

Reinforcement of Polyethylene Pipes with Modified Carbon Microfibers

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ABSTRACT. The surface properties of carbon microfibers (CMFs) are modified by chemical deposition of carbon nanofibers via the so-called ethylene processing. CMFs and the modified CMFs (MCMFs) are investigated as reinforcement additives to fabricate polyethylene (PE) composites with enhanced mechanical characteristics. The mechanical properties of the PE-MCMF composites are found to be better and favorable for applications under harsh climatic conditions such as those in Siberia. Improved adhesive interaction between MCMFs and PE is responsible for these enhanced mechanical properties.

Key words: Carbon microfibers, Surface and interfaces, Modified carbon microfiber, Polyethylene composite, Mechanical properties

INTRODUCTION

Carbon microfibers (CMFs) have been widely used to prepare polymeric composite materials.¹ CMFs have a small active specific surface area and are smooth. These characteristics of CMFs lead to weak adhesion with the polymer matrix.² Several methods have been proposed to alleviate these drawbacks - e.g., partial oxidation of the CMF surface (with acids, plasma, etc.) and chemical grafting³⁻¹¹ which can be employed to prepare modified carbon microfibers (MCMFs) that have a rough surface with a large specific area,⁵ which enhances adhesion at fiber-polymer interfaces and imparts high strength and fracture toughness.¹² Specifically, a number of studies have recently been devoted to the modification of CMFs via deposition of carbon nanofibers (CNFs)^{5,6,12-14} because carbon nanofibers (CNFs) are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus, respectively. This treatment is most commonly performed by catalytic chemical vapor deposition,³⁻¹¹ as in our previous studies on CMF surfaces.^{15,16}

Polyethylene (PE) is the most commonly used general-purpose thermoplastic polymer because of its excellent chemical resistance. PE can withstand attacks by strong acids or strong bases. It is also resistant to gentle oxidants and reducing agents. However, it has limitations under -15 °C, because its mechanical properties such as yield strength, crack resistance, and elasticity decrease significantly with

temperature.

In continuation of recent investigations on improved mechanical properties of polymer composites designed for use in the harsh Siberian climatic conditions,¹⁷⁻²⁰ the synthesis of MCMFs *via* chemical deposition of CNF, fabrication of PE-MCMFs composite, and the composite mechanical properties were investigated in this study.

EXPERIMENTAL

We used CMFs with 5–6 mm lengths and 5–7 μm diameters (VMN-4PKT, Carbon and Composite Materials Plant Limited Company, Russia), and several different PE (index 100) samples-namely, PE2NT11-9 (OJSC Kazanorgsintez, Russia), LH4100BL (Daelim Industrial Co. Ltd., Korea), PE6949Cblack (486H3) (OJSC Nizhnekamskneftekhim, Russia), and H1000PC (SCG Plastics Co. Ltd., Taiwan)-as the polymer matrix. The CMFs were modified by gas-phase ethylene processing with Ni as the catalyst^{15,21} in a rotary reactor,²² as shown in Fig. 1. Fiber-reinforced composites were fabricated by mixing melted PE with either CMFs or MCMFs^{16,22-25} at 180 °C. The resulting mixture was ground mechanically at 100 °C to obtain granules (2–5 mm in diameter) that were subsequently extruded with Plasti-corder (PL 2200, Brabender, Duisburg, Germany) at 180–200 °C.

The specific surface areas of the CMFs and MCMFs

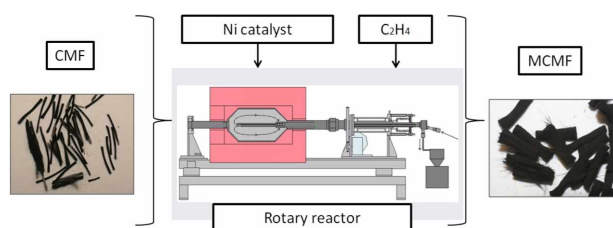


Figure 1. Schematic diagram for the ethylene processing.

were investigated using a pore size and surface area analyzer (ASAP-2400, Micromeritics, Norcross, GA, USA), and their morphology was observed by scanning electron microscopy (SEM, JSM-6460, Peabody, MA, USA) and transmission electron microscopy (JEM 1400, Jeol Ltd., Tokyo, Japan). Scanning electron microscopy (JEM 7800F, Jeol, Tokyo, Japan) was also used to study the interactions between the CMFs or MCMFs and the PE. The mechanical properties of PE and the CMF-PE composites were characterized using a UTS-2 universal testing machine (UTS Testsysteme GmbH, Ulm, Germany) according to the Russian government standards (GOST 11262-80).²⁶ The melting temperatures of several PE samples were estimated by differential scanning calorimetry (Fl Phoenix, NETZSCH, Selb, Germany), and their kinematic viscosity was measured using a capillary viscometer (Plasti-corder PL 2200, Brabender, Duisburg, Germany) at 180 °C and 15 rpm.

RESULTS AND DISCUSSION

Micrographs of the original CMFs and of the MCMFs used in this study are shown in *Fig. 2*. *Fig. 2(a)* shows that the CMFs form bunches with 5–7 μm diameters, and *Fig. 2(b)* shows that thermal treatment with $\text{Ni}(\text{NO}_3)_2$ leads to the formation of a nickel oxide layer on the surface of the CMFs. The CMFs increase in mass by 1% following ethylene treatment due to the deposition of CNFs at the CMF-Ni interface. As illustrated in *Figs. 2(c)* and *2(d)*, the Ni particles act as nucleation sites for CNFs that grow to a thickness of ~ 100 nm. Ethylene processing increases the specific surface area of the CMFs, with values (calculated using the Brunauer-Emmett-Teller theory)²⁷ of 0.3 m^2/g and 0.75 m^2/g obtained respectively for the CMFs and MCMFs.

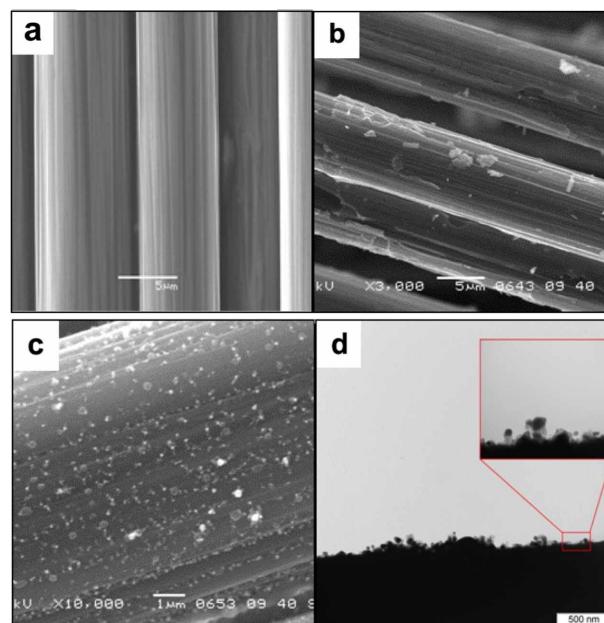


Figure 2. SEM of (a) original CMFs, (b) CMFs covered with a NiO layer, and (c) MCMFs, and (d) TEM of MCMFs.

Although the melting point, degree of crystallinity, and kinematic viscosity are given by suppliers of commercial PE, we measured these properties under same conditions and the results are listed in *Table 1*. These properties were necessary to determine the mechanical properties of polymer composites. Based on previous studies,^{14,15} a filler (CMF or MCMF) content of 10 wt % was chosen. *Fig. 3* shows that the mechanical properties of the PE-CMF and PE-MCMF composites vary according to the PE brand used. Further, the elastic modulus values of the LH4100BL-CMF and PE2NT11-CMF composites are higher than those of the LH4100BL-MCMF and PE2NT11-MCMF samples, respectively. However, H1000PC-CMF and PE6949Cblack (486H3)-CMF have a lower elastic modulus than H1000PC-MCMF and PE6949Cblack (486H3)-MCMF, respectively. These differences in elastic modulus reflect the differences in the kinematic viscosity of the PEs mentioned above. As shown in *Table 1* and *Fig. 3(b)*, the PEs with a low kinematic viscosity (LH4100BL and PE2NT11) form PE-CMF composites that have a higher elastic modulus than the corresponding

Table 1. Physical properties of commercial brands of polyethylene

Physical property	Polyethylene brand			
	LH4100BL	PE2NT11-9	H1000PC	PE6949C black (486H3)
Melting point (°C)	132.6	133.1	133.7	131.7
Degree of crystallinity (%)	52.3	57.3	57.5	43.6
Kinematic viscosity at 180 °C, 15 rpm (kPa·s)	11.9	12.9	15.0	14.8

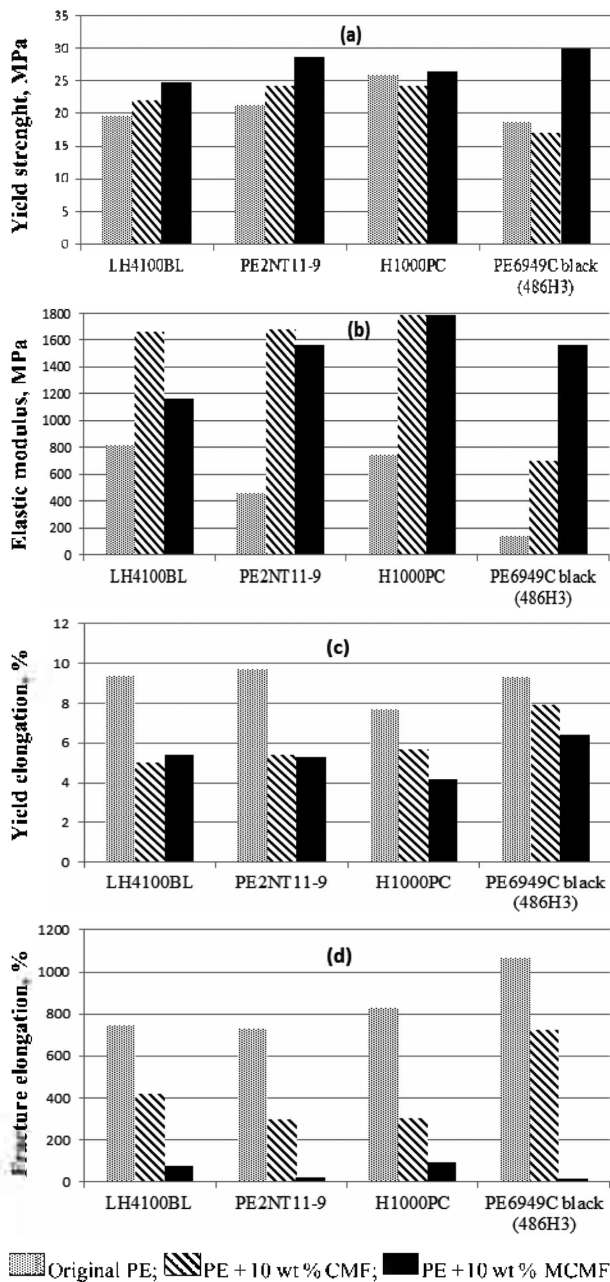


Figure 3. Mechanical properties of PE-CMFs composites: (a) yield strength, (b) elastic modulus, (c) yield elongation, and (d) fracture elongation.

PE-MCMF samples. For PEs with a high kinematic viscosity (H1000PC and PE6949Cblack (486H3)) in contrast, the PE-MCMF composites produced have a higher elastic modulus. The elastic modulus of the PE6949Cblack (486H3)-MCMF composite is 11 times higher than that of the pure PE. This substantial increase probably stems from the high macromolecular chain branching of PE6949Cblack (486H3).

As shown in Figs. 3(c) and 3(d), regardless of the PE

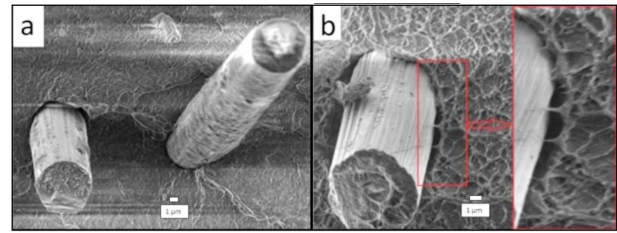


Figure 4. SEM of PE (PE6949C black (486H3)) composites with (a) CMFs and (b) MCMFs.

brand used, the PE-CMF and PE-MCMF composites all have significantly lower yield and fracture elongation than the original PEs. This degradation in the deformation characteristics is due to the high filler content of the composites. Because of the different matrix-filler interactions in the PE-CMF and PE-MCMF composites, the fracture elongation of the latter is lower than that of the former. SEM investigation results for all PE brands were similar, and representative micrographs are shown in Fig. 4. While in Fig. 4(a), few interactions are visible between the CMFs and the PE matrix, Fig. 4(b) highlights the enhanced filler-matrix adhesion achieved with MCMFs. This is due to the surface characteristics of the microfibers. Indeed, the CMFs have a smooth surface, whereas the surface of the MCMFs is rough with a high specific area. The CNFs on the surface of the MCMFs enhance their adherence to the polymer matrix, probably through van der Waals attraction between the CNFs and PE. These interactions explain that the higher yield strength, the lower yield elongation, and the lower fracture elongations are measured for the PE-MCMF composites.

CONCLUSIONS

Carbon microfibers (CMFs) were modified by depositing carbon nanofibers (CNFs) on the surface of CMFs via ethylene catalytic processing. The surface area of the resulting modified CMFs (MCMFs) is 2.5 times higher than that of the original CMFs. Polyethylene (PE)-MCMF and PE-CMF composites were then prepared, and the mechanical characteristics of the former were found to be better than those of the latter and of pure PE owing to the improved adhesion between the polymer matrix (PE) and the microfibers. This in turn is due to the greater roughness and larger specific area of the MCMF surface. These differences in matrix-filler adhesion are reflected in the different yield strength, elastic modulus, yield elongation, and fracture elongation. In conclusion, the mechanical properties of PE-MCMF composites are favorable for low-temperature applications.

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