Electronic Supplementary Material

The study and its application for rubber-modified plastics with higher heat resistance and higher toughness

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Starting materials

Diglycidyl ether of bisphenol-A (DGEBA, E-44, and supplied by SINOPEC Baling petrochemical CO., LTD. China), curing agent, methyl tetrahydrophenylanhydride (MeTHPA, by Jiaxing-Dongfang, China), curing initiator, triethanolamine (TEA, supplied by Jiamusi, China), Carboxylic nitrile-butadiene rubber latex (CNB-RL solid content 45%, nitrile content 26%, carboxylic content 2%, by weight, and supplied by Lanzhou China), nitrile-butadiene rubber latex (NB-RL solid content 45%, nitrile content 26%, by weight, and by Lanzhou China), and crosslinking agent, trimethyolo propane triacrylate (TMPTA, by Beijing Dongfang, China). They are directly used without any purification.

The preparation of CNBR-NP and NBR-NP

Preparing technology of Rubber Nanoparticles including CNBR-NP and NBR-NP was developed by our group. Its inventing patent has been issued in USA (USP6,423,760). CBN-RL or BN-RL with 5 phr TMPTA was irradiated with a cobalt-source with dosage of 25 KGy at dose rate of 50 Gy/min to make rubber nano-particle in their latex cross-linked and subsequently dried by spray dyer to obtain CNBR-NP and NBR-NP with less than 100 nm in diameter. Since the rubber nanoparticles have been cross-linked by irradiation, the cohesiveness between particles dramatically decrease and then can be individually re-dispersed in selected matrix such as epoxy resin.

Preparation of CNBR-NP and NBR-NP modified epoxy resin

First, a blend of 12 phr CNBR-NP or NBR-NP with 100 phr DGEBA was milled by a three-roll miller three times at room temperature. Then the blend was mechanically stirred for 30 min at 90 ℃ after addition of 75 phr MeTHPA. Subsequently, 1.5 phr TEA was added if necessary, and then the blend was degassed during stirring at 90 ℃ for 15 min. Finally, the blend was cast into a preheated PTFE mould, and was cured at 130 ℃ for 15 hours.

Measurements:

Izod impact strength without notches was measured with a impact machine (CEAST, AFS/MK3) according to testing standard GB 1843. Heat-distortion temperature was measured on a heat-distortion tester (148-HDPC-6) according to testing standard GB 1634. Glass transition temperature (T_g) was measured by DSC (Perkin-Elmer Pyris DSC-7) according to testing standard GB 19466.2. AFM images were scanned by Dimension 3100 AFM (Veeco Metrology Group, USA) at tapping mode with tip nominal spring constant of 2.8 N/m at room condition. Curing kinetics was monitored by means of DSC and in-situ FTIR (Nicolet AVATAR 360). DSC was performed from room temperature to 300 ℃ at a heating rate of 5 ℃/min under nitrogen, and in-situ FTIR was carried out at 130 ℃ for 20 min.

The AFM measurements and its sample preparation

For tapping mode AFM, during each cycle under ambient conditions the tip may go through several tip-sample force regimes. When tip interacts with sample surface, it is reasonable to assume that the tip-sample force interaction changes the force constant of the cantilever to an effective value $k_{eff} = k + \sigma$, where κ is the spring constant of tip and σ is the sum of the force derivatives of all attractive and repulsive forces acting on the cantilever. That is, the tip-sample interaction alters the resonance frequency of the cantilever to a new resonance frequency ω_{eff}.

The phase angle of the free cantilever, $\Delta\phi_f(\omega)$, is a steadily increasing function of ω with an inflection point at the resonance frequency ω_0. The phase angle of the interacting cantilever, $\phi_i(\omega)$, is the same as $\phi_f(\omega)$ except that its inflection point is at ω_{eff}. Therefore, when measured at ω_0, the phase shift $\Delta\phi_f(\omega) = \phi_f(\omega_0) - \phi_i(\omega_0)$, is negative when $\sigma < 0$ and positive when $\sigma > 0$. When σ is very small in magnitude compared with κ, the phase shift $\Delta\phi(\omega_0)$ is given by

$$\Delta\phi(\omega_0) \approx \frac{Q\sigma}{k} \propto \sqrt{\langle A\rangle} E^*$$

where the equation is valid when $\sigma > 0$. E^* is the effective modulus of the tip-sample system, which is close to Young's modulus of the samples when the tip is much stiffer than the sample, and $\langle A\rangle$ is the contact area A over one cycle of oscillation.[1]

Some literatures have reported that sample properties and characteristics such as the work of adhesion, local sample curvature and damping were all observed to affect the height and phase images. However, they also pointed out that carefully adjusting the set-point amplitude ratio $r_{sp} = A_{sp}/A_0$ to keep the tip/sample interacting force suitable, where A_0 is the amplitude of the free oscillation and A_{sp} is the set-point amplitude such that during the scanning the observed amplitude of oscillation is maintained at A_{sp} by adjusting the vertical position of the sample, tapping mode AFM can be used to qualitatively compare the relative hardness of heterogeneous regions in polymer in combination with the information of height images.[1,2] In AFM phase images brighter area is harder. The technique has been widely used to image distribution of heterogeneous phases with different hardness.[3-6] Therefore, the relative hardness of epoxy resin, rubber nano-particle and their interfaces can be qualitatively compared by AFM.

In the experiments, the sample used for AFM study was carefully cut by microtome with a glass knife at about -100 ℃ according to the procedures previously described.[7-9] A Dimension 3100 scanning probe microscope from Digital Instruments was operated in tapping mode under ambient conditions using commercial silicon microcantilever probes with a nominal spring constant κ of 2.8 N/m, a resonance frequency of 75 kHz, and tip height in the range of 10 μm ~ 15 μm. Topographic and phase images were obtained simultaneously. More detailed information was described in their figure captions.

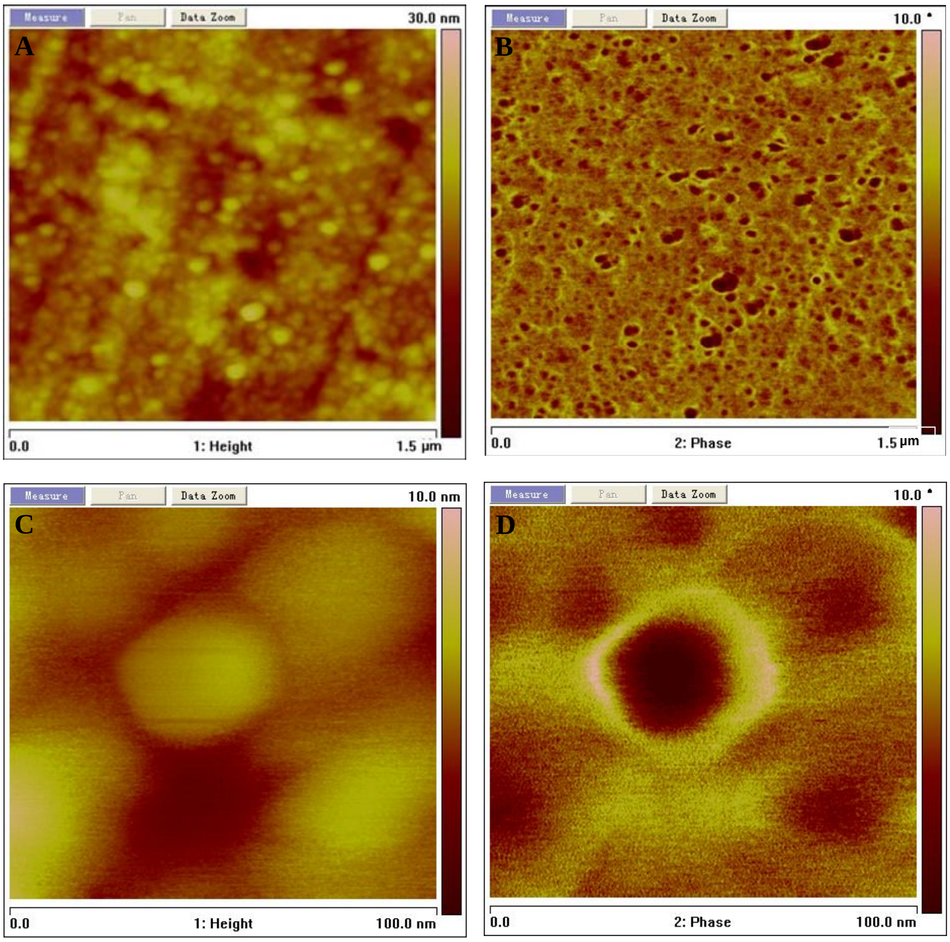

Fig. S-1 AFM height and phase images of epoxy resin toughened by 12 phr CNBR-NP. (A and B) AFM height image and height image; (C and D) magnified AFM height and phase image of a rubber nanoparticle. Their scanning conditions: for A and B scan rate of 1 Hz, a free-oscillation amplitude, A_0, of about 35 nm, and set-point ratio, r_{sp}, of about 0.55; for C and D scan rate of 4 Hz, a free-oscillation amplitude, A_0, of about 35 nm, and set-point ratio, r_{sp}, of about 0.55.

Fig. S-1 A and B were height and phase images of epoxy resin modified by 12 phr CNBR-NP. Since CNBR-NP was soft phase relative to epoxy resin, the brown spheres in phase image were CNBR-NPs, which corresponded to the raised spheres in height images. Their distribution revealed in the phase image was consistent with that in TEM image in Fig. S-2. Therefore, the selected value of r_{sp} was reasonable, and flipping of the phase contrast (i.e. the lighter regions become the darker regions and vice versus)[2] was excluded. Interestingly, the phase image revealed that there always existed a brighter ring surrounding every CNBR-NP, which showed that the formed interface was harder than epoxy matrix. Fig. S-1 C and D are height and phase images of a CNBR-NP in Fig. S-1 A. The brown sphere in phase image corresponded to the raised one with about same size in height image, which more clearly showed the brighter interface.

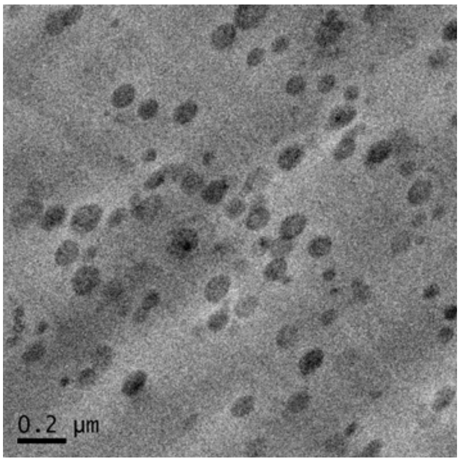

Fig. S-2 image of the epoxy resin toughened by 12 Phr CNBR-NP observed by TEM (Philips TECNAI 20). The specimens of less than 100 nm slices were cut by microtome with glass knife at ca. -100 ℃, which were stained by OsO_4 before TEM observing.

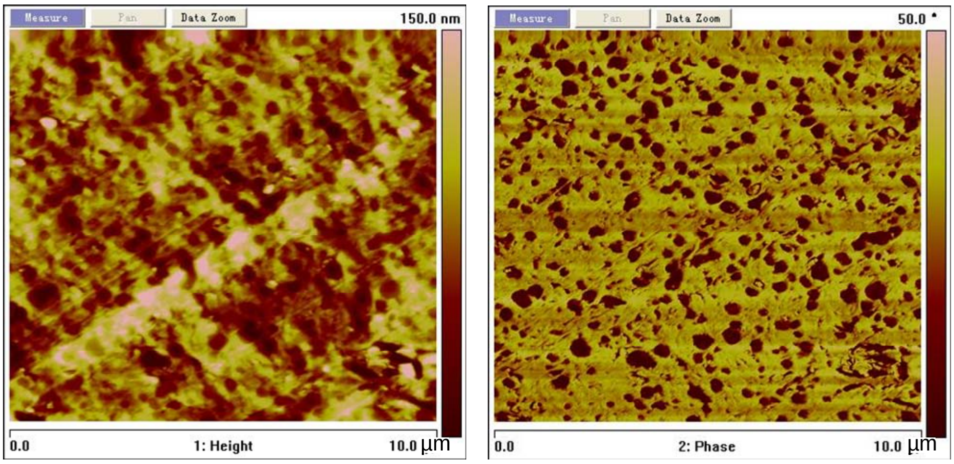

Fig. S-3 AFM height and phase images of polyamide-6 (PA6) toughened by 30 phr acrylate-rubber particles (ARP). A and B are AFM height and height images. Their scanning conditions: for A and B scan rate of 1 Hz, a free-oscillation amplitude, A_0, of about 35 nm, and set-point ratio, r_{sp}, of about 0.55. ARP was prepared according to the same procedure to CNBR-NP or NBR-NP described above.

In order to further confirm the formation of the rubber particle/epoxy resin interface even harder than epoxy resin, we introduced another system, acrylate-rubber nanoparticles (ARP) modified polyamide-6 (PA-6). Since PA-6 is a kind of thermoplastics no curing reactions took place in the system, dissimilar to the epoxy systems. Therefore, for the system, it is difficult to form an ARP/PA-6 interface harder than PA-6, similar to CNBR-NP/epoxy interface. The conditions for preparing AFM specimens and AFM observation were identical to that of CNBR-NP/epoxy systems.

Because ARP was much softer than PA-6, the brown spheres were ARP in the phase image of ARP/PA-6 system. In the height image, they corresponded to holes with same size. Differ from the CNBR-NP/epoxy resin system, no brighter ring surrounding ARP occurred as anticipated because no interface harder than PA-6 was formed. Therefore, those experimental results also confirmed the reliability of the technique that AFM phase images combining with height images could be used to qualitatively compare relative hardness of heterogonous phase in polymer.

Notes and References

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