Indentation Responses of a Graded Zirconium Phosphate–Filled Epoxy Resin

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ABSTRACT: The effects of load and time on the Vickers indentation responses of a graded zirconium phosphate (ZP)–filled epoxy resin are described. The hardness of this material is dependent on the concentration of ZP dispersed within the epoxy matrix. In the region poor in ZP, the hardness response is independent of load. In contrast, the hardness response in the region rich in ZP is profoundly load-dependent as a combined result of particle agglomeration and an indentation-size effect. When compared with the ZP-rich-epoxy, the ZP-poor epoxy exhibits a larger creep and a more pronounced elastic recovery in the Vickers impression. The nature and degree of deformation in the vicinity of Vickers contacts are also studied. During indentation the ZP-rich epoxy exhibits no contact-induced cracks but displays microscale plasticity, which can be associated with intergrain sliding, debonding, and grain push-out. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 931–935, 2001

Key words: Vickers indentation; epoxy; hardness; viscoelastic; zirconium phosphate; agglomerates

INTRODUCTION

Indentation testing offers a simple but versatile tool for determination of the mechanical properties of materials. Besides characterizing hardness and toughness, it has also recently been used to characterize residual stresses,[1,2] yielding stress,[3] Young's modulus,[4] thermal shock resistance,[5,6] and subsurface damage.[7]

Most indentation measurements, however, have been conducted on metals and ceramics. The reluctance of researchers in using indentation testing as a tool for studying the properties of polymeric materials may be attributed to the problem of pronounced elastic recovery or time-dependent behavior, which may complicate the computation and interpretation of results. Recent studies by Low and coworkers[8,9] have shown that the elastic recovery of epoxy or acrylic resin during Vickers indentation takes place only along the side faces but not along the diagonals, thus verifying the indentation test as a valid tool for characterizing the properties of polymeric materials. Indeed, in recent years, microhardness measurements have been widely used to study the hardness,[10–12] yield stress,[13] elastic modulus,[13,14] storage modulus and loss factor,[15] and glass-transition temperature.[12] of polymeric materials. Hitherto, the indentation method has not been reported to characterize the viscoelastic creep and hardness depth profile of a polymer system containing a *graded* concentration of filler.

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Figure 1 Scanning electron micrograph showing the platelet morphology of ZP powder.

In this study, we examine the effects of load and time on the responses of a functionally graded zirconium phosphate (ZP)–filled epoxy composite under Vickers indentation. The variations of hardness as a function of depth, load, and time are investigated. The influence of filler and viscoelastic flow on the hardness responses is discussed.

EXPERIMENTAL

The materials used for the synthesis of ZP-filled epoxy composite were epoxy resin *N,N,N′,N′*-tetra glycidylmethoxy diamine (TETRAD-X) and hardener 1,2-cyclohexanedicarboxylic anhydride (HHPA) supplied, respectively, by the Mitsubishi Gas Chemical Co. (Japan) and the Wako Junyaku Co. (Japan). The filler used was commercial α-zirconium phosphate (ZP) with a mean particle size of 1.8 μm, supplied by Dai-ichi Kigenso Kagaku Kogyo Co. (Japan). The platelet morphology of the as-received ZP is shown in Figure 1. A loading of 20 vol % ZP was mixed in an epoxy/hardener matrix and the mixture rotated in a Buchi Rotavapor rotary evaporator for 1 h. The well-mixed mixture was then poured into a Teflon-coated aluminum mold and placed in a vacuum chamber for degassing. Curing of the samples was performed in a ventilated oven at 90°C for 2 h, followed by 2 h at 180°C. Because of the effect of gravity, the denser ZP sedimented at the base of the mold, resulting in a graded composition with ZP-poor (~ 5 mm) and ZP-rich (~ 2 mm) regions on the top and bottom sides of the sample, respectively. The approximate concentrations of ZP in both regions are about 0.5–2 vol % and about 70–80 vol %, respectively.

To facilitate the process of sample polishing for Vickers indentation measurements, short bars (10 × 10 × 4 mm) of samples were cut and mounted in an acrylic resin. The samples were then polished with diamond paste down to 1 μm using a Struers Pedemat autopolisher. Vickers indentations were made at P = 2–300 N to measure hardness, determined here as

$$H = P/2a^2 \quad (1)$$

where P is the peak load and a is the impression half-diagonal. The effect of loading time (0–20 h) on the variations of hardness at 50-N load was performed to ascertain the viscoelastic nature of this material. The time-dependent strain $\epsilon(t)$ attributed to creep was calculated from the difference in diagonal lengths (d) between the initial (t_0) and continuous specified (t) loading times:

$$\varepsilon(t) = [d(t) - d(t_0)]/d(t_0) \quad (2)$$

RESULTS AND DISCUSSION

Indentation Response

The depth profile of hardness variations across the graded sample at P = 30 N is shown in Figure 2 As would be expected, the hardness was lower in the ZP-poor region and increased toward the ZP-rich region by virtue of an increasing harder filler content. The discontinuous rise in hardness

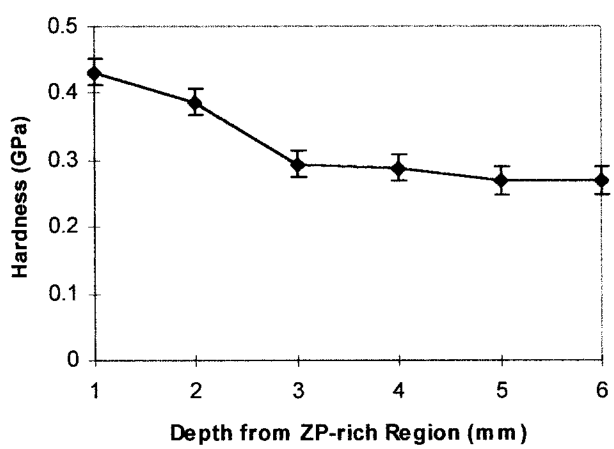


Figure 2 Depth profile hardness of the graded epoxy–ZP composite.

demarcates the boundary between the two regions. The graded nature of this polymeric system has been clearly revealed by the depth-profiling of hardness. To the best of our knowledge, this is the first time that microhardness has been used to establish the hardness depth profile of a functionally graded polymeric system.

The size of Vickers indentations in both ZP-rich and ZP-poor regions increased with an increase in the load. However, no radial cracks were observed, even at the maximum load (300 N) used. This is interesting because epoxy resin is known to have a relatively low fracture toughness (K_{ic}) of typically about 1.0 MPa $m^{1/2}$,[16] which is comparable to that of silica glass. The latter is well known to be very brittle and forms indentation cracks readily.[17] The absence of indentation cracks in the graded ZP-filled epoxy sample can be ascribed to: (a) low hardness (H_v) and (b) high critical load (P_c) to initiate cracks, where P_c is proportional to (K_{ic}^4/H_v^3).[17–19] Hence polymeric materials and metals hardly ever show radial cracks, except at very high loads. For instance, it would need a critical load of 800 kN to form indentation cracks in a mild steel.[17] Similarly, the critical load for epoxy can be calculated to be approximately 800 N, which is well beyond the loading capacity of the Zwick tester used.

The ZP-poor region displayed a star-shaped Vickers indent [Fig. 3(a)], which is not commonly observed in ceramics and metals. It appears that elastic recovery had taken place on the side faces but *not* along the diagonals of the indent. In contrast, the ZP-rich region displayed a more pyramidally shaped indent [Fig. 3(b)]. Fine microcrack-like defects can be clearly seen within the indent [Fig. 4(a)]. A closer examination reveals the presence of surface uplifts resulting from intergrain sliding, interfacial debonding, and grain push-out [Fig. 4(b)]. The presence of dispersed ZP in a concentrated amount has clearly modified the stress distributions and intrinsic deformation property of epoxy resin by virtue of mismatch in their thermal expansion coefficients and elastic moduli.

Figure 5 shows the variations of hardness as a function of load for ZP-poor and ZP-rich regions in the graded sample. The hardness of the former is virtually independent of load, a characteristic similar to that of brittle materials such as silica glass[20] and amorphous polymers.[8,9] In contrast, the ZP-rich region displays hardness that decreases as the load is increased. This load-dependent hardness characteristic is common in metals

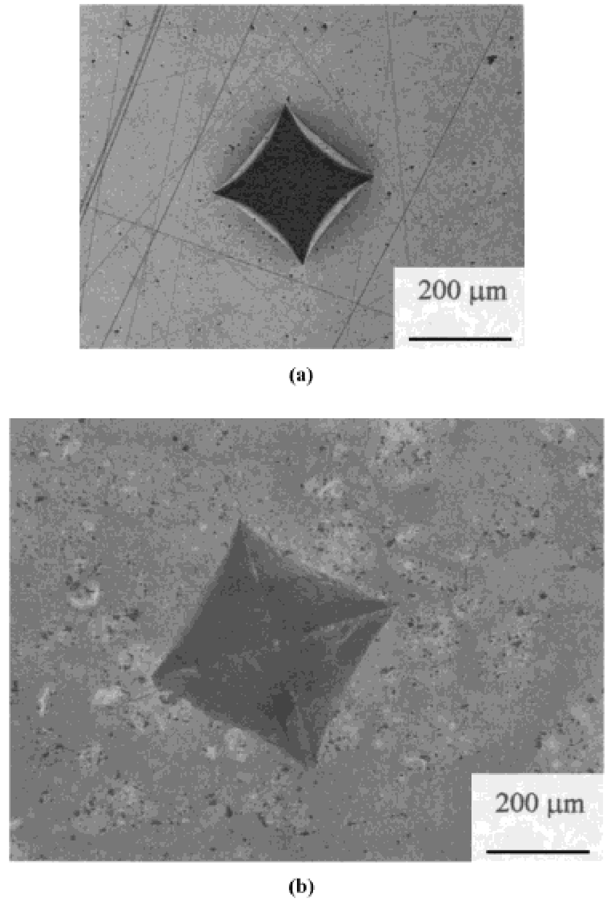
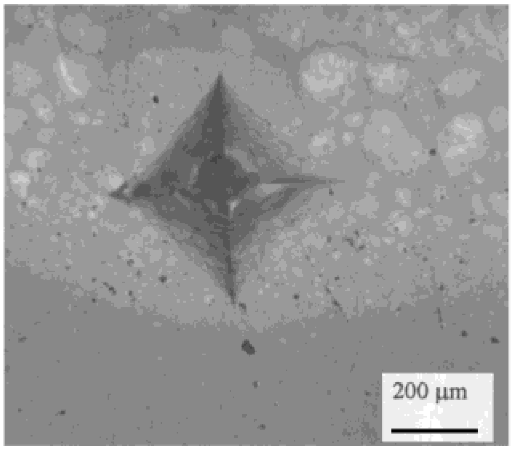


Figure 3 Morphology of a typical Vickers indentation in (a) ZP-poor epoxy and (b) ZP-rich epoxy.

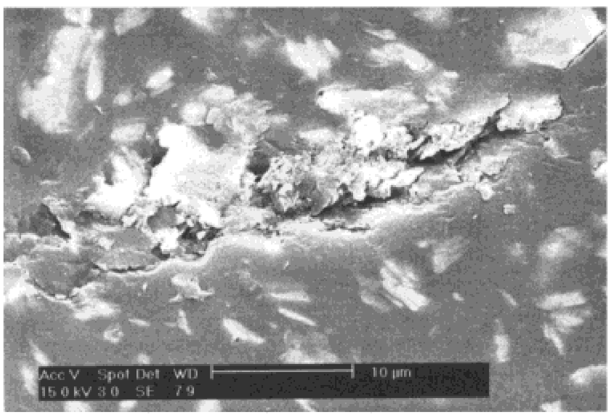
and has also recently been observed for Ti_3SiC_2,[21,22] a phenomenon that can be attributed to the effect of large grain size. At small loads, the contact dimension ($2a$) of Vickers impression is comparable to the agglomerated ZP grain size (Fig. 6), and the hardness measures properties similar to those of single agglomerated ZP grains; when $2a$ becomes much larger than the agglomerated ZP grain size at high loads, the hardness measures the bulk properties, with more epoxy matrix oriented for deformation by viscoelastic flow. It follows that the absence of load dependency of hardness in amorphous polymers may be the result of the lack of a grain size effect. Similarly, this load-dependent hardness behavior in the ZP-rich region will disappear if fine ZP particles could be uniformly dispersed within the epoxy matrix without formation of large agglomerates.

Viscoelastic Response

The viscoelastic nature of ZP-poor and ZP-rich regions during indentation is clearly revealed in



(a)



(b)

Figure 4 Optical micrographs showing microscale damage within the indentation in the ZP-rich region: (a) low magnification; (b) higher magnification.

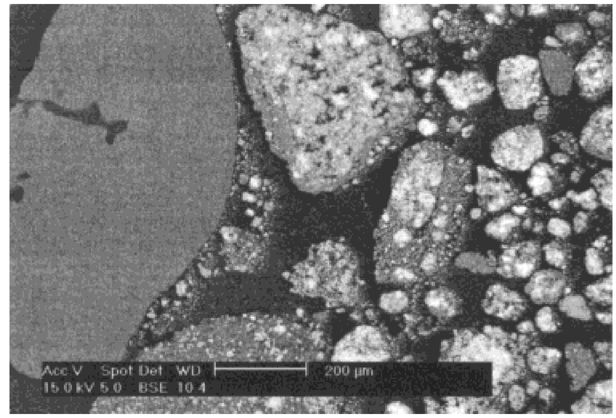


Figure 6 Scanning electron micrograph showing the formation of large ZP agglomerates in the ZP-rich region.

Figure 7 which shows the variations of hardness and creep strain as a function of continuous loading time. Over a period of 20 h, when compared to the ZP-rich region, the ZP-poor region showed a greater decrease in hardness but a larger increase in the associated creep strain. This suggests that

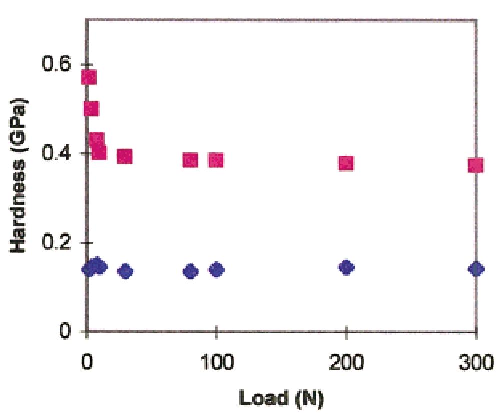
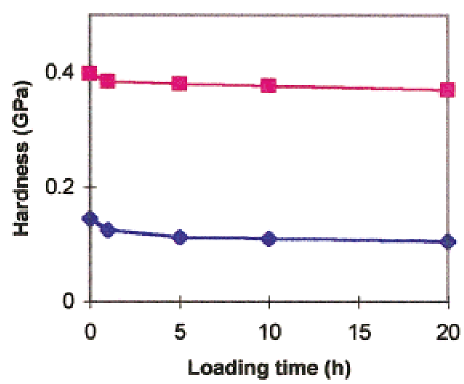
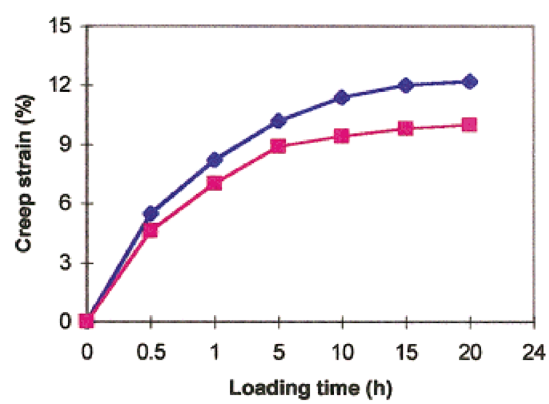


Figure 5 Variations of hardness as a function of indentation load for ZP-poor epoxy (◆) and ZP-rich epoxy (■).



(a)



(b)

Figure 7 Variations of (a) hardness and (b) creep strain as a function of loading time for ZP-poor epoxy (◆) and ZP-rich epoxy (■).

during prolonged loading, the size of indent increased with time as a result of both viscoelastic flow and relaxation processes. A smaller amount of hardness reduction and creep strain in the ZP-rich region may be attributed to the large concentration of ZP agglomerates, which reduces the effective volume fraction of epoxy matrix for viscoelastic flow.

CONCLUSIONS

The effects of load and time on the Vickers indentation responses of a graded ZP-filled epoxy sample have been examined. The hardness of this material is time dependent as a result of viscoelastic flow and relaxation processes. The elastic recovery in the Vickers impression takes place along the side faces but not along the diagonals. In contrast to the ZP-poor epoxy, the hardness of ZP-rich epoxy is dependent on load as a result of an indentation size effect. The latter also exhibits a smaller amount of creep and elastic recovery as a result of the presence of dispersed ZP, which reduces the effective volume fraction of epoxy matrix.

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