

# Morphology of acrylonitrile-vinyl chloride copolymer/silica/Na-montmorillonite nanocomposite and its enhanced thermal properties

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Acrylonitrile-vinyl chloride copolymer (AN-VC copolymer)/silica/Na-montmorillonite (Na-MMT) nanocomposites were prepared via solution blending in N,N-dimethylformamide (DMF). The solution was then extracted and dried to prepare the nanocomposite film. The transmission electron microscope (TEM) observation showed the silica was dispersed well in copolymer matrix after UV-light treatment; also, the X-ray diffraction (XRD) indicated the layered Na-MMT was exfoliated in copolymer chains. It was found that the AN-VC copolymer/silica/Na-MMT nanocomposites exhibited increased thermal stability.

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## 1. Introduction

Researches on polymer/silica and(or) clay nanocomposites are one of the most attractive research fields in material modification [1-4]. It is obviously indicated that polymer/inorganic hybrids have increased mechanical and thermal properties to extend its potential application in catalyse, electronics and auto fields. Among various composites, most are focusing on polymer/silica [5,6] and polymer/Na-MMT [7,8], expecting enhanced mechanical properties [9,10], flame-retarding [2] and gas barrier properties [11]. For the matrix materials, many polymers have been involved: polystyrene, poly(vinyl chloride), poly(ethyleneoxide), epoxy, polypropylene, poly(methyl methacrylate) and some biomaterials such as poly(L-lysine). Also, there are some studies focusing on PAN based nanocomposites, for example, PAN/porous silica and PAN/Na-MMT.

In PAN/porous silica case [12], the AN monomer was introduced into the porous silica matrix and photopolymerized to form the nanocomposite. In that study, the restraint of porous nano silica matrix may result in lower molecular weight. Meanwhile, the nano pores in the silica matrix could influence the crystallization of the PAN. X-ray diffraction patterns revealed that the PAN synthesized by photopolymerization in porous silica matrix showed amorphous morphology, while the PAN synthesized by thermal polymerization exhibited similar crystallinity.

In PAN/Na-MMT cases [8], Na-MMT layers were exfoliated during in-situ polymerization by emulsifier AMPS and PAN chains. And the nanocomposite exhibited

much more excellent properties than pure PAN. Choi reported that the high residual amount after thermal degradation of the PAN which resulted from the formation of ring compounds. Also, the elevated storage modulus was explained in term of the interaction between strong negative C≡N groups and exfoliated hydrophilic Na-MMT layers.

However, the research on co-incorporating of these two different form nano materials into polymer matrix, that is to say polymer/silica /Na-MMT nanocomposite has been rare. In our previous study, the silica and Na-MMT were introduced into the polyacrylonitrile matrix via in-situ polymerization and the nanocomposite exhibited better thermal stabilities and enhanced mechanical strength.

This work is a systematic investigation into the preparation and characterization of the acrylonitrile-vinyl chloride copolymer (AN-VC copolymer) nanocomposites. AN-VC copolymer/silica/Na-montmorillonite(Na-MMT) nanocomposites are prepared via solution blending in N,N-dimethylformamide(DMF).

X-ray diffraction (XRD) measurements show that the Na-MMT layers are fully exfoliated in the AN-VC copolymer matrix, the transmission electron microscopy (TEM) further confirm the exfoliation state of the Na-MMT layers. Also, TEM images reveal that the aggregation of nano silica was destroyed and the silica disperse well in the AN-VC copolymer matrix. To evaluate the thermal properties of the AN-VC copolymer nanocomposites, thermogravimetric analysis (TGA) was performed. All the results show that co-incorporation of the two nano materials into the AN-VC copolymer matrix

can result in enhanced onset temperature of thermal degradation of the copolymer matrix.

## 2. Experimental

AN-VC copolymer was purified and dried before dissolved in DMF. The layered Na-MMT and the silica were both treated by 1000W UV-light for 15 min before dissolved in DMF. The nano particles solution was then sonicated for about 30 minutes and blended with AN-VC copolymer solution thoroughly. Then the solution was poured into the culture dish. The solvent DMF was evaporated in a vacuum oven under normal pressure. The AN-VC copolymer/silica/Na-MMT nanocomposites(ASM) film was formed after about 12 hours. It was further extracted in a vacuum oven to get rid of the residual solvent DMF. The comparisons nanocomposites of AN-VC copolymer/silica(AS) and AN-VC copolymer/Na-MMT(AM) were also prepared via solution blending.

X-ray diffraction patterns of Na-MMT and nanocomposites were obtained by using Bruker AXS D8 Advance diffractometer with a scanning rate of  $2^\circ/\text{min}$  in a  $2\theta$  range of  $1.5\text{--}10^\circ$  under room temperature. The morphologies of the AN-VC nanocomposites were observed with JEOL JEM-2100 transmission electron microscope. The accelerating voltage is 120 KV. Thermogravimetric analyses (TGA) were carried out with TA instrument TGA2050 by heating from a room temperature to  $1000^\circ\text{C}$  with a rate of  $20^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere.

## 3. Results and analysis

### 3.1. Morphologies of AN-VC copolymer nanocomposites

Fig. 1 shows X-ray diffraction patterns of Na-MMT, AS, AM and ASM nanocomposites. Pristine Na-MMT exhibits a diffraction peak of the (001) plane at  $5.7^\circ$  in a  $2\theta$  value, and its basal spacing is 1.55 nm (curve (a)). Curve (b) is the result obtained for ASM. No diffraction peak is shown, indicating that the Na-MMT layers are exfoliated.

Choi et al. reported similar results for AM nanocomposites [8]. According to their studies, the basal space of the Na-MMT are enlarged in the aqueous solution of AN with surfactant 2-acrylamido-2-methyl-1-propanesulfonic acid. In this case, the Na-MMT layers can be fully exfoliated during solution blending in solvent DMF. Also, in AM case, there is no diffraction peak to indicate the exfoliation of the Na-MMT.

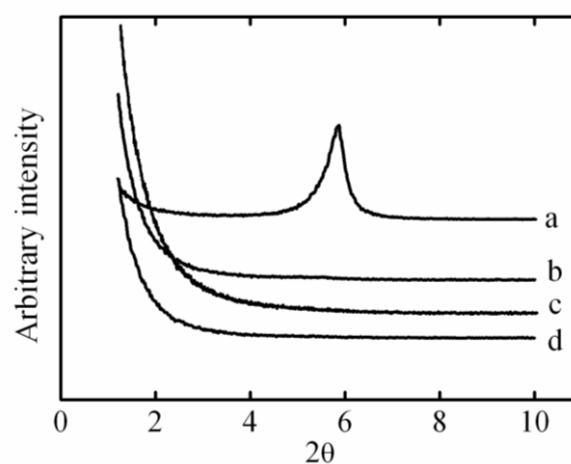


Fig. 1.  $0\text{--}10^\circ$  X-ray diffraction patterns of raw Na-MMT (a), ASM with 2.0wt% Na-MMT and 2.0wt% silica (b), AS with 4.0 wt% silica (c) and AM with 4.0 wt% Na-MMT(d).

Typical TEM photographs of ASM are given in Fig. 2(a). The dark slices stand for Na-MMT layers while the dark particles are silica. The AN-VC copolymer matrix appears as light region. The image of ASM reveals that the Na-MMT layers are exfoliated and well distributed, which further verifies the XRD results. Also, the aggregation of silica nano particles are destroyed and well distributed in the AN-VC copolymer matrix. It is also showed from Fig. 2(b) and (c), after lighted with UV-light and sonicated in DMF solution, the silica and Na-MMT can be dispersed well in AN-VC copolymer matrix.

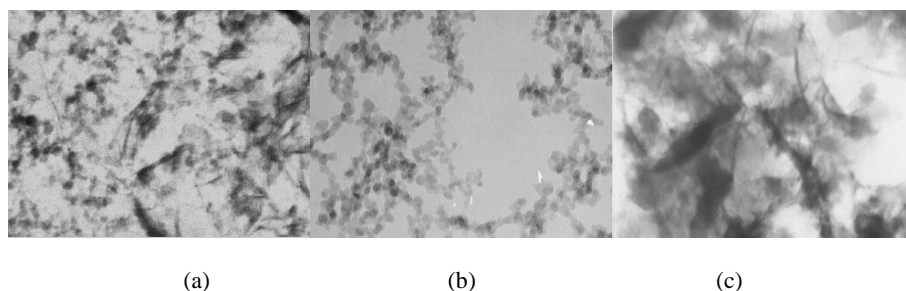


Fig. 2. TEM micrographs of ASM with 2.0wt% Na-MMT and 2.0wt% silica (a), AS with 4.0wt% silica (b) and AM with 4.0wt% Na-MMT(c).

### 3.2. Effects of co-incorporation of Na-MMT and silica on the thermal property

Fig. 3 shows the thermogravimetric graphs of the matrix AN-VC copolymer and its nanocomposites. Thermal decomposition of the matrix AN-VC copolymer chains occurs at about 300~400°C as shown by curve(a). The decomposition shifts toward higher temperatures when nano materials are incorporated into the AN-VC copolymer. For the nanocomposites with same nano materials loadings, i.e. 4.0 wt%, the ASM shows more enhanced thermal stabilities than either AS or AM.

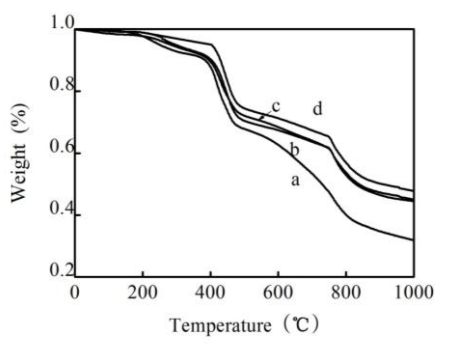


Fig. 3. Thermal gravimetric curves for AN-VC copolymer (a), AS with 4.0wt% silica (b), AM with 4.0wt% Na-MMT (c), and ASM with 2.0 wt% Na-MMT and 2.0 wt% silica (d).

Table 1. Degradation temperature when 20% and 40% weight lost.

weight lost	4.0 wt% nano material loading		2.0 wt% nano material loading	
	20%	40%	20%	40%
AN-VC copolymer	438	658	438	658
AS	450	783	432	778
AM	452	787	438	781
ASM (silica:Na-MMT=1:1)	474	798	460	790

### 3.3. Mechanism for enhanced thermal property of the nanocomposites

The enhanced thermal stability of AN-VC copolymer nanocomposites can be attributed to the interactions between copolymer chains and inorganic nano materials. Both the silica and Na-MMT have the Si-O groups on the surfaces of them. The AN-VC copolymer chains become cross-linked via the hydrogen bonds formed between Si-O groups and C≡N groups (Fig. 4). Such interaction can enhance the stability of the copolymer chains under temperature increasing, because the hydrogen bonds should absorb more heat to be destroyed before the chain degradation.

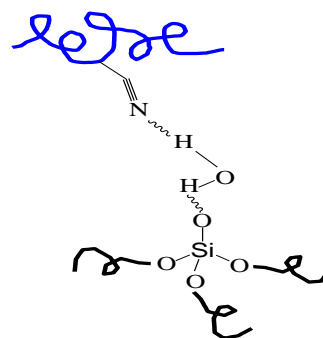


Fig. 4. The hydrogen bond structure formed between nano materials and AN-VC copolymer molecules.

More detailed information regarding the influence of the incorporation of nano materials on the thermal stability is shown in Table 1, the temperatures when 20% and 40% weight of nanocomposites lost are listed against nano material loading (for ASM, silica:Na-MMT=1:1).

For all nanocomposites examined, the decomposition temperatures are higher than that of AN-VC copolymer. Also, the 20% weight lost decomposition temperature increases with the nano material loading increasing; the situation of 40% weight lost decomposition temperature is the same. More evident enhanced thermal stability is demonstrated for the ASM systems. For instance, at 2.0 wt% nano material loading, the 20% weight lost temperature of ASM is 28°C higher than that of AS, and 22°C higher than that of AM. In case of 40% weight lost, the enhancement values are 12°C and 9°C, respectively.

Due to the strong interaction between the AN-VC copolymer chains and silica nano particles, a physical network can be formed and give rise to an enhanced thermal stability. On the other hand, the existence of the Na-MMT could prevent the out-diffusion of the volatile decomposition products because of its strip structure. Combination of these two effects can be the reason for the ASM nanocomposites showing superior thermal stability with respect to the AS and AM composites.

#### 4. Conclusions

AN-VC copolymer nanocomposites with silica, Na-MMT and silica/Na-MMT were prepared via solution blending in solvent DMF. XRD and TEM observations revealed that the Na-MMT layers were fully exfoliated and the aggregated silica particles were well dispersed in the copolymer matrix. After incorporated with nano materials, the thermal stability of the copolymer matrix was enhanced remarkably. Obviously, the co-incorporation of silica/Na-MMT into AN-VC copolymer matrix could get most excellent enhanced thermal stability. It is believed to be the combination of the interactions between silica/Na-MMT and AN-VC copolymer chains.

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