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Nodular Structure in Epoxy Resins

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Synopsis

Nodular morphology is observed on free surfaces, fracture surfaces, and etched surfaces of epoxy resins of widely different cure and chemistry. The influence of high- and low-energy substrates on nodule size is illustrated. Fine structure or "dimples" exist on several individual nodules, and various states of agglomeration of nodules are depicted. The possible relations between nodular morphology and adhesion phenomena are discussed.

INTRODUCTION

The morphology of thermosetting resins has been a subject of considerable practical and scientific interest to many investigators. It is well known that thermoset resins have considerably smaller tensile strengths than strengths predicted by either primary bond breakage or van der Waals bond breakage.[1] Various experimental techniques have subsequently indicated morphologic inhomogeneities that could explain these low tensile strengths.[2-6] Electron microscopy has indicated featureless resins in some cases and a nodular or micellar structure in others.[7-20] The most recent findings relate the size and number density of these nodules to the presence of plasticizer,[17] the effects of radiation damage,[20] and to the aging of the resin.[18] Both the low tensile strengths and nodular morphology of thermosets have been theoretically related to differences or nonhomogeneities in crosslink density,[3,8,22-28] though many investigators view thermosets as homogeneous, one-phase materials.

Interest in thermoset composite systems has renewed investigations of adhesion and failure of thermosetting resins. Properties of the thermosetting resin–reinforcing phase interfacial region have been related to the strength, fatigue resistance, and durability of the composite.[29] Consideration of the large stress fields occurring at these interfacial regions, and the displacement and/or destruction of the resin bonds in interfacial regions by a diffusing molecular species (notably water), considerably complicates the prediction of long-term strengths of composite systems.[29-31]

This study involves primarily an electron-microscopic investigation of several epoxy resin systems cured under different conditions, with some resins in contact with various substrates. Our objectives are, first, to firmly establish whether distinct nodular structures or domains can be produced in these thermoset amorphous systems and, second, to investigate the influence of composition, cure conditions, and substrates on the structure of the resin.

EXPERIMENTAL

Epoxy Systems Studied

Table I summarizes the chemistry of the resin systems used in these studies. Two types of epoxy resins were investigated: (1) systems based upon the diglycidyl ether of bisphenol A (DGEBA), which is the main component of Epon 828, and (2) systems based upon a triglycidyl ether of glycerol, which is the main component of Epon 812. The compositions made for this study are summarized in Table II.

Resins were manually mixed as thoroughly as possible. Inadequate or nonuniform dispersion of resin components could conceivably affect the properties of the cured product, but this was not investigated. After mixing, resins were promptly applied to glass slides or other substrates, or were poured into mold cavities.

Cure conditions are shown in Table II. The various cure conditions resulted in different degrees of crosslinking, hardness, and intensity of color in the cured blocks. Stoichiometric ratios of reactants were generally utilized, although an excess of accelerator (BDMA) was used with some Epon 812 resin mixtures. Curing was achieved by placing the samples in a preheated air oven. Postcure was accomplished by either transferring samples to a higher-temperature oven or by changing the oven temperature.

Substrates Studied

Various high and low surface energy substrates were employed to establish their effects on the epoxy structure. Free surfaces refer to surfaces cast against air. Table III indicates the substrates investigated, their surface preparation, and the method of application of the epoxy in the formation of the sample interface.

Microscopy Techniques

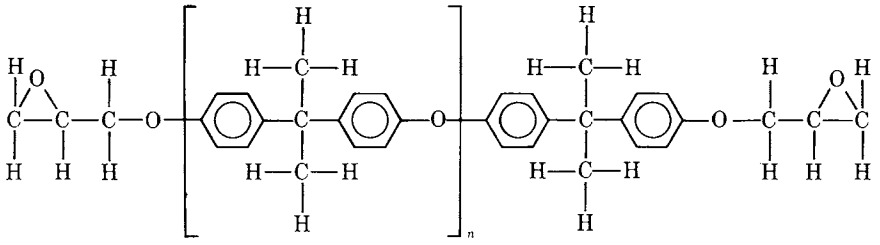
Two methods are employed to replicate surfaces and interfaces. The two-stage method of replication begins with the application of poly(acrylic acid) (PAA) of 26% water solution to the surface of interest, with the water then allowed to evaporate overnight. The brittle PAA replica is removed by mechanical prying using tweezers, and the replica is shadowed with Pt and a carbon film is deposited. The PAA is then dissolved in water and the carbon–Pt replica is floated onto electron microscope grids.

An experimentally more difficult one-stage (direct) replication method is also employed, in order to check for artifacts possibly produced by the PAA. Pt and C are shadowed directly onto the surface of interest, then PAA is placed on the backside of the carbon–Pt film. Again, mechanical prying removes the replica from the surface, which adheres to the PAA. The replica is again separated from the PAA by water flotation.

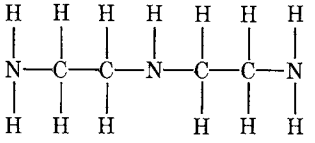
TABLE I
Epoxy Chemistry of Systems Studied

A. Epon 828 Systems

1. DGEBA (diglycidyl ether of bisphenol A) resin

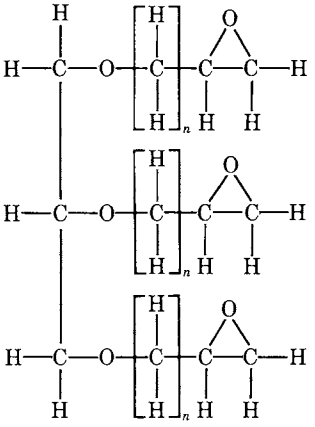


2. DETA (diethylene triamine) catalyst



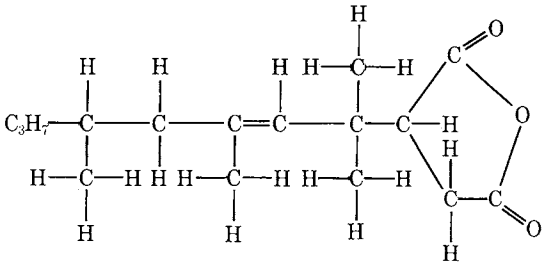
B. Epon 812 Systems

1. TGEG (triglycidyl ether of glycerol) resin



$n \sim 4$ to 5

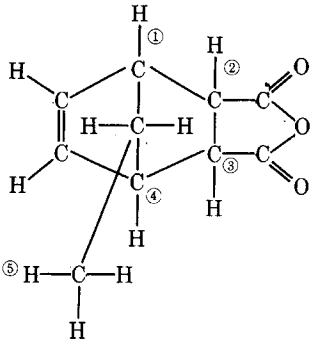
2. DDSA (dodecenyl succinic anhydride) catalyst



(*continued*)

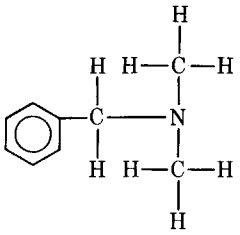
TABLE I (*continued*)

3. NMA (nadic methyl anhydride) catalyst



Note: NMA is a mixture of isomers in which methyl group ⑤ is bonded to any one of carbon atoms ① – ④.

4. BDMA (benzyldimethylamine) accelerator



Surface Fracture and Etching

Samples were fractured at room temperature and at liquid nitrogen temperature to observe bulk and interfacial morphology. Selective etching methods were also used to obtain information on the morphology beneath free and substrate-contacted surfaces. Acetone was used as a solvent etch. Some samples were immersed in boiling acetone or washed by condensing acetone in a cold-finger condensation apparatus. More severe chemical etching was achieved by immersion in 95–97% H_2SO_4 for various times and temperatures.

TABLE II
Composition and Cure of Epoxy Systems[a]

Composition	Cure
Epon 828 Resins	
1. 100 pbw (parts by weight) DGEBA + 11 pbw DETA	For all resins: Cure I: 2½ to 4 hr at 70–80° C. Cure II: 2½ to 4 hr at 70–80° C, then 24 hr at 130–150° C
Epon 812 Resins	
2. 62 pbw TGEG + 100 pbw DDSA + 1.5–3.0 pbw BDMA	
3. 100 pbw TGEG + 89 pbw NMA + 1.5–3.0 pbw BDMA	
4. Mixtures of (2) and (3)	

[a] A 20/80 Epon 812 resin indicates 20 pbw (2) and 80 pbw (3). Mixtures (2) and (3) correspond to the formulations A and B suggested by Luft[32] for ultramicrotome embedding applications.

RESULTS

In accord with other investigators, the electron microscopy of many of our epoxy systems indicates distinct nodular character of 10–60 nm in size (1 nm = 10 Å = 10^{-9}m). At times, these nodules are seen to aggregate into superstructures of about 100 nm size. The size of nodules remarkably increases near interfaces, while the bulk resin structure far from interfaces seems to be composed of densely packed smaller nodules. At times, the nodules appear to be part of extended networks; these networks are composed of pearl-like chains of nodules extending tens of nanometers. These observations pertain to both free and fractured surfaces.

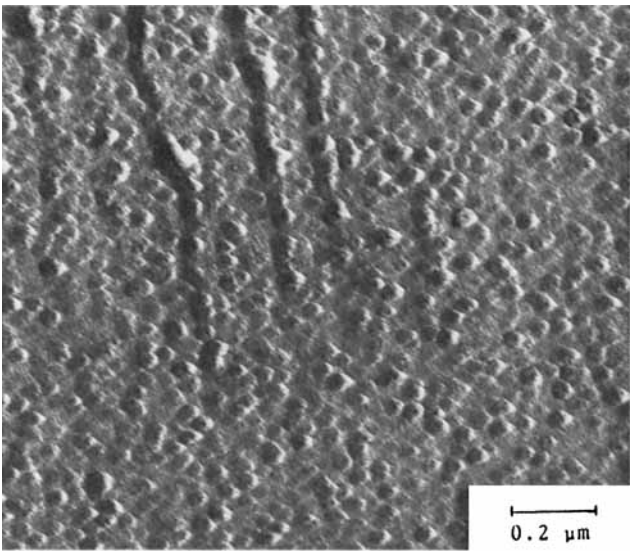
Again in agreement with other investigators, smooth, almost nodule-free surfaces were observed on some samples, especially those epoxy surfaces cured in contact with silicone elastomer and poly(tetrafluoroethylene). Etching often roughened the surfaces and gave strong indication of nodules beneath the smooth surfaces.

Replicas of Free Surfaces

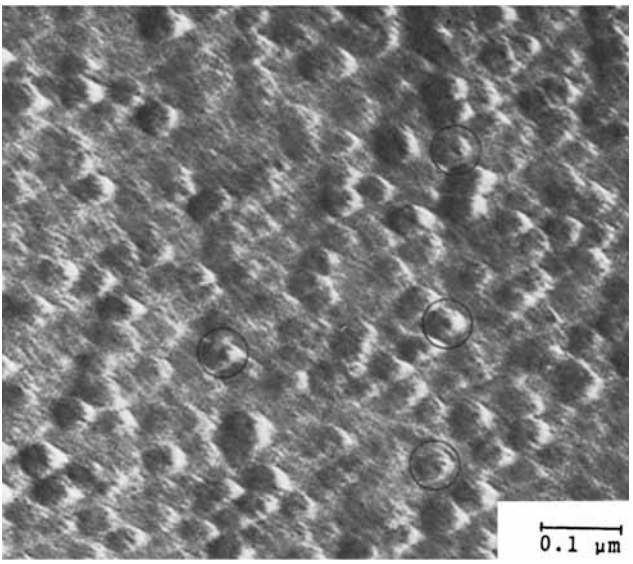
Examination of both free and fracture surfaces indicates that bulk-cured epoxy resins have a nodular morphology. (Figs. 1–18 are from two-stage Pt-C replicas, though one-stage replication corroborated these results.) Figure 1 shows an Epon 828 free surface, while Figure 2 shows an Epon 812 free sur-

TABLE III
Substrate Surfaces Used in the Study of Epoxy–Substrate Interfaces

Substrate	Source and Characterization	Preparation	Usage
1. Hollow glass microspheres	Emerson & Cuming Eccospheres R, of size mostly from 40 to 125 μm in diameter	cleaned in Chromerge cleaning solution (room temp., > 24 hr stirring), washed with large amounts of distilled water, oven dried	spheres added to resin during stir-mixing of the resin components
2. Silicone rubber	Ted Pella Co. #110 and 111, Polaron and Bojax microtome sample embedding molds	cleaned with Alconox detergent, acetone, distilled water	resin poured into mold cavities; cured block manipulated out of mold
3. Teflon PTFE film	du Pont TFE film, approx 3 mils thick	cleaned with Alconox detergent, acetone, distilled water	resin applied between PTFE films to form PTFE–epoxy–PTFE sandwich (copper wires used as spacers)
4. Copper wire	#10 Gauge electrical wire (with plastic insulation)	insulation stripped from wire, wire cleaned in detergent, distilled water, acetone	used as spacer, with PTFE film



(a)



(b)

Fig. 1. (a) Free surface replica of Epon 828 resin, cured ½ hr at 75°C + 24 hr at 150°C. (b) Enlargement of (a); "dimpled" nodules are circled.

face. Note, in both these figures, the chain-like character of agglomeration of the nodules. There are subtle "dimples" or ridges on many of the nodules in Figure 1 visible at high magnifications (Fig. 1B). A noteworthy feature of Figure 3 is the appearance of a network-like morphology in Figure 3, and Figure 4 displays large ridges, possibly due to surface shrinkage stresses. Both Figures 3 and 4 show dimpling on several nodules.

Compositional changes appear to have little effect on nodule size on these free surface replicas, though a change in Epon 812 resin composition from

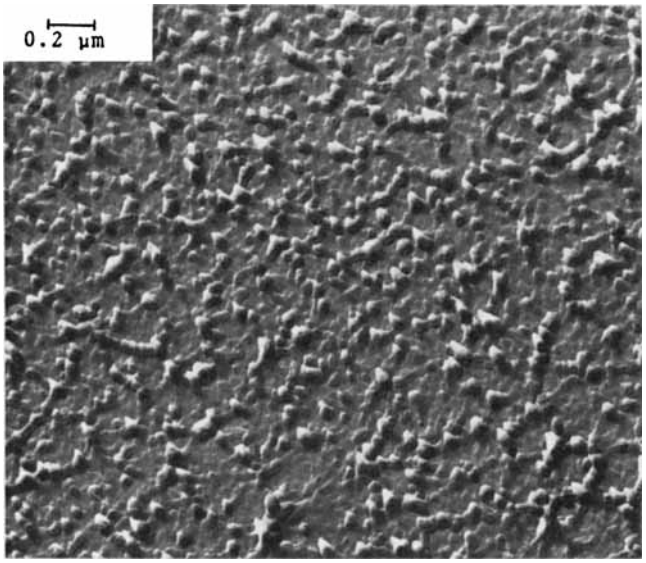


Fig. 2. Free surface replica of 20/80 composition Epon 812 resin, cured 3 hr at 75°C + 24 hr at 150°C.

100/0 to 50/50 to 20/80 compositions appears to give more network-like morphologies. The 100/0 compositions show nodules which seem more sharply bounded.

Incipient nodules are observed in barely cured systems as shown in Figure 5. The surface appears nearly smooth with periodic undulations occurring every 50–100 nm.

Replicas of Fracture Surfaces

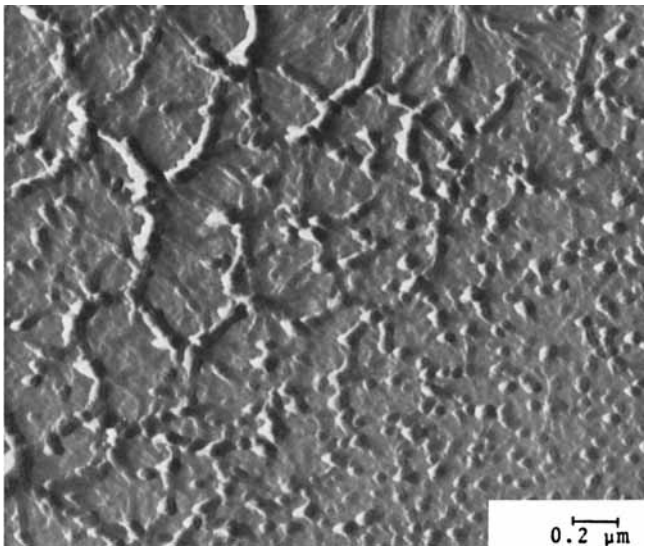
Fracture surfaces of the epoxy resins again clearly show nodules nearly identical in character with those seen on free surfaces. Figures 6, 7, and 8 show nodules with no apparent preferential alignment or connection with cleavage direction. Figure 8 does indicate some "loose" directional alignment but nothing suggesting periodic cleavage steps as observed on a more macroscale with some brittle materials, such as polystyrene.[37] Finally, nodules in Figure 6 again show the "dimpling" fine structure described above.

Replicas of Etched Surfaces

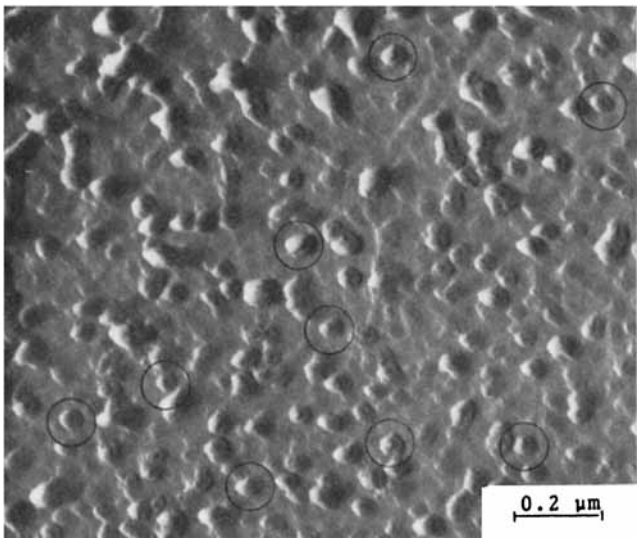
Nodular morphology is often observed on replicas of etched epoxy surfaces.

Acetone etching results in more severe attack on Epon 812 than on Epon 828 free surfaces. However, both etched systems show nodular morphology extensively, as seen in Figure 9. Sulfuric acid etching likewise effects a greater attack on Epon 812 resins (Fig. 10) than on Epon 828 resins, though the latter more clearly show nodular surfaces.

Figure 11 depicts a third type of etching which simulates environmental weathering. A 20/80 Epon 812 epoxy is cured within a silicone rubber block, then is placed within a Weatherometer (Atlas Sunshine (carbon-arc) Weath-



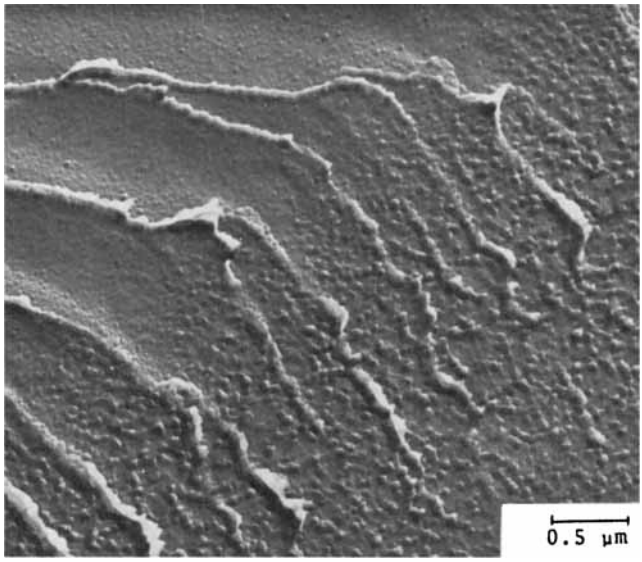
(a)



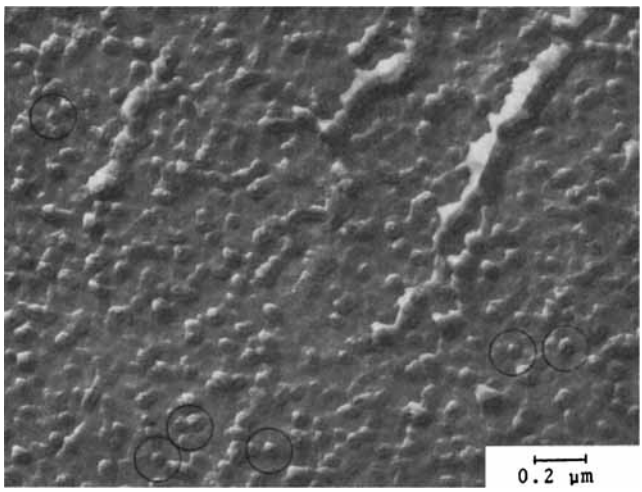
(b)

Fig. 3. (a) Free surface replica of 20/80 composition Epon 812 resin, cured 3 hr at 75°C + 24 hr at 150°C. (b) Enlargement of (a); "dimpled" nodules are circled.

erometer, Type XW) for 45 days, with each day effecting 6-hr exposure of the epoxy to a distilled water spray, followed by 18 hr of exposure to UV/visible radiation. Though the replica from this block has rather featureless regions (typical of silicone-contacted epoxy), the region depicted in Figure 11 indeed shows nodular character.



(a)



(b)

Fig. 4. (a) Free surface replica of 20/80 composition Epon 812 resin, cured 3 hr at 75°C + 24 hr at 150°C. (b) Enlargement of (a); "dimpled" nodules are circled.

Replicas of Epoxy Surfaces Contacted with Solid Substrates

Dramatic effects on nodule size are observed near interfaces with both Epon 812 and Epon 828 systems. Figures 12 and 13 are from an Epon 812–copper wire interface which was fractured at room temperature. Adhesion was extremely poor for these examples, and, from the micrographs, it appears

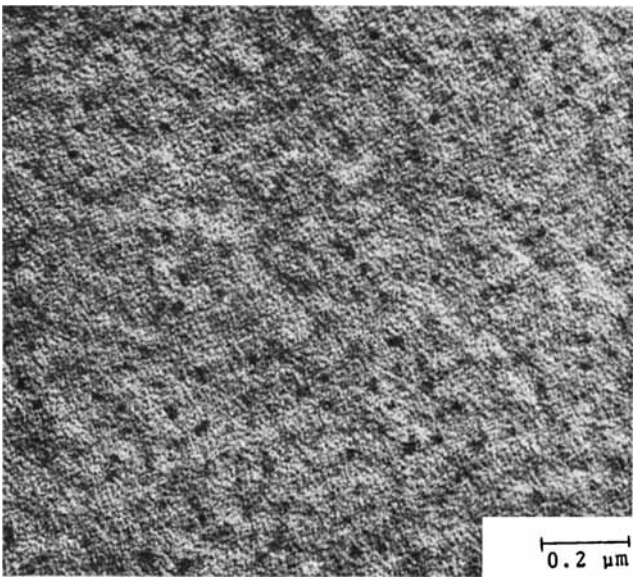


Fig. 5. Free surface replica of 100/0 composition Epon 812 resin, cured 2½ hr at 75°C.

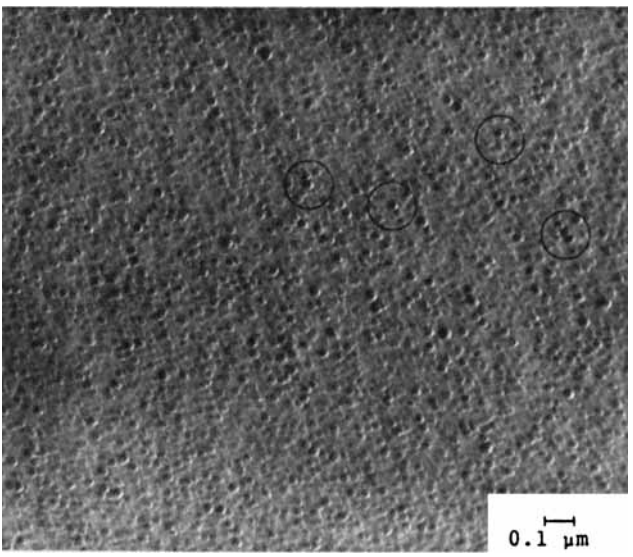


Fig. 6. Low-temperature fracture surface replica of Epon 828 resin, cured 2½ hr at 75°C. "Dimpled" nodules are circled.

that the contact between wire and resin during cure was not uniform. What is curious, however, is the appearance of very large-sized (~½ μ) supernodules, apparently composed of 10–60 nm nodules. The latter, small-sized nodules are also visible in these figures, and they predominate in Figures 14 and 15, illustrating both sides of another fractured epoxy–copper interface.

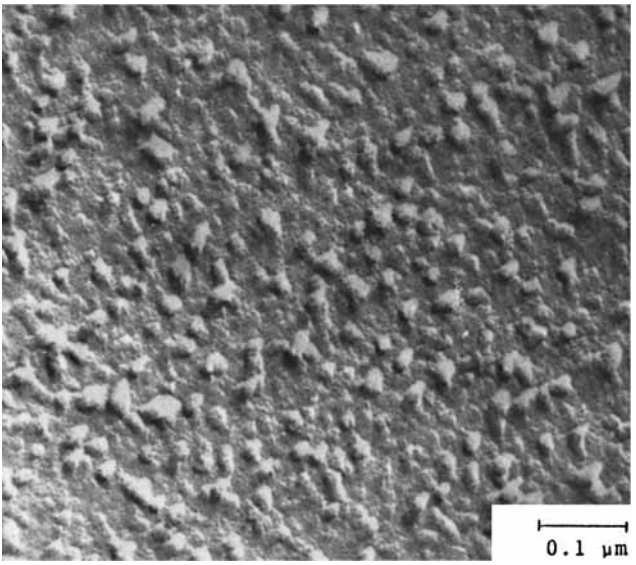


Fig. 7. Room-temperature fracture surface replica of 100/0 composition of Epon 812 resin, cured 4 hr at 80°C.

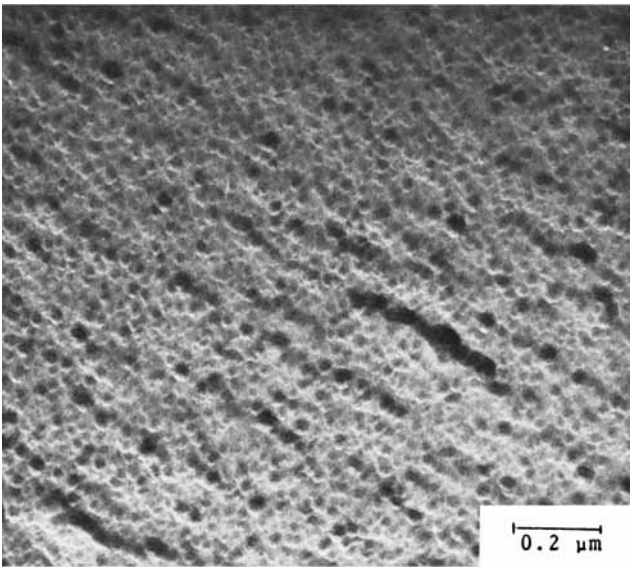


Fig. 8. Low-temperature fracture surface replica of Epon 828 resin, cured 2½ hr at 75°C.

Several epoxy–copper interfaces from systems of different preparation than in Figures 12 and 13 were much more difficult to separate (i.e., high copper–epoxy adhesion), yet their microscopy showed no significant difference in size, density of packing, or nature of supernodules. This preliminary and intuitively unsatisfying result may be related to the difficulties inherent in

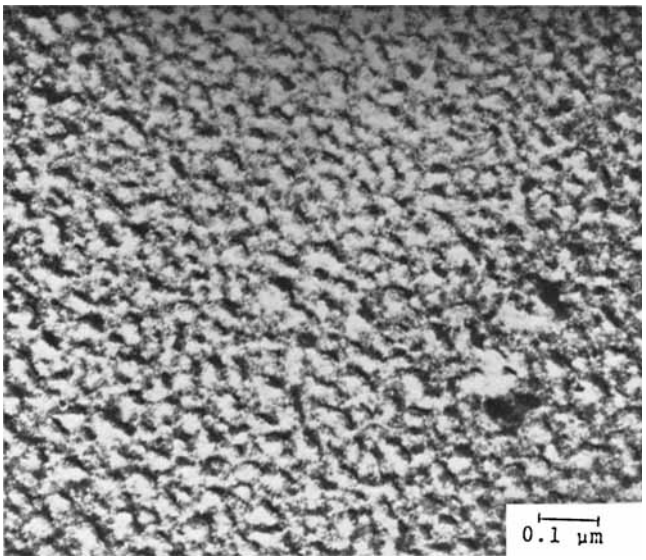


Fig. 9. Replica of Epon 828 resin, cured 4 hr at 80°C, fractured at room temperature, then etched by 60 min of immersion in boiling acetone.

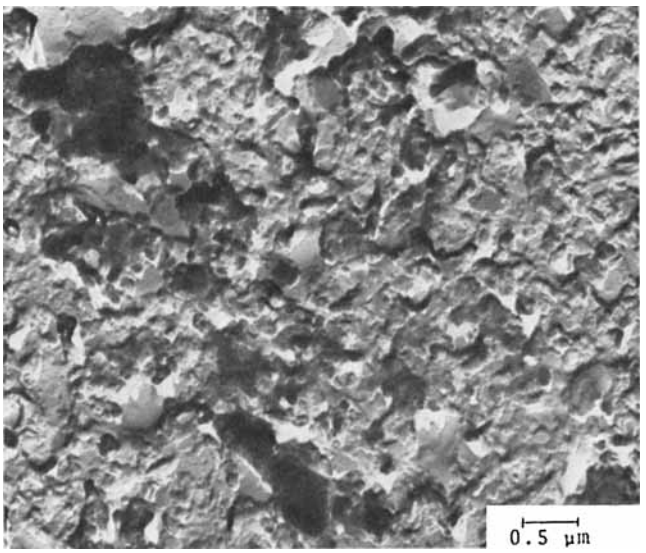


Fig. 10. Replica of 40/60 composition Epon 812, cured 3 hr at 70°C + 24 hr at 130°C, in contact with silicone rubber, then etched by 20 sec of immersion in 95–97% H_2SO_4, 49°C.

selective sampling of surfaces for replication, or to differences in locus of failure (interfacial vs. cohesive). It will be noted later that there likely was a layer of low molecular weight impurities on the copper wire before replication. Nonuniformities in this layer may relate to local variation in the strength of the epoxy "boundary layer," and to subsequent variations in locus

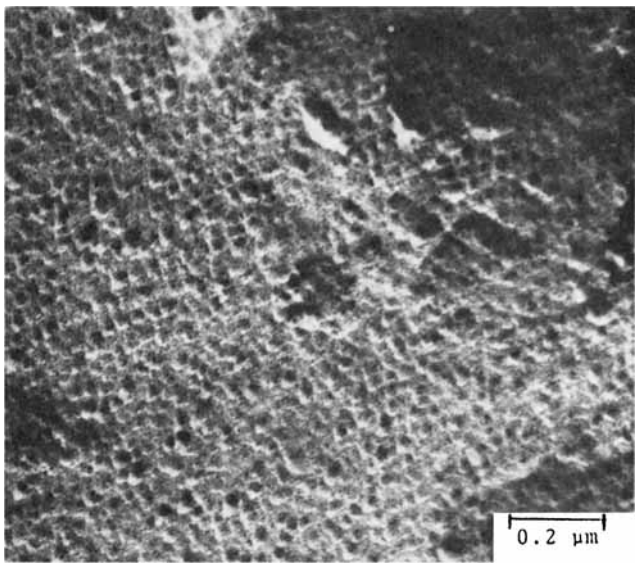


Fig. 11. Replica of silicone-rubber-contacted, weathered 20/80 composition Epon 812 resin, cured 2 hr at 70°C + 26 hr at 150°C.

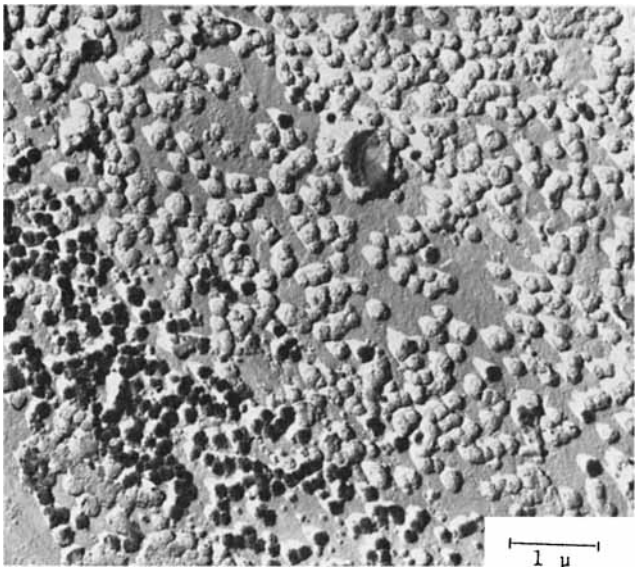


Fig. 12. Replica of epoxy side of copper wire/Epon 812 (100/0 composition) fractured interface, cured 4 hr at 80°C.

of joint failure along the wire. This may explain the absence of supernodules in Figures 14 and 15 as the result of joint failure far from the copper wire (i.e., cohesive epoxy fracture).

Silicone elastomer-contacted surfaces show smooth, almost nodule-free regions. However, evidence of nodules can be discerned by careful observation,

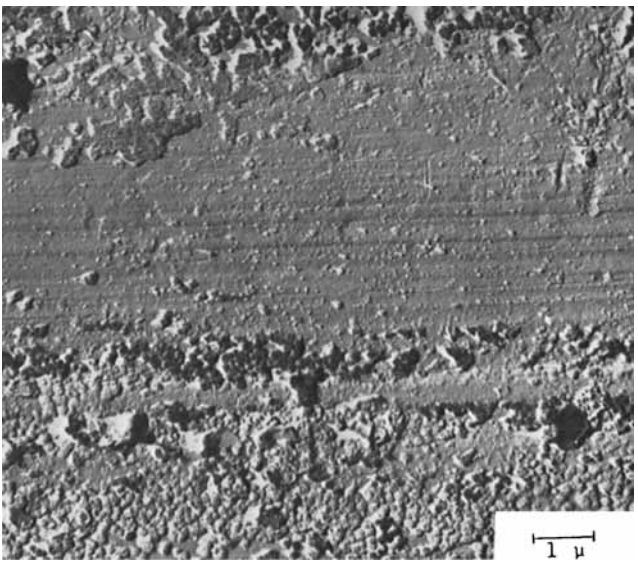


Fig. 13. Replica of epoxy side of copper wire/Epon 812 (100/0 composition) fractured interface, cured 4 hr at 80°C.

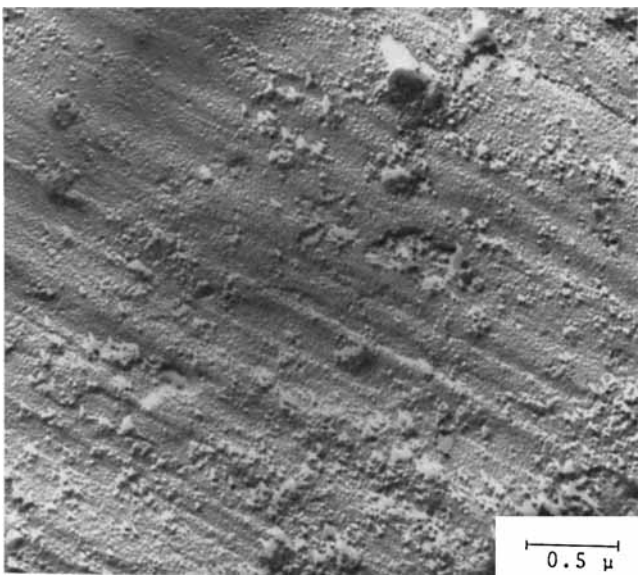


Fig. 14. Replica of copper wire side of copper wire/Epon 812 fractured interface, cured 4 hr at 80°C + 24 hr at 129°C.

and several silicone-contacted epoxy samples can be interpreted as displaying a thin superficial amorphous layer which obscures nodular morphology (see Fig. 16).

Electron microscopy of poly(tetrafluoroethylene)-contacted epoxy surfaces

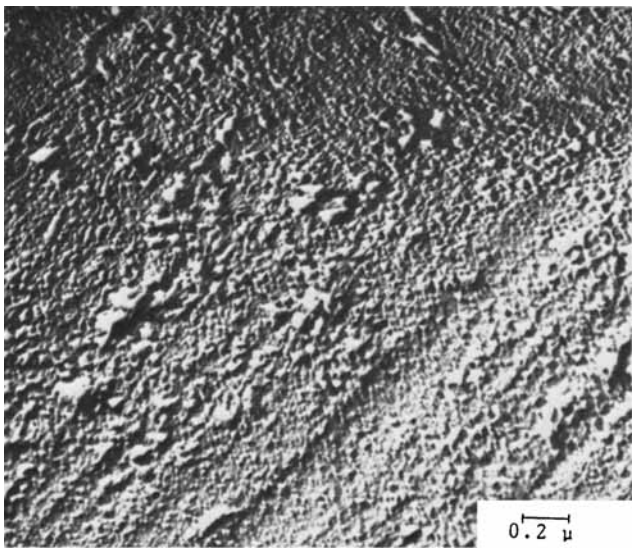


Fig. 15. Replica of epoxy side of copper wire/Epon 828 fractured interface, cured 4 hr at 80°C + 24 hr at 129°C.

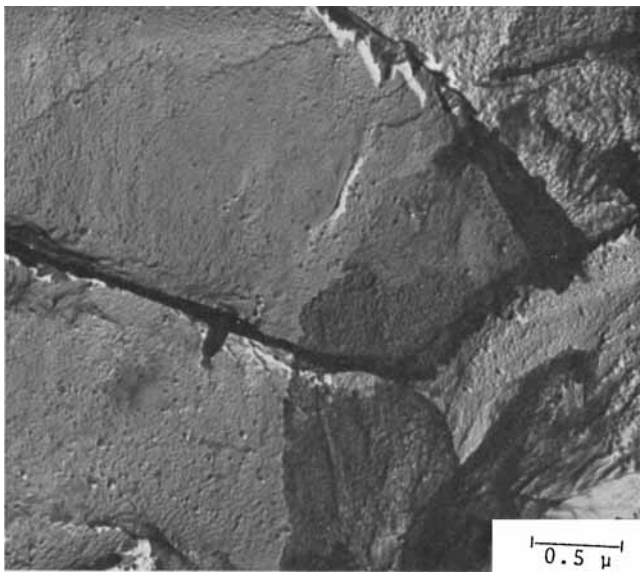


Fig. 16. Replica of silicone-rubber-contacted surface of 80/20 composition Epon 812 resin, cured 4 hr at 75°C + 24 hr at 133°C.

generally indicates nodules (see Fig. 17) appearing on rather smooth surfaces. Also discernible here are large nodules distributed randomly on the surface. It is possible that the resin only contacted the poly(tetrafluoroethylene) film at the points where supernodules appear. Low adhesion values were observed for these interfaces.

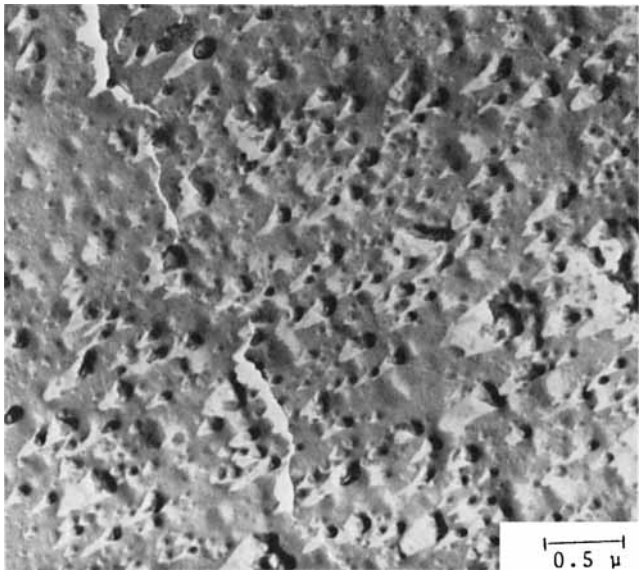


Fig. 17. Replica of epoxy side of PTFE/Epon 828 fractured interface, cured 4 hr at 80°C + 24 hr at 129°C.

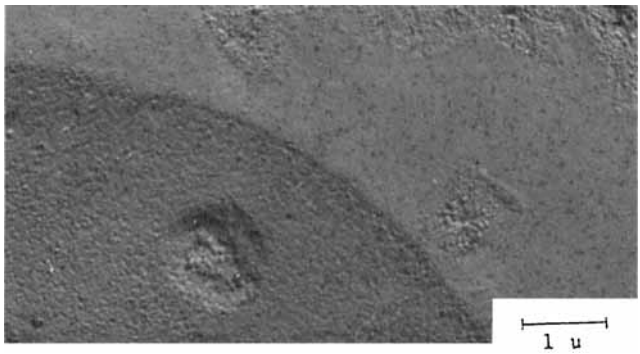


Fig. 18. Replica of scratched free surface of glass sphere-filled, 80/20 composition Epon 812 resin cured 4 hr at 75°C + 24 hr at 133°C.

DISCUSSION

From the electron micrographs, there is extensive evidence of a nodular character to nearly all the epoxy resin systems studied. The Epon 812 systems seem to show a less uniform size distribution of nodules than the Epon 828 systems. Also, the more rigid compositions of Epon 812 resins seem associated with a higher likelihood of formation of a network-like structure. The cause for this change in morphology is not well understood and appears to be difficult to control.

The size of the nodules appears to be strongly related to the presence of foreign substrates and inclusions. Low surface energy substrates cause little change in epoxy morphology adjacent to the surface, while other substrates show a strong influence on the epoxy morphology. We have observed a considerable increase in nodule size very near a glass–epoxy interface as shown in

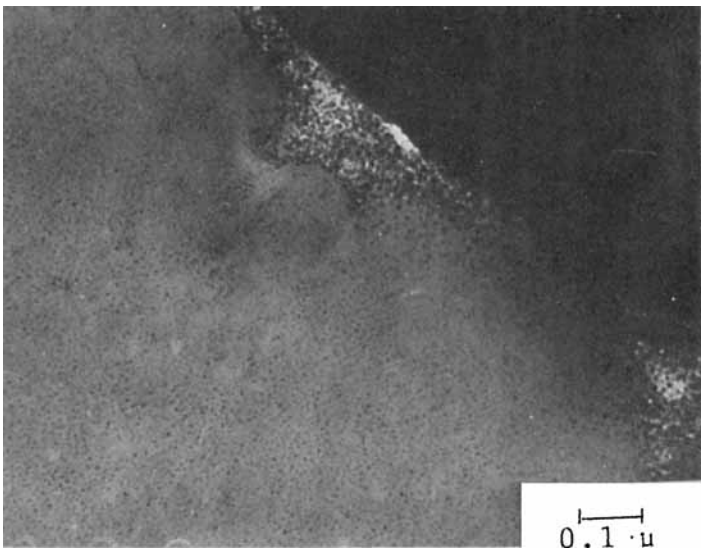


Fig. 19. Thin section of E-glass/Epon 828 interface, from J. L. Kardos.[7] Reproduced by permission of New York Academy of Sciences and Prof. J. L. Kardos.

Figure 18. Kardos[7] has observed similar results (see Fig. 19). Bascom[31] reviews the effect on the interfacial morphology of matrix thermosetting resins caused by adsorbed molecular species on embedded substrates, and several workers suspect a reduction in molecular mobility (and subsequent change in properties) within thermosets near rigid inclusions.[33–35]

The apparent logical link among all these findings is that nodule size increases with foreign dissolved material (plasticizer) as was observed by Kessenikh.[17] This could account for some of the above observations and is consistent with our findings from copper–epoxy interfaces.

Copper wire–epoxy interfaces were examined as an afterthought. The cleaning of the copper wire used in Figures 12 through 15 was inadequate to remove extruded plasticizer or other organic impurities deposited onto the wire by the electrical insulation originally covering it. Thus, the enormous structures seen in these samples are likely associated with diffusion of low molecular weights into the nodules. Consistent with this is the observation that no supernodules were observed at copper wire–epoxy interfaces when pains were subsequently taken to remove possible low molecular weight residues from the copper. (The increase in nodule size near glass inclusions is difficult to explain in terms of low molecular weight impurities, however, as a glance at Table III will indicate the small likelihood of substantial deposits of low molecular weight materials on the glass spheres.) Another possibility is that shrinkage stresses, which would be largest at interfaces, could play a significant role, as indicated in Figure 4 and as suggested by Manson and Chiu.[30]

Other curious aspects of our studies of bulk epoxy include (1) the lack of indication of nodules in ultramicrotomed epoxy sections,* and (2) the lack of

* Kardos has seen structure in microtomed epoxy–glass systems[7] of the same general size as our nodules (see Fig. 19). However, this structure does not appear nodular in his micrograph.

small-angle x-ray scattering. Both of these observations indicate that the electron density of the nodules is essentially uniform throughout the bulk. However, the latter statement is not inconsistent with theoretical suggestion that nodules are regions of higher crosslink density,[8] for an increase in crosslink density may only slightly affect the local electron density.

CONCLUSIONS

1. There is definite nodular formation throughout the epoxy resins studied.
2. The nodules have sizes ranging from 100 to 600 Å (10–60 nm).
3. At times, the nodules appear to align and form networks either at interfaces or in the bulk.
4. Nodules are observed to agglomerate into larger supernodules of up to ½ μ in size.
5. Teflon and silicone-rubber contact with epoxy seem to inhibit the appearance of nodules, while copper and glass surfaces induce large supernodules or increases in packing density of small nodules.
6. No consistent relation has been found among composition or cure, nodule size, and nodule density.
7. Slightly cured, soft epoxy resins show what may be interpreted as nodule precursors.
8. Some individual nodules surprisingly show a very subtle ridge-like fine structure on both fracture and free surfaces.

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