Tensile, Thermal, and Electrical Conductivity Properties of Carbon Fiber Reinforced Composites Using Itaconic Acid Based Dispersants

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Abstract: We prepared itaconic acid based dispersants (IBDs) by the copolymerization of itaconic acid with acrylic acid, acrylamide, or vinyl sulfonic acid, and compared the efficacy of the IBDs on carbon fiber (CF) dispersion in a water-based system, against that of sodium dodecyl sulphate (SDS) which is widely used as a dispersing agent. The procedure to fabricate nonwoven CF (NCF)/PP composites using IBDs includes the following steps: the synthesis of IBDs, the dispersion of CFs in water by the IBDs, the formation of a NCF, and hot pressing of NCF with polypropylene (PP) layer. We determined the tensile, thermal properties, and the electrical conductivity of non-woven CF/PP composites. It was found that using IBDs as a CF dispersing agent led to the CF/PP composites having better tensile, thermal, and electrical properties, as compared to when SDS was used as a dispersing agent.

Keywords: Carbon fiber, Nonwoven, Wet laid, Composite, Dispersion agent

Introduction

Nonwovens are engineered fabrics made from fibers. They are composed of parallel, cross or randomly laid fiber webs and are widely used in various applications. Their properties depend on the raw fibrous matter, bonding agent, production method, types of webs, and processing methods. The nonwoven webs can be classified according to the length of the fibers, and the manufacturing processes, such as the dry-laid or wet-laid processes.

The technology of wet-laid nonwovens was derived from the paper industry. In the paper industry, very short and fine fibers are used, whereas in the wet-laid nonwoven composites, long and rough fibers get a lot of attention. The preparation of wet-laid nonwovens demands large amounts of water and additives to obtain a good dispersion of the fibers in water. Therefore, the dispersion of fibers in water is a very important step in the wet-laid nonwoven fabrication technique. A large quantity of the fibers need to be dispersed in the medium as a state of a uniform distribution [1-3]. This implies that the state of fiber dispersion in water is of primary importance in determining the quality of wet-laid nonwovens.

Many researchers have studied the fiber dispersion using anionic and cationic surfactants. For example, Das *et al*. [4] studied the dispersion of cotton fibers treated with different concentrations of a cationic surfactant in water. Peng *et al*. [5] investigated the influence of three common dispersants

(sodium CMC, anionic polyacrylamide (APAM), and cationic polyacrylamide (CPAM)) on the dispersion of slag fibers in water. They reported that the optimal uniformity and stability of the fiber suspensions could be achieved by a combination of CMC and APAM. CMC was also used as a dispersing agent for polyester fibers in water [6]. Heo *et al*. [7] examined the effects of commonly used dispersing agents on glass and carbonized glass fibers using the wet-laid process. However, the effects of the dispersing agent on NCF in the wet-laid system have been rarely studied, irrespective of the various related studies.

During the process of preparing CF-reinforced composites, the tensile strength and modulus of composites are influenced by the dispersion and adhesion of fibers in the matrix [8-10]. Moreover, to improve the CF dispersion in the matrix, the surface activity of the CF papers and nonwovens can be enhanced by additives [11-13]. The additives play an important role in determining the end properties of the composite. Jabbour *et al*. used bleached eucalyptus kraft cellulose fibers as a novel binder for CF composite. The CFs were held with a homogeneous bleached eucalyptus kraft cellulose fibers network [14]. Yan *et al*. studied the fabrication of carbon fiber polyaniline composite using a facile polymerization route [15].

In this study, we synthesized IBDs, and used them to fabricate NCFs and their composites. The IBDs are copolymers based on itaconic acid (IA) and other comonomers. IA is selected as one of the top value added chemicals from biomass by the United States Department of Energy and is commercially produced by the fermentation of carbohydrates,

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or from sugars via biological methods [16,17]. It contains a hydrophilic carboxylic acid group, which can potentially enhance the CF dispersion in an aqueous medium. Also, we used three types of comonomers (anionic (acrylic acid), cationic (vinyl sulfonic acid) or nonionic (acrylamide) monomer) and compared their dispersing effects.

Experimental

Synthesis of Itaconic Acid Based Dispersants

We prepared three different copolymers of itaconic acid (IA, 97-65-4, Sigma Aldrich, USA) with acrylic acid (AA, 79-10-7, Sigma Aldrich, USA), acrylamide (AAm, 79-06-01, Sigma Aldrich, USA), or vinyl sulfonic acid (VSA,

3039-83-6, Sigma Aldrich, USA). The conditions and chemical structures of the copolymers for synthesizing the IBDs are shown in Table 1 and Figure 1, respectively.

We compared the CF dispersion effects of the IBDs to that of sodium dodecyl sulphate (SDS, 151-21-3, Sigma Aldrich, USA). For ionization the IBDs, 40 m*l* of sodium hydroxide (1310-73-2, Sigma Aldrich, USA) solution of 40 mol % based on carboxyl acid on IA was poured into a four-necked flask equipped with a stirrer, condenser, thermometer, and an argon line. The reactor was heated to 60 °C under the argon atmosphere. Potassium persulfate (7727-21-1, Sigma Aldrich, USA) was added in 1 wt.% of the total monomer content to the reaction mixture as an initiator. In the next step, the IA and comonomers such as acrylic acid, acrylamide, or vinyl

Table 1. IBDs' synthesis conditions by aqueous solution polymerization

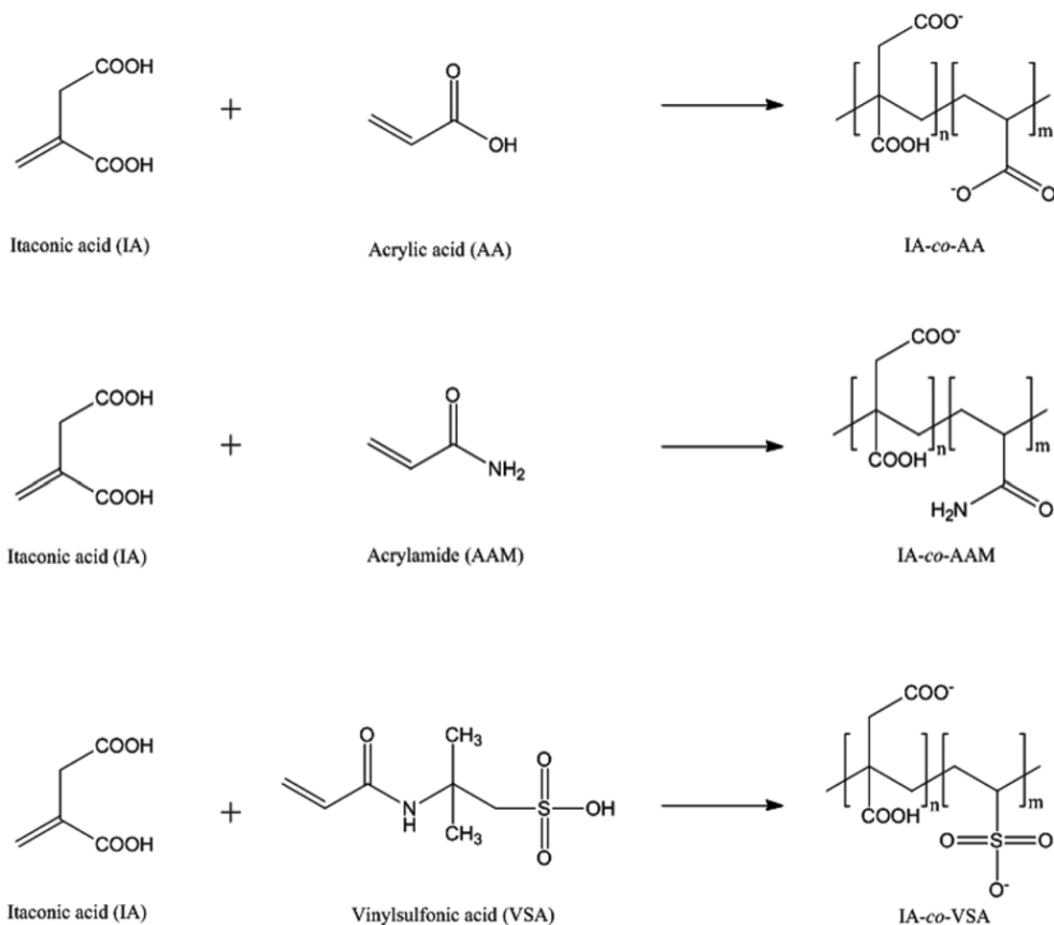| Name	Monomer A (mol)	Monomer B (mol)	Distilled water (m*l*)	Initiator (wt.%)	Stirring speed (rpm)	Temp. (°C)
IA-co-AA	Itaconic acid (0.4)	Acrylic acid (0.4)	50	Potassium persulfate (1.0)	250	60
IA-co-AAm		Acrylamide (0.4)				
IA-co-VSA		Vinyl sulfonic acid (0.4)				

Figure 1. Synthesis of itaconic acid based dispersants: IA-co-AA, IA-co-AAm, and IA-co-VSA.

sulfonic acid were added. The comonomers were used after removing the inhibitor by passing them through alumina columns. The polymerization was stopped when further stirring became impossible due to the high viscosity of the reaction medium. The products were quenched into ethanol, dried in a vacuum oven (OV-11, JEIO Tech, Korea) at 60 °C for 24 h, and finally ground.

Preparation of the Nonwoven Carbon Fiber (NCF)

The CFs (Torayca, T700SC-12K, 800 tex) were cut to pieces of 5-6 mm length using a fiber-cutting machine (FiDoCut; Fiber Dosing and Cutting system, Schmidt & Heinzmann GmbH & Co., Germany). CFs (3.0 g) were dispersed in 3000 ml of distilled water along with 0.3 g of the dispersing agent (copolymeric IBDs or SDS), the samples are denoted as shown in Table 2. The medium was continuously stirred using a magnetic stirrer for 1 h. The dispersed CF were allowed to settle down on a wire mesh (10 cm×10 cm) placed at the bottom of the wet-lay device. The NCF thus formed on the wire mesh was taken out and dried in an oven at 60 °C for 24 h.

Preparation of the NCF/PP Composites

We manufactured the NCF/PP composites using the laminating and hot pressing process. The laminated composite was composed of three layers that have a weight of 30±5 g/m^2 per layer, as shown in the Table 3. The NCF layer was sandwiched between two PP layers. The resultant PP/NCF/PP composites were hot-pressed using a compression-molding machine (MH-15, MASADA SEISAKU SHO, Japan). The compression molding conditions were as

follows: preheating at 230 °C for 5 min, pressing at 2.5 MPa for 1 min, and then cooling to room temperature.

Characterization

The structure of the IBDs was characterized by Fourier transform infrared spectroscopy (FT-IR) (Thermo Nicolet, NEXUS, USA). The molecular weight of the copolymers was determined using a binary high performance liquid chromatography (HPLC) pump (Waters 1525, USA) and a refractive index detector (Waters 2414, USA) using a three columns connected in series (Ultrahydrogel™ 1000, 500, and 250 columns, Waters, Ireland) with a mobile phase. The mobile phase was 0.1 M $NaNO_3$ in aqueous medium, and the flow rate was 1 ml/min. The measuring temperature and injection volume were 40 °C and 20 μl, respectively. The surface morphologies of the NCF were examined by a digital camera (PL 150, SAMSUNG, Korea), optical microscope (CKX41, OLYMPUS, Japan), and field emission scanning electron microscopy (FE-SEM, SU8010, Hitachi, Japan). The settling rate of CF in the aqueous medium was measured immediately after stopping the stirring. The sedimentation levels were monitored and recorded at 15, 30, 60, 360, and 720 min.

The tensile properties of the NCF/PP composites were measured according to the ASTM D638 standard by a universal testing machine (UTM, H5K-T, Tinius Olsen, USA) at a constant cross-head speed of 2 mm/min. The electrical conductivity of the NCF and the composite were determined using a sheet resistance meter (CMT-100S, AIT, Korea) at 25 °C room temperature using the four-point probe technique.

Results and Discussion

The FTIR spectra of the IBDs are shown in Figure 2. In all the IBDs, an intense peak at 1700-1730 cm^{-1} associated with the carbonyl C=O stretch of the carboxylic group in itaconic acid was observed. The broad band at 3400-2900 cm^{-1} and the sharp peak at 1215 cm^{-1} are associated with the O-H and C-O stretching of carboxylic acid, respectively. IA-co-AA contains all of the above peaks, since IA-co-AA mainly consists of carboxylic groups. Figure 2(b) depicts the spectrum of IA-co-AAm. The absorption bands appearing at 3500-3300 cm^{-1} are due to the amide groups of acrylamide in the IA-co-AAm copolymer. The sulfonate peaks at around 1300 cm^{-1} and 1040 cm^{-1} in the IR spectrum of IA-co-VSA (Figure 2(c)) are clear evidence of the incorporation of vinyl sulfonic acid groups into IA.

To choose a proper dispersing agent, the polarities of the target materials and the solvent medium should be considered. SDS, an amphiphilic surfactant, is generally used to disperse hydrophobic polymeric materials into aqueous solutions. SDS is known to be especially effective for dispersing carbon nanotubes or carbon black in aqueous solutions [18-

Table 2. Summary of NCF preparation conditions

Name	Water input (L)	Carbon fiber input (g)	Dispersing agent	
			Type	Input (g)
NCF$_{CONT.}$			-	
NCF$_{I-AA}$			IA-co-AA	
NCF$_{I-AAm}$	3	3	IA-co-AAm	0.3
NCF$_{I-VSA}$			IA-co-VSA	
NCF$_{SDS}$			SDS	

Table 3. The preparation of NCF/PP composites

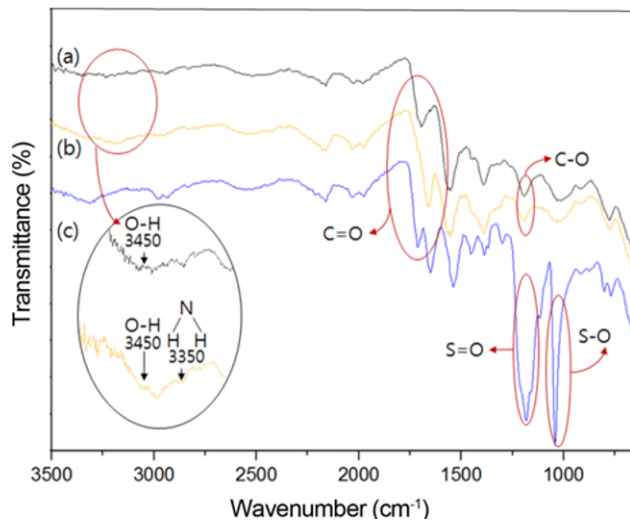| Name	NCF		PP input (g/m^2)
	Type	Input (g/m^2)	
NCF$_{CONT.}$/PP	NCF$_{CONT.}$		
NCF$_{I-AA}$/PP	NCF$_{I-AA}$		
NCF$_{I-AAm}$/PP	NCF$_{I-AAm}$	30±5	30±5 (per layer)
NCF$_{I-VSA}$/PP	NCF$_{I-VSA}$		
NCF$_{SDS}$/PP	NCF$_{SDS}$		

Figure 2. The FT-IR spectra for IBDs; (a) IA-co-AA, (b) IA-co-AAm, and (c) IA-co-VSA.

Table 4. Molecular weight characteristics of the dispersing agents

Name	GPC		
	M_n^a	M_w^b	PDI[c]
Control	-	-	-
IA-co-AA	139,600	1,423,400	10.19
IA-co-AAm	135,000	1,073,000	7.95
IA-co-VSA	125,000	624,700	5.00
SDS	-	-	-

[a]Number-average molecular weight, [b]weight-average molecular weight, and [c]polydispersity index (M_w/M_n).

21]. From the molecular weight analysis using aqueous GPC (gel permeation chromatography) (Table 4), we found that the average molecular weights of the IBDs were above 120,000, whereas that of SDS was relatively low, i.e., less than 20,000, although the polydispersity index (PDI) of SDS was much lesser.

The dispersion of CFs in aqueous medium using IBDs (Figure 3(b-d)) seems to be better than that of the control sample or with SDS. Because the IBDs have both hydrophobic and hydrophilic groups, they can be pulled onto the surface of the CFs by van der Waals or electrostatic interactions, and thus enhance the hydrophilicity and wettability of the CFs. Furthermore, we theorize that as the IBDs have a relatively high molecular weight and are polymeric in nature, they can effectively microencapsulate the CFs. Peng *et al*. [5] found that the dispersion of short slag fibers in aqueous solutions was affected by the wetting mechanism, electrostatic stabilization, and steric stabilization. Since SDS is amphiphilic, it is capable of microencapsulating hydrophobic materials in aqueous medium; however, in the case of the NCF$_{SDS}$ system, it was not very effective in dispersing the CFs in the aqueous medium. This phenomenon can be explained by the fact that the molecular weight of SDS is too small for it to microencapsulate the CFs in our system. On the other hand, the IBDs were much more effective in dispersing the CFs in the aqueous medium. This phenomenon could be attributed to not only electrostatic stabilization, but also to the steric stabilization effect of the IBDs.

Using IBDs as the dispersing agents helped the CFs to de-bundle into individual fibrils and form stable aqueous dispersions. Figure 4 illustrates a possible model for the covalent and hydrogen bonding between the functional groups on the surface of the CF and the functional groups of the IBDs. The hydroxyl and epoxy groups on the surfaces of the CF can interact with the functional groups (-COOH, -OH, -CONH, -SO$_3$H) of the IBDs, through hydrogen bonding. This results in the enhancement of CF dispersity in the water based system.

The settling rate of the CFs with different types of dispersing agents is shown in Figure 5. In the case of the NCF system with IBDs, the sedimentation volume remained
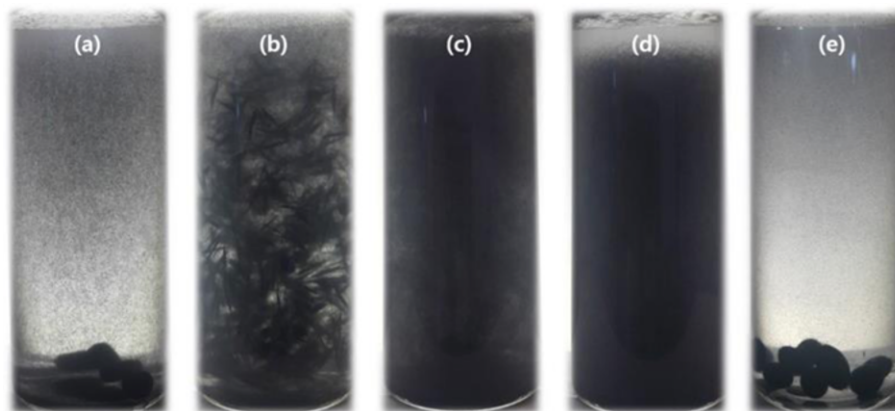

Figure 3. Digital photos of CF dispersions in water at room temperature, 5 min after stopping the stirring; (a) NCF$_{CONT.}$, (b) NCF$_{I-AA}$, (c) NCF$_{I-AAm}$, (d) NCF$_{I-VSA}$, and (e) NCF$_{SDS}$.
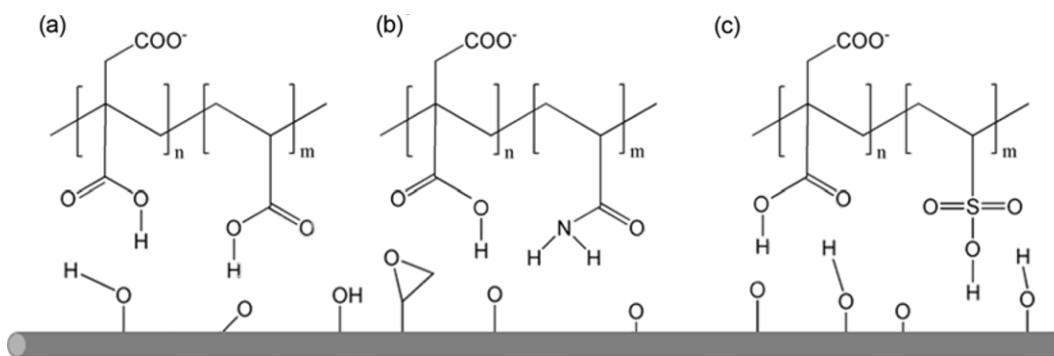
Figure 4. Possible interactions between CF and IBDs; (a) NCF_{I-AA}, (b) NCF_{I-AAm}, and (c) NCF_{I-VSA}.
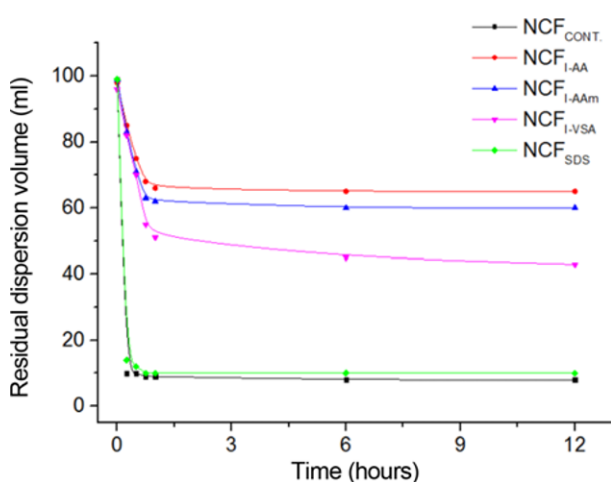

Figure 5. Settling rate of CFs in aqueous medium.

constant after a certain time period. Such constant levels are due to the formation of stable CF dispersions upon using IBDs. On the contrary, in the case of the NCF_{SDS} and NCF_{CONT} systems, we found that the dispersion stability of the CFs was very poor due to fiber-aggregation as shown in Figure 3. There is the difference of the settling time between NCF_{I-AA}, NCF_{I-AAm}, and NCF_{I-VSA}, which is expected to be caused by the different viscosity associated with molecular weight of each dispersant.

The morphologies of the NCF, as examined by optical microscopy and SEM, are shown in Figures 6 and 7, respectively. The bundles of CFs were not well spread in the NCF_{CONT} (a), and NCF_{SDS} (e) systems. However, they are uniformly distributed and formed by 2D orientation in the NCF_{I-AA} (b), NCF_{I-AAm} (c), and NCF_{I-VSA} (d) systems. The good dispersion and 2D orientation of CFs positively affect the mechanical and electrical properties of the composites.
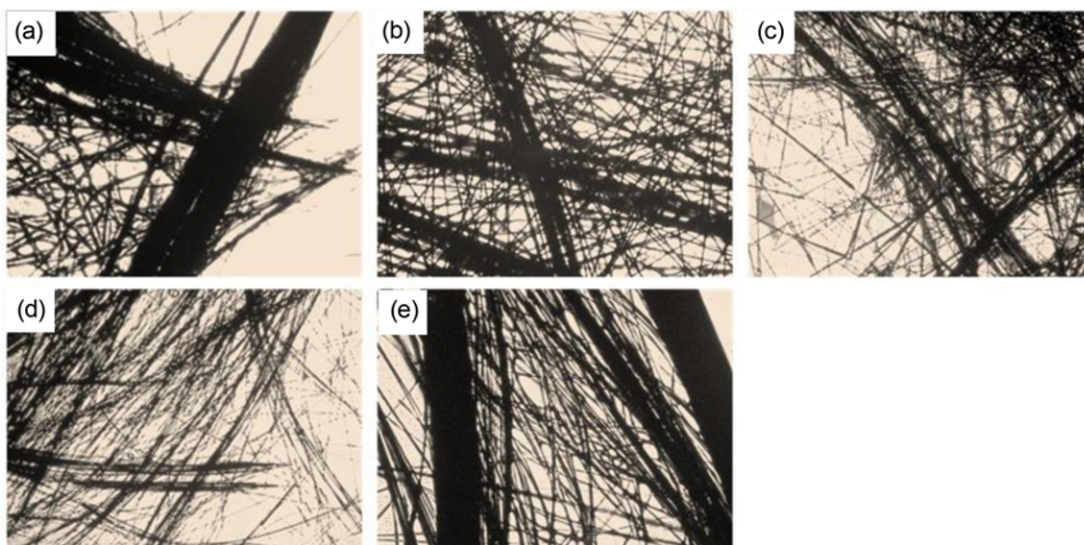

Figure 6. Optical microscopy images (× 40) of NCF with different dispersing agents; (a) NCF_{CONT}, (b) NCF_{I-AA}, (c) NCF_{I-AAm}, (d) NCF_{I-VSA}, and (e) NCF_{SDS}.
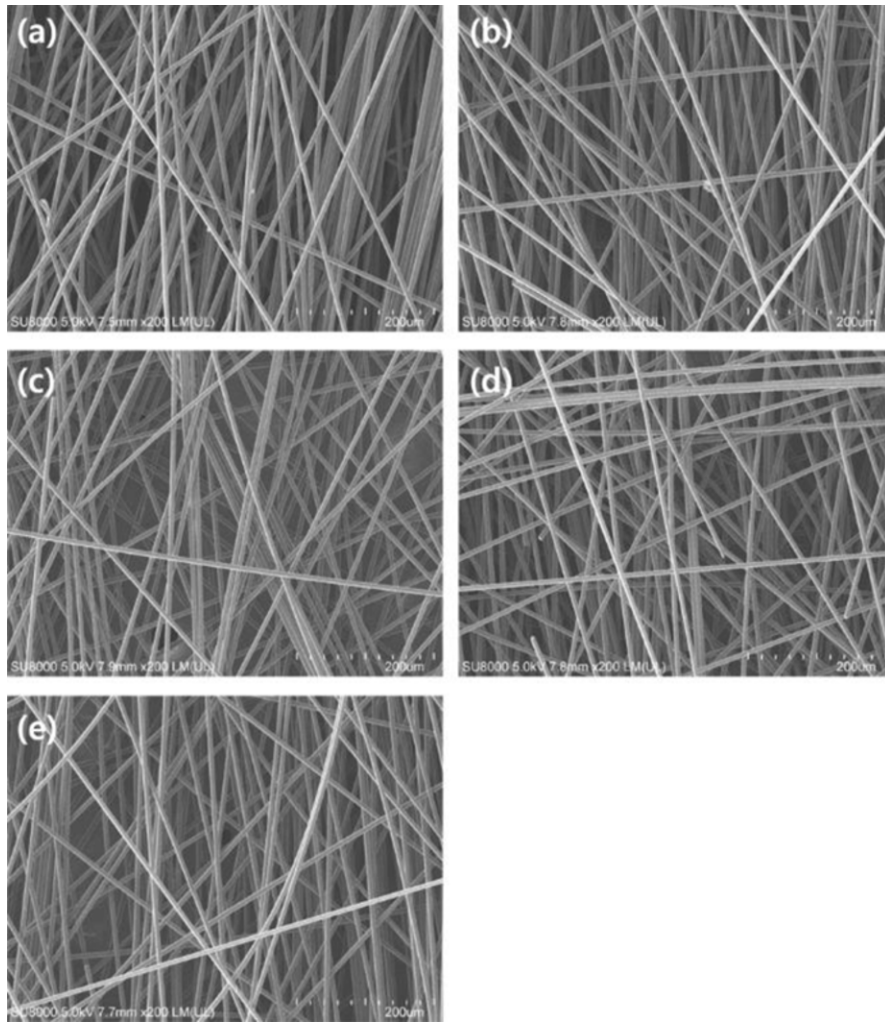
Figure 7. SEM images of NCF with different dispersing agents; (a) NCF$_{CONT.}$, (b) NCF$_{I-AA}$, (c) NCF$_{I-AAM}$, (d) NCF$_{I-VSA}$, and (e) NCF$_{SDS}$.
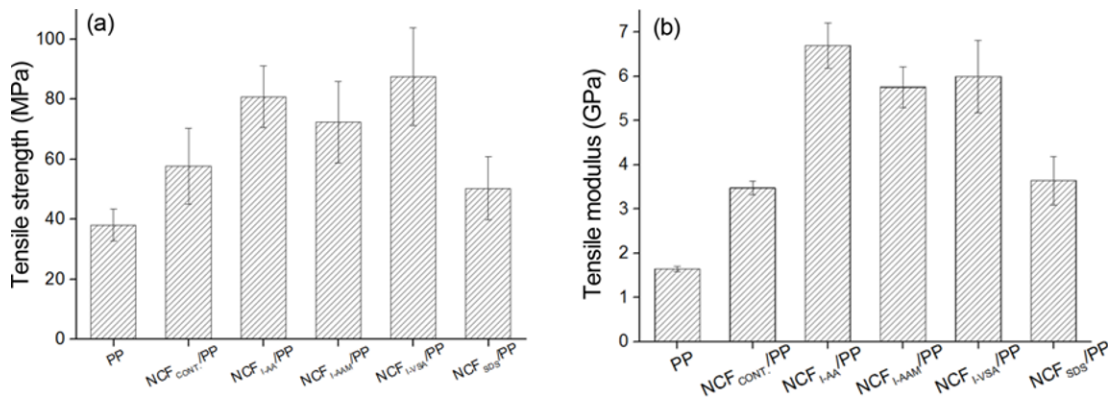

Figure 8. Tensile properties of NCF/PP composites; (a) tensile strength and (b) tensile modulus.

[21] When the fibers are not well dispersed, it can induce the emergence of pores and holes in the matrix, leading to poor mechanical properties of the composites.

Figure 8 shows the changes in the tensile strength and tensile moduli of the NCF/PP composites with or without dispersing agents. The tensile properties of the NCF/PP composites with IBDs as the dispersing agents (NCF$_{I-AA}$/PP, NCF$_{I-AAm}$/PP, and NCF$_{I-VSA}$/PP) were higher than those of
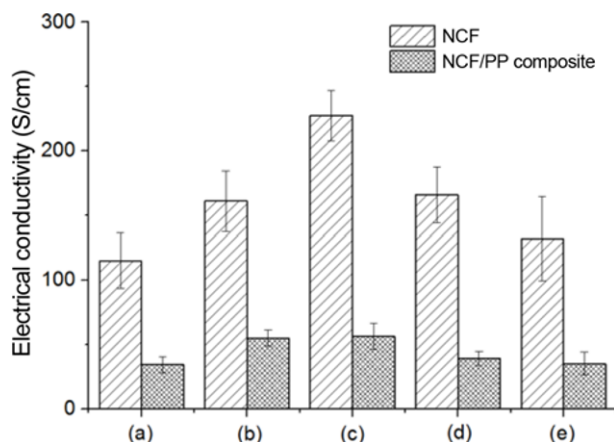
Figure 9. Electrical conductivity of NCF and NCF/PP composites using various dispersing agents; (a) control, (b) IA-co-AA, (c) IA-co-AAm, (d) IA-co-VSA, and (e) SDS.

$NCF_{CONT.}/PP$ and NCF_{SDS}/PP. Well-dispersed CFs are important in order to induce good tensile properties in the NCF/PP composites.

As shown in Figure 9, the electrical conductivity is related to the dispersion state of the CFs. The electrical conductivities of the NCF/PP composites using IBDs as a dispersing agent (NCF_{I-AA}/PP, NCF_{I-AAm}/PP, and NCF_{I-VSA}/PP) are far higher than those of $NCF_{CONT.}/PP$ and NCF_{SDS}/PP composites. These phenomena are mainly due to the de-bundled and well-dispersed state of the CFs in the aqueous medium [8-12], as shown in Figure 6.

Conclusion

In this work, we developed three novelty dispersing agents based on itaconic acid with different comonomers – acrylic acid, acrylamide, and vinyl sulfonic acid. These IBDs were then incorporated in NCFs and NCF/PP composites, and their effect on the tensile, thermal, and electrical properties was analyzed. The functional groups of the IBDs could interact with the hydroxyl and epoxy groups on CF surfaces via hydrogen bonding. Such interaction helped the development of a stable CF dispersion in water.

From the sedimentation and morphological observations, we found that the IA-co-AA, IA-co-AAm and IA-co-VSA copolymers are good dispersing. The NCFs using IBDs were uniformly distributed with 2D orientation and were well-dispersed. The IBDs helped the CF de-bundle into individual fibrils and induced the formation of stable aqueous dispersions. These phenomena helped to enhance the tensile properties and the electrical conductivity of the NCF/PP composites. In particular, the tensile properties of the NCF/PP composites using IBDs were much higher than those of $NCF_{CONT.}/PP$ and NCF_{SDS}/PP composites, owing to the well-divided and uniformly distributed fibers in the composites.

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