Polyvinyl Chloride / Attapulgite / Micro-crystalline Cellulose (MCC) Composites Preparation and Analysis of the Role of MCC as a Compatibilizer

Bo Wang,[a,c] Hai-Rong Zhang,[a,b] Chao Huang,[a,b] Xue-Fang Chen,[a,b] Si-Lan Shi,[a,c] Lian Xiong,[a,b] Jun Luo,[a,b,*] and Xin-De Chen [a,b,*]

To improve the performance of polyvinyl chloride (PVC), composites incorporating polyvinyl chloride (PVC), attapulgite nanoparticles (ANPs), and microcrystalline cellulose (MCC) were successfully prepared. The composites had higher vicat softening temperatures (VSTs) and the MCC had a great influence on mechanical properties of the composites. When MCC was added from 0 to 5 per hundred parts of PVC (phr), the mechanical properties of the composites increased, but the mechanical properties of the composites decreased when the MCC was more than 5 phr. The tensile breaking stress, tensile strength, and impact strength were maximized with increases of 19.76 N (4.1%), 29.66 MPa (15.5%), and 13.8 MPa (7%) when 5 phr MCC was added. Infrared spectral analysis indicated that MCC and ANPs were present in the composites. Scanning electron microscopy showed that the composites system was distributed into two phases, which indicated that MCC in composites was dissolved in the PVC matrix, and some of MCC coated the surface of ANPs as a compatibilizer. Overall, this study provided a promising method for PVC modification to improve its performance.

Contact information: a: Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China; b: R&D Center of Xuyi Attapulgite Applied Technology, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Xuyi 211700, PR China; c: University of Chinese Academy of Sciences, Beijing 100049, China;
* Corresponding author: cxd_cxd@hotmail.com; luojun@ms.giec.ac.cn

INTRODUCTION

Polyvinyl chloride (PVC) is a thermoplastic resin that is generated by the homopolymerization of vinyl chloride (VC) or copolymerization of other monomers. PVC can be processed into all sorts of plastic materials through mixing, plasticization, and molding. Using different types and proportions of processing aids, a series of products can be produced, including hard, semi-hard, soft, transparent, and non-transparent PVC. Product types can include PVC copolymers or alloys, synthetic fibers, engineering plastics, coatings, adhesives, thermoplastic, elastomers, foams, sealants, and different types of special functional materials. PVC materials have good fire resistance and high strength, and thus they are widely used in construction and industry. The annual production of PVC materials is lower only than that of polyethylene (PE) (Yang *et al*. 2005; Huang *et al*. 2010; Mendez *et al*. 2011; Zhu *et al*. 2012). However, the thermal stability of PVC is poor; it starts to decompose when heated to 100 °C, and the decomposition rate is accelerated when the temperature is over 150 °C (Braun 1981). Furthermore, the vicat softening temperatures (VSTs) of PVC materials are usually under 80 °C (Kamira and Naima 2006), which

restricts its application. Therefore, various fillers have been used to improve the thermal performance of PVC in order to broaden the scope of its application. PVC can be modified by nano-$CaCO_3$, silica, and montmorillonite, and such modification can increase mechanical properties, thermal properties, and processing fluidity of PVC (Kaczmarek *et al*. 2003; Chen *et al*. 2004; Xiong *et al*. 2005).

Attapulgite is a clay mineral with a chain-layered transition structure that is primarily magnesium aluminum phyllosilicate (Galan 1996). Attapulgite shows fibrous appearance macroscopically and the nanoscale channels in its structure enable it to have a very large specific area (Bradley 1940). Attapulgite has advantages such as low density, light color, and low hardness. Thus, it can be easily processed into attapulgite nanoparticles (ANPs). The porous and hollow structure can provide conditions for chemical modification or use for composites. Because of the special structure and the unique colloidal properties, such as dispersion, water absorption, and saline alkali tolerance, as well as high decolorization ability, good plasticity and adhesive properties, they have been widely used in petroleum, chemical engineering, building materials, paper making, medicine, agriculture, printing, and many other industries (Liu *et al*. 2008). ANPs have a good filling performance for polymer materials (Bradl 2004). However, ANPs dispersibility in polymers needs to be improved through surface modification. Recently, ANPs studies have become a hot spot as a polymer filler (Volle *et al.* 2011).

The reduced availability of fossil resources and environmental pollution have become key factors affecting the development of the world economy, which make it imperative to develop alternative, sustainable, and renewable materials. One of the directions of current research is using cellulose to replace non-renewable or non-degradable materials for polymer reinforcement (Favier *et al*. 1995; Karnani *et al*. 1997; Glasser *et al*. 1999). Cellulose is one of the most abundant natural renewable resources, offering the advantages of low cost, low density, high mechanical properties, good thermal stability, renewability, and degradability. Compared to biomass materials such as starch, nature fiber also has outstanding properties including a highly developed crystalline structure, regular morphology, large length diameter ratio, large specific surface area, and high modulus. It has been extensively studied and used to reinforce polymer (Favier *et al*. 1995; Dubief *et al*. 1999; Angles and Dufresne 2001; Grunert and Winter 2002; Noishiki *et al*. 2002; Mathew and Dufresne 2002). As a reinforcing filler, MCC has been used in many polymer systems, including PE, polycaprolactone (PCL), glycerol plasticized starch, styrene, epoxy resins, and cellulose acetobutyrate (Nakagaito *et al*. 2005; Oksman *et al*. 2006; Wu *et al*. 2007; Alemdar and Sain 2008). The interaction between chlorine atom of PVC and the hydroxyl group of the MCC may contribute to compatibility between them. However, studies on its application in attapulgite nanoparticle compounded systems have rarely been reported.

In this study, the PVC/ANPs/MCC composites were successfully prepared, and the composites were characterized by infrared spectroscopy, VSTs, mechanical testing, and scanning electron microscopy.

EXPERIMENTAL

Feedstock Sources

PVC S1000, having an average degree of polymerization of 1100, was obtained from Shandong Qilu Petrochemical Engineering Co. Ltd (China). ANPs were obtained

from Xuyi, Jiangshu Province, China. MCC was obtained from Aladdin Industrial Corporation, (China). The lubricant stearic acid was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Thermal stabilizer (zinc stearate, 7138G-6) was obtained from Shenzhen AIMSEA Industrial Co. Ltd (China). Epoxidized soybean oil (ESO) was obtained from Guangzhou Dongfeng Chemical Industrial Co., Ltd (China).

Experimental Method
Preparation of PVC/ANPs/MCC composites material

Formulation recipes of the composites are shown in Table 1. The term "phr" in the table indicates the added amounts of ingredients relative to 100 parts of PVC by mass. The mixture was mixed by high-speed agitation at 100 °C for 10 min, and then the powered mixture was fed into twin-screw extruder (Jiangsu Kemao Machinery Co. Ltd., SHJ-20, China) to prepare tablets with an extrusion temperature of 180 °C. The tablet blend was then dried in an air-oven at 80 °C for 12 h. An injection molding machine (Haitian Plastics Machinery Ltd., China, JU 10000 II) was then used to prepare the tablet mixture into sample bars and the injection molding temperature was set at 180 °C.

Table 1. Formulations of the PVC/ANPs/MCC Composites (phr)

Number	PVC	Stabilizer	Lubricant	ESO	ANPs	MCC
PVC0	100	4	2	5	5	0
PVC1	100	4	2	5	5	5
PVC2	100	4	2	5	5	10
PVC3	100	4	2	5	5	15
PVC4	100	4	2	5	5	20
PVC5	100	4	2	5	5	25
PVC6	100	4	2	5	5	30

FT-IR

In preparation for FT-IR, the composites were pressed into slices by a heating pressing machine (120 °C, 12 MPa) for 3 min. FT-IR tests were performed on a Bruker (Germany) Tensor 27 spectrometer, taking 32 scans for each sample.

Determination of VSTs

The samples were placed on a vicat softening point tester (Chengde Kecheng Testing Machine Co. Ltd., China, XWB-300A) equipped with acupressure needles with a length of 3 mm and cross sectional area of 1 mm^2 and heated in an oil bath with samples submerged into the oil by 35 mm. Then a 5-kg weight was placed on the load beam. The temperature elevation rate was 120 °C /h. The temperature was recorded when the needles of the device pierced into the sample to a depth of 1 mm. Evaluation of each sample was repeated three times.

Mechanical properties testing

The tensile (testing speed, 5 mm/min) testing was conducted by a universal testing machine (The Zwick Roell Group, Germany, Z005 TN) at room temperature. The impact strength of the samples was measured by an impact testing machine (Instron Company, USA, Ceast 9050) at room temperature. All of the data were obtained from five parallel samples and then averaging the value.

SEM

The morphology of the samples was observed by scanning electron microscope (Hitachi, Japan, S-4800) operated at 2.0 kV and 10 mA in order to observe the compatibility at the tensile fractured surface of the sample. All the samples were coated with platinum to reduce charging effects.

RESULTS AND DISCUSSION
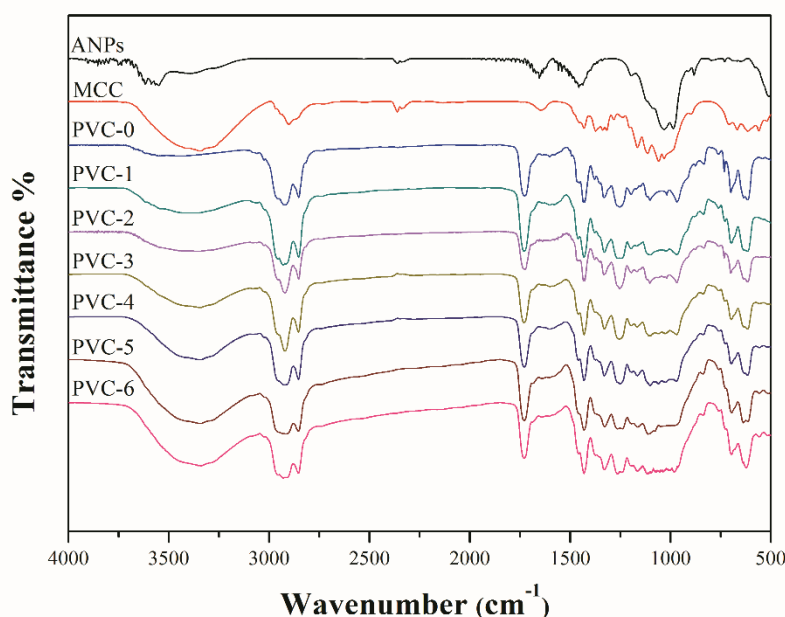
Infrared Spectra Analysis of PVC/ANPs/MCC Composites

Fig. 1. FTIR spectrographs of PVC/ANPs/MCC composites

Figure 1 shows the FTIR spectra of ANPs, MCC, and PVC. The spectrum of the MCC showed a peak near 3348 cm^{-1}, which is related to the hydroxyl stretching vibration of cellulose. The peak at 1649 cm^{-1} can be attributed to the hydroxyl stretching vibration of adsorbed water (Lojewska *et al*. 2005). The peaks at 1373, 1317, 1163, 1056, 1028, and 894 cm^{-1} corresponded to cellulose. The peaks at 1056 and 1025 cm^{-1} corresponded to ether C-O-C and C-O-H stretching vibrations of sugar rings. The peak at 894 cm^{-1} is associated with the presence of a glycosidic bond. The spectrum of the ANPs showed that a peak was observed at 3627 cm^{-1}, which is related to the hydroxyl stretching vibration of peaks of aluminum and/or magnesium species; the peak at 3618 cm^{-1} can be ascribed to the hydroxyl stretching vibrations of adsorbed water; the peaks at 3587 and 3546 cm^{-1} corresponded to the bending vibrations of zeolite water in the channels of attapulgite (Blanco *et al*. 1989). The peak at 1651 cm^{-1} can be attributed to adsorbed water, and the peaks at 1031 and 989 cm^{-1} were related to Si-O stretching and Si-O-Si and Si-O-Al vibrations (Zhang *et al*. 2010).The spectrum of PVC-0 showed a peak at 1722 cm^{-1}, which is related to the carbonyl group of the additive such as ESO, zinc stearate, and stearic acid. The peaks at 1427, 1328, and 966 cm^{-1} were related to CH_2, while the peak at 1251 cm^{-1} can be attributed to the

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stretching vibration of CHCl. The strong peak at 696 cm^{-1} is related to C-Cl. In comparison with the spectrum of MCC, ANPs, and PVC-0, the spectra of PVC showed an additional peak at 1163 cm^{-1}, which can be attributed to the cellulose (Lojewska *et al*. 2005), and the peaks at 3548 and 1652 cm^{-1} corresponded to the ANPs (Zhang *et al*. 2014). These observations indicated that MCC and ANPs were present in the PVC.

Vicat Softening Temperature Analysis of PVC/ANPs/MCC Composites

Generally, VST analysis is used to evaluate the thermal properties and reflect the mechanical properties of materials as they are being heated. Although the VST of a material cannot be directly used to evaluate the actual application temperature, it can be used to guide quality control of the material. Higher VSTs suggested that the material has better dimensional stability, smaller thermal deformation, larger rigidity, and higher modulus. It can be seen in Fig. 2 that the VSTs of the composites gradually increased as the MCC concentration was increased. This was probably due to the fact that chain segments of the PVC increased their motility when the temperature was increased, as PVC was the main bearing phase when the filler content was low. The fillers dispersed in the PVC matrix served as supporting points. Thus, a higher content of filler is expected to provide more supporting points (Xiong *et al*. 2005). With increased MCC, the resistance to internal rotation of macromolecular chains of the PVC was increased. Thus, the degree of movement resistance of chain segments of PVC increased as well; on the other hand, because of the poor interfacial compatibility between ANPs and PVC, with the same amount of ANPs added, the VSTs increased gradually as the amount of MCC was increased. It can be inferred that MCC may have acted as the compatibilizing agent between ANPs and PVC.
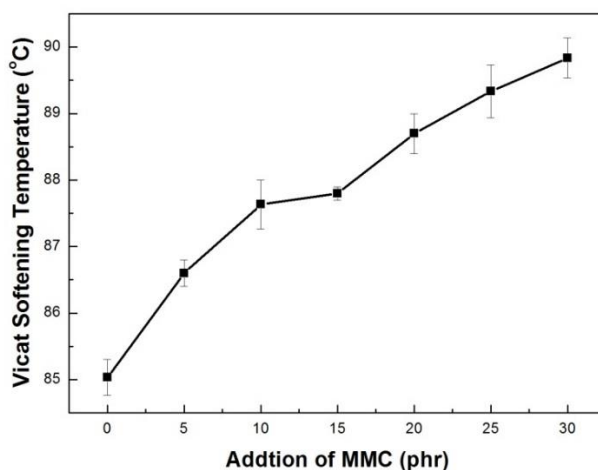

Fig. 2. VSTs of PVC/ANPs/MCC composites

Mechanical Property Analysis of PVC/ANPs/MCC Composites

Results for mechanical properties of PVC/ANPs/MCC composites are presented in Figs. 3 and 4. The tensile curves of composites are indicated in Fig. 3. The yield stress and yield strain of the composites gradually decreased after MCC was added, whereas elongation at break increased when 5 phr was added and all elongations at break gradually decreased with more addition of MCC.
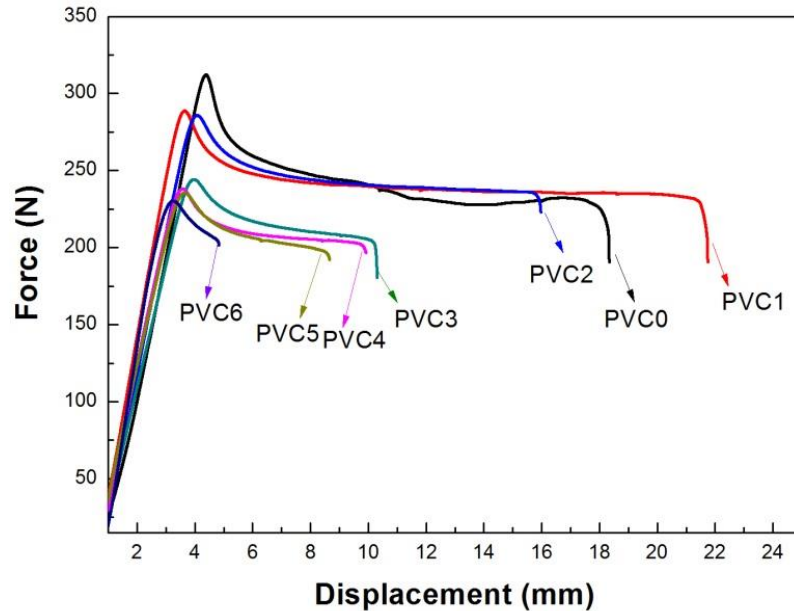
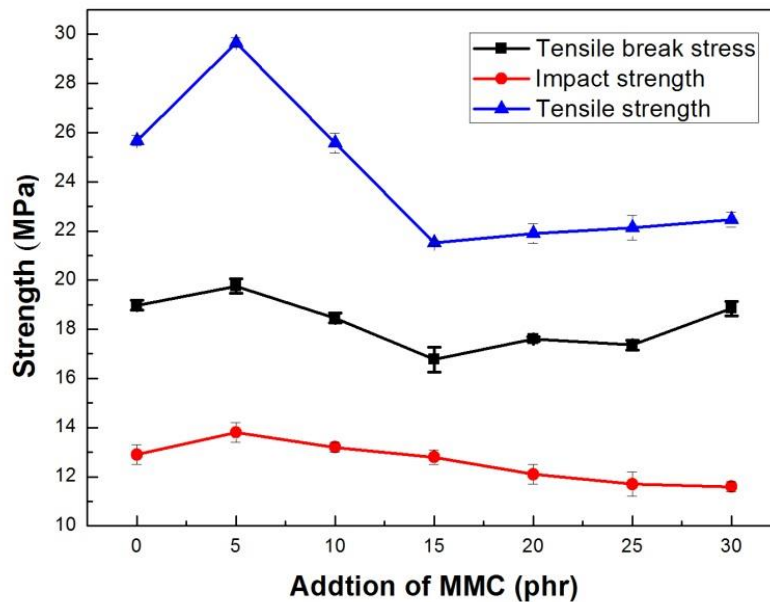**Fig. 3.** Tensile curve of PVC/ANPs/MCC composites

Fig. 4. Mechanical properties of PVC/ANPs/MCC composites

Trend analysis of the mechanical properties obtained from the tensile tests indicated that the concentration of MCC had different effects on various mechanical properties. The results showed that MCC has complex effects on composites. It is worth mentioning that the curves of PVC composites without MCC after reaching the yield strain point and before

complete break were initially flat, then they gradually dropped, whereas composites with MCC added did not show this phenomenon.

It was shown that the tensile properties were improved with the addition of 5 phr of MCC. It can be seen that when MCC was added from 0 to 5 phr, the tensile breaking stress, tensile strength, and impact strength of the composites increased and reached a maximum (4.1%, 15.5%, and 7%). When more than 5 phr of MCC was added, the tensile properties and impact properties of composites decreased. ANPs can cause the PVC to exhibit shear band and silver grain effects in response to stress, which in the process of producing shear band and silver grain can absorb lots of energy. However, when the concentration of ANPs was increased, stress concentration points and defects were produced during formation of the composites. Thus the composites declined in the ability to withstand external damage, which can reduce the performance of the mechanical properties. The mechanical properties of the composites were dependent on the strength of the polymer, the filler, and the bond strength of the interface between the polymer and filler. After MCC was added, mechanical properties of composites were better than that of PVC-0. It was shown that the formation of ANPs and PVC interfacial bonding strength was higher. The main reason for this phenomenon may be that ANPs will be coated by MCC, so that the compatibility between ANPs and PVC was increased. Thus the results provided contributing evidence that the MCC served as a compatibilizing agent in the composites.

SEM Morphology Analysis of PVC/ANPs/MCC Composites

Scanning electron microscopy was used to further analyze the effects of MCC on the blending state of composites (Fig. 5). It can be seen that the matrix phase of PVC and inorganic phase of ANPs all contributed to the morphology.

It was shown that the MCC was well distributed within the PVC matrix. The MCC did not affect the two-phase distribution, and when the MCC concentration was increased, the distance between MCC and PVC matrix became smaller, which increased the interaction force of MCC and PVC matrix. The increase of interaction force of MCC and PVC matrix provide a possibility for MCC can improve the interfacial adhesion between PVC matrix and ANPs.

Moreover, with more MCC added, the distribution of ANPs became more uniform. This indicated that the interfacial adhesion between ANPs and PVC was better; thus the compatibility between PVC and ANPs was improved significantly. These phenomena indicated that the MCC might have coated ANPs and acted in the role of compatibilizer between PVC and ANPs.
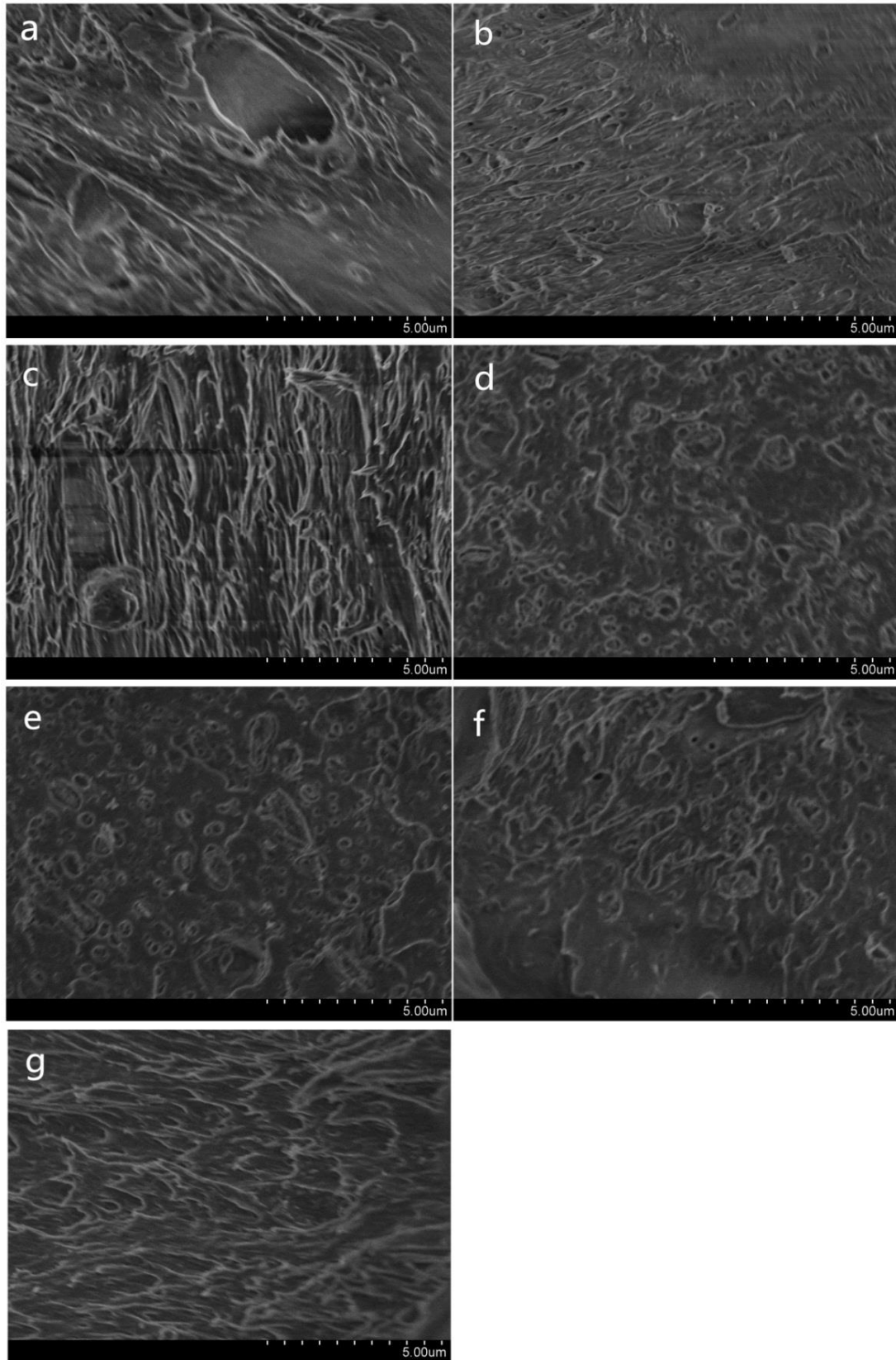
Fig. 5. SEM micrographs of PVC/ANPs/MCC nanocomposites with MCC contents of (a) 0 phr, (b) 5 phr, (c) 10 phr, (d) 15 phr, (e) 20 phr, (f) 25 phr, and (g) 30 phr

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CONCLUSIONS

1. In this study, composites were prepared with polyvinyl chloride, attapulgite clay, and micro-crystalline cellulose (PVC/ANPs/MCC). FT-IR results indicated that MCC and ANPs were present in the composites.

2. The vicat softening temperature (VSTs) results for the composite showed that the thermal stability was greatly improved by the addition of MCC.

3. MCC had a great influence on the mechanical properties of the composites. When 5 phr MCC was added, the composites achieved the maximum elongation at break, tensile strength, and impact strength, with increases of 19.76 N (4.1%), 29.66 MPa (15.5%), and 13.8 MPa (7%). These results provide evidence that the interfacial compatibility of the PVC and ANPs was getting better and also indicate that MCC played the role of compatibilizer in the composites.

4. SEM morphology showed that as more MCC was added, the distribution of ANPs was more uniform, which indicated that the compatibility between PVC and ANPs improved significantly. Accordingly, the MCC might have coated ANPs and acted in the role of compatibilizer between PVC and ANPs.

ACKNOWLEDGMENTS

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