Microstructure and Mechanical Properties of Nanocomposites Compounded with Polyolefin and Hydrophobizing Agent-Treated Cellulose Nano Fibers

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Keywords: Composite material, Cellulose nano fiber, Mechanical property, Surface treatment

Abstract

The objective of this study is to investigate surface modifications occurring on CNFs and the mechanical properties of nanocomposites consisting of polyolefins and hydrophobizing agent-treated CNFs. We discovered a new preliminary special agent that enables strong interactions between CNF surfaces. Using a twin-screw extruder operating at 130 rpm and at 180–200°C, CNF nanocomposites were prepared by melt-compounding polyolefins (HDPE) with CNFs treated with the preliminary special agent. Tensile tests were carried out to assess the effects of CNF content and loading rate on the mechanical properties of the nanocomposites. In addition, the dispersion states of the CNFs in the HDPE were examined using an optical microscope. Because no agglomerates of CNFs with diameters greater than 10 μm can be found in the composite, it can be inferred that the CNFs are homogeneously dispersed within the HDPE matrix. The relationship between the mechanical properties and the microstructure of CNF nanocomposites is disussed.

1. Introduction

In recent years, various measures have been taken on a global scale to tackle environmental issues such as global warming and resource depletion. In the industrial sector, in particular, saving resources and energy is important for future economic growth, and thus, it is essential for manufacturers to be considerate toward the environment. In the field of polymers, for example, attention has been focused on biomass as a natural resource. There is ongoing research into biomass composite materials that utilize wood, which accounts for the vast majority of biomass.Cellulose Nano Fiber (CNF) is expected to be utilized in various fields because of its attractive properties such as high strength, high rigidity, and low coefficient of linear expansion, and its use as a filler for resins is also desirable [1,2]. CNF is obtained by the nanonization of cellulose, which is a component forming the skeleton of plants and constitutes approximately 50% of the plant. Of the1 trillion 800 billion tons of biomass known to exist on Earth, 99.99% is found in plants. Moreover, 92–95% of plants are timber, the raw material of the CNF, which implies that the availability of this resource is 10 times that of petroleum. CNF contains many hydroxyl groups and is a hydrophilic material. When forming composites with hydrophobic polymer materials, it is essential to impart hydrophobicity to the CNF. The purpose of this study is to develop an inexpensive CNF dispersion technology for the hydrophobization of CNF. Tensile tests were performed and the dispersion structure of the CNF was observed by focusing on the CNF/polyolefin resin composite materials prepared by melt kneading. The effects of the addition of a hydrophobic agent on the dispersibility of CNF and the tensile properties of the composite material were examined.

2. Experimental procedure

2.1 Test materials

Table 1 shows the test materials used in this study. The matrix of the composite material was High Density Polyethylene, HDPE powder (Creolex; Asahi Kasei Chemicals Co., Ltd.), the CNF was a crystalline cellulose nanofiber (Asahi Kasei Chemicals Co., Ltd.), and a phosphite-based heat stabilizer and a hindered phenol-based heat stabilizer were used as stabilizers. Furthermore, for deployment of the CNF composite material in various fields, 0.1 g of each stabilizer was used for 100 g of the composite material. Table 2 shows the blending conditions for each composite.

Table 1 Materials used in this study.

Material	
Matrix	HDPE(High Dentisity Polyrthylene) (Asahikasei Chemicals Corporation)
CNF	Cellulose nanocrystal (Asahikasei Chemicals Corporation)
Surface modifier	HA(Hydrophobizing Agent)
Graphene	GE(Graphene) 10 μm (ITEC corporation)
	GN(Graphene Nanoplatelets) 5,15,25 μm (XG Sciences coporation)
Thermal stabilizer	PTS (Phosphite based thermal stabilizer) HPTS (Hindered phenol based thermal stabilizer)

Table 2 Blending conditions for each composite.

| | PE(wt%) | CNF(wt%) | HA(wt%) | Graphene | | PTS(wt%) | HPTS(wt%) |
				GE(wt%)	GN(wt%)		
PE	100	–	–	–	–	0.1	0.1
3wt%CNF/PE with HA	96.4	3	0.6	–	–	0.1	0.1
5wt%CNF/PE with HA	94.4	5	0.6	–	–	0.1	0.1
5wt%CNF/PE without HA	95	5	–	–	–	0.1	0.1
10wt%CNF/PE with HA	89	10	1	–	–	0.1	0.1
10wt%CNF/PE without HA	90	10	–	–	–	0.1	0.1
5wt%CNF/GE/PE with HA	93.4	5	0.6	1	–	0.1	0.1
5wt%CNF/GN/PE with HA	93.4	5	0.6	–	1	0.1	0.1

2.2 Fabrication of composite materials

2.2.1 Stirring of CNF

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After blending the HDPE powder, CNF, and each stabilizer, the mixture was stirred with a high-speed rotary mixer (Laboratory Blender, Waring Co.).

2.2.2 Melt kneading

For melt kneading, a composite-type kneading extruder (IMC-1853 type, Imoto Seisakusho Co., Ltd.) and a small kneading machine (Xplore MC15, Xplore instruments Co., Ltd.) were used. The conditions of kneading were as follows: a set temperature of 180 ℃, a blade rotation (composite-type kneading extruder) or screw rotation speed (Xplore MC15) of 130 rpm, and time of 10 min.

2.3 Observation of CNF dispersion state

The extruded composite was pelletized, made into a film of approximately 100 μm in thickness by hot pressing (AH-2003C, AS ONE Co.), and observed under a microscope with transmitted light (100× and 500× magnification).

2.4 Processing of the specimen

The pelletized composite material was formed into a 1 mm-thick rectangular plate by hot pressing and then punched using a lever press cutter (Toyo Seiki Seisakusho K.K.). The shape of the test piece conformed with the 1B-type dumbbell according to the JIS K7127 standard [3].

2.5 Tensile tests

Tensile tests were performed using a universal material testing machine (Autograph AG-E type, Shimadzu Corporation). The crosshead speed was varied between 10, 50, 100, and 200 mm/min.

3. Results and discussion

3.1 Dispersed CNF

Figure 1 shows the results of the optical microscope observation of CNF dispersed in various composite materials. Results (a)–(d) refer to the use of a composite-type kneading extruder: (a) shows the CNF dispersion in the absence of a hydrophobizing agent and (b)–(d) show the CNF dispersion in the presence of a hydrophobizing agent, observed at 100× and 500× magnification. The images reveal that compared with the case without a hydrophobizing agent (a), the addition of a hydrophobizing agent (b)–(d) improved the dispersibility of CNF. Furthermore, a large difference in the degree of dispersion of the CNF for different amounts of the added hydrophobizing agent was not found in the optical microscopic observations.

Similar to Fig. 1, Fig. 2 shows the optical microscopy results for a composite material prepared using a small kneader. Compared with (b)–(d) in Fig. 1, the use of the small kneader improved the dispersibility of CNF. Moreover, the addition of a hydrophobizing agent further enhanced the CNF dispersibility, as can be seen by comparing Fig. 2 (a) with (b).

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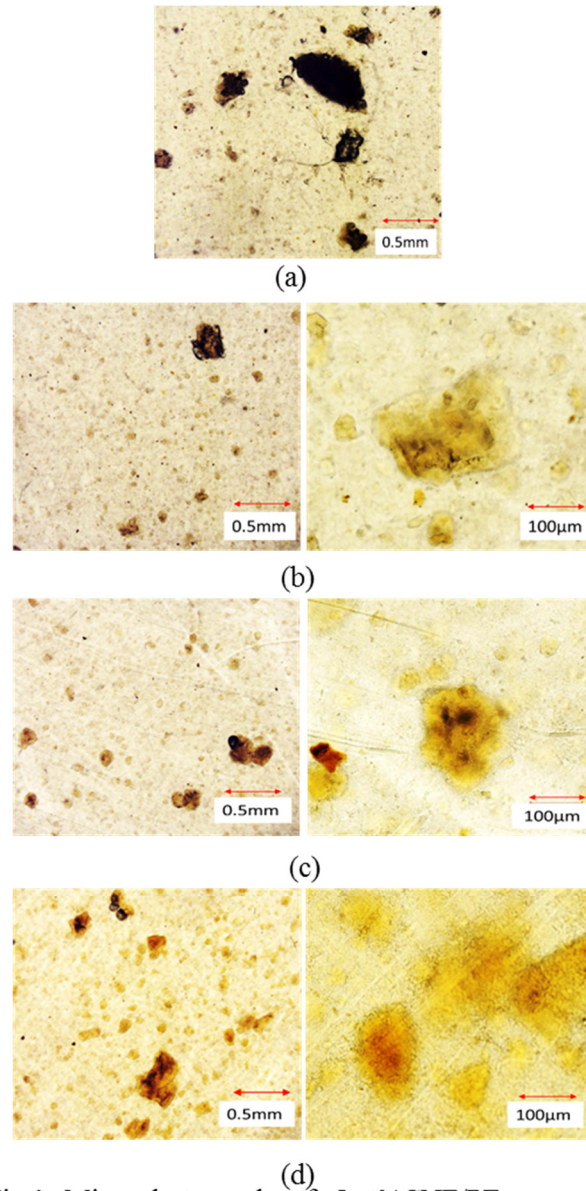
Fig.1 Microphotograph of 5wt%CNF/PE composites with/without HA fabricated by using IMC-1853 kneading machine:(a)CNF:HA=10:0; (b)CNF:HA=9:1; (c)CNF:HA=8:2; (d)CNF:HA=7:3
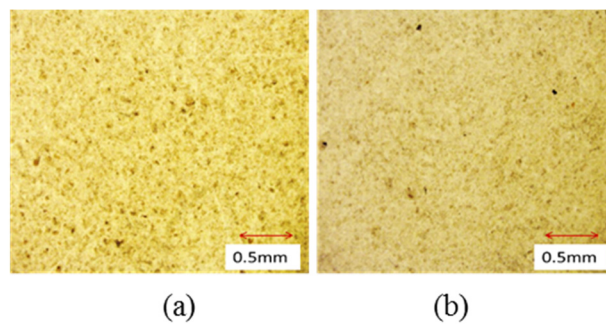
Fig.2 Microphotograph of 5wt%CNF/PE composites with/without HA fabricated by using Xplore kneading machine:(a)CNF:HA=10:0; (b)CNF:HA=9:1

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3.2 Tensile properties

Figure 3 shows the stress–strain diagram obtained in tensile tests performed with a crosshead speed of 10 mm/min for a neat PE and for various composite materials. Each composite material was produced using the composite-type kneading extruder. The tensile strength of the 5 wt.% CNF/PE composite material obtained by adding a hydrophobizing agent increased significantly compared with the results obtained without the addition of a hydrophobizing agent, and it was even slightly higher than that of neat PE. This is presumably because of the improved dispersibility of the CNF caused by the addition of the hydrophobizing agent, which enables the expression of the characteristics of CNF as a reinforcing agent. However, the breaking strain of the 5 wt.% CNF/PE composite material combined with a hydrophobizing agent was slightly lower than that of the composite material without the hydrophobizing agent. This reduction is probably because the deformation of the resin was restricted because of the dispersion of the CNF. In contrast, compared with PE alone, the tensile strength of the 3 wt.% CNF/PE composite material obtained by adding a hydrophobizing agent was reduced, despite the breaking strain showing comparable values. Because the CNF content is low in the 3 wt.% CNF/PE composite, the characteristics of CNF as a reinforcing agent are most likely not developed, and the CNFs.
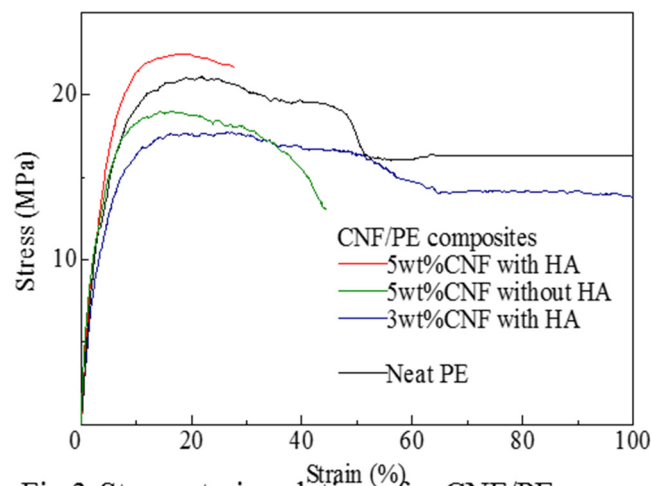

Fig.3 Stress-strain relations for CNF/PE composites with/without HA and neat PE fabricated by using IMC-1853 kneading machine

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