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Core-shell particles with an acrylate polyurethane core as tougheners for epoxy resins

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Epoxy resins form the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fibre composites. They exhibit high strength, stiffness and temperature resistance, but their cured resins have one drawback: they are brittle and have poor crack resistance. One of the most common approaches of improving the toughness of epoxy resins is through incorporation of dispersed reactive liquid rubbers [1–4]. The problem encountered with toughened epoxy resins with reactive liquid rubbers is incomplete phase separation; some of the rubber can remain dissolved in the epoxy phase, leading to a reduction in the glass-transition temperature of the cured resin [5]. Although reactive liquid rubbers remain popular for toughening epoxy resins, there has been growing interest in the use of preformed toughening particles because they have the potential to avoid some of the problems of reactive liquid rubbers [6, 7].

Dispersing reactive liquid polyurethane rubbers in epoxy resin is a popular approach to improve the toughness of epoxy resins [8–10]. But investigations on preformed polyurethane toughening particles have not been reported before. In this paper we have prepared a new type of core-shell polyurethane latex particle in which acrylate polyurethane with a double bond was copolymerized with butyl acrylate to be the core, then methyl methacrylate polymerized around the core to be the shell in order to avoid the latex forming a membrane during separation of latex particles. The core-shell particles have been used as a modifier for epoxy resins and had a beneficial effect on toughening epoxy resins.

In this work, acrylate polyurethane was prepared by a three-stage reaction under nitrogen atmosphere. In the first stage, a prepolymer of polyurethane was synthesized with Toluene-2,4-diisocyanate (TDI) (69.8 g, 0.4 mol) and polyether polyols N-210 (200 g, $\bar{M}_n = 1000$, $\bar{f} = 2$) at 75 °C for 2 hrs and at 80 °C for another one hour with 5 drops of Dibutyltin dilaurate as catalyst. In the second stage, the prepolymer chain was extended with 2,2-Bis (hydroxymethyl) propic acid (DMPA) (13.41 g, 0.1 mol) and some acetone was used to reduce the viscosity of the solution. In the third stage the prepolymer was capped with 2-hydroxyethyl methylacrylate (HEMA) (26.0 g, 0.2 mol) at 56 °C for 6 hrs. The change of —CNO group around 2300 cm^{-1} in each stage can be seen from curves in Fig. 1. It can be seen from Fig. 1 that —CNO was nearly exhausted in the third stage.

The core-shell latex was prepared by two-stage emulsion polymerization at 70 °C. In the first stage, seed emulsion was prepared by free emulsion polymerization. The acrylate polyurethane was emulsified with ammonia, then reacted with butyl acrylate (BA) for 6 hrs in which $K_2S_2O_8$ and $NaHSO_3$ were used as initiators. In the second stage, the seed emulsion was reacted with methyl methacrylate (MMA) in which sodium dodecyl sulphate was used as emulsifier and tripropylence glycol diacrylate (TPGDA) was used as cross-linking agent. MMA was added continuously for 2.5 hrs then polymerized for about 3 hrs. The structure of core-shell latex stained with phosphotungstic acid was shown in TEM photograph (Fig. 2).

The core-shell latex was coagulated with NaCl aqueous solution and frozen for 48 hrs. After being filtered, washed with distilled water several times, dried at room temperature for 48 hrs and ground to a powder, the finial powder was dispersed into epoxy resins (Shell Epon 828) with a three-roll miller and cured with the

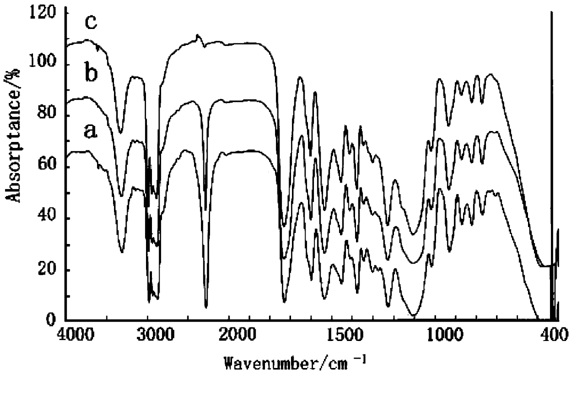

Figure 1 IR spectra of the products for the three-stage reaction.

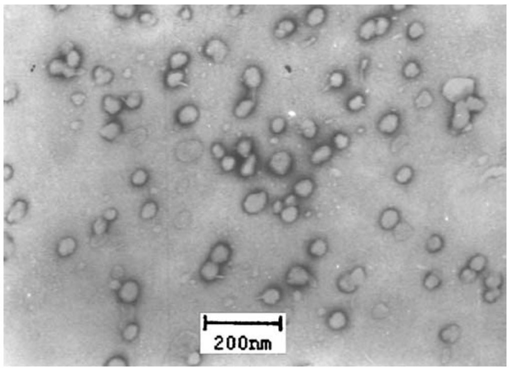

Figure 2 TEM photograph of core-shell latex.

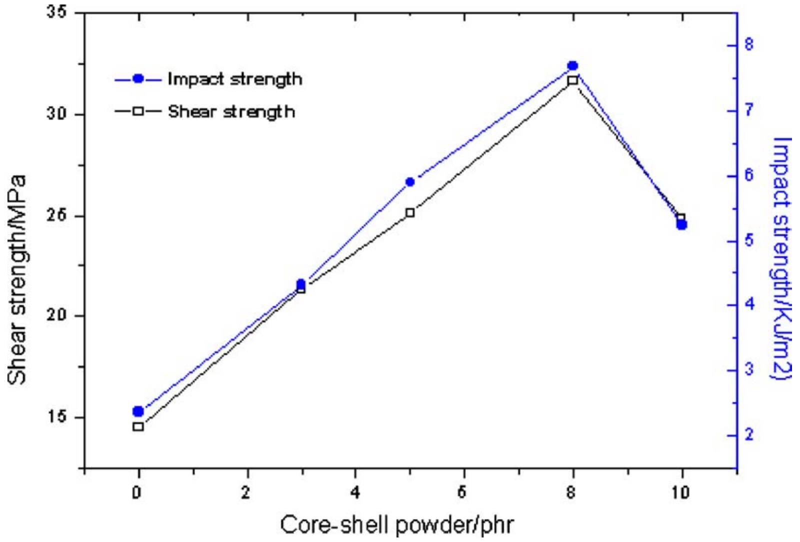

Figure 3 Mechanical properties of epoxy resins and its blends with core-shell powder.

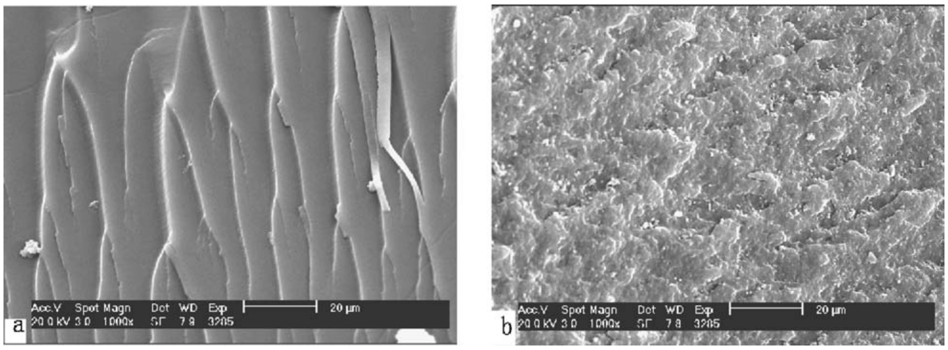

Figure 4 SEM photomicrographs for the fracture surfaces of modified epoxy having core-shell particles: (a) 0 and (b) 8 phr.

self-prepared curing agent. Shear strength and impact strength were measured after seven days. The toughening effects on mechanical behavior can be seen in Fig. 3.

From Fig. 3, it is clear that as the contents of core-shell powder increased, shear strength and impact strength of the epoxy adhesive increased gradually and reached the peak at 8 phr. At the peak, its shear strength and impact strength are 2.2 and 3.3 times that of unmodified epoxy adhesive, respectively.

The impact behavior of the modified epoxy resins can be explained in terms of the morphology observed by SEM. The SEM microphotographs for unmodified epoxy and 8 phr core-shell particles are shown in Fig. 4. From the photograph of Fig. 4a, we can see the smooth glassy fractured surface with cracks in different planes in the case of the unmodified epoxy. This indicates a brittle fracture of the unmodified epoxy, which leads to its poor impact strength. However, the fracture surface of the modified epoxy is teeming with accidented morphology and stress whitened zones as may be seen from Fig. 4b. The generation of the voids arising from the cavitations of core-shell particles can dissipate the fracture energy, so its impact strength was improved remarkably which is in accordance with other works [11–13] in the case of epoxy resin modified with core-shell particles.

In conclusion, the core-shell particles used as modifier for epoxy resins can improve the toughness of the cured resin greatly and the optimum contents of core-shell particles was 8 phr.

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