

Preparation of Epoxy Blends with Nanoparticles by Acoustic Levitation Technique

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ABSTRACT: Three types of blends consisting of nano-Al₂O₃ particles, polyester, and epoxy resin were respectively prepared as suspended small balls in an acoustical levitator with a microgravity state. The microstructures of the blends were compared to those with identical composition prepared in a normal gravity field. The results showed that the nanoparticles were deposited at the bottom of blends, and the polyester possessed a sphere-crystalline-dispersed phase when the blends were prepared in the normal gravity field.

However, the nanoparticles can be dispersed into epoxy resin at a nanoscale, and the polyester transformed to a highly dispersed amorphous phase when the blends were prepared by the acoustic levitation technique. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 84–89, 2002

Key words: microstructure; nanocomposites; microgravity simulation

INTRODUCTION

To simulate an outer space environment such as a microgravity condition, and avoid undesired normal gravity, levitation techniques provide a promising way to prepare blend materials with a uniform microstructure to eliminate the influence of the difference in specific gravity between the components. It is well known that electromagnetic levitation is a good candidate. However, the applications of the electromagnetic levitation are limited in metallic materials with conductivity.^{1–4} Other techniques have to be established for nonconductive materials such as organic and polymer materials. In this field, acoustic levitation shows a good prospect and attracts much attention,^{5–8} such as containerless protein crystal growth in rotating levitated drops⁹ and the measurement for the growth velocity of dendritic ice.¹⁰

There are many attempts on the optimization in the composition of the blends to obtain excellent properties.^{11,12} The comprehensive properties of blends depend not only on the properties of each component, but also on the morphologies of microstructure.

Hence, it is important to examine the microstructural morphology of the blends selected.

Engineering thermoplastics are novel modifying materials of epoxy resins from the viewpoint of the maintenance of mechanical and thermal properties. The modifications of epoxy resins with various types of ductile thermoplastics have been studied to improve the toughness of epoxy resins.^{13–15} In the present investigation, polyester is used to modify epoxy resin due to its high modulus, great tensile strength, and good heat-resistance.

In the present work, epoxy resin blends are prepared in both normal gravity and microgravity fields by a single-axis acoustic levitator, respectively. The investigation focuses on the analysis of the needed physical conditions of acoustic levitation and the comparison of the microstructural morphologies of the blend materials prepared in the two fields. For the use of acoustic levitation to prepare polymer blends, this article presented a relatively novel approach.

EXPERIMENTAL

Physical conditions for acoustic levitation

The acoustic levitator as shown in Figure 1 creates the levitation force resulting from the resonance of acoustic waves. The acoustic levitator consists of three principal components: a transmitting terminal of acoustic waves—a plate 25 mm in diameter, a reflex terminal of acoustic wave—a slightly concave circular reflector 30

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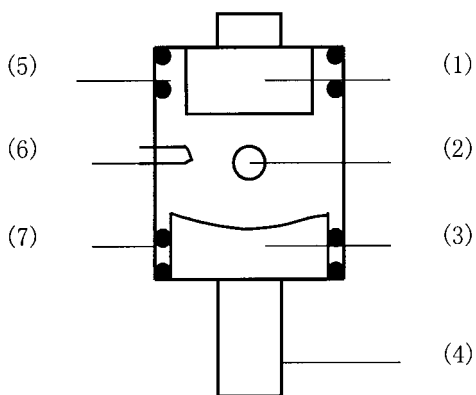


Figure 1 Schematic configuration of acoustic levitator. (1) Sound source; (2) levitated specimen sphere; (3) reflector; (4) vertical adjuster; (5) heater; (6) thermocouples; (7) heat-resistant glass tube.

mm in diameter, and a heating chamber. They are coaxially arranged to create a large lifting force in the vertical direction. The distance between the transmitting plate and the reflector of acoustic levitator is adjustable within a certain range to produce a standing wave along the axial direction.

Preparation of epoxide blends on normal gravity field

A commercially available E-6101 bisphenol A type of epoxy resin with 0.43 N/100 g of epoxy value and polyester (Polyethylene terephthalate or PET) with $1.9 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ of the average molecular weight, and/or nanoparticles were added into a 250-mL enamelware cup with stirring and a heater. The mixing operations were carried out at 250°C for 20 min until the added polyester was resolved completely. After the mixing was cooled at 200°C, maleic anhydride used as a curing agent was added into the cup and stirred uniformly. The compositions of blends were listed in Table I. Some of them were at once cooled to room temperature with an ice-water bath and then used to prepare the blends in the acoustic levitation. Most of the mixings were poured into the preheating mold at once, and then put it into a vacuum oven at 200°C for 2 h. Subsequently, the cured epoxy resins were brought out of the oven, and cooled to room temperature and then taken out of the mold.

The use of acoustic levitator

The small sphere with about 5 mm in diameter composed of the above-mentioned mixing was moved into the heating chamber from the movable upper plate of the acoustic levitator. After the distance between the transmitting plate and reflector of the acoustic levitator had been adjusted to a certain position, the small sphere was levitated steadily. Then the heating chamber of the acoustic levitator was gradually heated up to 200°C with an electric heater, and remained for 2 h to harden the specimen. After cooled to room temperature, the specimen was used to observe the microstructure by transmission electron microscope (TEM).

Morphologies observation

Some impact fracture surfaces of the specimens prepared with normal gravity field were observed with a scanning electron microscope (S-2700, Hitachi, Japan), which were coated previously by sputtering with gold metal to achieve a conducting and protecting layer.

Some slices with a thickness of 70 nm were first machined with Slicing Machine (LKB NOVA, Sweden) and then dyed with OsO_4 to enhance the contrasting color of photographs.

Finally, they were used to observe the phase structure by transmission electron microscope (JEM-2000EX, Japan).

RESULTS AND DISCUSSION

Physical conditions of acoustic levitation

Assuming that the particle velocity and sound pressure of standing wave in an ideal fluid are

$$v = v_0 \sin(kz) \cos(\omega t) \quad (1)$$

and

$$p = -p_0 \cos(kz) \sin(\omega t) \quad (2)$$

where v_0 is the maximum particle velocity, k the acoustic wave number, z the axial coordinate, p_0 the maximum sound pressure, ω the angular frequency ($\omega = 2\pi f$, f = frequency), and t time.

TABLE I
Composition of Blends

Materials	Supplied by	Blend 1	Blend 2	Blend 3
EP (phr)	Yueyang Chemical Co., China	100	100	100
PET (phr)	Xinqiang petroleum Chemical Factory, China	0	16	16
Nano- Al_2O_3 particles (phr)	Beijing Physics Institute, Academic of China Science, China	8	0	8
Maleic anhydride (phr)	Xi'an Chemical Reagent Factory, China	30	30	30

phr: the added mass parts relative to *per hundred parts matrix resin*.

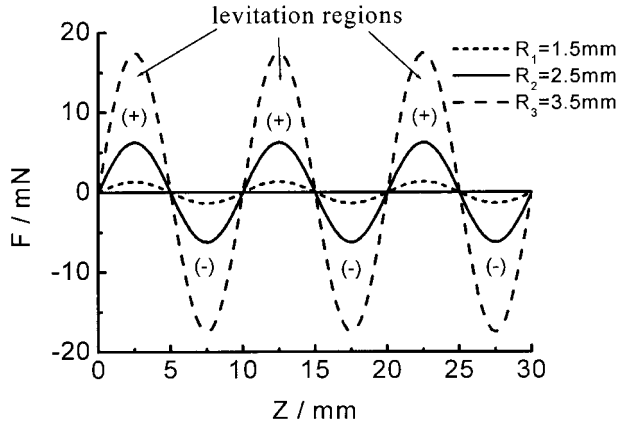


Figure 2 The acoustic levitation force as a function of the axial coordinate.

The acoustic levitation force of a small sphere ($R \ll \lambda$) in the field is obtained by Gor'kov¹⁶ as

$$F = \frac{5}{6} \pi R^3 k \rho_0 v_0^2 \sin(2kz) \quad (3)$$

where R is the radius of a spherical sample in the acoustic field, ρ_0 the density of the medium. The acoustic levitation force F was plotted as a function of the axial position z of the sphere with a different radius in Figure 2. Because F is positive, there are three isolated levitation regions between the transmitting plate and the reflector. Each levitation region is divided into both stable and unstable subregions corresponding respectively to negative dF/dz and to positive dF/dz shown in Figure 3.¹⁷

The suspending force F can be decomposed into the radiation forces in the direction of axis F_x and radial F_r , respectively

$$F_z = \pi R^3 \rho_0 v_0^2 k_z \sin 2k_z z [(5/6) \cos^2 k_r r - k_z (k_r/k)^{1/2}/2] \quad (7.4)$$

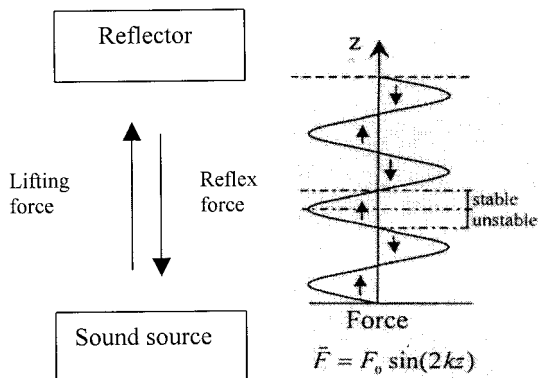


Figure 3 The variation of the levitation force in the axial direction.

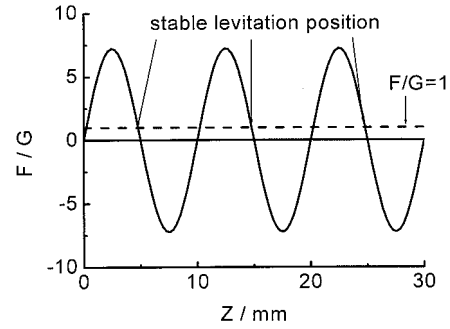


Figure 4 F/G vs. axial coordinate.

$$F_r = \pi R^3 \rho_0 v_0^2 \sin 2k_r r [(5/6) \cos^2 k_z z - (k_z/k)^{1/2}/2] \quad (7.5)$$

where k_z and k_r are, respectively, wave number in the axis coordinate z and radial coordinate r .

It is necessary that the maximum of the levitation force produced by the acoustic field is more than or equal to the gravity of the sample to achieve the purpose of levitation of the used polymer materials. They are given by

$$G = \frac{4}{3} \pi R^3 \rho_s g \quad (4)$$

$$\frac{F}{G} = \frac{5}{8} \frac{k \rho_0 v_0^2 \sin(2kz)}{g \rho_0} \geq 1 \quad (5)$$

where ρ_s is the density of levitated materials, g is the acceleration of gravity.

In the present works, $k = 200\pi \cdot \text{m}^{-1}$, $\rho_0 = 1.21 \text{ kg} \cdot \text{m}^{-3}$ (air at 298 K), $v_0 = 20 \text{ m} \cdot \text{s}^{-1}$, $\rho_s = 1.34 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$ (the density of cured epoxy resin). It can be calculated that the levitation regions of the small sphere are confined to $2.48 \text{ mm} < z \leq 5.01 \text{ mm}$, $12.52 \text{ mm} < z \leq 14.96 \text{ mm}$, and $22.46 \text{ mm} < z \leq 24.72 \text{ mm}$ ($R = 2.5 \text{ mm}$). The stable levitation positions of small sphere center ($R = 2.5 \text{ mm}$) is 4.73 mm, 14.77 mm, and 24.72 mm apart from the reflector, as shown in Figure 4.

The temperature variation during the curing period

The temperature variation of the heating chamber of the levitator for the epoxy resin/nano- Al_2O_3 particles blends during the curing period was shown in Figure 5, including three periods: heating period, constant temperature, and cooling period. It needs to be noted that, when the heating velocity was almost constant, an exothermic peak emerged in the curve of heating period.

During the initial period of heating (the temperature was below 120°C), the levitated sphere was viscous liquid. When temperature reached at 120°C , a great

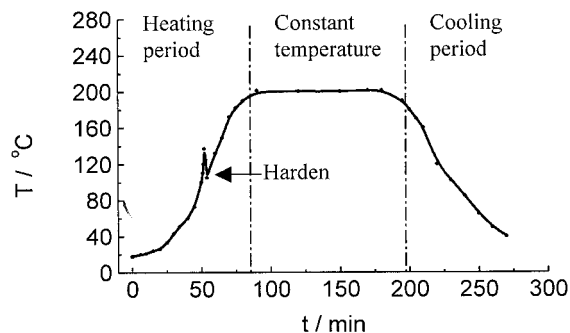


Figure 5 Variation of temperature vs. curing time.

deal of reactive heat was released and an exothermic peak emerged, which indicated that the curing reaction between epoxy resin and curing reagent has started. In the period of curing, the crosslinked density of the specimen was increased with the increased reaction time. It should be emphasized to carefully adjust the distance between the transmitting plate and the reflector to steadily levitate the sphere, because the density of material changed remarkably. After the peak, the levitated sphere was converted to harder gel, which indicated that the crosslinked density has been greater and greater, which resulted in increased rigidity. During the constant temperature period, the crosslinked density of the sphere was increased slowly, and the sphere was levitated steadily. In the meantime, the distance between the transmitting terminal of acoustic waves and reflector was certainly adjusted.

The morphologies of microstructures

Epoxy resin/nano- Al_2O_3 particles blend

In the normal gravity, it is impossible that nanoparticles can be directly dispersed at nanoscale into the epoxy resin. When mixed, the added nano- Al_2O_3 particles were easily separated from the epoxy matrix, as shown in Figure 6. That is, during the initial curing stage of the mixture, the rapid deposition of the particles resulted from their great difference in the specific gravity with epoxy resin, which has very low viscosity when the curing temperature was at 200°C.

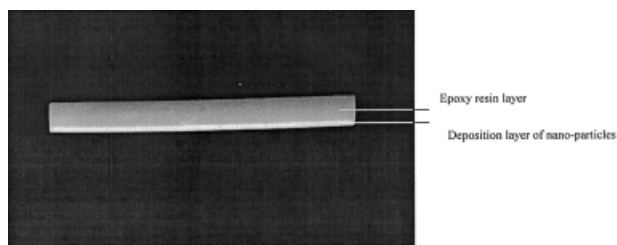


Figure 6 Nanoparticles/epoxy resin blend specimen prepared in normal gravity.

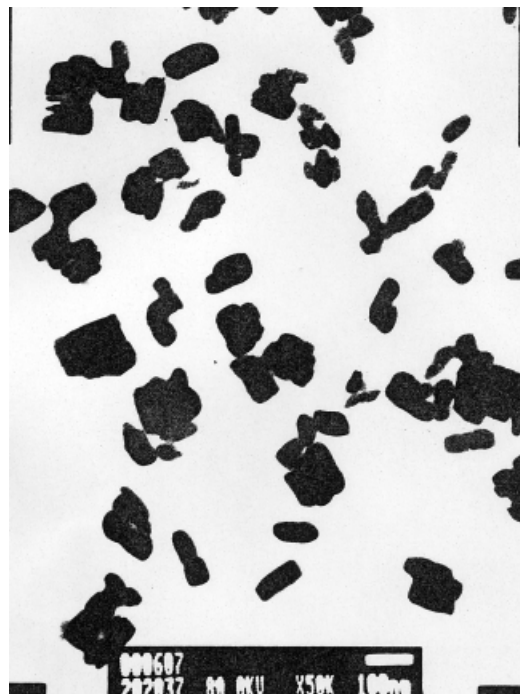


Figure 7 TEM photograph of nanoparticles/EP blend prepared by acoustic levitation.

Additionally, the nanoparticles with a large specific surface, driven by their great mutual action forces, have a strong tendency to agglomerate in the epoxy with low viscosity.

By acoustic levitation, nanoparticles can be directly dispersed at nanoscale into the epoxy resin, as shown in Figure 7, which was not achieved in the normal gravity. In general, the more uniform the nanoparticles being dispersed, the better the mechanical properties of blends was. Strong interface action contributed greatly to the mechanical properties of the epoxy matrix, which should result in the improvements on both impact and tensile strength.

In the acoustic levitation, the small ball was prepared in a microgravity state acted by suspended



Figure 8 SEM observed impact fracture surface of polyester/epoxy resin blends prepared in the normal gravity.



Figure 9 TEM micrograph of PET/EP blends prepared by an acoustic levitation.

force, in which the difference in specific gravity between nanoparticles and epoxy resin can be neglected. Moreover, the action forces of sound wave F_z and F_r played a strong vibrating function in dispersing the nanoparticles.

Polyester/epoxy resin blend

The SEM observation results of polyester/epoxy resin blend prepared in a normal gravity field is shown in Figure 8, and the polyester dispersed state in the epoxy resin was sphere-crystals, owing to chemically induced phase separation (CIPS).

The TEM photograph of the blend prepared by an acoustic levitation is shown in Figure 9, in which sphere-crystals could not be found. That is, polyester appeared in the amorphous dispersed phase, which indicated that the molecule chains of polyester had a highly dispersed degree in the epoxy matrix. The highly dispersed amorphous state of polyester implied the great ability of plastic deformation compared with that of ball crystals with a highly congregating degree when the blend was acted by impact force.¹⁸ Therefore, the amorphous dispersing state of the polyester would improve the toughness of the epoxy resins.

Nano- Al_2O_3 particles/polyester/epoxy resin blends

Normally, as indicated above, nano- Al_2O_3 particles could not be dispersed uniformly into epoxy resin unless there was an absence of gravity. However, the nanoscale dispersion of the particles can be achieved by a blend of the polyester/epoxy resin being formed as interpenetrating networks even in the normal gravity field, as shown in Figure 10(a).¹⁹ In the same composition, this ternary system was also prepared by an acoustic levitation technique, and its microstructure is shown in Figure 10(b). The nanoparticles were prior to

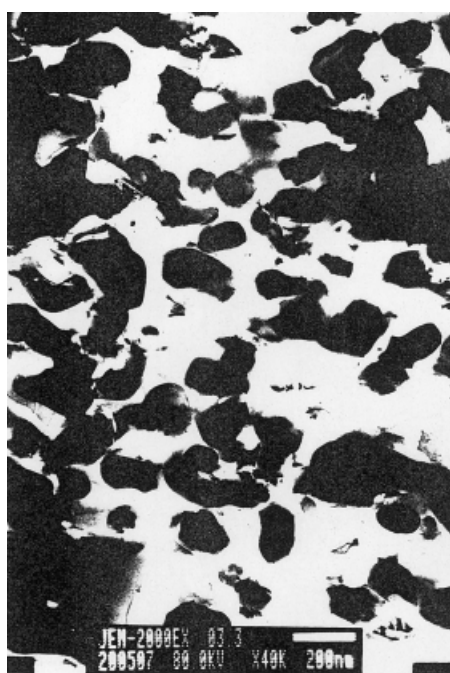


Figure 10 TEM micrographs of the ternary system. (a) Preparation in normal gravity; (b) preparation in an acoustic levitator.

be located and dispersed in the polyester in both preparation methods. Meanwhile, this is this kind of sorption that prevented the formation of polyester crystals, and intensively restricted the segment motion of polymer molecules as well as polarization tropism in the electric field.²⁰ However, for the ternary system prepared by the acoustic levitation, the interface between the nanoparticles and polyester was fuzzy, which implied that the adhesion of the interface was better than those with clear interface prepared in normal gravity.

CONCLUSION

1. The acoustic levitation technique effectively simulates a microgravity condition, which can eliminate the difference in specific gravity between epoxy resin and nanoparticles or polyester, and provides the ideal physical environment for the preparation of polymer blends with nanoparticles in a highly uniform microstructure.
2. The morphologies of blends prepared in a microgravity field by an acoustic levitator were remarkably different from those in normal gravity field. For the former, the nanoparticles can be uniformly dispersed in the epoxy matrix, and the polyester was a highly dispersed amorphous state. For the latter, it is impossible that the nanoparticles was directly dispersed at a nanoscale into epoxy resin, and the polyester-dispersed phase in the epoxy matrix was of sphere-crystal-line structure.
3. For the nano- Al_2O_3 particles/PET/EP ternary system, the adhesion of the interface between

nanoparticles and polyester by the acoustic levitation technique was better than that prepared in a normal gravity.

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