Preparation of Latent Curing Agent for Epoxy Resin by Encapsulation Technology

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Abstract. The microcapsule-type curing agents DDM-PMMA and IZ-PU were prepared by solvent evaporation method and interfacial polymerization method, respectively. The surface morphology of the two microcapsules was characterized by SEM. The coating efficiency and latency were analyzed by DSC analysis of the one-component adhesive composed of the microcapsule-type curing agent and epoxy resin. Two encapsulation methods were compared in terms of hydrophilicity or lipophilicity of the core material, formation time of the microcapsules, coating efficiency and latency of the microcapsules.

1. Introduction

Epoxy resins are widely used as electrical materials, coating materials, adhesives, aerospace materials and composite materials because of their high adhesion strength, excellent chemical resistance and thermal insulation, etc. [1] The curing agents for epoxy resin, such as amines and anhydrides, are commonly used with high curing activity [2]. However, the high activity curing agent has a short storage period and cannot be used in one-component adhesive or prepreg. The latent curing agents with low curing activity at room temperature, such as dicyanamide and dianodiphenyl sulfone, can be used in one-component epoxy system, but the reaction temperature required for the curing reaction is often too high to be widely used. [3] In comparison, the microencapsulation of the commonly used highly active curing agent is a feasible and economic method. The curing agent is embedded in a wall material so that the curing agent is separated from the epoxy resin. Thus, the curing reaction of epoxy resin can be controlled by the breakage or permeability of the wall material [4, 5].

Since the microencapsulation technology was reported in the 1930s, several methods for preparing microcapsules have been described, including interfacial polymerization, in-situ polymerization, spray drying, and solvent evaporation, etc. The study on microcapsule-type curing agent has attracted much attention. The spray drying process is simple, but the microcapsules obtained are a mixture of the core material and the wall material, so the active ingredients cannot be completely embedded. Therefore, the spray drying method is not suitable for the preparation of microcapsule-type curing agent for epoxy resin. Interfacial polymerization, and solvent evaporation are common methods for preparing microcapsule-type curing agent. In our previous study [6, 7], a microcapsule-type latent curing agent was prepared by solvent evaporation method with dianodiphenylmethane (DDM) as the core material and PMMA as the wall material. We also prepared a microcapsule-type latent curing agent with imidazole (IZ) as the core material by interfacial polymerization of triethanolamine (TEOA) and diphenylmethane diisocyanate (MDI). In this paper, the two encapsulation processes and microcapsule-type latent curing agents obtained were analyzed.
2. Results and Discussion

2.1. Encapsulation of Hydrophilic or Lipophilic Core Material

The encapsulation process for solvent evaporation method is relatively simple to control, and many studies have been reported [8, 9]. Encapsulation of the lipophilic core material (e.g., DDM) can be carried out by solvent evaporation. DCM is a commonly used volatile solvent for precipitating wall materials. The stability of the emulsion has an important influence on the core/shell structure of the microcapsules. The microcapsules formed in stable emulsions generally have a smooth surface and a regular spherical appearance, indicating that the oil phase droplets remain stable before the solidification of the microcapsules. However, the precipitation of wall materials depends on the evaporation process of volatile solvent in oil-in-water emulsion or water-in-oil-in-water emulsion. The long time for evaporation makes the diffusion of lipophilic DDM from the oil phase to the aqueous phase non-negligible, resulting in a lower core content. Due to the relatively large variety of hydrophilic core material (e.g., amines curing agent), interfacial polymerization techniques using water-in-oil emulsions may be more applicable for encapsulation.

Figure 1. SEM images of DDM-PMMA and IZ-PU microcapsules
(a) DDM-PMMA microcapsules; (b) IZ-PU microcapsules

Imidazole is a commonly used curing agent with high activity. The microencapsulation of imidazole and its derivatives has been reported. Dong et al. [10] and Min et al. [11] prepared the microcapsule of 2-methyl imidazole as the core material by spray drying method. Ham et al. also studied the preparation of microcapsule curing agent for polymer-enclosed imidazole by solvent evaporation [12, 13]. The hydrophilic nature of imidazole makes it more suitable for dispersion in water-in-oil emulsions. Moreover, the interfacial polymerization technique requires relatively short time for the solidification of the microcapsules. However, compared with aqueous phase, the viscous oil phase results in a certain degree of adhesion of the formed microcapsules, but this does not affect its dispersion in epoxy resin. And the residual IZ dispersed on the surface of the adhered microcapsules is difficult to remove with water and ethanol.

Figure 1(a) shows the SEM images of the DDM-PMMA microcapsules. It shows that the DDM-PMMA microcapsules prepared by solvent evaporation method has a smooth surface and a regular spherical appearance. Figure 1(b) shows the SEM images of the IZ-PU microcapsules prepared by interfacial polymerization. It shows that the IZ-PU microcapsules prepared by interfacial polymerization has a relatively small particle size.

2.2. Curing Behavior of the Microcapsule-type Curing Agent for Epoxy Resin

Thermal curing behavior of the DDM-PMMA microcapsules to epoxy resin was examined by DSC under argon atmosphere. The curing exothermic values of DDM-PMMA/EP adhesives with different DDM-PMMA contents were normalized to the values of heat flow per gram of epoxy resin. Figure 2 shows the relationship between the curing exothermic values per gram of epoxy resin and the
DDM-PMMA content. The inflection point of the curve corresponds to the proper DDM-PMMA content of the DDM-PMMA/EP adhesive, indicating complete curing of epoxy resin.

The curing exothermic values of the DDM-PMMA/EP adhesives with the same content of DDM-PMMA microcapsules prepared under different conditions were compared to optimize the preparation parameters. Figure 3 shows the curing exothermic values of the DDM-PMMA/EP adhesives with DDM-PMMA microcapsules as curing agent. The DDM-PMMA microcapsules corresponding to different preparation processes are labeled DPM1, DPM2, DPM3 and DPM4, respectively. The higher the curing exothermic value, the higher the core content of the microcapsule curing agent.

The DSC curves of IZ-PU/EP adhesives are shown in Figure 4. The DSC curve for the original IZ-PU/EP adhesive was marked as 0day, and IZ-PU/EP adhesives after sealed storage for 15days and 30days, were marked as 15d and 30d.

**Figure 2.** The curing exothermic values of DDM-PMMA/EP adhesive vs. DDM-PMMA content

**Figure 3.** The curing exothermic values of DDM-PMMA/EP adhesive with different DDM-PMMA microcapsules
Figure 4. DSC curves of IZ-PU/EP adhesives
(a)-(d) corresponding to the IZ-PU microcapsules of IPM1-IPM4

As shown in Figure 4, the curing exothermic values of 15d and 30d samples are lower than the value of original IZ-PU/EP adhesive. The reduced value is due to the curing reaction of IZ-PU and EP during the storage period. The curing degree of the sample can be estimated by the ratio of the reduced value of the corresponding sample to the original value. The curing degrees of IZ-PU/EP adhesive corresponding to IPM1, IPM2, IPM3 and IPM4 after sealed storage for 15days and 30days are shown in Figure 5.

As discussed above, the residual IZ dispersed on the surface of the adhered microcapsules is difficult to remove by washing. The residual IZ is in direct contact with the epoxy resin, causing a certain degree of curing of the adhesive during storage. However, the one-component adhesive with a curing degree lower than 10% has little effect on the viscosity and applicability of the adhesive.

The original value of curing exotherm and the curing degree of the stored IZ-PU/EP adhesive at room temperature are the main evaluation criteria for evaluating the coating efficiency and latency of IZ-PU microcapsule. As shown in Figure 5, sample IMP2 has a relative low curing degree value after sealed storage at room temperature for 30days, compared with the other three samples. It can be inferred that the shell-core structure of corresponding IZ-PU microcapsule may have the most efficient coating. As the initial curing exothermic value corresponding to sample IMP4 is the highest among the four samples, that is to say, the core content of corresponding IZ-PU microcapsule is higher than the others. Therefore, the coating efficiency and latency of IMP4 might be better than IMP2.
Figure 5. The curing degrees of IZ-PU/EP adhesives after sealed storage for 15 days and 30 days

3. Conclusions

Solvent evaporation method and interfacial polymerization method were used to prepare the microcapsule-type curing agents DDM-PMMA and IZ-PU, respectively. The application of different encapsulation processes depends on the hydrophilicity or lipophilicity of the core materials. In terms of the latent curing agent suitable for epoxy resin, according to the above results, interfacial polymerization method may be more efficient than solvent evaporation method.

Summarized as follows:

1. Due to the high reactivity of diisocyanate, the interfacial polymerization is rapid, and the shell of the microcapsules is formed quickly, so the diffusion of the core material into the outer phase is much less, compared with solvent evaporation method.

2. Since hydrophilic curing agents for epoxy resin (e.g., amines) are more common than lipophilic curing agents, interfacial polymerization techniques using water-in-oil emulsions may be more applicable for encapsulation.

3. Due to the higher curing efficiency of IZ and the higher core content of IZ-PU microcapsules, the mass fraction of IZ-PU microcapsules required to cure epoxy resin is much lower than that of DDM-PMMA microcapsules. Therefore, the wall material introduced by the microcapsules has a relatively small influence on the mechanical strength of the cured resin.

4. References

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