ABS/Iron Nanocomposites Prepared by Cryomilling

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ABSTRACT: Acrylonitrile-Butadiene-Styrene (ABS)/iron nanocomposites have been prepared by cryomilling (high-energy ball milling under cryogenic temperature), and a microstructure of iron network in ABS matrix was obtained. The blending scale and homogenization of ABS/iron nanocomposites are observed by Atomic Force Microscope (AFM). The morphology and structure of cryomilled composite powders are characterized by means of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and X-ray Diffraction (XRD). The results indicate that upon cryomilling for 20 h, ABS and Fe are intimately blended with the single composite particle size less than 100 nm, the Fe phase domains less than 50 nm, and Fe grain size reduced to 20 nm. Both the fast rate of homogenization and size reduction are mainly attributed to the introduction of cryogenic temperature and comilling. The evidences suggest that cryomilling is a capable and promising technique for the production of polymer/metal nanocomposites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 501–505, 2006

Key words: nanocomposites; cryomilling; atomic force microscopy; microstructure

INTRODUCTION

Polymer/metal nanocomposites have the probable potential applications in electrode materials, new plating, information storage, electro-magneto shielding and so on,[1–3] and they not only provide the sum of the individual contributions from polymer and metal components but also may have the possibility of providing remarkable properties unknown in conventional materials. For instance, it owns the light weight and easy processing merits of polymers and peculiar light, electricity, and magnetic performance of nanometer metals; in addition, nanometer iron particles embedded in an insulating matrixlike (ceramic or polymer) exhibit coercivity values orders of magnitude higher than that of bulk iron.[1,2] To Polymer/metal nanocomposites, the traditional fabrication methods are *in situ* filling and direct dispersion. These methods rely on processing the materials in melt or in solution. However, it is impossible to get homogeneous blending when the contents of filling material is high or the polymers used are of high melt viscosity. One way to solve these problems is to process the materials in solid state, which avoids the thermal and solvent problems while provides almost infinite design flexibility. So the solid-state methods, such as mechanical alloying[4] and solid-state shear pulverization (S^3P),[5] are becoming more prevalent in recent years. Mechanical alloying is a well-established technique for processing metals and ceramics with fine microstructures since 1960s.[6] It is a high-energy ball-milling process in which the repeated fracture and welding of powder particles, arising from ball-powder collision events, enables true alloy powders to be formed from mixtures of elemental powders.[7] In 1988, Shaw[8] firstly explored the concept that mechanical alloying could be applied in polymer field. To embrittle polymer and overcome its viscoelastic nature, ball milling of polymer was carried out under cryogenic temperature induced by cryogenic media such as liquid nitrogen. This adapted technology was mostly referred as cryogenic mechanical alloying or cryomilling. Up to present, cryomilling has become an effective method to improve blending intimacy and enhance compatibility between polymers[9–12]; however, little attention has been given to fabricating polymer/metal composites via cryomilling. As a matter of fact, even the efforts to prepare polymer/metal composites by ambimilling (ball milling under ambient temperature)[2,3,13] were rarely made. Ishida and Tamaru[3] milled polytetrafluoroethylene (PTFE) with

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Cu and Ni, and reported that the mean size of mixture particles was about 20 μm after milling for 21 h. Mikko Karttunen[13] mixed high density polyethylene with copper, and the final particle size of copper was less than 10 μm after milling for 20 h. Besides, Giri[2] prepared Fe and polyethylene mixture, and reported that the average grain sizes of iron were 32 and 9 nm after milling for 25 and 150 h, respectively. Nanoscale blending in polymer/metal composites has never been obtained by ball milling in previous researches, although the grain size of metal could be reduced into nanometer by prolonged milling. In our present work, we attempt to produce ABS/iron nanocomposites by cryomilling using a stirring mill.

EXPERIMENTAL

The starting materials used in this study were ABS resin powder (Dp611) and atomized Fe powder (commercial grade). Before use, ABS and Fe were dried at 80°C for 4 h to dehydrate water. Sample of ABS_{1-x}–Fe_x (x denotes volume fraction) with $x = 0.1$ was cryomilled in a stirring mill at a rotating speed of 900 rpm. Appropriate amounts of ABS, Fe, and stainless steel balls (6 and 8 mm in diameter, a ball-to-powder weight ratio of 60 : 1) were put into a stainless steel vial. The temperature inside the inner vial was maintained at −150°C or so by introducing liquid nitrogen into the outer vial and the resulted nitrogen gas was introduced into the inner vial to supply a protective atmosphere. The cryomilling duration added up to 20 h with several interruptions so that the vial could be opened and a small portion of powders could be taken out for different analysis.

Morphology of the cryomilled powder was characterized by Scanning Electron Microscopy (SEM, *S*-520, 20.0KV) and Transmission Electron Microscopy (TEM, JEM-100CX, and 100.0KV). SEM observation was carried out with gold-coated powder samples. TEM specimens were prepared by dispersing the powders in ethanol and collecting them onto 200-mesh copper grids. The blending intimacy was evaluated with Atom Force Microscopy (AFM, Multimode Nanoscope 3) applying the tapping mode. AFM samples were prepared by compacting blended powders at 150°C for 10 min and then polishing the compact surface. X-ray Diffractometer (XRD, D8 ADVANCE, and Cu Kα radiation) was used to follow the refinement of Fe grains.

RESULTS AND DISCUSSION

Morphology changes of particles during cryomilling

Figure 1 shows the morphology of original powders and cryomilled powders. ABS particles generally are big blocks with a size of 60 μm [Fig. 1(a)], while Fe particles are spheroids either in single (large) or in cluster (small) [Fig. 1(b)], and the particle size of Fe is less than 30 μm.

From the particle's morphology changes during cryomilling, it is easy to find that the comminution of ABS/Fe divides into two stages. Flake shape appears in the early hours, as reported in ambimilling of polymer/metal systems.[3] ABS/Fe blended powders first deform seriously into irregular blocks [Fig. 1(c)] and then get flattened to flake-like morphology [Fig. 1(d)]. The particles become smaller and thinner, and then pile together randomly with increasing milling time [Fig. 1(e)]. In the second stage, the flakes are pulverized into equiaxied dimensions [Fig. 1(f)] other than cold-welded to lamellar structures like in ambimilling. With further milling, these equiaxied particles become submicron in size (about 500 nm), and they have a tendency to agglomerate and form the conglomeration with size as big as 10 μm [Fig. 1(g)]. No remarkable change is induced by continuing milling to 20 h [Fig. 1(h)], which indicates that the comminution limit might have been reached.

To further observe the inner structure characteristics of the equiaxied particles observed in SEM image, we attained their transmission electron microscope images. Shown in Figure 2 are the TEM image and the electron diffraction pattern of ABS/Fe composite powders cryomilled for 20 h. The size of the whole block in Figure 2(a) is about 400 nm, and its size is corresponding to that of the submicron equiaxied particles observed in the SEM image. The electron diffraction spots in Figure 2(b) indicate that there are many Fe nanocrystallines in Figure 2(a), but we nearly could not distinguish Fe particles from ABS. This result reveals that the submicron equiaxied particles observed in SEM image contain both ABS and Fe, but the positional relationship between ABS and Fe could not be confirmed.

Changes of Fe grain size during cryomilling

To follow the grain refinement of Fe during cryomilling, we did the XRD test to the blended powders cryomilled for different times. The XRD spectra of blended powders with increasing milling time are shown in Figure 3. In the unmilled powders (0 h), Fe may be covered by ABS because of its smaller particle size and lower volume fraction, and so the intensities of Fe peaks are relatively weak. In the early stage during cryomilling, the intensities of Fe peaks increase (3 h) and reach a maximum (5 h), while the intensity of ABS peak weakens gradually and nearly disappears after cryomilling for 5 h. We consider that this phenomenon may be explained from the viewpoint of structural evolution: with milling continued, ABS gradually becomes surrounded by Fe (for more de-

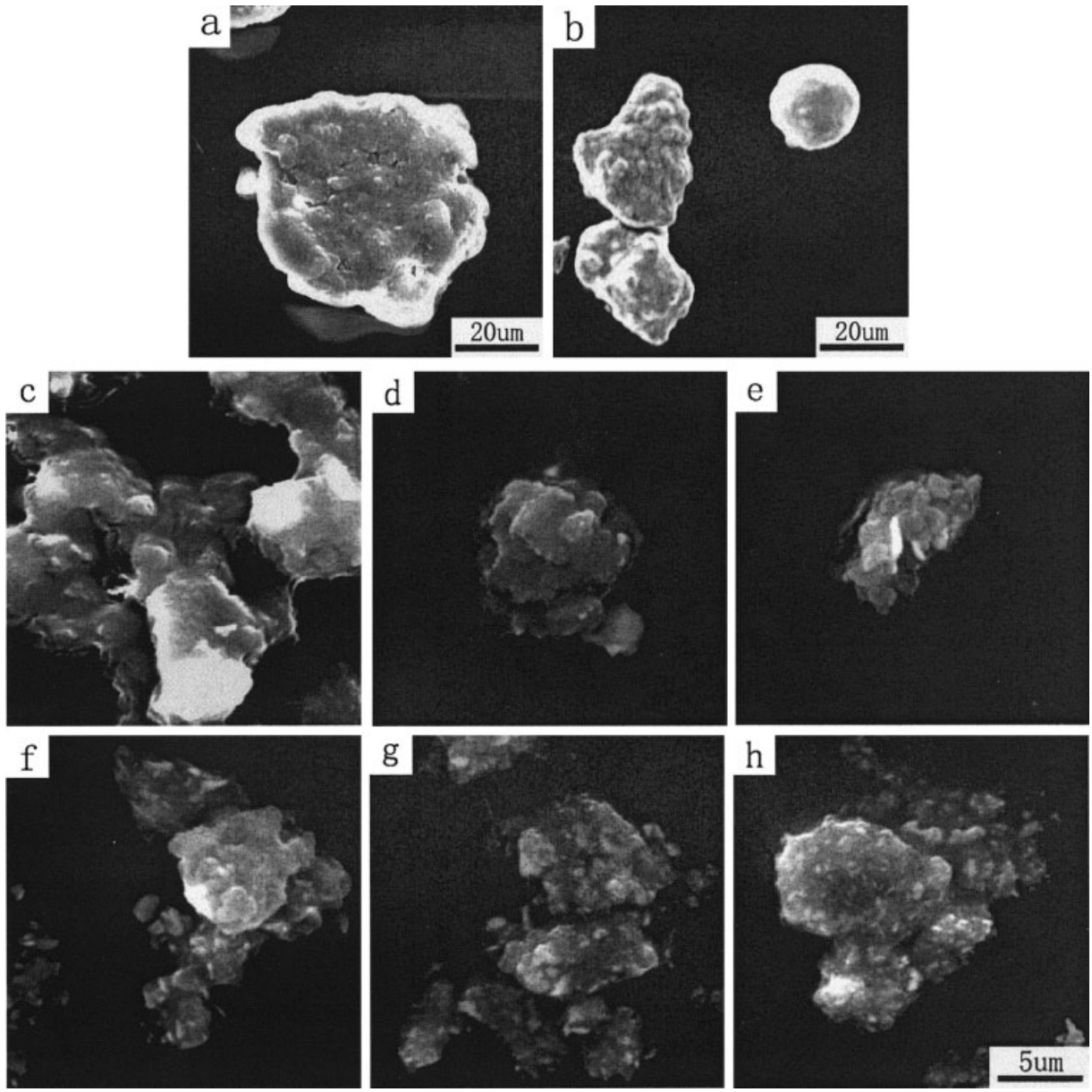

Figure 1 SEM images of original ABS (a), Fe (b), and their blended powders cryomif led for different time (in hours): (c) 1, (d) 3, (e) 5, (1) 10, (g) 15, and (h) 20. The scale marker for c, d, e, f, g, and h images is shown in h.

tails, see the following section) and the ABS surface exposed to X-rays decreases relatively. Further cryomilling makes Fe peaks weaken and broaden (15 and 20 h) because of the refining of Fe grains. We have calculated the average grain size of Fe for (110) reflection at different milling times from the line broadening using the Scherrer equation[14] given by

$$D = 0.89\lambda/\beta \cos \theta$$

where D is the grain size, λ is the wavelength of the radiation used, and β is the full width at half maximum after making the correction due to instrumental broadening, and θ is the scattering angle. The average grain size of Fe decreases with increasing milling time and the values achieved by 15 and 20 h' cryomilling are 22 and 20 nm, respectively.

Microstructure of ABS/Fe nanocomposites and dispersion of Fe

The blending intimacy of ABS and Fe after 20 h' cryomilling could be evaluated by the AFM image shown in Figure 4. Figure 4(a) is the surface morphology, the height change in which is less than 80 nm. Figure 4(b) is the phase mapping of the same micro-zone as Figure 4(a). Because ABS and Fe do differ in mechanical properties, the dark and bright areas in Figure 4(b)

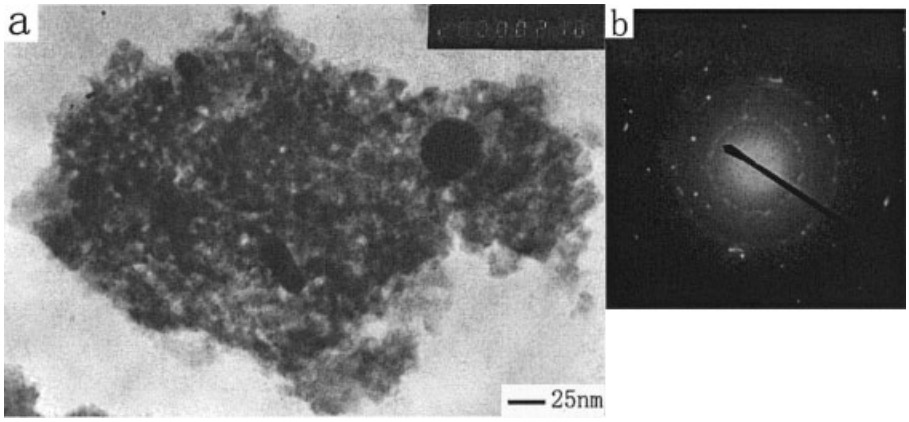

Figure 2 TEM image (a) and diffraction spot (b) of ABS/Fe blended powders cryomilled for 20 h.

should correspond to different phase states. Judged from the volume fraction (10% Fe), the bright and dark domains should be Fe and ABS, respectively. In Figure 4(b), a novel feature found is that the bright Fe phase shows a crosslinked network in the black ABS matrix, and this microstructure feature will be advantageous to conductibility of the composite, since the Fe networks can easily form conductive paths. Comparison of the morphology and the phase figure reveals that the small particles in Figure 4(a) are composite particles containing both ABS and Fe, and Fe phase surrounds ABS phase like shown in the black square in Figure 4. So when the composite powders are hot-pressed together, the external Fe particles link together and form networks like shown in Figure 4(b).

In the novel composite microstructure, ABS phase is surrounded by Fe phase and Fe phase forms the crosslinked network in ABS matrix, and we consider that this structure should be connected with the material nature at cryogenic temperature. The impact strength of ABS and Fe is about 1 J/cm^2 and 18 J/cm^2 at liquid nitrogen temperature,[15,16] respectively. That is to say, at the cryomilling temperature, Fe is ductile relatively comparing with ABS, and so it easily forms the flake structure relatively and surrounds the brittle ABS phase.

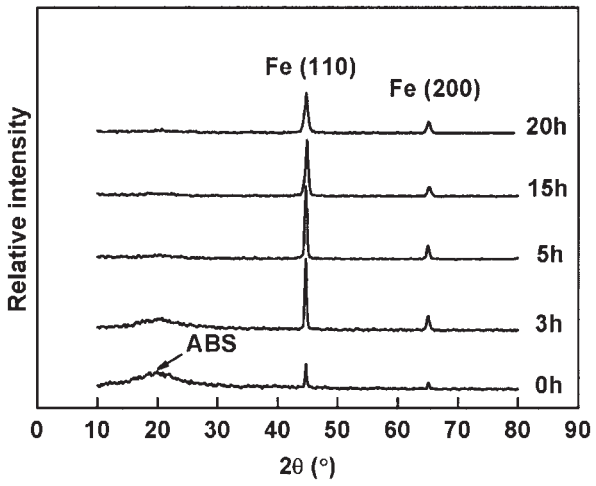

Figure 3 XRD patterns of ABS/Fe blended powders cryomilled for different time (h).

We count that the single composite particle size is less than 100 nm from Figure 4(a), and Fe phase domains are less than 50 nm from Figure 4(b). These indicate the ability and efficiency of cryomilling to refine the metal and polymer materials and blend them in nano scale.

As mentioned earlier, Fe grains get refined into 20 nm in average by 20 h' cryomilling, contrasting with ambimilling (32 nm and 9 nm of Fe grain sizes in PE/Fe after milling for 25 and 150 h, respectively).[2] Our speed rate is much faster; besides, the single composite particle of ABS and Fe is less than 100 nm, and they attain the nanoscale blending, while during comparable time ambimilling could only attain micron scale blending in polymer/metal systems.[3,13] Cryogenic temperature and comilling are considered the main factors contributing to the faster rate of refinement. Both ABS and Fe have a ductile–brittle transition, at −84°C[15] and −26°C[16], respectively. At −150°C as milled in our work, the fracture fashion of both ABS and Fe changes from ductile (ambimilling) into brittle (cryomilling). In ambimilling, ductile ABS and Fe deform easily, which not only consumes a large part of the mechanical energy input, but also facilitates cold-welding and form lamellar structure, since the flake structures formed own large flesh surface. In cryomilling, however, brittle ABS and Fe are easy to produce the large stress concentration and fracture in a short milling time; therefore, cryomilling accelerates the refinement process. Comilling is of great benefit to the reduction of the phase domain size, and the mechanism could be attributed to the re-

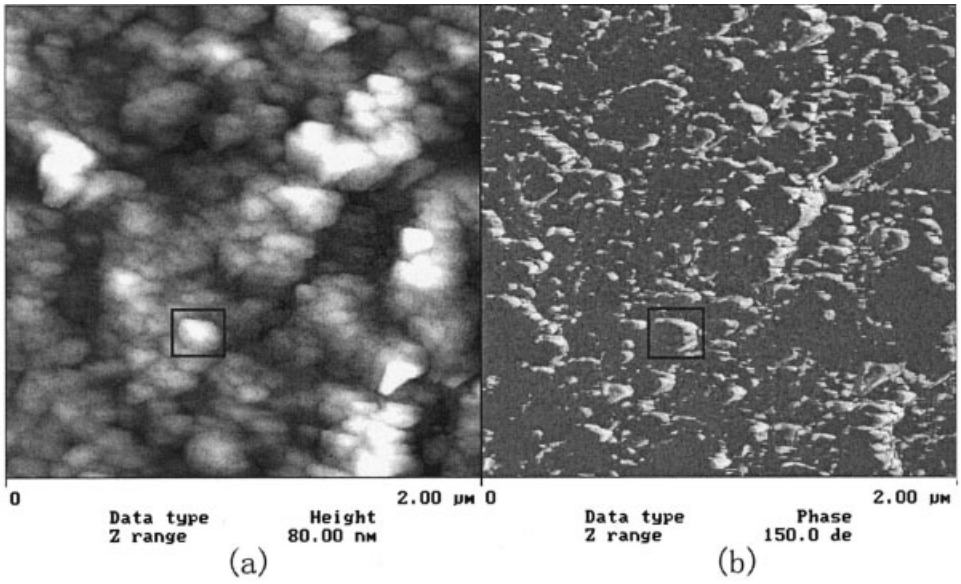

Figure 4 AFM images (tapping mode) of ABS/Fe composite powders cryomilled for 20 h and compacted for 10 min at 150°C. (a) height image and (b) phase image are of the same area. The vertical scales (z) are 0–80 nm (height image) and 0–150° (phase image). The bright domains are Fe phase in b.

striction of cold-welding. Comilling can effectively reduce the contacting chances between particles of the same kind, and so the chances of the cold-welding decrease among the same kind particles; besides, the cold-welding is not prone to produce between metal and polymer due to their different surface nature. Therefore, the total speed rate of cold-welding falls down, and the phase domains decrease much more.

CONCLUSIONS

ABS/Fe nanocomposites have been successfully obtained by cryomilling. The cryogenic temperature and comilling greatly enhance the size reduction by improving fracture and restricting cold-welding. Both particles and grains refine with much faster speed rate, and the comminution limit is moved to the finer end inaccessible to ambimilling process. 20 h's cryomilling pulverizes the single ABS/Fe composite particle smaller than 100 nm and refines Fe grains about 20 nm. In the hot-pressed ABS/Fe composites, Fe domains are less than 50 nm and form crosslinked network in ABS matrix, which predicts a good conductibility of the composites with the low content of the conductive metal filler. Thus, the revealed capability of cryomilling to pulverize and blend ABS/Fe makes it a promising technique for the production of polymer/metal nanocomposites.

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