and dried in air for 480 h: (○, △) as-received specimen, (●, ▲) treated specimen.

a higher peak value at 20°C in comparison with the untreated specimen showing a broad curve with a peak at 50°C . In general the plasticizers lower the α relaxation temperature, while the β relaxation is unaffected. Therefore the relaxation phenomena observed in our treated specimen may be distinguished from a usual plasticization effect. The sharper β relaxation at 20°C implies that side-chain motions of the ester group in PMMA [11] are promoted by the residue (acetonitrile and water), and further predicts a higher ductility and impact resistance at room temperature.

Fig. 4 shows the tensile properties of the specimens which were presoaked in the reagent for different periods of time and then dried. For both the specimens presoaked for 6 h and 12 h, brittle fracture behaviour is commonly observed. In these cases fracture occurs at lower stress and strain values compared to the virgin sample, which fractured at a stress of 84 MPa and a strain of 9 %. Such facile fracture behaviour seems to be attributable to a residual tensile stress generated in a specimen surface during the drying process. In contrast to these specimens, yield phenomenon clearly takes place at 57 MPa and a fracture strain of 58 % is obtained for the specimen presoaked for 18 h and then dried. In addition, the specimen which was immersed in the reagent for 24 h and then dried also yields at 42 MPa and its fracture strain is achieved at about 148 %. In these specimens showing clear yield behaviour we could not find any crazes, but instead a diffuse shear band was observed. The appearance of the fractured specimen presoaked for 24 h is shown in Fig. 5. It is noted that the PMMA

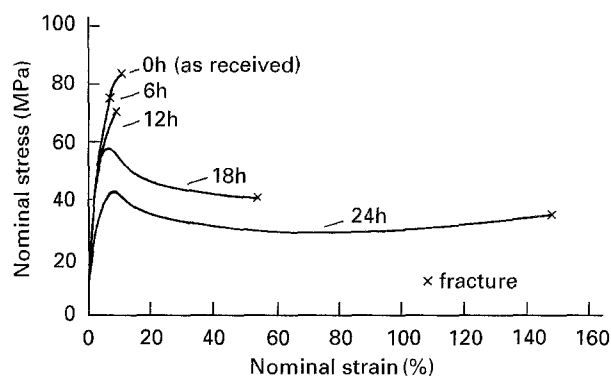


Figure 4 Tensile deformation curves for the specimens soaked in the reagent for various periods and then dried for 480 h.

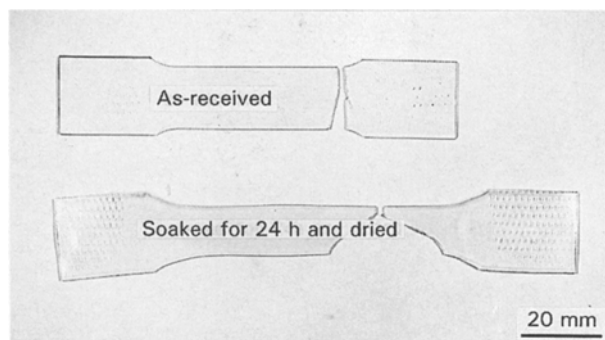


Figure 5 Appearance of the fractured specimen presoaked for 24 h and dried.

specimen changed to a highly ductile polymer while maintaining its transparency. Fig. 6 shows the relationship between the toughness, i.e., the total energy for fracture per unit volume and the presoaking time.

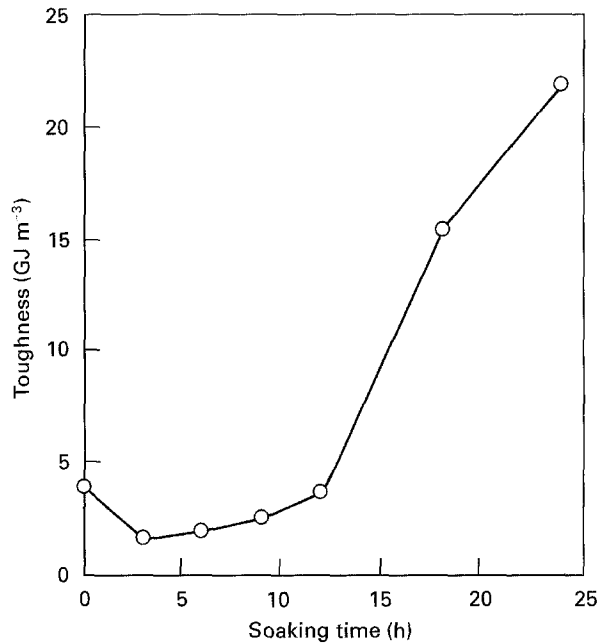


Figure 6 Relation of toughness to soaking time in the reagent.

The toughness dramatically increases with an increase in the presoaking time above 18 h.

Fracture surfaces of the specimens treated for different presoaking times are shown in Fig. 7(a–c). In the as received specimen (Fig. 7a) one may observe a number of parabola marks indicating secondary crack formation induced by the stress field at the front of the advancing main crack, which is generally accompanied by craze formation. In the specimen presoaked for 6 h and then dried (Fig. 7b) an outer layer clearly distinguished from the inner region is observed. The outer layer is thought to be produced by swelling under case II diffusion of the acetonitrile aqueous solution, and reasonably plasticized by the residue even after drying. However, as previously mentioned, a tensile residual stress may be generated in this layer during the drying process by the same mechanism as that which Thomas and Windle have proposed for the PMMA–methanol system [12]. Both the plasticization effect created by the residue and the tensile residual stress will create a lower applied stress for craze nucleation and ease to fracture. A relatively large crazed-area formed in the outer layer shown in Fig. 7b may support this interpretation. Fig. 7c shows a tilted SEM image of the fracture surface of the specimen presoaked for 24 h and dried, for which shear yielding clearly occurred. It is emphasized that from a fracture origin on the outer edge a very smooth

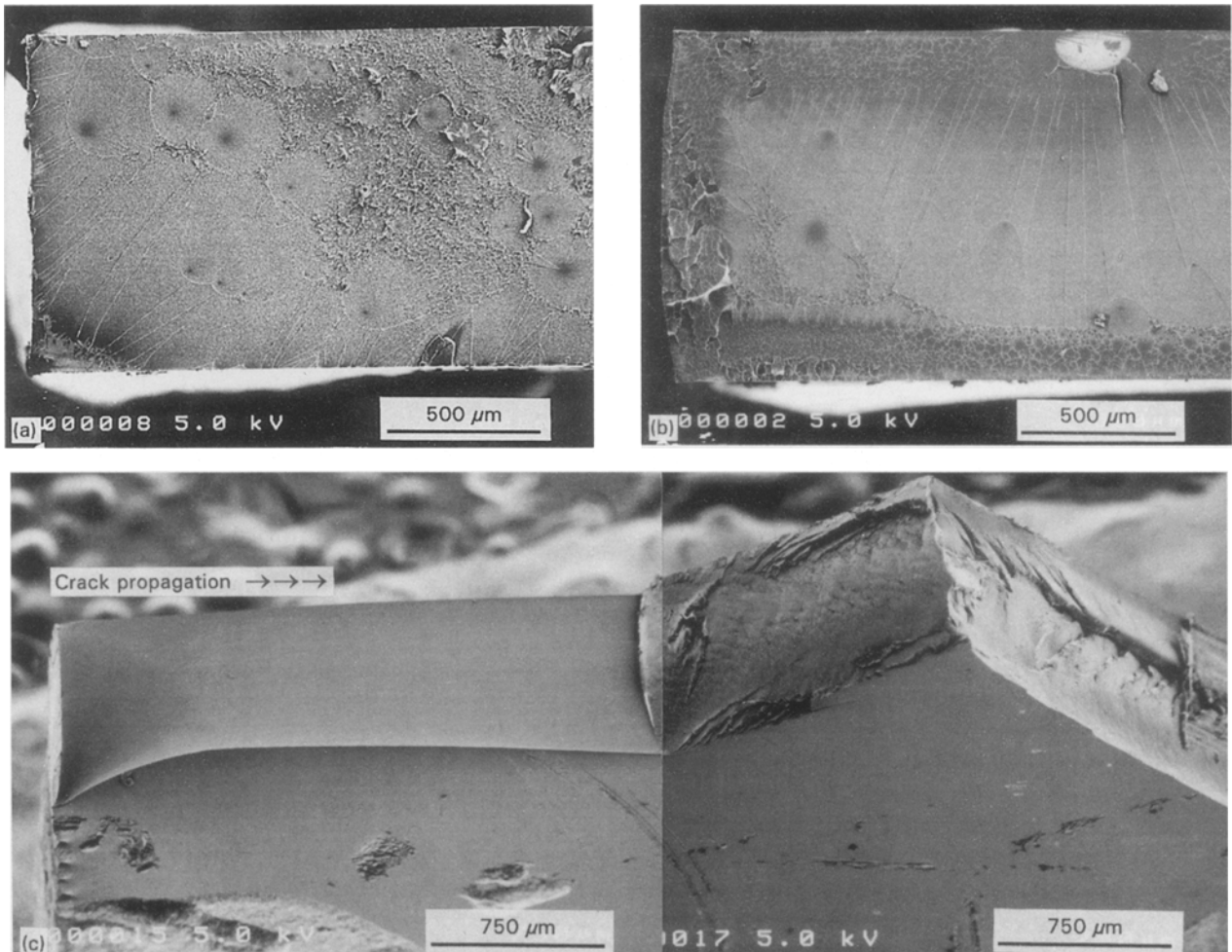


Figure 7 Fracture surfaces of tensile specimens: (a) as-received, (b) soaked for 6 h and then dried for 480 h, (c) soaked for 24 h and dried for 480 h.

fracture surface extends with no vestiges of crazing and that the fracture mode abruptly changes from normal-stress dominated fracture to a shear dominated one. This type of fracture resembles that observed for polycarbonate (PC) which is known as a typical ductile polymer showing large elongation after shear yielding. Thus it may be concluded that the treatment of soaking in a 40 vol % acetonitrile aqueous solution for a time period greater than 18 h and subsequent drying for more than 200 h can change PMMA to a completely ductile polymer without the use of a crazing mechanism.

It is of interest to consider why such a dramatic change in the tensile fracture behaviour of PMMA takes place. Acetonitrile is a polar solvent [13], and probably forms a cluster with water. If the cluster remains in the dried sample, it may be sited in close vicinity to the ester group of the PMMA side chain through dipole interactions between the nitrogen atom of acetonitrile and the carbonyl carbon atom of the ester group and/or the carbon atom of acetonitrile and the carbonyl oxygen atom of the ester group. There will also exist some interactions between water and PMMA. Such interactions will raise intra- and inter-chain mobility of the side chain, and consequently promote β relaxation and thus produce a clear $\tan \delta$ peak at room temperature. These effects will eventually change brittle PMMA to a completely ductile state. The mechanism discussed above, however, is only hypothetical at the present stage, because as previously noted the structure and state of the residue remains to be elucidated. A nuclear magnetic resonance (NMR) study will be performed to solve this problem [14].

4. Conclusions

A simple method to enhance the ductility of PMMA by applying absorption and desorption of a 40 vol % acetonitrile aqueous solution was examined using dynamic viscoelastic measurements and tension tests performed in air. For a specimen presoaked in the reagent for 24 h and subsequently dried for 480 h, in which a concentration of the penetrant of 5.5 wt % remained, shear yielding takes place without crazing, and the fracture strain reaches 148 %. The storage modulus at room temperature before the tension test

has a value of about 82 % of that of the virgin specimen. In addition, the transparency of PMMA is almost preserved until fracture. Such enhanced ductility may be related to a higher peak of the β relaxation at room temperature caused by the residue in the treated specimen. In order to improve the mechanical performance of PMMA, in addition to the usual method of rubber particle dispersion, the introduction of some smaller molecules has been shown to be effective and should be further investigated more extensively [15].

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