Dramatic Improvement in Mechanical Properties of GNs-Reinforced HDPE Nanocomposites

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ABSTRACT: Graphite nanosheets (GNs) modified with sodium dodecyl benzene sulfonate (SDBS) was prepared and then incorporated into high-density polyethylene (HDPE). The GNs/HDPE nanocomposites displayed pronounced enhancements of the mechanical properties. With a load of 10 wt % of the modified GNs, the nanocomposites exhibited an increase of about 290% in the elongation at break as well as an increase of about 14% in the elastic modulus in comparison with neat HDPE.

Scanning electron microscopy (SEM) shows a notable microscopic orientation of the matrix and GNs in the strained nanocomposite specimen, which may play an important role in the dramatic increase in the elongation at break. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2029–2034, 2010

Key words: graphite nanosheets; mechanical property; reinforcement; nanocomposites

INTRODUCTION

Graphite/polyethylene composites have been studied intensively in recent years owing to the expected advantages of improving the electrical properties of composites. Accordingly, the presence of graphite particles has also great influence on the mechanical behavior of polymeric composites.[1–6] However, little effort is devoted to investigating the mechanical property. Introduction of fillers usually leads to the decrease in the ductility of polymers, e.g., elongation at break.[7,8] Similar trends are also seen in many graphite-reinforced polymeric composites,[4,9,10] whereas this seems to be unexpected and disappointed for practical applications.

According to the literature, fillers have different effects on the reinforcement of composites. Clay nanolayer-reinforced nanocomposites have an increase in both tensile strength and elongation at break.[11–14] And Liang et al. reported that the tensile strength of carbon nanotubes (CNTs)/epoxy resin nanocomposites increased by 18.3% and the rate of elongation increased by 92.8% when the content of CNTs was 0.75%.[15] Chemically similar to CNTs and structurally analogous to layered clay,[16–18] graphite has the potential to be an outstanding nanofiller in the form of individual graphene layers or nanoscale layered stacks. Our previous work[19] prepared a new kind of nanofillers-Graphite nanosheets (GNs) by sonicating expanded graphite, with the high aspect ratio (up to 250).

Despite potential advantages, like most nanomaterials, effective dispersion of two-dimension flakes in the polymer matrix is practically impossible by prevalent direct melt processing, thus significantly limiting industrial applications.[20–22] GNs, which have a high specific surface area, are inclined to form agglomerates or even restack to form graphite through van der Walls interactions unless well separated from each other. The prevention of aggregation is of particular importance for GNs because most of their unique properties are only associated with individual sheets. Attempts to prevent this aggregation have mainly focused on attaching polymers or surfactants to the surface of sheets to hold them apart.[23,24]

Surfacants have been widely used in petroleum, textile, daily chemical and so on. By being adsorbed on the surface or coating the surface partly, the surfactants reduce the aggregation of sheets.[25] Compared to simple direct mechanical blending process, blending compatibilization can be improved and nanoscale dispersion in polymer blends is also attained after the modification of GNs.[26] Herein, the industrial products of GNs were chosen and a typical surfactant, which is practical and economical, was selected to modify GNs so as to improve mechanical performaces of polymer/GNs nanocomposites.

EXPERIMENTAL

Materials

GNs, provided by Fujian Kaili Specialty Graphite. Figure 1 shows the typical character of GNs. As seen
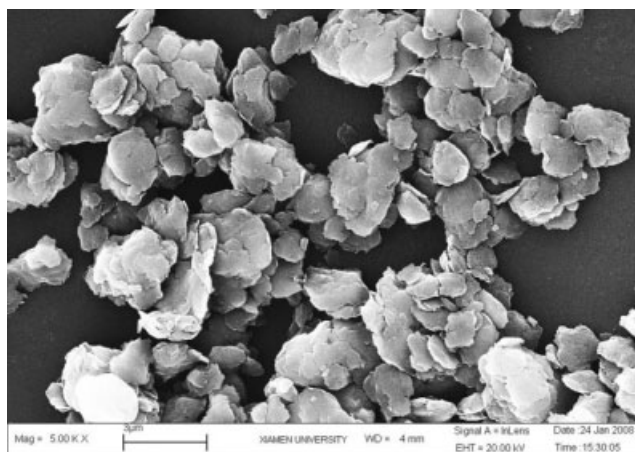
Figure 1 SEM image of graphite nanosheets.

in Figure 1, the used GNs having a diameter of 1–5 μm and the thickness ranging from 10 to 50 nm. It also clearly shows that GNs have a large diameter-thickness ratio and some small sheets are on the surface of large sheets.

Commercial grade of high-density polyethylene (HDPE, BK 160–4604) was purchased from Saudi Arabia with melt-index (MI) of 8 g/10 min. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Xilong Chemical, Shantou, Guangdong Province, China.

Modification of GNs

Ten gram of GNs were immersed into 200 mL ethanol solution and sonicated for 5 min. SDBS (0.1 g) of 1 wt % GNs was dissolved in 100 mL 98% ethanol solution. During magnetic stirring process, the as-prepared modified solution was added into GNs ethanol solution, followed by continuously stirring for 30 min. GNs solution was filtrated before being rinsed thoroughly with double distilled water, and then dried at 100°C for 12 h. The modified graphite nanosheets (MGNs) were prepared.

Preparation of nanocomposites

To obtain uniform dispersion of nanocomposites, HDPE and MGNs were mixed firstly in high-speed mixer for 15 min, then the Internal Mixer was employed, in which the mixture were fed to prepare HDPE/MGNs composites with the mixing temperature of 140°C and the speed of 45 r/min. For comparison, HDPE/GNs composites were fabricated under the same condition.

Mechanical property test and characterization

Tensile strength and impact strength were measured on a tensile tester (CMT6000, Shenzhen, China) and

an impact test machine (ZBC-4, Shenzhen, China), both of which were in accordance with the testing standard of Chinese GB1040-92. The samples for tensile and impact test were prepared through the universal sample machine (CGP, Quanzhou, China).

Scanning electronic microscopy (SEM) was performed on a JSM-6700F field-emitting scanning electron microscopy (JEOL) at the operating voltage of 15KV. A thin coating of gold about 10 nm in thickness was sprayed on the surface of samples to bear any static charges.

Thermal analysis was carried out on a differentia scanning calorimeter (Perkin–Elmer DSC-7). The heating rate was 10°C /min under the protection of nitrogen flow with the scanning temperature from room temperature to 180°C.

RESULTS AND DISCUSSION

Mechanical properties of HDPE/GNs nanocomposites

The detailed tensile mechanical properties of HDPE nanocomposites at different concentrations of GNs and MGNs are given in Figure 2. It is obviously seen in Figure 2(A), that both kinds of test samples undergo a dramatic increase in ductility at low fillers loadings, high to 44.83 and 131.41% of elongation at break separately (compared to neat HDPE). It is quite the opposite of the usual effect of adding a particulate filler to a polymer. When GNs loading is up to 20 wt %, both composites become brittle.

Generally, elongation at break decreases with increasing the content of the filler, which is described by Nielsen's model.[27] However, such behavior is valid only for particles having spherical shape assuming perfect adhesion between phases. Many fillers do not fulfill these conditions, such as GNs used in the experiment.

The increased toughness of GNs/HDPE nanocomposites compared to neat HDPE can be explained by the strengthening and toughening mechanism of inorganic fillers.[28] GNs improve the whole mould quantum and the effect of dispersing stress based on it. Moreover when the material is forced, the concentrating stress made by GNs causes the cutting bend in the polymer matrix and therefore the whole toughness of the material is improved.

It also shows that higher elongation at break of GNs/HDPE nanocomposites modified with 1 wt % SDBS is achieved than that of the unmodified counterparts shown in Figure 2(A). The result indicates that the surfactant is in favor of the increased elongation at break. The other tensile properties and impact properties are also improved as the increase of elongation at break, shown in Figure 2(B–D).
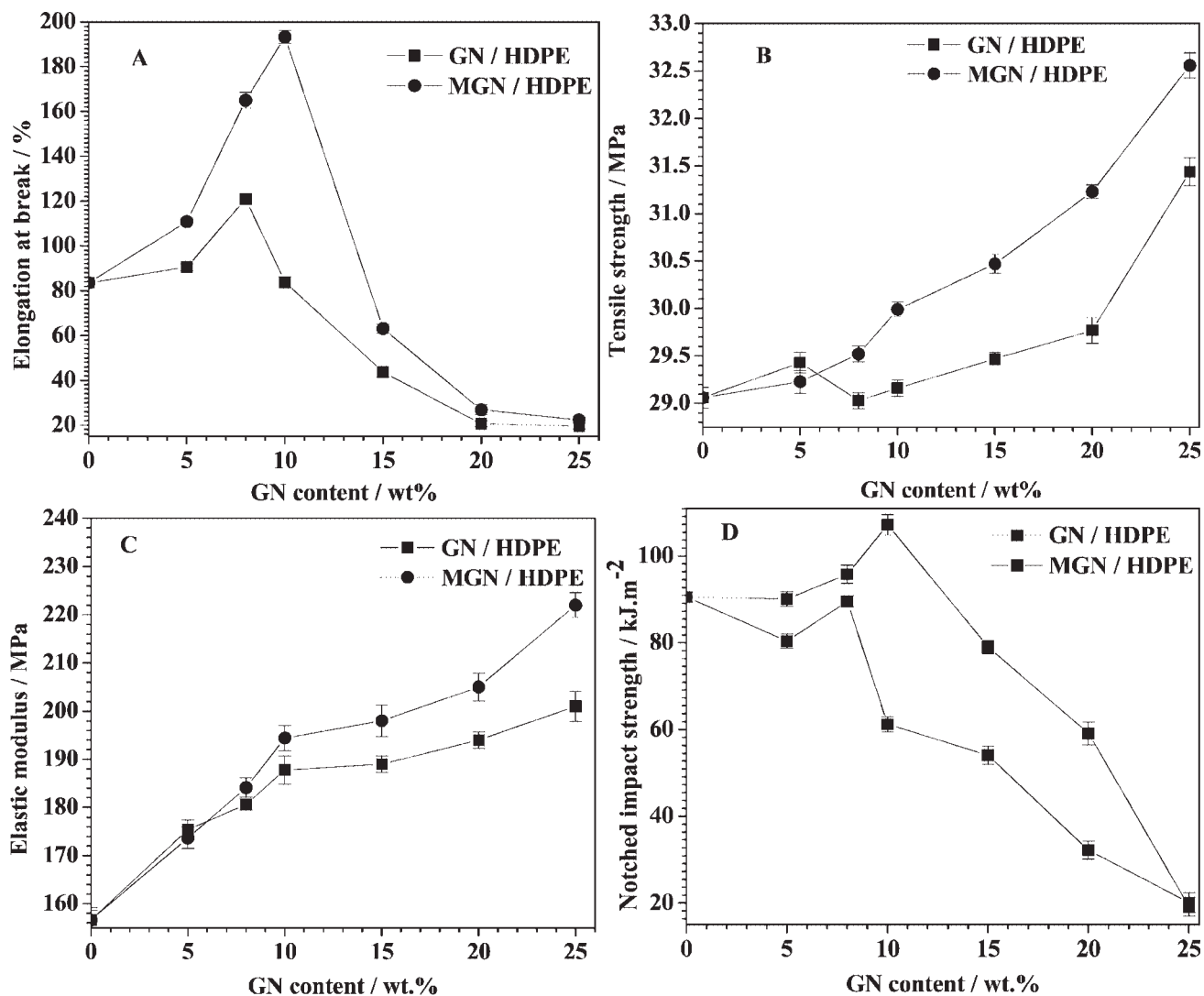
Figure 2 Mechanical properties of GNs/HDPE and MGNs/HDPE nanocoposites (1 wt % SDBS) (A) elongation at break, (B) tensile strength, (C) Tensile modulus, and (D) impact strength.

The argument is supported by the results of the surfactant control experiment (Fig. 3), which shows that a more remarkable increase in the elongation at break occurred as compared to that of pristine HDPE when 0.8 wt % SDBS was used. The sharp increase was observed in Figure 3(A), from the value of 83.51% (neat HDPE) to the value of 323.2% at filler concentration of 10 wt %. From Figure 3(B–D), it can be drawn that the tensile strength, elastic modulus and impact strength increase with the elongation at break increasing at 0.8 wt % SDBS, which is extraordinary exciting. In Figure 3(B,C), both the tensile strength and elastic modulus are inclined to decrease; however, they increase when the surfactant loading is over 0.5 wt %. This variety is mainly because of the increased interaction between the good coated GNs and the matrix. They are decreased again after 1 wt % surfactant. The impact strength tends to decrease and then increase above

the point of 2 wt % surfactant. It can be suggested that 10 wt % GNs modified with 0.8 wt % SDBS reinforced HDPE nanocomposites showed the best balance of mechanical properties, especially dramatic elongation at break.

In Figure 4, compared to pristine HDPE the crystallinity of nanocomposites decreases because of the adding of GNs. Yet the trends in crystallinity with respect to the same content of GNs are similar with and without SDBS surfactant. That is to say, the surfactant is little responsible for the crystallinity of nanocomposites.

Tensile fracture of HDPE/GNs nanocomposites

Features of tensile specimens is shown in Figures 5 and 6. The fracture toughness of polymer depends upon the chain disentanglement from the entangled network as well as chain rupture under stress,[29]
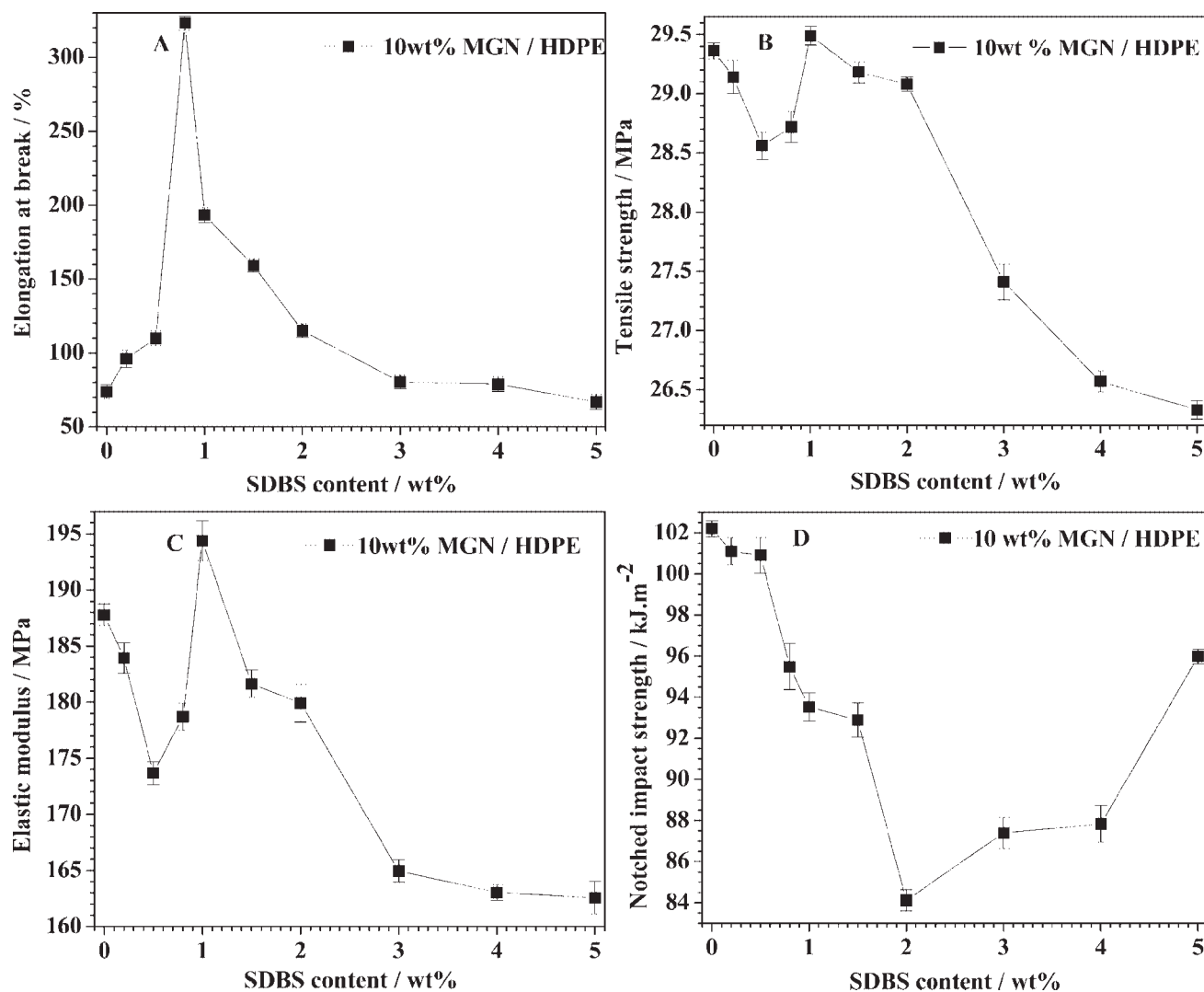
Figure 3 Mechanical properties of 10 wt % GNs modified by SDBS enhanced HDPE nanocoposites (A) elongation at break, (B) tensile strength, (C) Tensile modulus, and (D) impact strength.

which has been revealed by numerous pioneer studies. In such a sense, the macroscopic failure can be related to the microscopic molecular orientation of strands in the deformed molecular network because chain disentanglement or rupture always leads to chain recoiling and thus reduces molecular orientation.[30] Due to the addition of the surfactant, the orientation of GNs is acheived in Figure 6 compared to Figure 5, which may result in the macroscopic orientation of PE. The remarkable increase in the elongation at break compared to that of pristine HDPE is mainly attributed to the layered graphite nanosheets linked to the HDPE molecules through the surfactant rather than the surfactant itself.

However, due to the inserted surfactant, the level of adhesion of the filler to the matrix is improved. In the tensile procedure, if the adhesion of the interface between the filler and the matrix is higher than the interaction between gathered GNs, sliding of
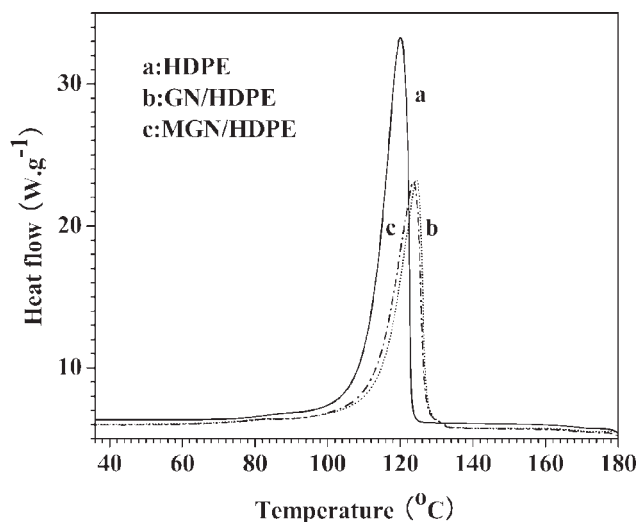

Figure 4 DSC curves of 10 wt % GNs and MGNs enhanced HDPE nanocomposites near melting point.

oriented flakes could occur each other (see Fig. 6), which may contribute to the increased elongation at break. What's more, the uniform dispersion of graphite nanosheets in the nanocomposite affords a marked improvement in the elongation at break, tensile strength, modulus, and impact strength.

CONCLUSIONS

In this article, GNs- and MGNs-reiforced HDPE nanocomposites were prepared. It has been demonstrated that GNs can typically reinforce the mechanical properties of HDPE/GNs and GNs treated with 0.8% SDBS leads to a quite dramatic increase of about 290% in elongation at break and about 14% in elastic modulus in comparison with that of neat HDPE. Both the impact strength and tensile strength are improved simultaneously. The surfactants attached to the sur-
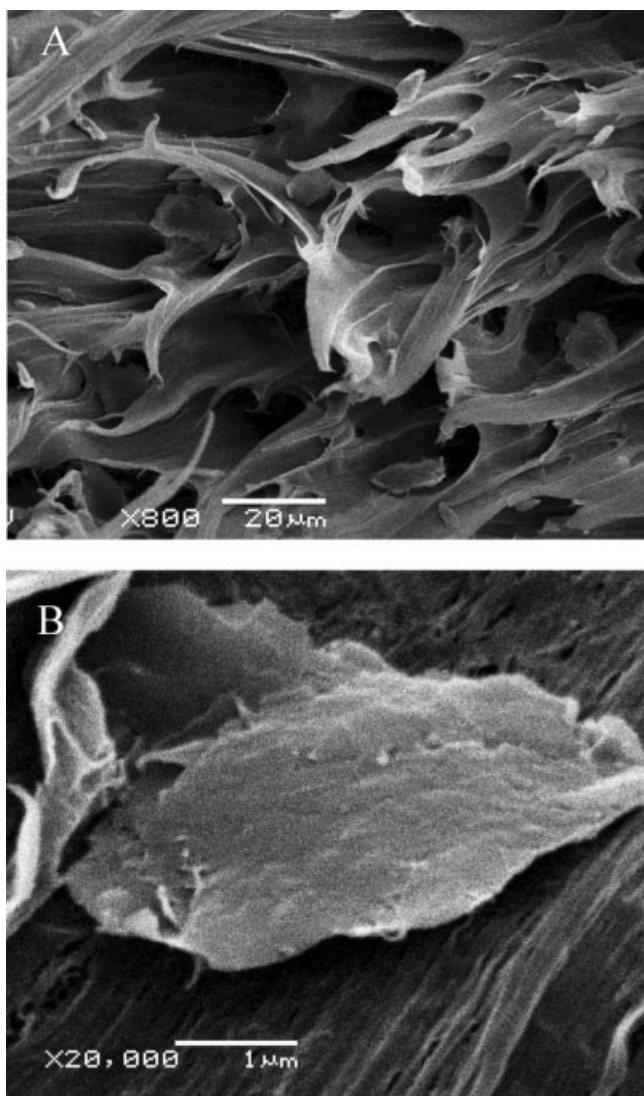

Figure 6 Tensile failure features of 10 wt % MGNs with 0.8 wt % SDBS modified enhanced HDPE nanocomposites (A) overview of fracture surface and (B) GNs dispersed in the matrix on the fracture surface.

face of nanosheets provided notable advantages in the dispersion of GNs in HDPE and the interfacial-strength between the filler and the matrix, both of which make for the increase in mechanical properties. SEM suggested the sliding of layered graphite nanosheets linked to the HDPE molecules through the surfactant could occur, which may contribute to the increased elongation at break. Though the remarkable elongation at break attracts tremendous interests, the mechanism should be further researched.

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Figure 5 Tensile failure features of 10 wt % GNs enhanced HDPE nanocomposites (A) overview of fracture surface and (B) GNs dispersed in the matrix on the fracture surface.
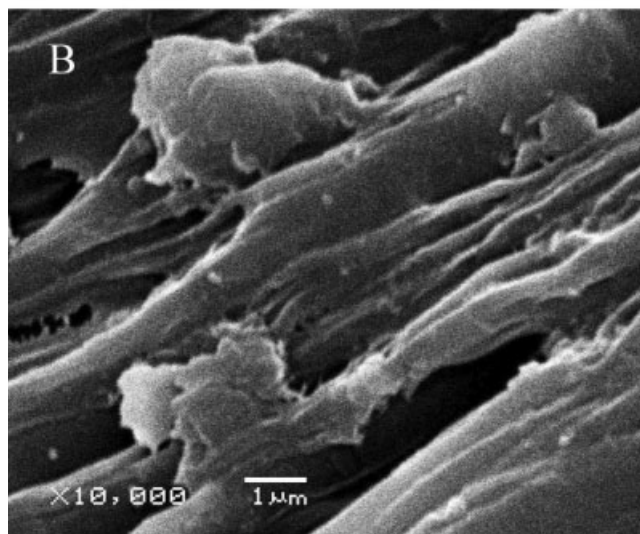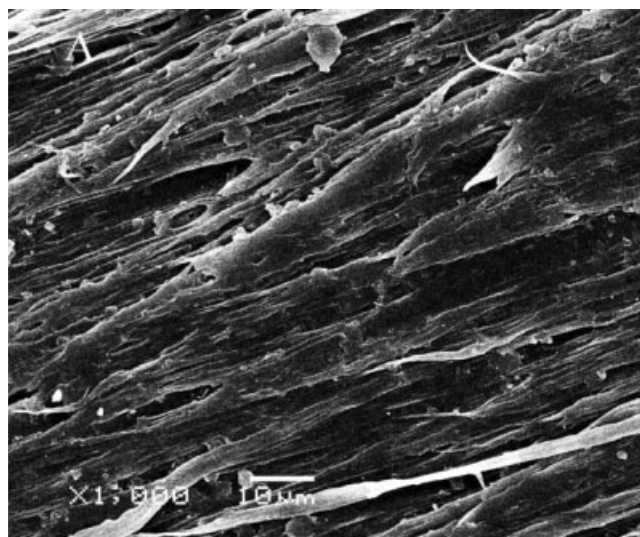
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