Dynamic Mechanical Properties of Dental Base Material Reinforced with Glass Fiber

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ABSTRACT: Dynamic mechanical properties of poly(methyl methacrylate) (PMMA) reinforced with glass fibers were investigated. The composite used as dental base material contained other additives for different purposes to give the same appearance as natural dentals. The fiber–polymer bonding and orientation of fibers in polymer matrix are very important in the application of the product. To see that, the fibers were treated with silane and compared with untreated fibers. The commercial polymer and monomer used were the heat-cured type. However, in addition to heat curing, γ-radiation was also used in curing. This gives much improved material in terms of mechanical properties. The voids, which cause mechanical failure in the material, will be minimal in number with irradiation curing. The results showed that the orientation of all fibers were not regular. This could be observed from the micrographs and DMA behaviors of samples. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1683–1697, 2002

Key words: dental base material; poly(methyl methacrylate); reinforcements; glass fibers; DMA

INTRODUCTION

In prosthodontics literature,[1–6] several techniques were proposed to improve the mechanical behavior of poly(methyl methacrylate) (PMMA), commonly used as a denture base material. The incorporation of various reinforcing agents, such as carbon (graphite),[2,7–8] aramid,[9–10] ultrahigh modulus polyethylene,[4–5] and glass fiber,[11–15] into acrylic resin matrix has provided the improvement in mechanical properties of material. It increases the flexural strength and reduces the number of midline fractures occurring mainly in the vulnerable upper plate, resulting in enhanced fatigue resistance and rigidity. Glass fibers have drawn the most attention, because of their esthetic qualities and easy manipulation. Therefore, much research has been conducted[11–15] on the physical and mechanical properties of PMMA reinforced with glass fibers. There are controversial arguments related to the property gain for the use of coupling agents (adhesives) between polymer matrices and the reinforcement fibers. The use and type of adhesive has a great effect on the mechanical properties of the fiber–polymer composite construction. According to some reported results,[15] untreated fibers act as inclusion bodies in the acrylic resin mixture and instead of reinforcing, actually weaken the resin. Various chemicals are used as adhesive, but various si-

lane-coupling agents were used to obtain optimal bonding.

Many authors[15–16] showed that the silanized glass fibers used as reinforcement increased the fracture resistance and transverse strength of PMMA specimens studied. Another concern is fiber concentration. Stipho[16] stated that the reinforcement of PMMA acrylic resin with low glass fiber concentration gave the best fracture strength and deformation results. It was concluded that the incorporation of fiber should be limited to 20%, in standard dental process, because of the deleterious effects on the dough formation properties above this percentage. In addition to improvements made in physical and mechanical properties of reinforced denture base material, the rheological properties are also affected. This can be shown in terms of molecular size and distribution, glass transition temperature (T_g) and so on. The rheological flow of polymer is related to T_g, because flexible chains tend to have low values of T_g and stiffer chains cause a large increase in T_g. The importance of T_g during the cleaning procedure of denture material to avoid distortion in material was shown before.[17] The value of T_g can also have great influence on the dimensional stability and internal stresses during the polymerization.[3] A variety of techniques such as thermal mechanical analysis (TMA), differential scanning calorimetry (DSC), and dynamical mechanical analysis (DMA) can be used to study the property improvement of denture base material with reinforcement. However, the transition of glassy to rubbery states can best be resolved by DMA. As a result of this analysis, the relationship between the dynamic properties and the structural parameters (crystallinity, molecular weight, crosslinking, etc.) with respect to external variables (such as temperature, time, frequency-type deformation) can be explained.

Recently, we suggested γ-rays[18] as an alternative to other curing methods such as heat, chemical initiator, light, and microwave in dental applications. Because γ-rays have better penetration properties without increasing the local high temperature in material, they can increase the degree and rate of curing as well as convert monomer to polymer much more effectively. Therefore, the mechanical properties of dental material should improve more when using γ-rays as curing technique. Because γ-rays can produce radical centers on the chain of polymer, it also may help the grafting between the adhesive and PMMA,

which will be resulted with stronger bonding between them.

This study aims to determine the DMA investigation results on the effect of random, loose, short cut-glass fibers on some rheological properties of heat-cured PMMA denture base resin polymerized by heat at different cycles or irradiated γ-rays at different total doses. The glass fibers used will be treated with a silane-coupling agent or untreated in different experimental runs. The effect of the percentage of glass fiber will also be investigated. The distribution of E-type glass fibers in polymer matrix and the attachment of adhesive will be observed by stereomicroscope.

EXPERIMENTAL

Material and Methods

Powder PMMA polymer and liquid monomer (Meliodent Bayer Dental) were heat-cured denture base acrylic raw materials. They were used without further purification. The E-glass fiber used (Cam Elyaf Sanayii, A.™, Turkey) were produced according to specification of ISO 9002. They contained 54% SiO_2, 17.5% CaO, 14.0% Al_2O_3, 8.0% B_2O_3 as main ingredients. The density of fibers were 2540 kg m^{-3}, axial tensile modulus was 76 GPa, and axial tensile strength was 1.5 GPa.

The dynamic mechanical measurements were carried out on a DMA 983 (TA Instruments, U.K.). The stereomicroscope was a Nikon SMZ-2T (Japan).

Procedure

The samples in this study consist of three groups. They are a controlled group, a not-reinforced dental base material (PMMA), PMMA reinforced with silane-untreated glass fibers, and PMMA reinforced with silane (type A174)-treated glass fibers. The concentration of fibers in polymer were 3, 5, 10, 15, and 20 wt %. It is not possible to have more than 20% of fiber in composite material because of incompatibility. The composites were prepared by weighing the masses with 0.1 mg accuracy.

The glass fibers were silane (gamma methacyloxypropyl trimethoxy silane) treated in a Petri dish by wetting with excess silane. After waiting a few minutes, the fibers were squeezed between paper towels to remove the excess silane on the surface. The fibers were then dried in air for 20
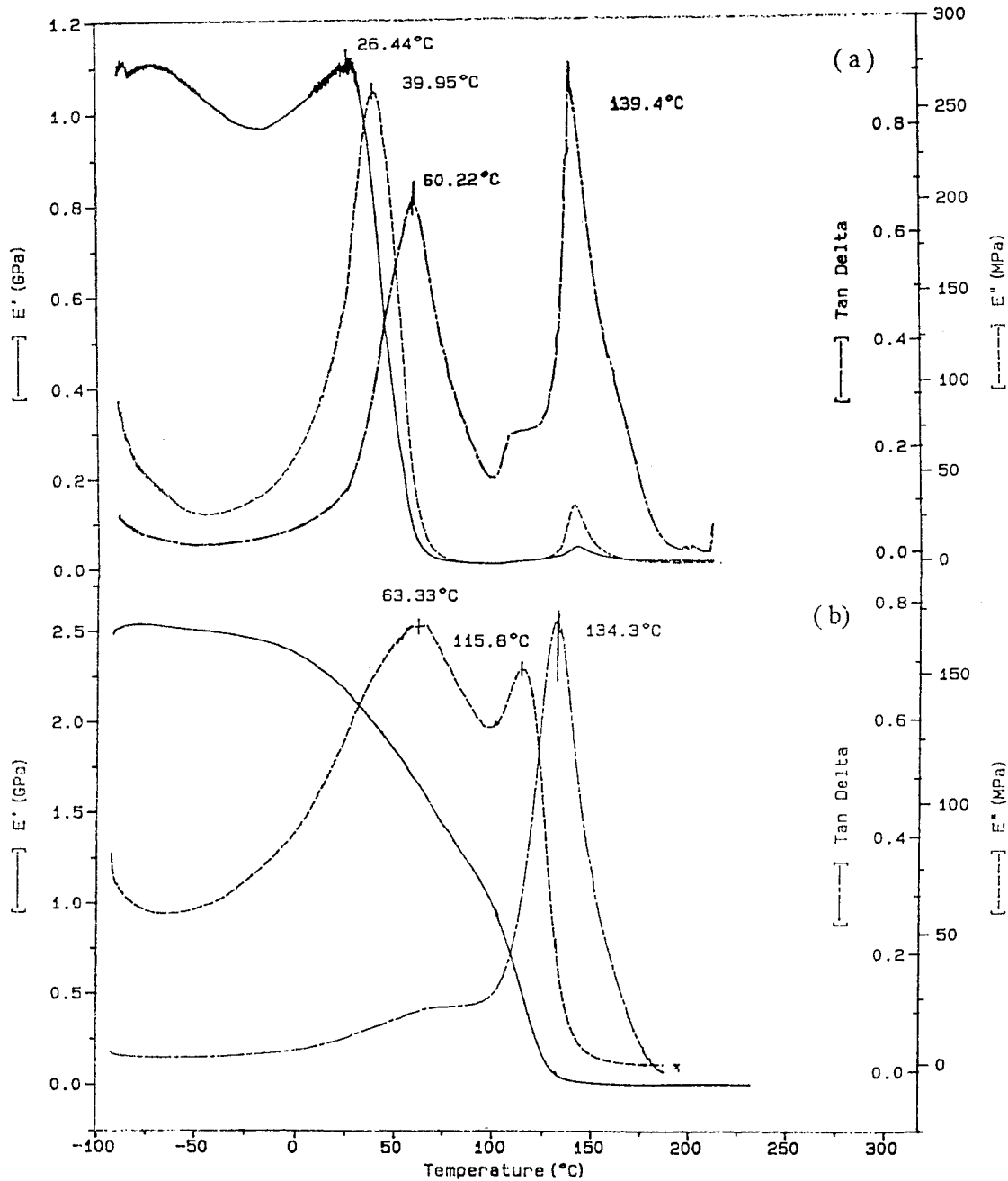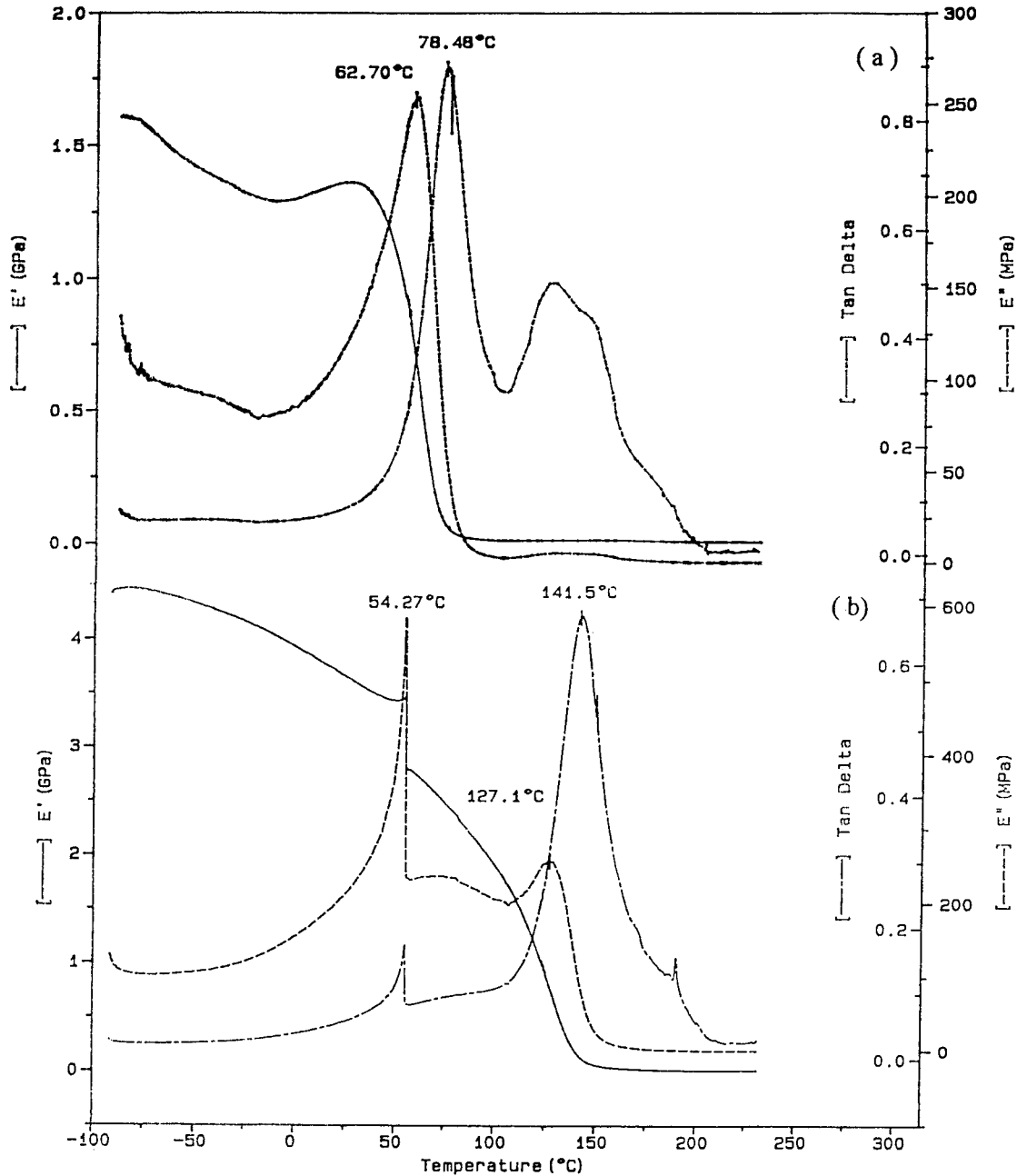
Figure 1 The DMA scan of PMMA heat cured for (a) 15 min, (b) 180 min.

min at room temperature. The silane-treated fibers were well mixed with polymer powder in a mechanical mixer and liquid monomer was added in a weight ratio of 2.2 : 1.0. It was mixed well to make A homogenous dough. Then, the dough was placed in the space created by wax pattern in the mold ($4 \times 1.3 \times 0.2$ cm dimensions). The pressure was applied and polymerization carried out at 60°C in a constant temperature water bath for 30

min. The samples were then cured either by (1) heat at boiling water temperature (96°C) for 15, 45, 60, 120, and 180 min or (b) gamma-ray irradiation for 3.5, 24, and 75 h with a dose rate of 0.014 Mrad/h. The control group was heat-cured by the same procedure.

Silane-untreated samples were prepared by a similar technique, but not treated with silane, and the fibers were mixed with liquid monomer

Figure 2   The DMA scan of PMMA reinforced with 3% silane-untreated glass fiber and heat cured for (a) 15 min, (b) 180 min.

and wetted before adding powder polymer to make dough.

The surface of the samples was polished with grinding paper (number 500) to finish the sample preparation for DMA tests.

RESULTS AND DISCUSSION

The DMA scan of heat-cured dental base material (PMMA) samples used as control group (contain-ing no glass fiber) are given in Figure 1. The scan of samples heat-cured for 45, 60, 120, and 180 min were almost identical with some shifts in peak position. Therefore, the DMA scan for 15-min [Fig. 1(a)] and 180-min curing [Fig. 1(b)] are given. After 15-min curing, the storage elastic modulus is about 1.1 GPa and there are two peaks at 60 and 139°C in the spectrum of tan δ. After 45- to 180-min curing range, the storage modulus increased to about 2.5 GPa and became more
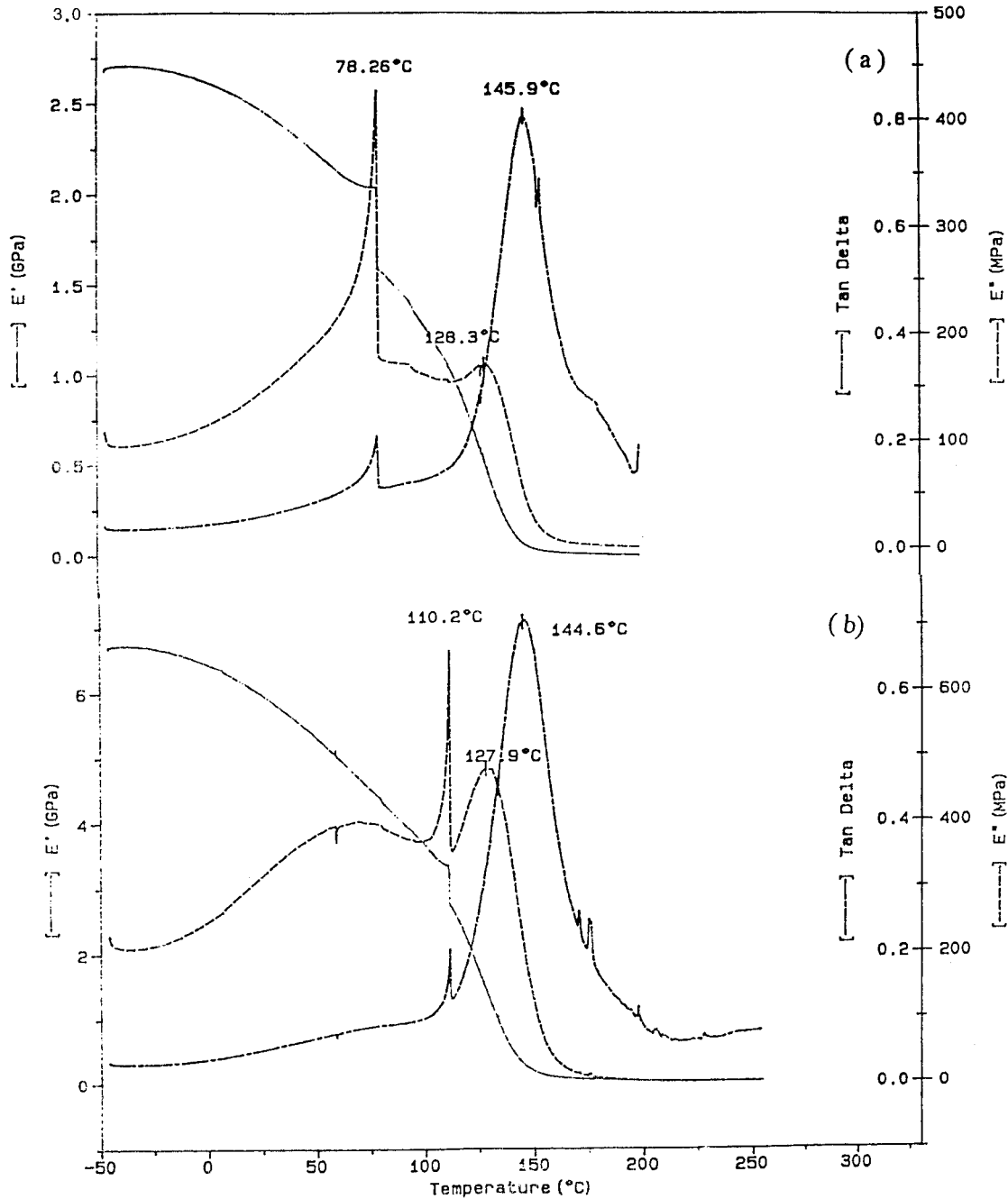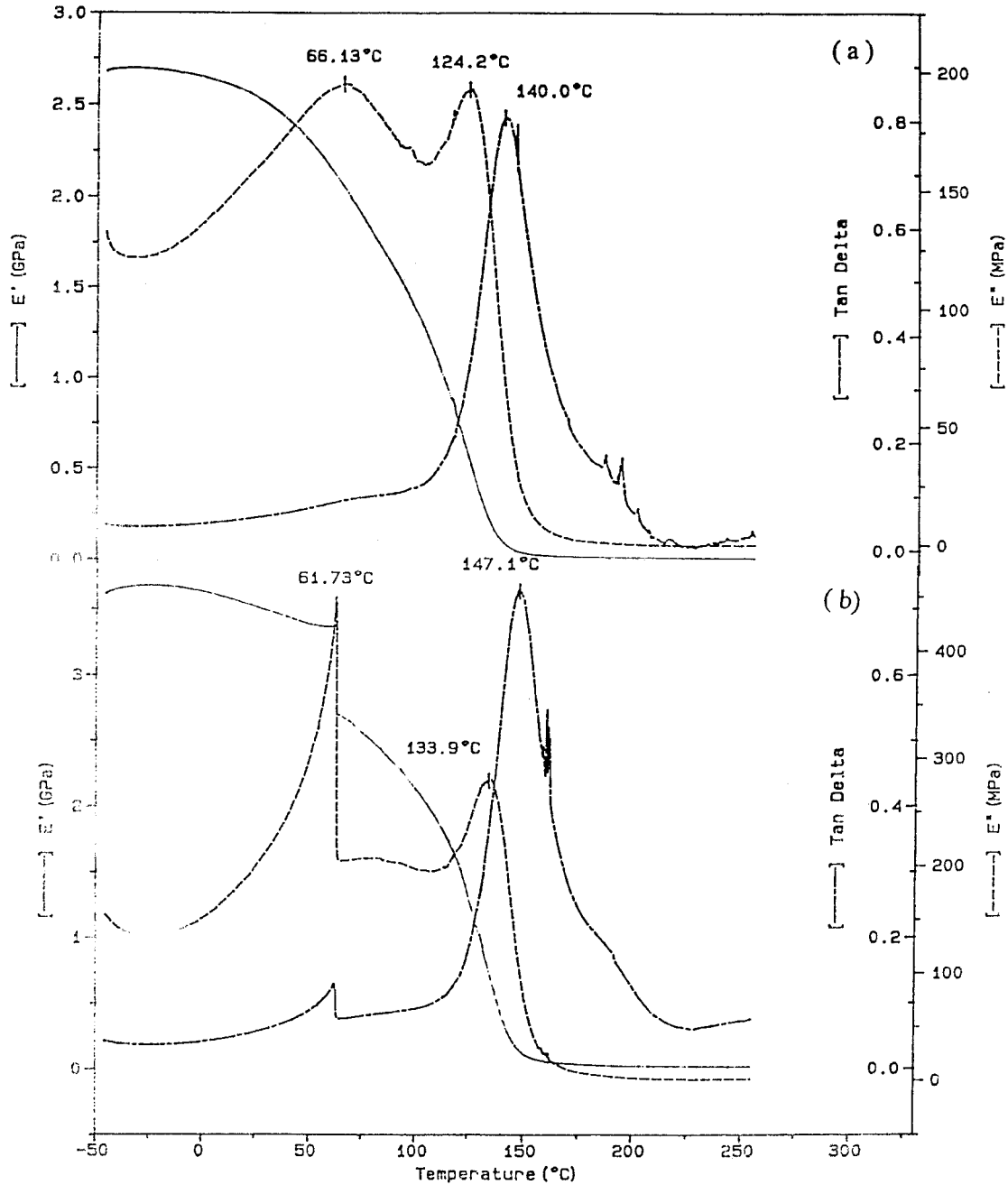
Figure 3 The DMA scan of PMMA heat cured for 60 min and reinforced with (a) 5% and (b) 20% silane-untreated glass fiber.

smooth. The tan δ curves now give only one peak at 134°C, which shows complete crosslinking of polymer. The lost modulus E'' also has the shape corresponding to crosslinked polymer.[3]

The preparation of samples with reinforcement agent required very careful attention in terms of the percentage of reinforcing agent, their orientation, and bonding to polymer. The voids that may exist in composite material are the source of mechanical weakness. Thus, to decrease the number of voids to minimum level, the glass fibers were treated with silane. This will make a good adhesion between polymer–glass fiber and prevent the void formation. Therefore, samples with a different percentage of silane-untreated and silane-treated glass fibers were studied with DMA.

Figure 4 The DMA scan of PMMA heat cured for 60 min and reinforced with (a) 5% and (b) 20% silane-treated glass fiber.

The DMA scan of PMMA reinforced with 3% silane-treated glass fiber for 15-min and 180-min curing periods are given in Figure 2. The spectrum for 45-, 60-, and 120-min curing was almost identical to that of 180-min curing. The general trend of the change in storage modulus, E', and lost modulus, E'', are quite similar to that of the control group. However, after 45-min curing, the sharp decrease of E' is observed at about 54°C. This behavior is most probably due to the phase separation of glass fiber from brittle polymer. After 15-min curing, the polymer is not completed and material is relatively soft. The E' begins a sharp decrease at lower temperature (63°C). However, after 180-min curing [Fig. 2(b)], the E' value reaches to about 4.5 GPa and the plateau
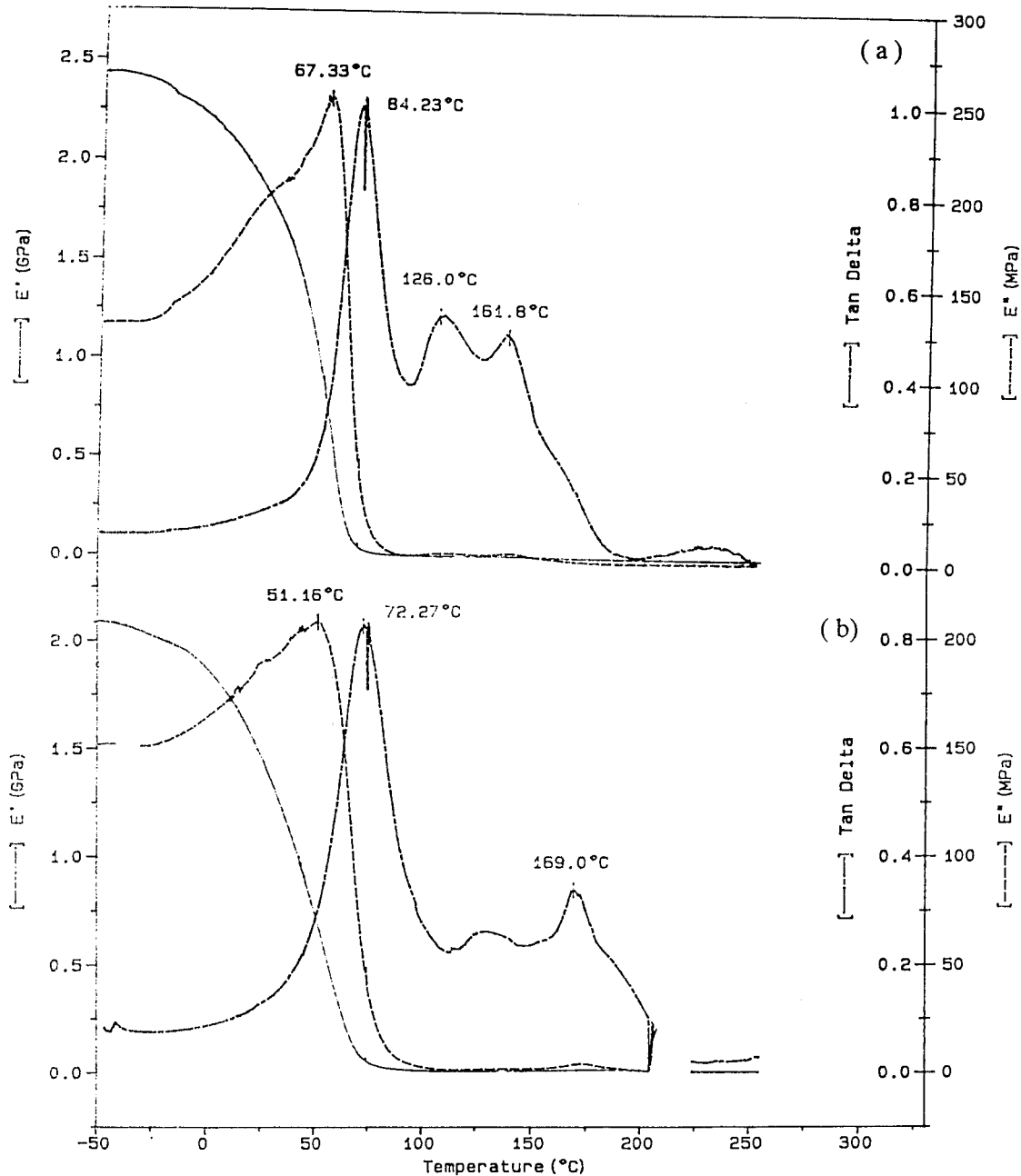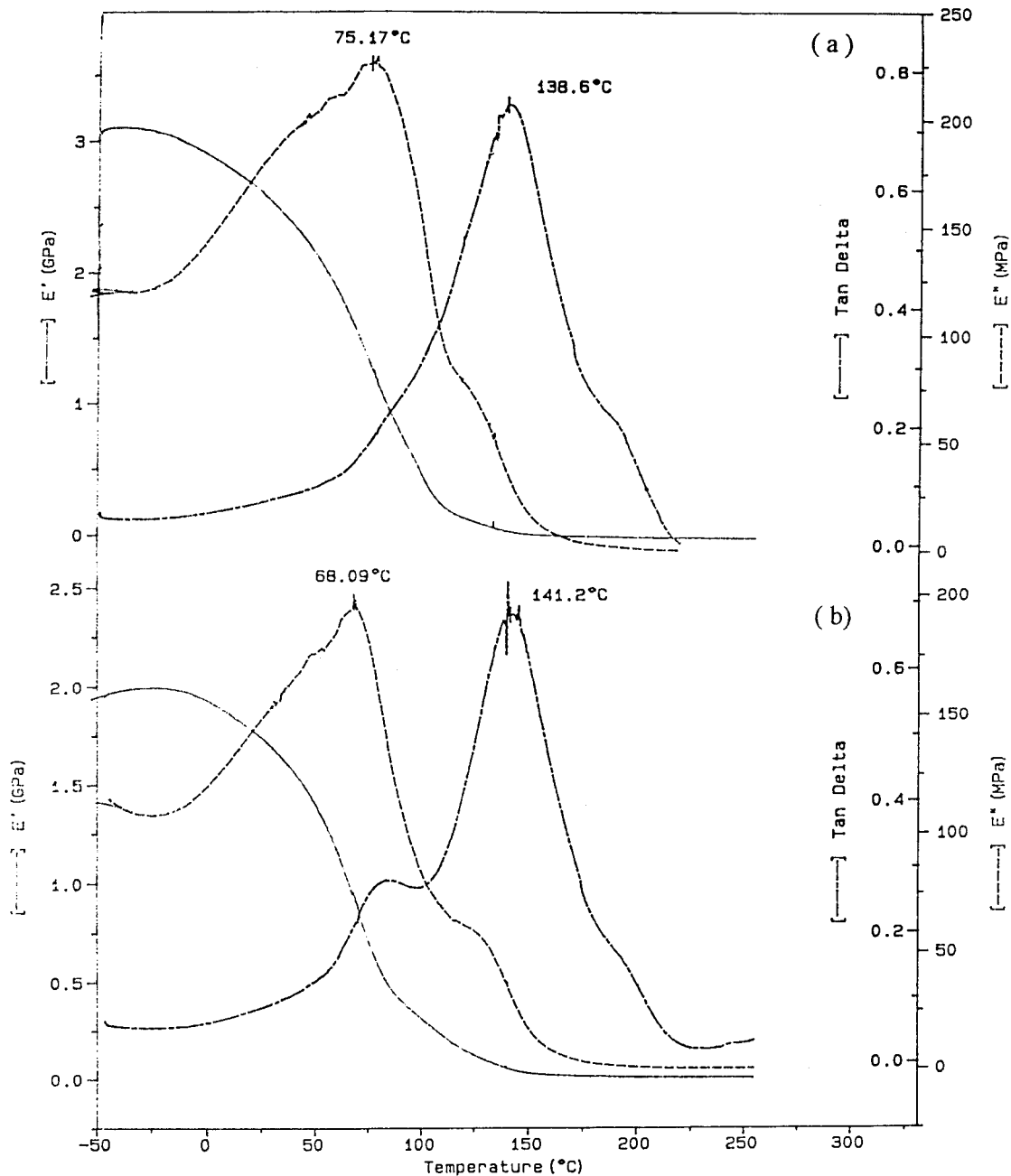
Figure 5 The DMA scan of PMMA reinforced with 3% (a) silane untreated, (b) silane-treated glass fiber and γ-cured with 52.5-krad dose.

range is now increased up to about 140°C. The tan δ curve shows two relaxations[19] (α-, β-) corresponding to T_g temperature of main chain and ester group, but only one peak of α-relaxation for backbone chain after 180-min curing. The molecular mass has a large effect on the glass transition range, where viscous flow transforms to a plateau range of rubberlike behavior. Up to 15-min curing, the liquid monomer gives low molec-

ular weight polymer chain, but when the curing period increased, the chain became longer and crosslinking increased. As a result, the larger molecular chains will have more entanglements between themselves and glass transition temperature reaches to a limited value independent of molecular mass.

The effect of percentage fiber in DMA behavior of material is observed in Figures 3 and 4. The
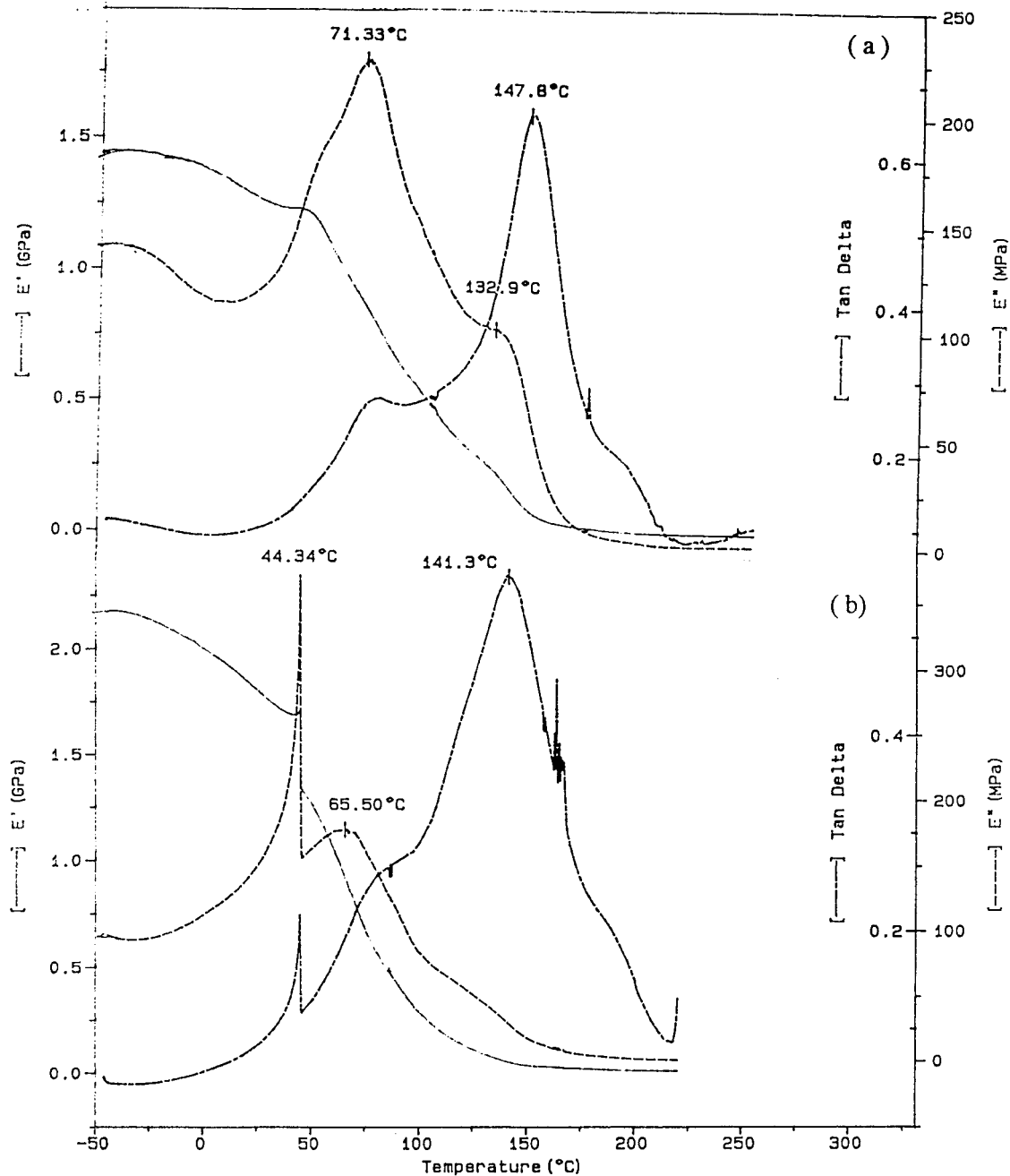
Figure 6 The DMA scan of PMMA reinforced with 3% (a) silane-untreated, (b) silane-treated glass fiber and γ-cured with 360-krad dose.

DMA for 5–10% and for 15–20%, respectively, are similar. Therefore, the results for 5 and 20% are given in the figures. The first one gives DMA scans of silane-untreated glass fiber reinforcement and the second one gives DMA scans of silane-treated glass fiber reinforcement. The heat-cured time for each sample is 60 min, at which crosslinking is almost completed. In silane-untreated glass fiber reinforced samples, tan δ

curve shows a main peak of α-relaxation at about 145°C [Fig. 3(a)], which shows small variation with an increase of percentage glass fiber. The E' value (glass transition plateau) increases with an increase in percentage fiber, reaching to about 6.4 GPa when 20% glass fiber is added [Fig. 3(b)]. The break in E' curve is also observed similar to that in Figure 2(b). However, the temperature at which the phase separation observed increased
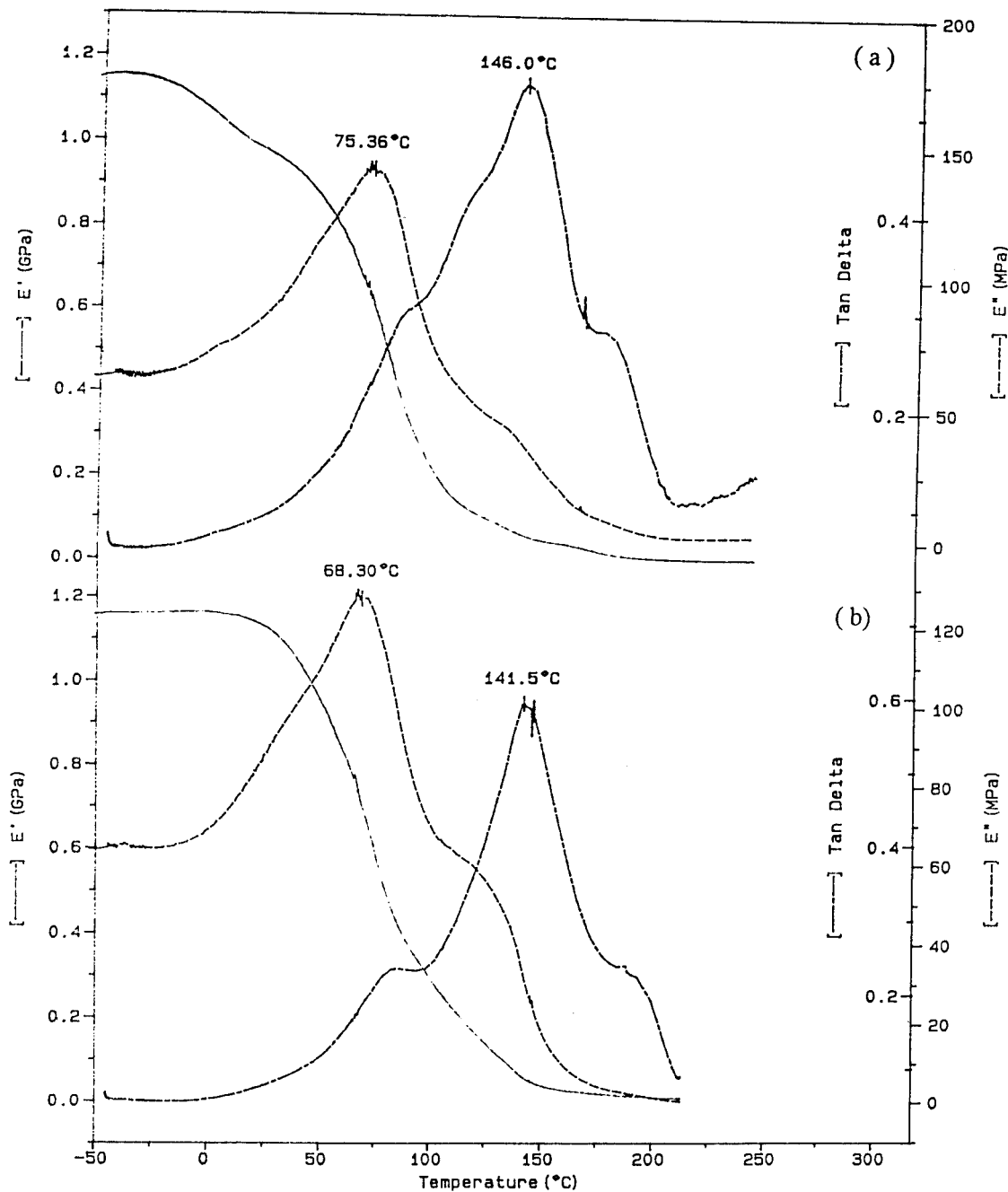
Figure 7 The DMA scan of PMMA reinforced with 15% (a) silane-untreated, (b) silane-treated glass fiber and γ-cured with 360-krad dose.

and the drop range in E' decreased with percentage of fiber. The behavior of tensile lost modulus, E'', shows a regular change with an increase in percentage fiber. The two peaks become more distinct, and the first one now is sharper than that of the controlled samples (with no fiber reinforcement) in Figure 1(b). The sharpness of peak is due to a steep decrease of E' at that temperature.

The DMA scans of samples reinforced with silane-treated glass fibers are shown in Figure 4. The T_g is now about 140°C and does not change much with an increase in the percentage of fiber up to 15%, but showed appreciable change with the 20% [147°C; Fig. 4(b)] fiber addition. When the 5% fiber is added, the DMA of the sample [Fig. 4(a)] is similar to that of the unreinforced sample
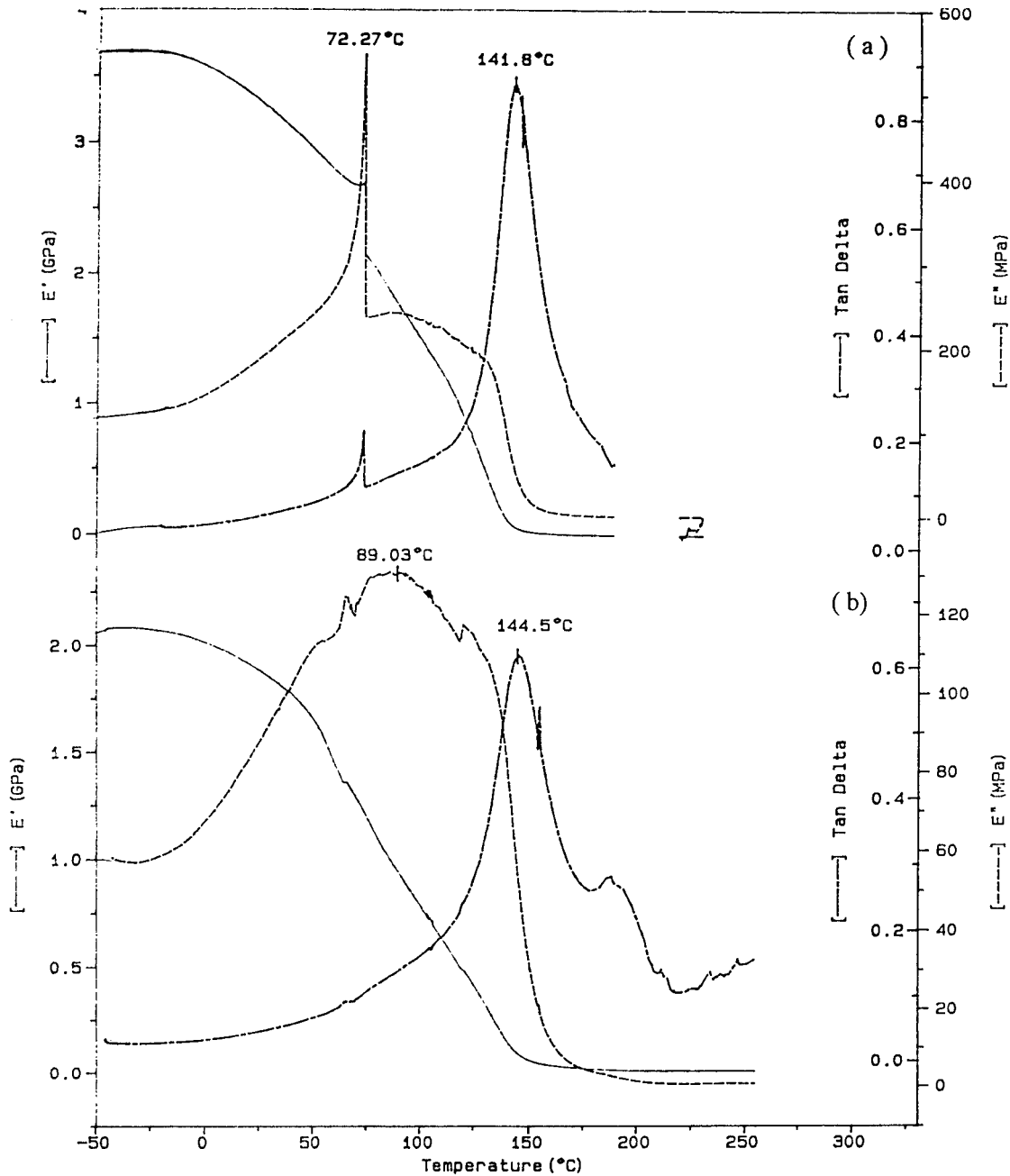
Figure 8 The DMA scan of PMMA reinforced with 20% (a) silane-untreated, (b) silane-treated glass fiber, and γ-cured with 360-krad dose.

[Fig. 1(b)] with an increase in the values of E' and glass transition temperature. This shows high compatibility between polymer and reinforcing agent at this concentration. However, the phase separation takes place at a higher concentration [Fig. 4(b)].

The curing with γ-rays is expected to give much improved mechanical behaviors for several reasons. γ-Radiation penetrates into material without creating a local temperature increase, which results with the minimum residual monomer and voids in the material. γ-Rays also can initiate chemical crosslinking without distorting the orientation of reinforcing fiber in PMMA. The DMA scan of 3% glass fiber reinforced PMMA cured with 52.5 krad total dose γ-irradiation is

Figure 9 The DMA scan of PMMA reinforced with 5% (a) silane-untreated, (b) silane-treated E-type glass fiber and γ-cured with 1125-krad dose.

shown in Figure 5. The glass transition plateau is longer for silane-untreated fibers [Fig. 5(a)] and γ-relaxation temperature is higher. However, the α- and β-relaxation temperatures are higher for silane-treated fiber reinforced PMMA [Fig. 5(b)]. In both samples, the curing is not completed and initial value storage tensile modulus, E', is almost the same.

When the total dose rate of irradiation increased to 360 rad (Fig. 6), the greatest change was observed in the peak shape of tan δ curve. The α-relaxation peak (T_g for main chain) became predominant, and γ-relaxation peak (T_g for —CH$_3$ side group) disappeared in both silane-untreated [Fig. 6(a)] and silane-treated [Fig. 6(b)] 3% fiber-reinforced PMMA samples, but the β-relaxation
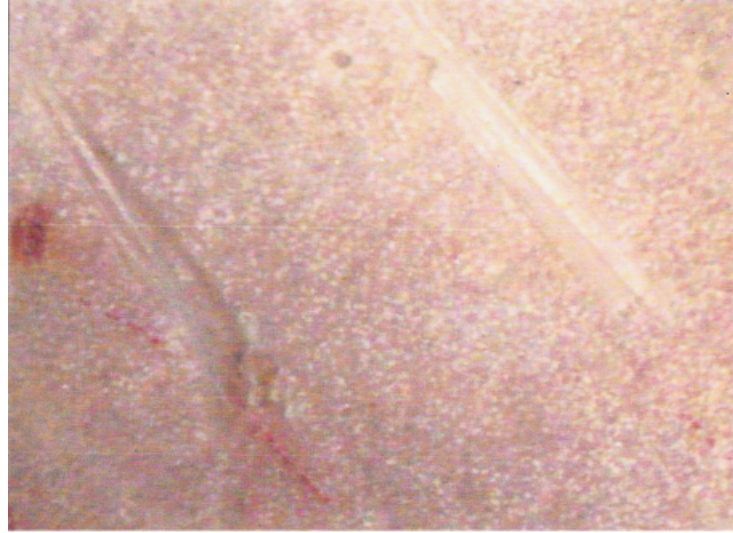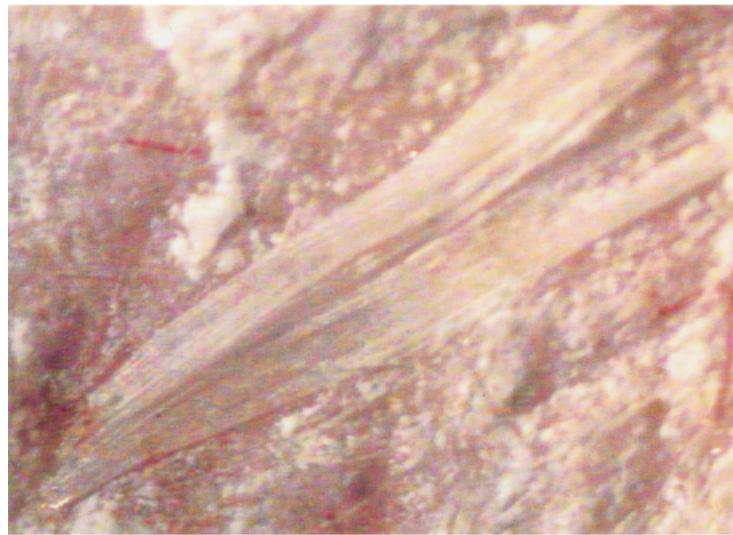
(A)
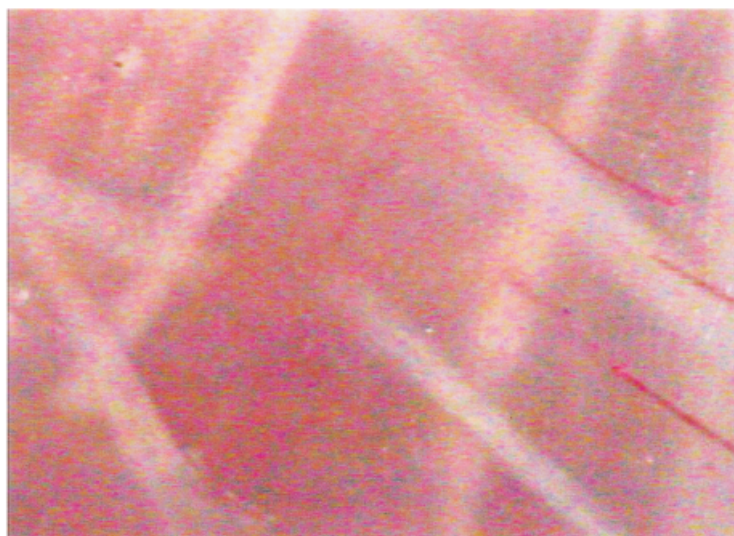
(B)

Figure 10 Stereomicroscope photograph of 10% (a) silane-untreated, (b) silane-treated glass fiber reinforced and 60-min heat-cured samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peak (T_g for ester side group) was observed as a shoulder in the silane-treated sample. The E' value was slightly decreased with an increase of irradiation dose, and a little lower for the silane-treated sample. However, the α-relaxation temperature was higher for the silane-treated sample.

The effect of percentage increase of reinforced glass fiber in samples irradiated for the same total doses (360 krad) is shown in Figures 7 and 8. In Figure 7, the fiber concentration is increased to 15% and in Figure 8 the fiber concentration is increased to 20% for (a) silane-untreated and (b) silane-treated fibers. The gen-

(A)

(B)

Figure 11 Stereomicroscope photograph of 10% (a) silane-untreated, (b) silane-treated glass fiber reinforced and 360-krad dose γ-cured samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

eral peak shape of the tan δ curve is similar in all cases with some variation in peak position and shape for the α-relaxation. It is also similar to the samples in Figure 6. The initial value of E' decreased with an increase in percentage fiber and a break is observed in curve for 15%

fiber-reinforced sample [Fig. 8(b)]. This can be explained with general behavior changes. Most probably, it is related to sample preparation, because there seems to be a phase separation of fibers because of their orientation and distribution in the PMMA matrix.

(A)

(B)

Figure 12   Stereomicroscope photograph of 20% (a) silane-untreated, (b) silane-treated glass fiber reinforced and 360-krad dose γ-cured samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Because the crosslinking is still not completed for this total dose when looking to general shape of curves and compared to that in Figure 1(b), the irradiation dose was increased to 1125 krad. Even though this total dose is also small, it is almost sufficient for complete crosslinking. The corre-

sponding DMA scans are shown in Figure 9. There is a break in the E' curve for the 5% silane-untreated glass fiber [Fig. 9(a)], which is not observed for other samples. The explanation might be the same as for sample in Figure 8(b). The general shape of the tan δ curve for all samples

shows almost complete crosslinking. The initial values of E' values are low for all samples with small variations.

The distribution and orientation of glass fibers in the polymer matrix are shown in Figures 10-12. Generally, the fibers are not well oriented in the polymer and some of them are attached to each other, causing poor packing. Therefore, the expected improvement cannot be achieved. The optical photograph of (a) silane-untreated and (b) silane-treated samples containing 10% glass fiber and 1-h heat cured are shown in Figure 10. The fibers in silane-treated samples appear to be oriented more randomly and cross each other. When similar samples are gamma cured with 360 krad total dose [Fig. 11(a,b)], the samples are more opaque and fiber distribution shows some differences from that of heat-cured samples. This may be due to stronger bonding of fiber to polymer by ionizing radiation. Also, in heat curing, the high temperature may cause distortion in position (orientation) of fibers in polymer matrix. When the fiber percentage is increased to 20% (Fig. 12), the sample becomes more heterogeneous and orientation of fibers shows more random distribution. The random distribution is more apparent for silane-treated [Fig. 12(b)] samples. The conventional sample preparation must be reconsidered and fibers should be well oriented to increase flexural strength of dental base material.

CONCLUSION

Different improvements are carried out in preparation of dental base materials. The first one is the reinforcement with glass fibers, and the second improvement is to use γ-rays for the curing of the material. The optimum curing period by heat or irradiation dose not change with the percentage of fiber. However, increasing the percentage of fiber to about 20% causes the problem of compatibility between fiber and polymer. When the percentage of fiber is increased, the orientation of fibers becomes more irregular and the number of voids formation become larger. This can easily be observed from a photograph of the samples. When

curing is done with γ-rays, the DMA spectra show the reduction in phase separation and the decrease in the number of voids. On the other hand, silane treatment causes the glass fiber to bond to each other as well as with the polymer matrix. The bonding of glass fibers to each other results in more disturbed structure and random orientation of fibers. Thus, the void numbers are greater after silane treatment.

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