

Scanning electron microscope study of a filled food-contact epoxy resin

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A scanning electron microscope (SEM) study (magnifications 50 to 35 000 times) of the microstructure of a food-contact epoxy resin composed of epichlorohydrin glycol, bisphenol-A and methylenedianiline was undertaken in order to predict its reaction to food fluids. Observations revealed a smooth, homogeneous surface zone and a heterogeneous interior zone, the multi-laminar aspect of which appeared to be influenced by the concentration and particle size of the filler but not by the nature of the resin support. No differences between samples as a function of their curing temperature were observed under SEM. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Epoxy resins are increasingly being used for synthetic linings of food storage vats and water towers to ensure water-tightness, and more recently to line the inside of drinking-water pipes as part of their renovation.

Epoxy resins are based on prepolymers formed by the addition of epichlorohydrin glycol to a polyalcohol, most often bisphenol-A (BPA). The prepolymer is linear, with hydroxyl groups along the chain and terminal epoxide groups^{1,2}. Crosslinking is obtained by the addition of a hardener reacting with both groups. The most-frequently used hardeners are aliphatic polyamines, aromatic polyamines and acid anhydrides³. The end product is a three-dimensional, thermosetting resin. In order to improve the physical and mechanical properties or to facilitate utilization of the epoxy resins, additives such as reactive thinners, flexibilizers, plasticizers, colourants, solvents and fillers are incorporated.

For food-contact epoxy resins, epichlorohydrin glycol, BPA, bisphenol-F and primary aromatic and aliphatic amines are used. Inorganic fillers are incorporated at concentrations of the order of 35% w/w of the total mixture. The present tendency is to avoid addition of solvents since they are volatile, mobile (risk of migration), odorous and toxic.

Like all food-contact materials, epoxy resins are regulated. In Europe, they must conform to the food-contact suitability criteria described in the Council Directives 89/109/EU⁴ and 90/128/EU⁵. In particular, they must not release substances into the foodstuff fluids. The migration of compounds into food is a well-established phenomenon^{6–12} and the degree of migration can be tested.

Migration is related to the structure of the epoxy resin¹³. Within the three-dimensional network, epoxy resins can present several typical faults that form during crosslinking^{14,15}:

- 1) more or less ordered, high crosslinked zones;
- 2) slightly crosslinked zones with a looser structure; and
- 3) micro-spaces containing non-linked molecules (free components, adsorbed compounds).

Under these conditions, the penetration of fluids into the resin and the release of molecules not linked to the resin structure would be favoured.

Therefore, with a view to being able to predict the behaviour of epoxy resins towards food fluids, we undertook a study of their microstructure using electron microscopy. As far as we know, few articles have been published on the study of epoxy resins using this method. We were able to refer to two articles by Mijovic^{16,17}, who used transmission electron microscopy to study epoxy resins composed of epichlorohydrin glycol, BPA and diethylenetriamine, without filler. For our samples, which were opaque to the incident electron beam due to their thickness and the presence of filler, the use of transmission electron microscopy would have required microtome cutting of frozen samples. We preferred instead to use scanning electron microscopy (SEM) for which sample preparation causes minimal modifications to the structure. This communication presents the results of this study.

Experimental

Epoxy resin samples. A food-contact epoxy resin was provided by the manufacturer. The stated composition was epichlorohydrin glycol and BPA, with methylenedianiline (MDA) as hardener.

The resin was applied to a support by the manufacturer in stoichiometric proportions of prepolymer and hardener. Different samples in the form of rectangular sheets 30 cm² area × 900 ± 100 µm thick were prepared for the study of:

- 1) microstructure—inorganic filler: mixture of iron oxide (6% w/w) and barium sulfate (27% w/w). Samples mounted on stainless steel, cured for 7 days at 20°C, stored for 1 month at 4°C;

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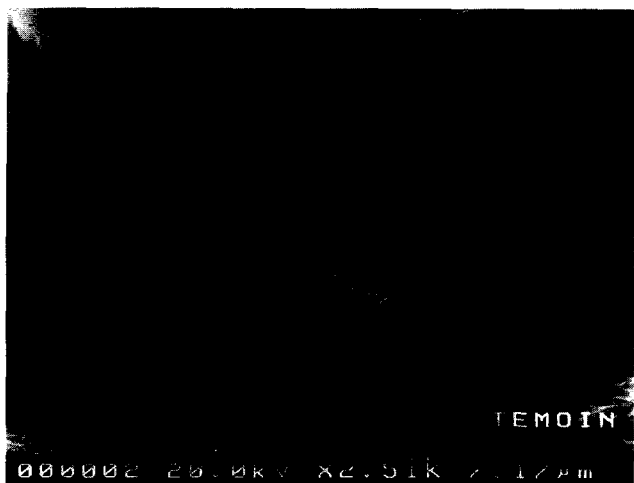


Figure 1 SEM image of the surface zone (a) and the fracture zone (b) of a sample containing filler ($\times 2500$)

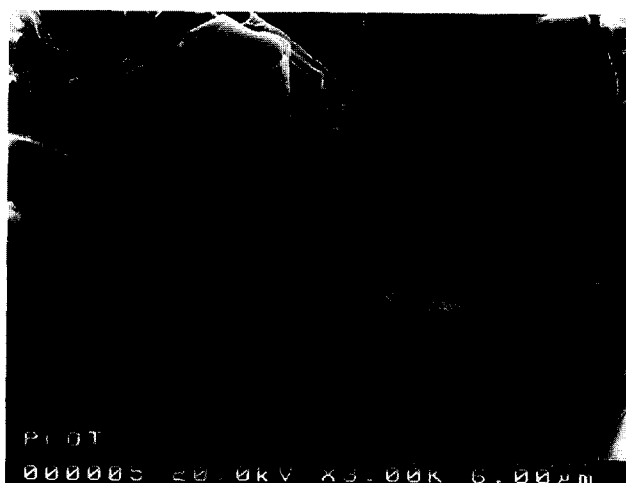


Figure 3 SEM image of the fracture surface of a sample containing filler ($\times 3000$)



Figure 2 SEM image of the fracture surface of a sample containing filler ($\times 100$)

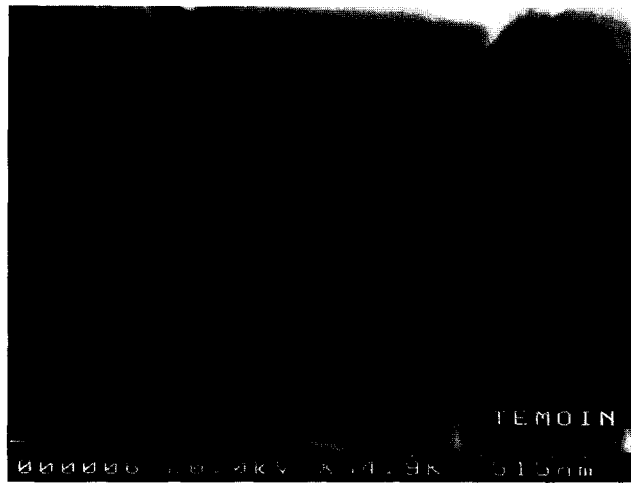


Figure 4 SEM image of the fracture surface of a sample containing filler ($\times 35000$)

- 2) influence of filler concentrations—inorganic filler: 0, 10, 24.5 or 44.5% w/w (maximum possible) of iron oxide. Samples mounted on stainless steel, cured for 7 days at 20°C, stored for 1 month at 4°C;
- 3) influence of filler particle size—organic filler: 35% w/w poly(vinyl chloride) (PVC) as 20, 100 or 800 μm diameter spheres. Samples mounted on stainless steel, cured for 7 days at 20°C, stored for 1 month at 4°C;
- 4) influence of support—no filler. Samples mounted on different supports: aluminium, stainless steel, glass or wood, cured for 7 days at 20°C, stored for 1 month at 4°C;
- 5) influence of curing temperature—inorganic filler: mixture of silica (26% w/w) and titanium oxide (7% w/w). Samples mounted on stainless steel, cured for 7 days at 5, 20, 50 or 90°C, stored for 1 month at 4°C.

Preparation of samples. The samples were removed from their supports, then broken up manually into pieces approximately 20 mm² in size. These fragments allowed microscopic examination of the surface and the fracture.

Scanning electron microscopy. The samples were examined under Hitachi 5400 scanning electron

microscope with an acceleration voltage of 20 kV, allowing magnifications of up to $\times 35000$ for the samples studied. Prior coating of the samples with a 10–15 nm layer of gold–palladium was performed using a Polaron SC500 system.

Results and discussion

Microstructure. SEM revealed two zones:

- 1) a smooth and homogeneous surface zone. Observation at $\times 2500$ (Figure 1) revealed a thin surface with a heterogeneous structure visible underneath (small clear spots); and
- 2) a heterogeneous fracture zone. At $\times 100$ magnification it appeared granular, resembling a polymer filter (Figure 2). At greater magnification, it appeared multi-laminar. This structure favours the existence of free spaces (Figures 3 and 4). We also noted the presence of bubbles, imprisoned during application of the resin on the support (Figures 2 and 5). The interior of these bubbles resembled the surface zone, suggesting a surface phenomenon favoured by air or by rapid cooling.

The homogeneous surface zone could form a barrier to

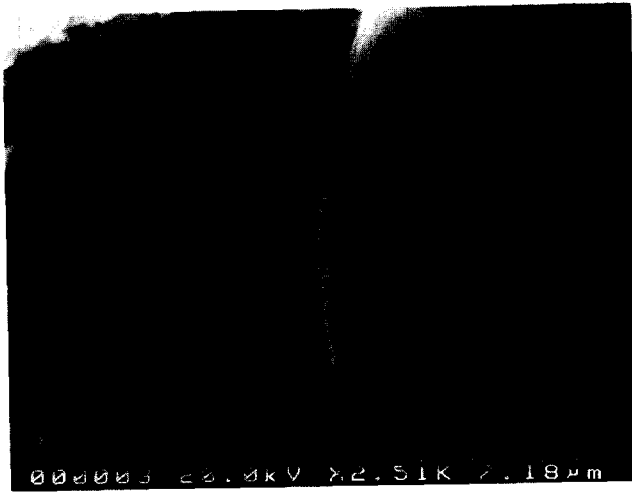


Figure 5 SEM image of a bubble in the fracture surface of a sample containing filler ($\times 2500$)

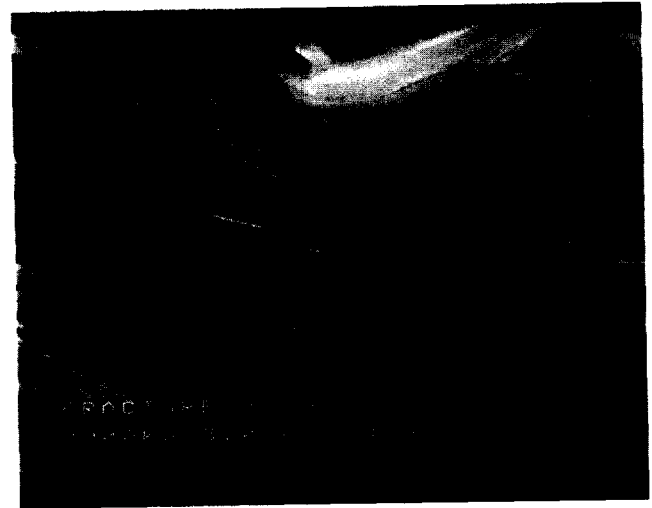


Fig 8 SEM image of the fracture surface of a sample containing 24.5% filler ($\times 3500$)

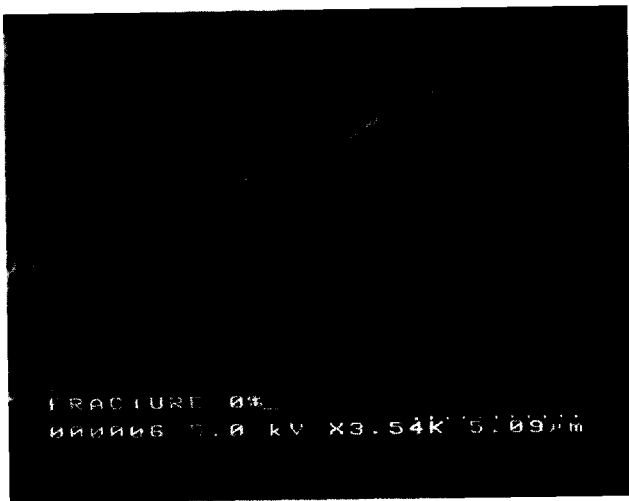


Figure 6 SEM image of the fracture surface of a sample without filler ($\times 3500$)

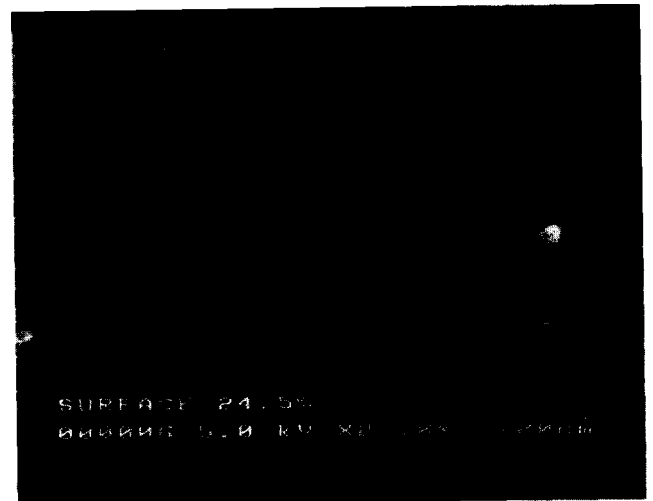


Figure 9 SEM image of the surface zone of a sample containing 24.5% filler ($\times 25\ 000$)

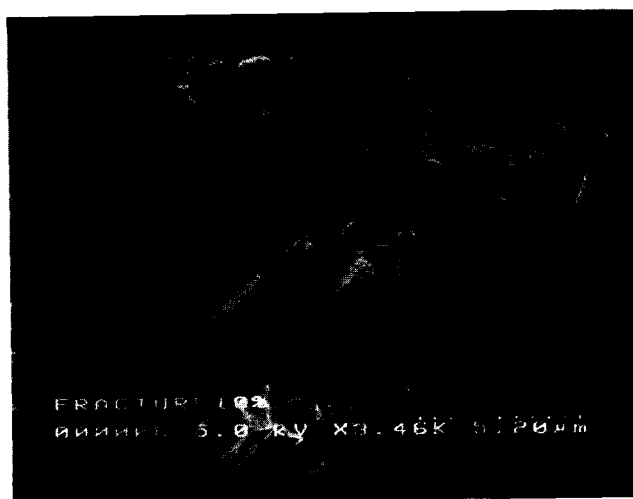


Figure 7 SEM image of the fracture surface of a sample containing 10% filler ($\times 3500$)

exchange between the resin and the food fluids. We are currently trying to evaluate this barrier effect. On the other hand, in the heterogeneous zone, the free spaces would facilitate penetration of food fluids, thereby

increasing the surface of exchange within the resin. In addition, they could house bacteria.

Influence of filler concentration. Using transmission electron microscopy, Mijovic^{16,17} reported on the morphological heterogeneity of the epoxy resin studied (without filler). This heterogeneity, characterized by the presence of nodules, was observed only at a magnification of $\times 135\ 000$. At lower magnifications, the resin appeared homogeneous. In our case, the heterogeneous structure, observed at a magnification of $\times 100$, could have been due to the presence of filler.

The following results concern the study carried out on samples containing increasing percentages of inorganic filler: 0, 10, 24.5 or 44.5% (iron oxide). The fracture zone was studied at $\times 50$, $\times 100$, $\times 1000$, $\times 3500$ and $\times 25\ 000$ magnification. Without inorganic filler it appeared completely homogeneous (Figure 6). The multi-laminar structure appeared at a filler concentration of 10% and intensified proportionally at higher concentrations (Figures 7 and 8). The surface zone was studied at the same magnifications without being able to detect any significant differences between the samples. At $\times 25\ 000$

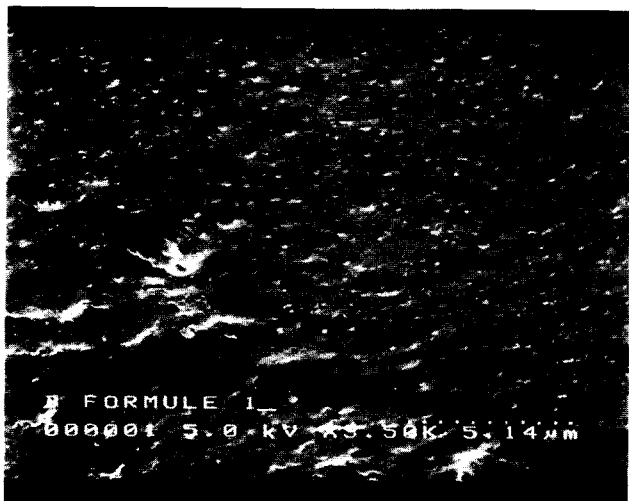


Figure 10 SEM image of the fracture surface of a sample incorporating 20 μm diameter PVC spheres (×3500)

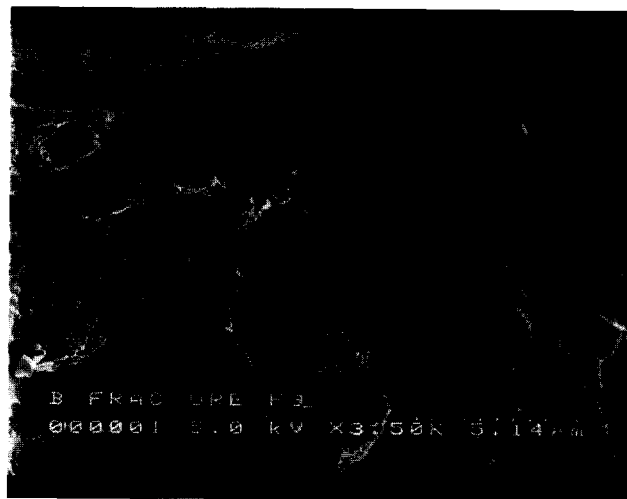


Figure 12 SEM image of the fracture surface of a sample incorporating 800 μm diameter PVC spheres (×3500)

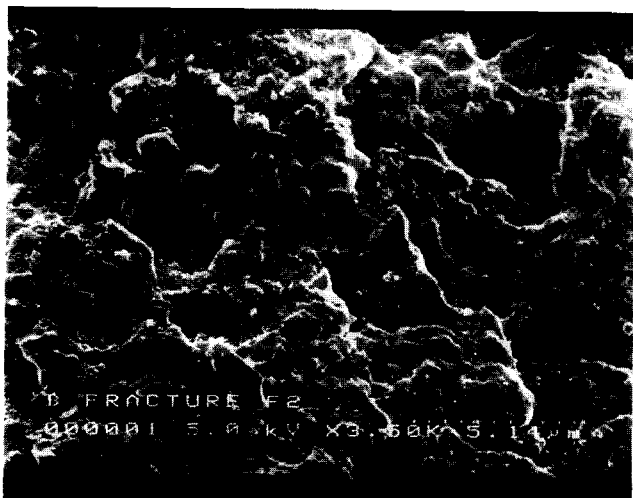


Figure 11 SEM image of the fracture surface of a sample incorporating 100 μm diameter PVC spheres (×3500)

magnification, all surface zones showed microcracks around 9 nm across (Figure 9).

Influence of filler particle size. Samples were prepared incorporating graded PVC spheres of 20, 100 or 800 μm diameter. The fracture zone was studied at ×100, ×1000, ×3500 and ×25 000 magnification. The heterogeneous structure of the fracture surface was visible only in the samples containing 100 or 800 μm diameter spheres (Figures 10, 11 and 12). The PVC spheres appeared coated with the epoxy resin and occasionally aggregated. At ×25 000 magnification, no differences between the surface zone of the samples were observed.

From these results, it seems that homogeneous resin structure is obtained with well-dispersed filler of small particle size. We are currently studying the influence of the nature of the filler.

Influence of the support material. It was also necessary to verify that the heterogeneous structure observed in the fracture zone was not the result of internal tension from retraction of the resin (0.1–0.5%¹⁴). The support can affect this via the phenomenon of adherence or

thermal conductivity¹⁸. Four different supports were therefore tested to evaluate their influence on the microstructure of a sample without filler.

At ×100, ×1000, ×3500 and ×25 000 magnification no differences were observed between the samples concerning the surface zones, the fracture zones or the zones of resin/support contact.

Influence of curing temperature. The curing temperature can influence the quality of crosslinking, as indicated by the glass transition temperatures¹⁹. However, at ×100, ×1000, ×3500 and ×25 000, no significant differences were observed between the surface zones or fracture zones of samples cured at 5, 20, 50 and 90°C.

Conclusion

Scanning electron microscopy of an epoxy resin revealed:

- 1) a smooth, uniform surface zone, which appears to form a mechanical barrier to resin–contact medium exchange. This seems to be confirmed by solvent penetration tests currently in progress;
- 2) an interior, heterogeneous zone, with a multi-laminar structure apparently related to the presence of filler. By favouring the penetration of fluids, this structure would accelerate the phenomenon of migration and could also constitute a favourable site for the attachment and development of bacteria. For these reasons, we are continuing our studies to evaluate the chemical, toxicological and bacteriological risks that this microstructure might pose.

The effect of fillers on the internal structure can be explained by one or more of the following phenomena: coating of the fillers by the resin, occasional aggregation of the fillers, and differential dilation phenomena caused by heat flow from the network during curing differing according to the medium traversed (resin or filler). The smooth and homogeneous aspect of the surface zone could be the result of a rapid and uniform cooling with limited differential dilation.

The demonstration by SEM of the importance of the filler should enable an evolution in the formulation of epoxy resin-based coatings with a view to ensure better

food security. With the same aim, SEM could be used to evaluate the attachment of the epoxy resin to the support (observation of the resin/support interface).

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