

Reduction in Percolation Threshold of Injection Molded High-Density Polyethylene/Exfoliated Graphene Nanoplatelets Composites by Solid State Ball Milling and Solid State Shear Pulverization

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ABSTRACT: Previous work showed that high density polyethylene (HDPE)/exfoliated graphene nanoplatelets (GNP) nanocomposites fabricated with melt extrusion followed by injection molding had a relatively high percolation threshold of between 10 and 15 vol % GNP loading. To lower the percolation threshold of injection molded HDPE/GNP nanocomposites, two special processing methods were investigated: solid state ball milling (SSBM) and solid state shear pulverization (SSSP). Results have confirmed that the percolation threshold of HDPE/GNP nanocomposites could be reduced to between 3 and 5 vol % GNP loading by these two approaches. The mechanism

by which SSBM and SSSP are capable of producing lower percolation is to coat the polymer surface with GNP platelets which facilitates the formation of conductive networks during injection molding. However, it was found that HDPE/GNP nanocomposites obtained from these two techniques exhibited lower mechanical properties at high GNP loadings. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 525–535, 2012

Key words: injection molding; mechanical properties; nanocomposites; nanotechnology; polyolefins

INTRODUCTION

Electrically conductive polymeric composites are materials of high interest because of the potential advantages of these materials in many applications such as for electromagnetic interference (EMI) shielding devices, rechargeable batteries, electronic devices, light emitting diodes (LEDs), gas sensors, supercapacitors, and photovoltaic cells.^{1–4} The advantages in selecting these polymeric composites over traditionally used materials such as metals or ceramic are their low density, low susceptibility to oxidation/chemical corrosion, good barrier properties, and low cost. Additionally, polymeric composites can be manufactured into complex shapes without expensive secondary processing steps.⁵

Among all the conductive fillers, carbon black is by far used the most due to its abundance in nature and low price. However, composites filled with carbon black generally require large filler concentra-

tions to attain percolation and adequate electrical conductivity as a result of the low aspect ratio of carbon black and the large electron “hopping” distance between carbon aggregates.⁶ The large amount of carbon black added in the composites to reach high electrical conductivity results in a polymer melt with extremely high viscosity, making it difficult to process with traditional processing methods such as extrusion and injection molding.⁷

Recently carbon nanotubes (CNTs) have been intensively explored as the conductive filler in polymers on account of their exceptional mechanical, electrical, and thermal properties, and potentially low percolation threshold.⁸ Many articles have appeared in the literature describing the processing and resulting electrical and/or mechanical properties by fabricating CNTs-filled polymeric nanocomposites for a number of applications.^{9–12} However, due to the poor yield and costly fabrication and purifying process, the price of CNTs in the market is still high, which limits the commercial applications of CNTs to date.¹³

To achieve a high electrical conductivity in polymeric composites but low cost and easy processing, graphite based materials are gaining more and more research attention. Polycrystalline graphite is a material that consists of extended networks of sp²-hybridized carbons (i.e., large sheets benzene rings) in a

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planar layered structure (graphene), resulting in excellent thermal and electrical conductivity within this graphitic basal plane. Exfoliation of these graphite layers and dispersion into polymers offers the potential to produce multiple conductive pathways in the composites at low graphite concentrations.¹⁴ Furthermore, it is found that fully exfoliated graphite nanosheets are as effective in conductivity enhancement as CNTs due to their two-dimensional lattice of sp²-bond carbon and extremely high aspect ratio.¹⁵ Based on this principal, a new form of graphite-based nanomaterial, exfoliated graphene nanoplatelets, GNP, has been under investigation in the Drzal group for several years.^{16,17} Previous work has already shown that incorporation of GNP into high density polyethylene (HDPE) could greatly enhance the mechanical and thermal properties by applying melt extrusion and injection molding.^{18,19} But as for the electrical conductivity, HDPE/GNP nanocomposite fabricated by this conventional compounding method was found to have a percolation threshold higher than 10 vol % GNP loading. This threshold value is generally much higher than the nanocomposites filled with CNTs by similar processing methods.²⁰ The high percolation threshold of HDPE/GNP nanocomposites is a result of the GNP re-aggregation during melt extrusion and preferential platelets alignment in the injection molding due to the large aspect ratio and planar shape of GNP as described in the previous study.¹⁹ Thus, the superb electrical properties of GNP cannot be as yet fully translated into good electrical conductivity of GNP nanocomposites.

To lower the percolation threshold of GNP nanocomposites, several nontraditional processing methods have been investigated such as solution intercalation method in polypropylene/GNP system,²¹ *in situ* polymerization method in nylon 6/expanded graphite²² and polyaniline/expanded graphite²³ system and polymerization filling technique in polystyrene/exfoliated graphite²⁴ system. These methods have demonstrated that the percolation threshold values in these polymer/graphite composites were all significantly reduced compared with the samples made by the melt extrusion. However, since extrusion and injection molding is still the major processing method used for manufacturing the thermoplastics in industry because of its design flexibility, low cost and labor, short cycle time, and minimum scrap loss,²⁵ a method to reduce the percolation threshold in extrusion and injection molded nanocomposites remains an area of high interest. Solid state ball milling (SSBM) and solid state shear pulverization (SSSP), which are the techniques both suitable for extrusion and injection molding, are reported in this study to lower the percolation threshold and enhance the electrical conductivity for HDPE/GNP nanocomposites.

EXPERIMENTAL

Materials

In this research, HDPE pellets with the trade name Marlex[®] HXM 50100 (density 0.948 g/cm³, ASTM D1505; flow index 10.0 g/10 min, ASTM D1238) were obtained from Chevron Phillips Chemical Company.

Exfoliated graphene nanoplatelets, GNP, were prepared with acid intercalated natural crystalline graphite followed by rapid exfoliation in a microwave environment. The graphite rapidly heats as a result of coupling with the microwave radiation and the intercalants quickly and completely vaporize resulting in "clean" expanded graphite. The exfoliated graphite particles undergo significant expansion (~500×) forming a worm-like structure. This worm-like structure is then mechanically grounded to form the individual graphene nanoplatelets which have the thickness less than 5 nm and a diameter around 15 μm (GNP-15). GNP-15 can be further reduced in diameter by vibratory milling, resulting in graphene nanoplatelets with the same thickness but having the diameter around 1 μm (GNP-1). The details of the exfoliation process and the morphology of GNP-1 and GNP-15 can be found elsewhere.¹⁶

Processing

Melt extrusion and injection molding

Melt extrusion of HDPE/GNP nanocomposites was carried out in a DSM Micro 15cc Compounder, (Vertical, corotating, twin-screws microextruder) operating at 220°C for 5 min at a screw speed of 100 rpm. The composite melt was then directly transferred in the melt state to a Daga Micro injector with the $T_{\text{barrier}} = 220^\circ\text{C}$ and $T_{\text{mold}} = 90^\circ\text{C}$. The injection pressure applied for injection molding of flexural coupons were around 0.6 MPa. The melt extrusion and injection molding systems are shown in the Figure 1(a,b) respectively.

Solid state ball milling and injection molding

The starting material for SSBM is a mixture of GNP and HDPE powder (diameter ~100 μm) which was obtained from the cryogenic milling of as-received HDPE pellets. SSBM process was carried out in a SPEX SamplePrep 8000D Dual Mixer/Mill[®] system which is shown in the Figure 2. The mixture of GNP and HDPE powder at selected volume ratios (1, 3, 5, 10, and 15 vol % GNP loading) was added into a stainless steel vial where six steel balls (two large balls: 1/4 in. in diameter and four small balls: 1/8 in. in diameter) were used as the milling medium. SSBM time was kept at 200 min which could

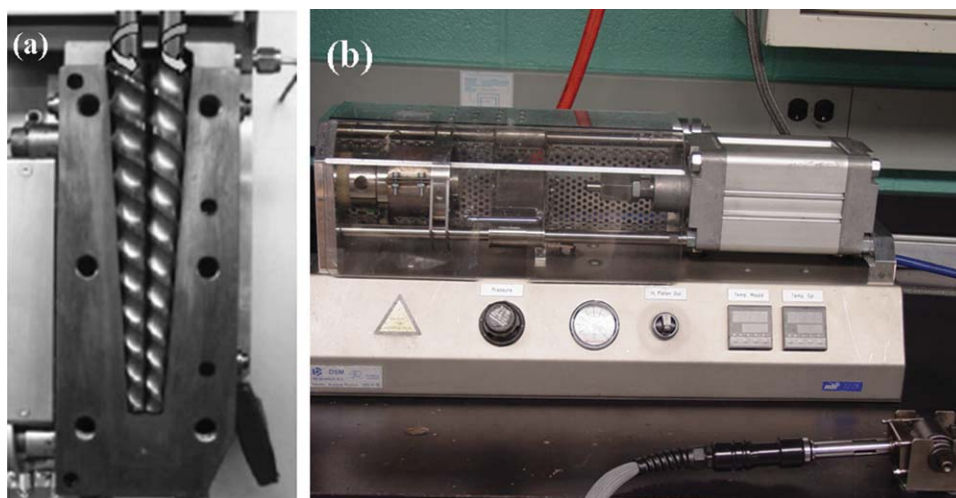


Figure 1 (a) A DSM Micro 15cc Compounder, (vertical, corotating, twin-screws microextruder); (b) A Daca Micro injector. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

produce a powder with each HDPE particle uniformly coated with GNP platelets. The morphology of HDPE powder after 200 min SSBM with and without GNP-15 is presented in the Figure 3. From Figure 3(a), it is noted that the diameter of HDPE particles is reduced from 100 μm to around 20 μm due to the high energy ball milling. And from Figure 3(b), we can see that the HDPE particle is uniformly coated with GNP-15 platelets and the size of most GNP-15 platelets is also reduced (less than 10 μm) according to the SEM image of higher magnification [Fig. 3(c)]. The GNP coated HDPE powder was then injection molded to make flexural coupons for mechanical properties and electrical conductivity test under the same injection conditions as described above.

Solid state shear pulverization and injection molding

The solid state shear pulverization process (SSSP) was originally devised and explored in the Torkel-

son Group in Northwestern University as a method for polymer blend compatibilization.^{26,27} Here, we introduce the SSSP technique as a novel strategy to fabricate HDPE/GNP nanocomposites. SSSP was conducted with a Leistritz Micro 27 twin extruder (27 mm screw diameter, $L/D = 48$, corotation). HDPE pellets (as-received) and GNP with selected volume ratios (1 vol %, 3 vol %, 5 vol %, 10 vol %, and 15 vol % GNP loadings) were fed at a feed rate of 100 g/h into the extruder in which they were pulverized to yield a powder mixture output. The screw rpm was 200 and the barrel temperature was kept around 20°C by the cooling coils surrounding the barrels to ensure that the polymer remained in the solid state. The process of SSSP is schematically shown in the Figure 4. According to the SEM images of Figure 5, the SSSP technique also results in a uniform GNP coating on the surface of HDPE particles. However, the size of HDPE particles after SSSP (>100 μm) is much larger than those processed with SSBM, which is due to the much shorter processing



Figure 2 SPEX SamplePrep 8000D Dual Mixer/Mill[®] system and its steel vial set.

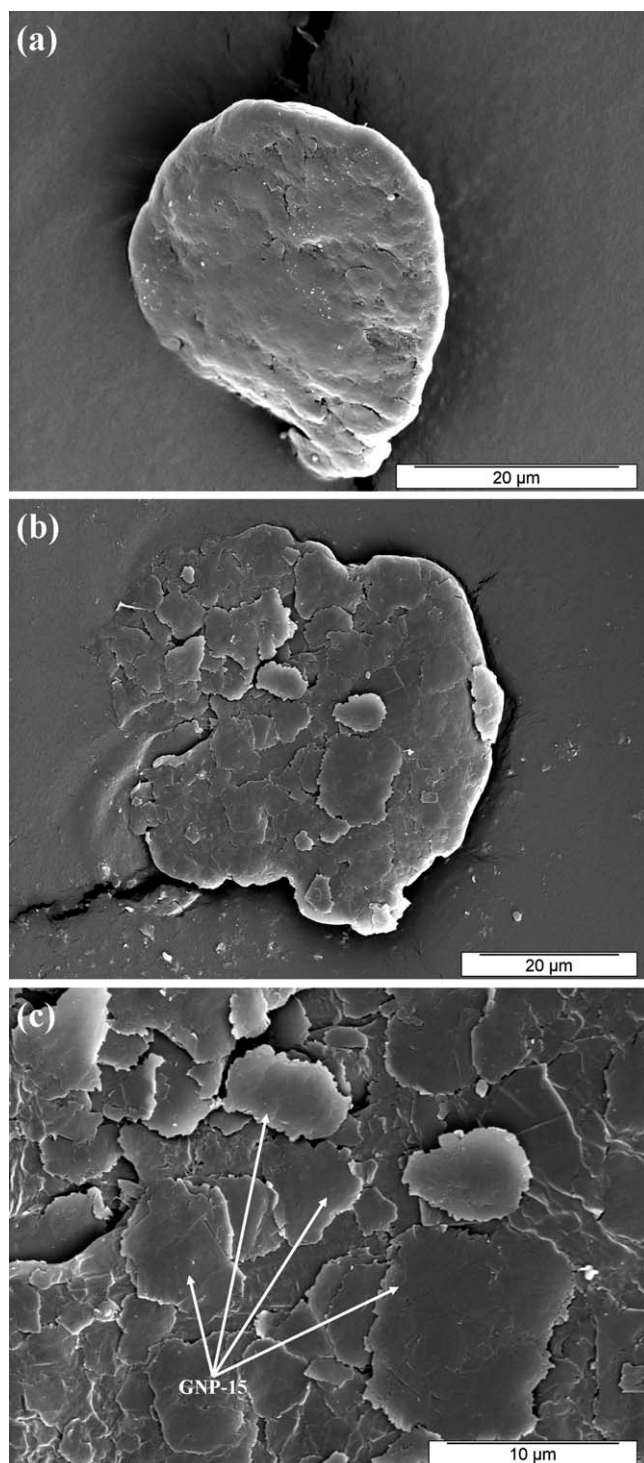


Figure 3 SEM images of HDPE powder after 200 min SSBM without GNP-15 ($\times 2000$) (a); HDPE powder after 200 min SSBM with GNP-15 at low magnification ($\times 1500$) (b) and high magnification ($\times 3700$) (c).

time in SSSP (several minutes vs. 200 min). The pulverized HDPE and GNP powder mixture was then injection molded to make flexural coupons for mechanical properties and electrical conductivity test under the same injection conditions as described above.

Characterization methods

Mechanical property

A UTS SFM-20 machine (United Calibration Corp.) was used to measure the flexural properties. Flexural coupons were tested under 3-point bending mode at a flexural rate of 0.05 in./min following the ASTM D790 standard.

Electrical resistivity

The electrical resistivity of HDPE/GNP nanocomposites was measured along the material flow direction (in-plane resistivity), using impedance spectroscopy by applying the two-probe method at room temperature. Samples with dimensions of 10 mm \times 3.15 mm \times 12.15 mm (length \times thickness \times width) were cut from the middle portion of the flexural coupons. The two surfaces connected to the electrodes were first treated with an O₂ plasma (14 min, 375 W) to remove the top surface layers which are rich in polymer and then conductive silver paste coated to ensure good contact of the sample surface with the electrodes. The resistance of samples was measured and converted to resistivity by taking the sample dimensions into account.

Scanning electron microscopy (SEM)

The preparation of SEM samples in this study included epoxy mounting, grinding, polishing, and etching steps. First, HDPE/GNP specimens for microscopic examination were mounted with epoxy in cylindrical sample holders to maintain a flat surface over the entire grinding area. After the epoxy was fully cured, the samples were then carefully grounded and polished. Plasma etching was applied at the last step to remove the polymer in top surface layers allowing the GNP platelets to stand out. A JEOL (model JSM-6400) SEM with an accelerating voltage of 10 kV and a working distance of 15 mm was then used to collect the SEM images. Samples were also gold coated of a few nanometers in thickness to avoid charging.

RESULTS AND DISCUSSION

Electrical conductivity of SSBM HDPE/GNP samples

The in-plane (material flow direction) electrical resistivity of HDPE/GNP nanocomposites made by conventional DSM extrusion and injection molding (DSM HDPE/GNP) is displayed in the Figure 6. For the in-plane resistivity, it is seen that at concentrations between 10 vol % and 15 vol % of GNP, there is a large decrease in the resistivity both for HDPE/GNP-1 and HDPE/GNP-15 nanocomposites. This

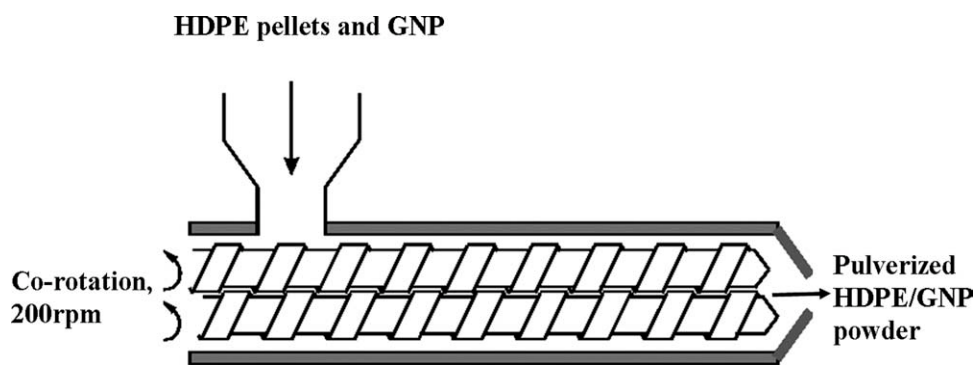


Figure 4 A schematic view of the SSSP process.

concentration range (10–15 vol %) is thus noted as the percolation threshold for DSM HDPE/GNP nanocomposites. The percolation threshold is defined as the concentration where a connected assembly of conductive particles is formed within a polymer matrix. At this concentration of the conductive filler, the electrical conductivity of the composite significantly increases and it becomes electrical conductive.²⁸ The high percolated threshold for DSM samples is mainly due to the GNP aggregation during extrusion and the preferential filler orientation and alignment during injection molding. The morphology of DSM HDPE/GNP-1 and HDPE/GNP-15 samples at 5 vol % GNP loading is shown on the Figure 7 as an example. From Figure 7(a), it can be seen that all the GNP-1 particles align parallel along the material flow direction and they are totally separated by the polymer matrix. The resistivity of this GNP-1 sample is therefore high at 5.6×10^{10} ($\Omega \cdot \text{cm}$). GNP-1 aggregates can also be found in the Figure 7(a) which is the indication of insufficiency of DSM extrusion for good GNP separation and dispersion. From Figure 7(b), it is concluded that GNP-15 platelets also exhibit preferential alignment with no interparticle connection and extremely large aggregates can be easily detected. In summary, aggregation along with GNP alignment leads to poor interconnections between GNP platelets which results in the low electrical conductivity of DSM HDPE/GNP nanocomposites.

The in-plane electrical resistivity of HDPE/GNP nanocomposites obtained from the SSBM method and the comparison with the DSM samples is presented in the Figure 8. As indicated in this Figure, SSBM HDPE/GNP nanocomposites have the in-plane percolation threshold of just 3 to 5 vol % GNP loading compared with the threshold value of 10 to 15 vol % for the DSM samples. Huge reduction in percolation threshold clearly suggests better formation of conductive networks in the resulting SSBM nanocomposites. In addition, the absolute electrical conductivity of SSBM HDPE/GNP samples from 3 vol % to 15 vol % GNP loading is found to be

greatly higher which further confirms the substantial improvement in electrical conductivity by the SSBM process.

SEM images of SSBM HDPE/GNP-1 and SSBM HDPE/GNP-15 nanocomposites at 5 vol % GNP loading are presented in the Figures 9 and 10, respectively. The morphology helps explain why

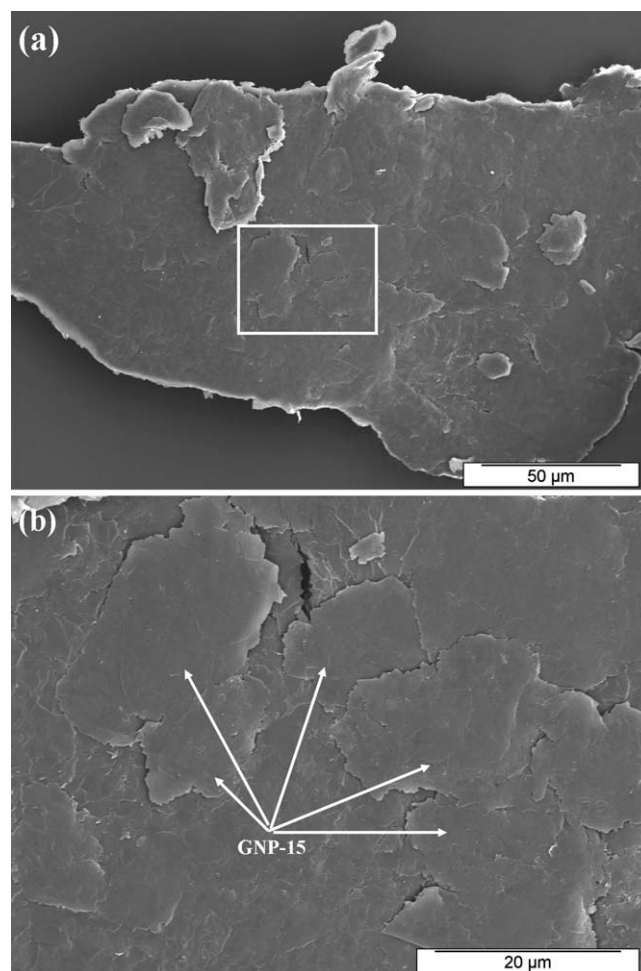


Figure 5 SEM images of HDPE pellets after SSSP with GNP-15 at (a) low magnification ($\times 550$) and (b) high magnification ($\times 2000$, enlarged rectangular area in the image (a)).

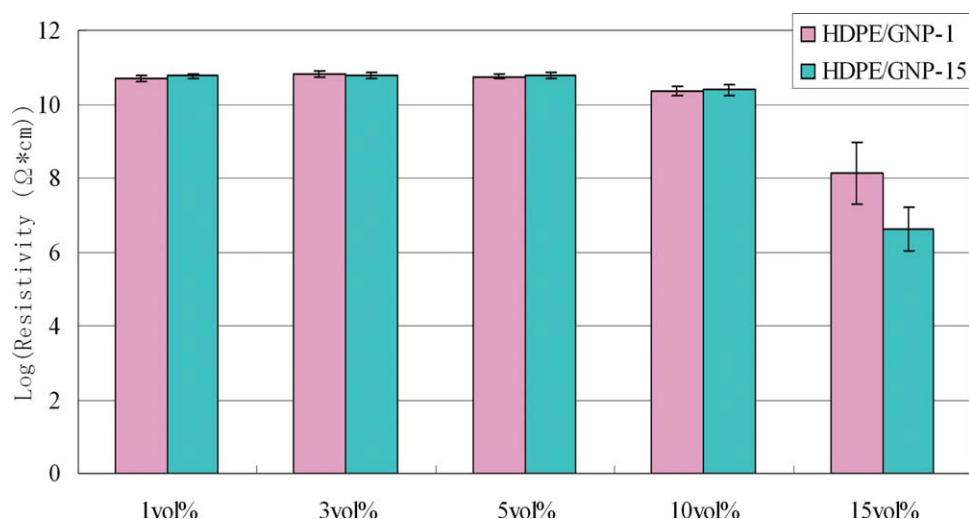


Figure 6 In-plane electrical resistivity of DSM HDPE/GNP nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

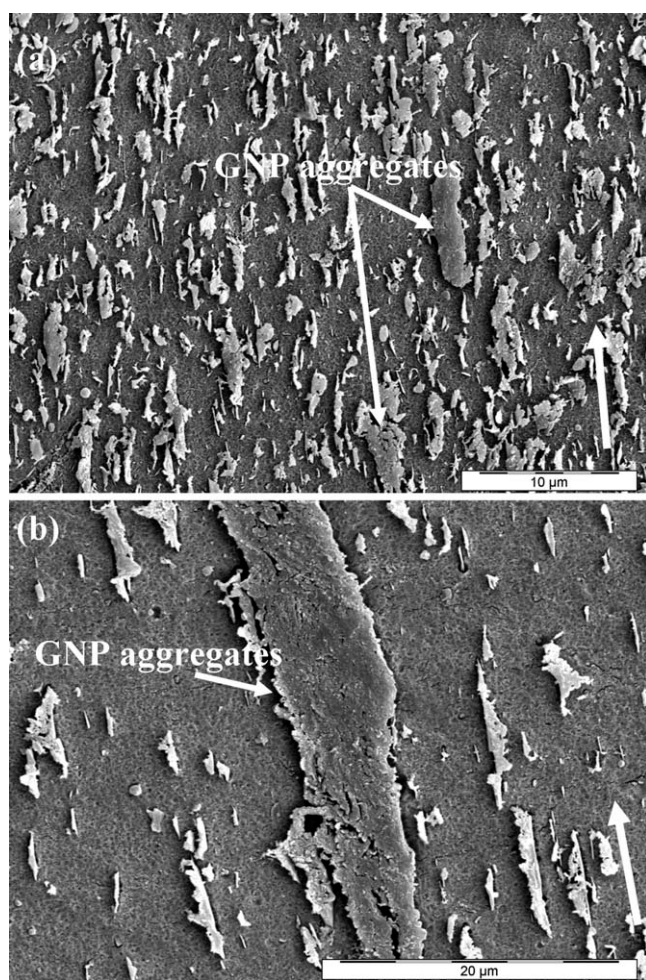


Figure 7 SEM images of DSM HDPE/GNP nanocomposites at 5 vol % GNP loading. The arrow on the right bottom indicates the material flow direction during injection molding. (a) GNP-1 sample (magnification $\times 3000$); (b) GNP-15 sample (magnification $\times 3000$).

SSBM HDPE/GNP nanocomposites have a lower percolation threshold and higher electrical conductivity. From Figure 7, it is noted that for DSM HDPE/GNP-1 nanocomposites [Fig. 7(a)], GNP-1 platelets are relatively homogeneously dispersed in the HDPE matrix with preferential alignment along the flow direction. However, for the SSBM sample [Fig. 9(a)], it is clear to see that there exist alternate polymer-rich regions and GNP-rich regions in the polymer matrix. The SEM image with higher magnification [Fig. 9(b)] shows that GNP-1 nanoplatelets are all intersecting with each other forming conductive pathways in the GNP-rich regions. It is believed that the presence of such conductive pathways throughout the polymer matrix significantly reduces the percolation threshold and increases the electrical conductivity of HDPE/GNP-1 nanocomposites.

The formation of this unique morphology by the SSBM process is supposed to be the result of the high-energy ball milling, which produces compression and shear forces to the GNP aggregates to shear them apart and get GNP platelets separated. HDPE powder is thus homogeneously coated with individual GNP platelets as indicated in the Figure 3. When the GNP coated HDPE powder undergoes the injection molding process, the high velocity material flow forces HDPE to melt and fuse into one phase (polymer-rich regions), and the GNP platelets originally coated on the surface move along together to re-aggregate, forming another phase (GNP-rich regions or conductive pathways). This kind of the conductive pathway formation during injection molding is schematically illustrated in the Figure 11. From Figure 10(a,b), the SSBM HDPE/GNP-15 sample also exhibits alternate polymer-rich regions and GNP-rich regions resulting in conductive pathways for

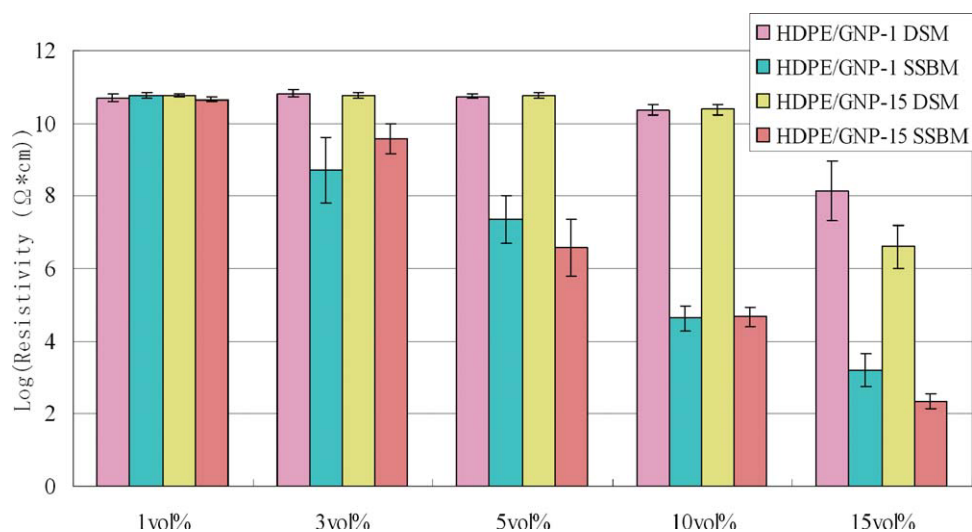


Figure 8 In-plane electrical resistivity of SSBM HDPE/GNP nanocomposites and its comparison with DSM HDPE/GNP samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

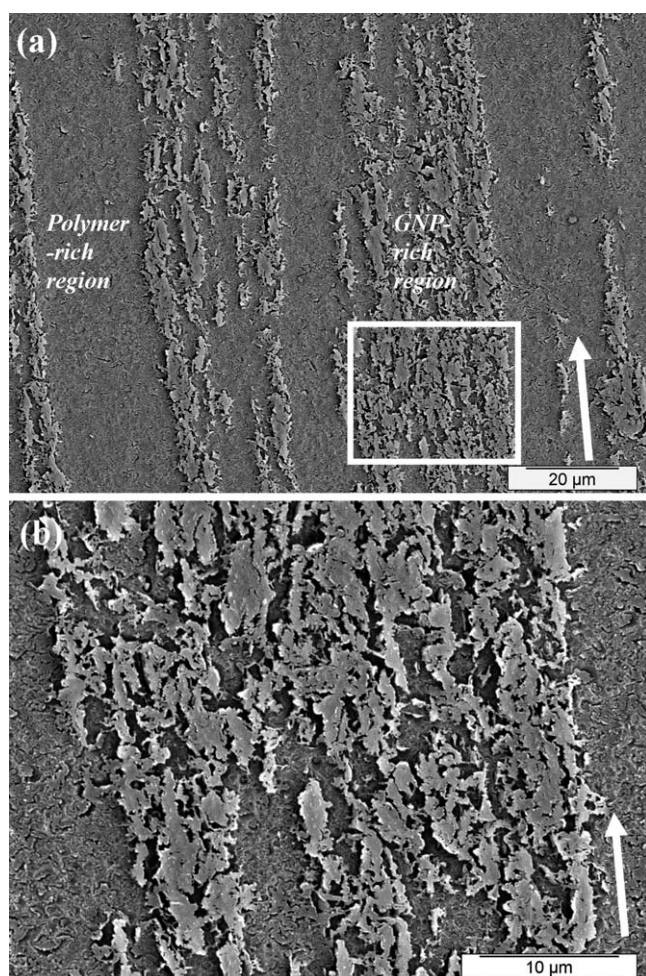


Figure 9 SEM images of SSBM HDPE/GNP-1 nanocomposites at 5 vol % GNP loading. (a) Low magnification image ($\times 1000$); (b) high magnification image ($\times 3000$, enlarged rectangular area in the image (a)). Arrows in the images indicate the material flow direction during injection molding.

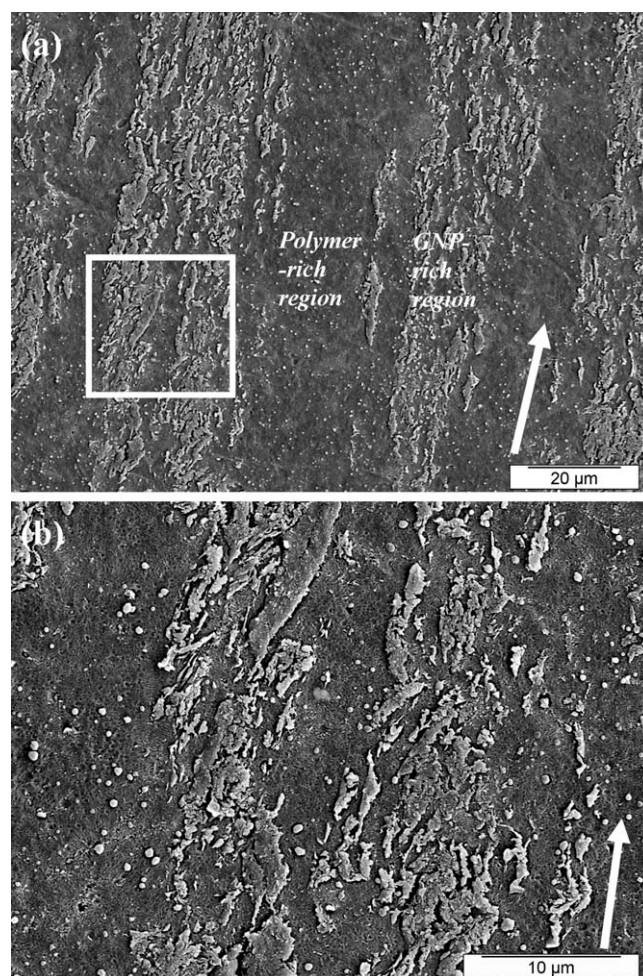


Figure 10 SEM images of SSBM HDPE/GNP-15 nanocomposites at 5 vol % GNP loading. (a) Low magnification image ($\times 1000$); (b) high magnification image ($\times 3000$, enlarged rectangular area in the image (a)). Arrows in the images indicate the material flow direction during injection molding.

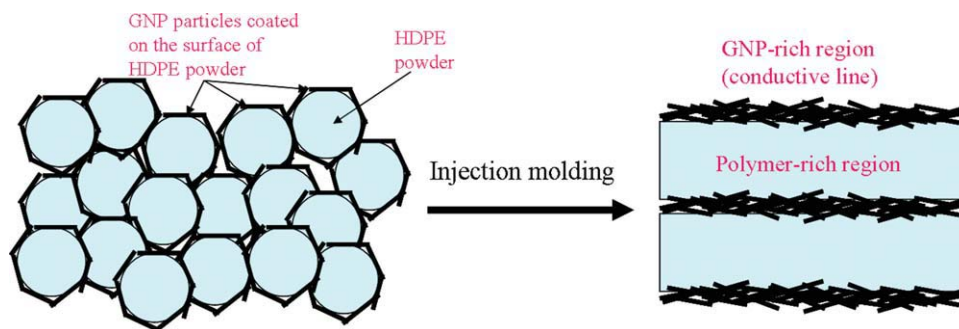


Figure 11 Formation of conductive pathways in SSBM HDPE/GNP nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electron transportation in the GNP-rich regions. In this case, it is concluded that the SSBM process substantially improves the electrical conductivity of HDPE/GNP nanocomposites due to the selective aggregation of GNP platelets at HDPE-GNP interfaces which results in continuous conductive pathways in the HDPE matrix during injection molding.

Electrical conductivity of SSSP HDPE/GNP samples

From the previous section, the advantage of the SSBM process is clear that SSBM could significantly increase the in-plane electrical conductivity of HDPE/GNP nanocomposites. However, SSBM is a discontinuous process and only a small amount of material can be produced each time which may constrain its potential for industrial application. To overcome this deficiency, solid state shear pulverization (SSSP) is introduced here which is capable of producing large amount of materials continuously within a relatively short time. Figure 12 compares the in-plane electrical resistivity of HDPE/GNP

nanocomposites fabricated by the SSSP process and the samples made from the DSM extrusion. From Figure 12, it is concluded that the in-plane electrical conductivity of SSSP HDPE/GNP nanocomposites is also significantly enhanced and the percolation threshold is reduced to only 3 to 5 vol % GNP loading as well. The morphology of the SSSP HDPE/GNP-15 sample at 5 vol % GNP loading is shown in the Figure 13, which also exhibits polymer-rich regions and GNP-rich regions and they appear to be very similar to those in the SSBM samples (Figs. 9 and 10). The mechanism of formation of alternate polymer-rich and GNP-rich regions by the SSSP technique is therefore considered to be the same as that of the SSBM method. In the GNP-rich regions, electron pathways are found to be nicely constructed because of the well-connected GNP aggregates, which greatly contribute to the enhanced electrical conductivity of the resulting nanocomposites.

The comparison between the SSSP and SSBM methods in improving the electrical conductivity for HDPE/GNP nanocomposites is presented in the Figure 14. According to this Figure, it is observed

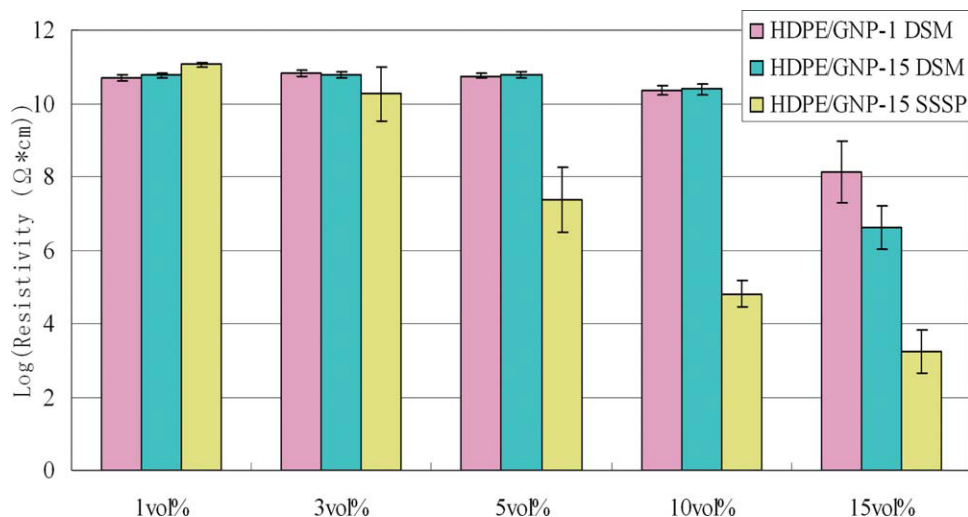


Figure 12 In-plane electrical resistivity of SSSP HDPE/GNP-15 nanocomposites and its comparison with DSM HDPE/GNP samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

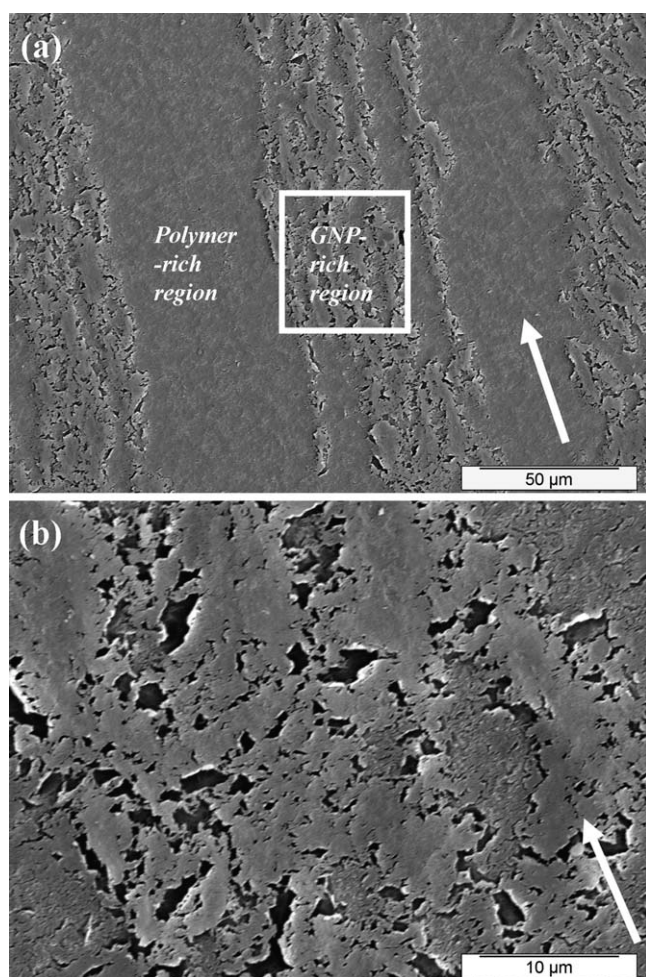


Figure 13 SEM images of SSSP HDPE/GNP-15 nanocomposites at 5 vol % GNP loading. (a) Low magnification image ($\times 600$); (b) high magnification image ($\times 3000$, enlarged rectangular area in the image (a)). Arrows in the images indicate the material flow direction during injection molding.

that SSSP HDPE/GNP nanocomposites exhibit competitive electrical conductivity to the SSBM samples both in the percolation threshold and the absolute conductivity at most GNP loadings (except for 15 vol % GNP loading). However, due to its capability of continuous mass production and much shorter processing time, the SSSP technique is believed to be more promising for its potential in industrial application.

Mechanical properties of SSBM, SSSP, and DSM HDPE/GNP nanocomposites

According to the discussion above, application of SSBM and SSSP methods can both improve the electrical conductivity of HDPE/GNP nanocomposites significantly. However, nanocomposites are often expected not only to have good electrical conductivity but also excellent mechanical properties. Bipolar plates in the proton exchange membrane fuel cells and EMI shielding and electrostatic discharge (ESD) protection materials for aerospace are just two examples.^{29,30} In this case, Figures 15 and 16 compare the flexural strength and flexural modulus respectively, between the SSBM, SSSP HDPE/GNP nanocomposites, and the DSM HDPE/GNP counterparts of which the excellent mechanical properties have already been demonstrated in an earlier study.¹⁸ As a baseline for comparison it is noted that virgin HDPE fabricated by the SSBM and SSSP methods shows higher flexural strength and modulus than the sample made from the DSM melt extrusion. It has been known that high energy ball milling in SSBM and high pressure shear deformation in SSSP both produce molecular chain scission and breakage.³¹ The breakage of polymer chains most often produces

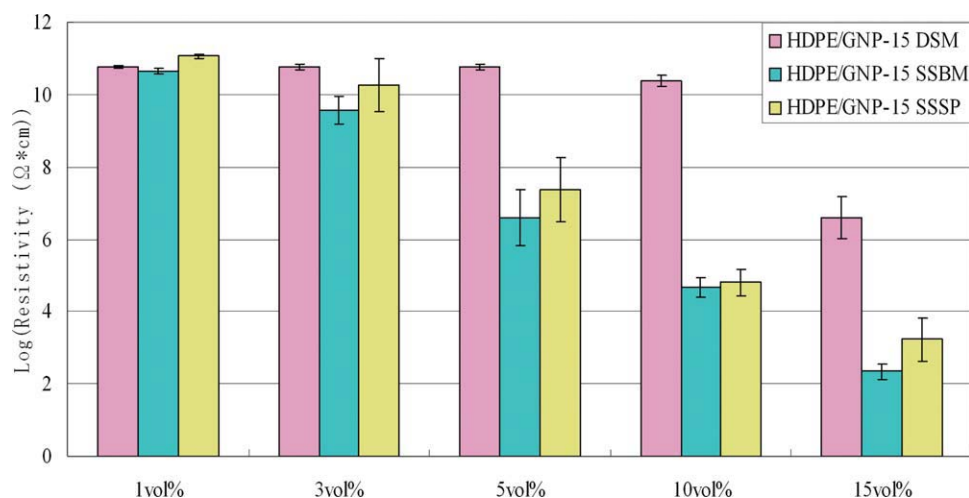


Figure 14 In-plane electrical conductivity of 5 vol % HDPE/GNP-15 nanocomposites made by DSM, SSBM, and SSSP methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

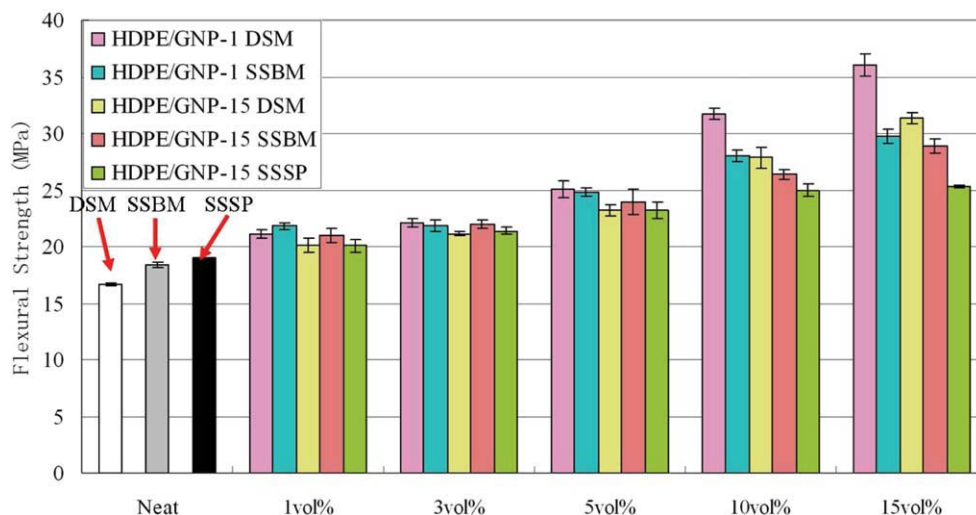


Figure 15 Flexural strength of HDPE/GNP nanocomposites made by DSM, SSBM, and SSSP methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

free radicals which in turn lead to the crosslinking in the polymer. This crosslinking phenomenon induced by SSBM or SSSP mainly contributes to the enhanced flexural properties of virgin HDPE. And for the flexural properties of HDPE/GNP nanocomposites, SSBM and SSSP samples exhibit comparable flexural strength and modulus to the DSM samples with GNP loadings up to 5 vol %. At higher GNP loadings, however, SSBM and SSSP HDPE/GNP nanocomposites show inferior flexural properties. On the basis of morphology analysis for the SSBM and SSSP samples described above, the reduced mechanical property is mainly due to the poor GNP dispersion in the polymer matrix. GNP platelets in those nanocomposites are not uniformly distributed and the severe GNP aggregation in the GNP-rich regions form stress concentrations similar to those

voids in the composites which result in a decrease of flexural strength and modulus.

CONCLUSIONS

Although the percolation threshold of HDPE/GNP nanocomposites fabricated by conventional extrusion and injection molding is high, this study demonstrates that it could be significantly reduced by the SSBM and SSSP techniques before injection molding to improve the electrical conductivity of HDPE/GNP nanocomposites. GNP platelets are found to be uniformly coated on the surface of HDPE particles after the SSBM or SSSP processing as confirmed by SEM images. During injection molding, those GNP platelets on the surface of polymer tend to selectively aggregate at HDPE-GNP interfaces to form

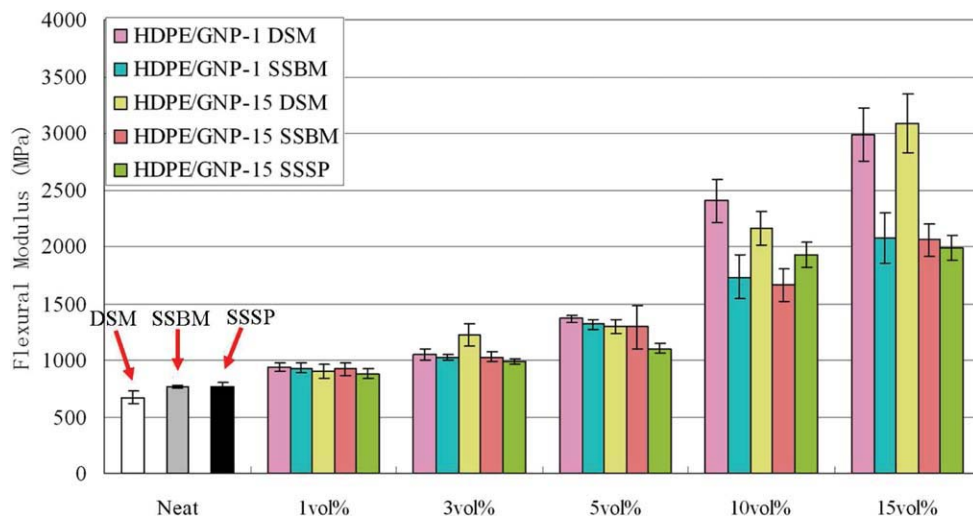


Figure 16 Flexural modulus of HDPE/GNP nanocomposites made by DSM, SSBM, and SSSP methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the GNP-rich regions (conductive pathways). The electrical conductivity of HDPE/GNP nanocomposites is therefore substantially increased by the existence of these well-connected GNP conductive pathways in the resulting nanocomposites. The mechanical properties of SSBM and SSSP HDPE/GNP nanocomposites have also been investigated. Because of the severe GNP aggregation in the GNP-rich regions as shown in their morphology, reduced mechanical properties are observed for SSBM and SSSP HDPE/GNP nanocomposites at high GNP loadings.

The mechanisms by which the SSBM and SSSP methods are capable of enhancing the electrical conductivity of HDPE/GNP nanocomposites appear to be similar. While SSBM is a viable batch method, SSSP is a continuous method that can produce larger amount of material at shorter time. These two methods are believed to have wide applicability to all thermoplastic nanocomposites systems.

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