

Nanocomposites of Vinyl Chloride–Acrylonitrile Copolymer and Silica

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ABSTRACT: Vinyl chloride–acrylonitrile (VC–AN) copolymer was synthesized through emulsion copolymerization. VC–AN copolymer/silica nanocomposites were prepared by solution blending of copolymer and silica in a common solvent, *N,N*-dimethylformamide (DMF). The rheology studies show that the shear-thinning behavior of the VC–AN copolymer solution becomes less distinct as nano particles are introduced. It was also found that the viscosity of the copolymer solution decreases with adding small amount of nano particles. Transmission electron microscopy observations indicate that the UV-treated silica could disperse well in the copolymer matrix. Differential scanning calorimeter studies suggest that the presence of the silica suppresses crystallization of the AN segments in the copolymers. Because of the interactions between copolymer chains and inorganic particles, the thermal stability and mechanical strength of the VC–AN copolymers are improved considerably. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 43: 3127–3134, 2005

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INTRODUCTION

The interesting physical and chemical properties of nanostructured materials are well recognized for decades. Particles with nano size have some specific properties, such as the mini-size effect, surface and interface effects, which can result in the difference of properties between nanostructured materials and macro bulk materials. Introduction of the nano materials into polymer matrix can lead to substantially enhanced thermal and mechanical properties of the polymer material, due to the mini-size effect, surface, and interface effects of the nano materials. This kind of composites, the so-called nanocompo-

sites, has gained more attention recently.^{1–3} For the nanocomposites, the matrix materials are usually polypropylene, poly(vinyl chloride), polyacrylonitrile, and so on. A widely used nanoparticle for the enhancement is silica.

Sol–gel reaction of tetraethoxysilane (TEOS) in the polymer matrix is a commonly used method for the preparation of the silica nanocomposites. In these cases, the polymer could be 3-glycidoxypropyltrimethoxysilane (GLYMO),⁴ polyacrylamide,⁵ poly(vinylidene fluoride–tetrafluoroethylene) (P(VDF–TFE)),⁶ styrene-based triblock copolymer,⁷ isobutylene–styrene triblock copolymer,⁸ and 2-hydroxyethyl methacrylate polymer.^{9,10} Some novel or outstanding properties of the composites emerge with the introduction of the nano silica. For example, the GLYMO coating modified by the ZnO/SiO₂ could be dense, flexible, abrasion resistant, and UV absorbent. The yield strength, yield strain, and tensile strength

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of the P(VDF–TFE)/nano SiO₂ composites are considerably increased with respect to the matrix polymer.⁶ Marked improvements of the flame-retarding and thermal properties are also reported for poly(methyl methacrylate)/SiO₂ nanocomposites.¹¹

Another method to prepare silica nanocomposites is *in situ* polymerization. For instance, the TEOS solution is catalyzed by acid to form silica particles via repeated hydrolysis and condensation.^{9,10,12} Polymer/nano silica composites can also be obtained by melt blending. In this case, the matrices could be epoxy resin,¹³ polypropylene, and so on. Melt blending is also used for preparation of nanocomposites containing nano materials other than silica, such as montmorillonite (MMT).

Solution blending is widely used in material preparation and processing.^{14–19} However, for nanocomposite preparation, solution blending is used rarely.^{17–19} The solution has relatively low viscosity, which can lead to a good dispersing state of the nano materials. The commonly used nano material in solution blending is MMT, while there are few reports about silica used in solution blending to prepare the nanocomposites. Krikorian and Kurian reported the preparation of poly(L-lysine)/MMT nanocomposites via solution blending.¹⁸ In their studies, the polymer matrix and MMT are both well dissolved in deionized water, the nano material and matrix could incorporate thoroughly to form perfect dispersing state. Therefore, both the thermal stability and the mechanical properties are increased significantly. Pramanik and Srivastava reported a study regarding the preparation of rubber-clay nanocomposites through solution blending.¹⁹ Ethylene vinyl acetate (EVA) being dissolved in organic solvent can delaminate the MMT layers. It was found that the tensile strength of nanocomposites is 1.6 times higher than that of the neat EVA matrix.

Vinyl chloride (VC)–acrylonitrile (AN) copolymer is an important flameproof material,²⁰ which can be dissolved well in the organic solvent *N,N*-dimethylformamide (DMF). And the nano-sized silica treated by UV-light can also disperse well in the solvent DMF. As a result, it is feasible to prepare the nanocomposite of VC–AN copolymer/silica by solution blending.

In the present research work, nanocomposites of VC–AN copolymer/silica with various copolymer-to-nano silica compositions were prepared via solution blending. Nanocomposite morpholo-

gies were studied by transmission electron microscopy (TEM). Thermal properties of nanocomposites were measured with differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA), while the mechanical properties were investigated by mechanical tester. The results of these studies presented herein reveal successful nanocomposite formation with VC–AN copolymer and silica, resulting in the improvement of the thermal stability and the enhancement of the mechanical properties, compared with the VC–AN copolymer matrix.

EXPERIMENTAL

Materials

The vinyl chloride–acrylonitrile (VC–AN) random copolymer was synthesized by emulsion polymerization. Measurements of molecular weight and distribution were performed with SERIES 200 (PerkinElmer, Inc) GPC. The number average molecular weight of the copolymer is 1.46×10^5 and the polydispersity is 1.83. The compositions of the copolymer were measured with element analyzer (Elementar Vario EL III). The N, C, H contents (wt %) are 7.66, 46.71, and 5.31% respectively, and the Cl content is calculated accordingly as 40.32%. It is concluded that the random copolymer contains 69.3 mol % VC segments and 30.7 mol % AN segments. The modified silica with nano size was provided by Degussa Co. Ltd.

Preparation of the Nanocomposites

VC–AN copolymer was purified by repeated precipitation from a DMF solution in a large volume of deionized water. Then the copolymer was dried in the oven at 60 °C for about 12 h and dissolved again in DMF. The solution was stirred overnight. The silica was treated by 1000 W UV-light for 15 min. It was stirred for about 2 h after dissolved in DMF and stabilized overnight. The silica solution was sonicated for about 30 min before use.

The silica solution and polymer solution were mixed together thoroughly and sonicated for 30 min again. Then the solution was poured into the culture dish. The solvent DMF was evaporated in a vacuum oven at 60 °C under normal pressure. The solid nanocomposites film was formed 12 h later. It was further dried in a vac-

uum oven for 48 h at 70 °C and subsequently cooled to ambient temperature under vacuum. The final nanocomposites film was optically clear.

Rheology Studies

The blending solution was sonicated again for about 30 min. The concentration of the copolymer solution was kept at about 6 wt %, and the nano silica content in the solutions are 0, 1.0, 1.5, 3.0% (wt %), respectively. The solution samples were stirred for several minutes a day over at least two weeks. The rheological experiments of the sample solutions were carried out on a rheometer (Haake Rheo Stress 600) at 25 °C.

TEM Observations

The morphologies of the nanocomposites were observed with TEM (JEM-1200-EXII) with 120 kV accelerating voltage. The nanocomposite films were microtomed into ultrathin (<100 nm thickness) slices with a diamond knife under room temperature after embedded in the epoxy matrix. The slice samples were put on the copper grids before observation.

Thermal Analysis

The nanocomposite thermal behavior was measured with TA Instruments DSC (1090B) and TGA (SDTA DSC851e). DSC and TGA were performed on pieces of nanocomposites films. These experiments were carried out under dynamic nitrogen flow with a heating rate of 10 °C/min.

Mechanical Analysis

The nanocomposites were cut into strip-like samples with the dimension of 50.0 (L) × 7.0 (W) × 0.5 (H) mm³. The tensile strength of these samples was tested on the AG-2000A (Shimadzu) mechanical tester under room temperature. Each experiment was carried out on at least three strips for every specimen.

RESULTS AND DISCUSSION

Rheological Studies

Figure 1 depicts the normalized shear viscosity as a function of shear rate for the VC-AN copolymer solutions. As it can be seen, the viscosity of the matrix VC-AN copolymer solution decreases with the shear rate on log-log plot.

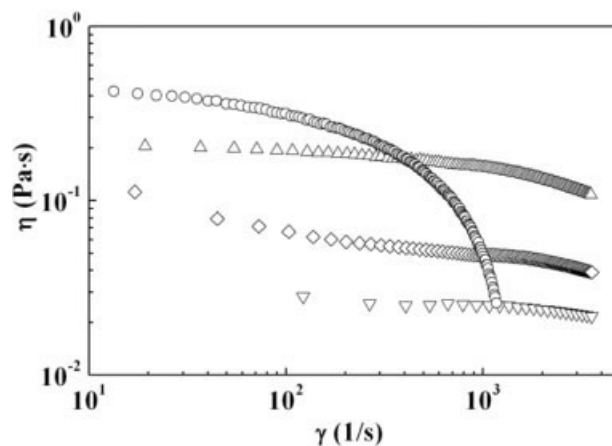


Figure 1. Constant shear viscosity versus shear rate for VC-AN copolymer/SiO₂ solutions with SiO₂ content of 0 wt % (○), 1.0 wt % (△), 1.5 wt % (◇), and 3.0 wt % (▽) at 25 °C.

However, the shear-thinning behavior of the polymer/nano particle solutions becomes less distinct and the viscosity of the blending solutions changes slightly when the shear rate increases, exhibiting Newtonian fluid flow behaviors. It can also be noted that with the introduction of nano silica, the solution viscosity decreases. The decrease in viscosity with the addition of nano particles is contradicted to the classical rheology stemming from the pioneering work of Einstein that if a rigid filler material is added to a suspension, the shear viscosity will be increased.²¹ For the VC-AN copolymer/nano SiO₂/DMF solution, the interactions between the silica and copolymer chains such as hydrogen bonding could change the polymer chain conformation and decrease the hydrodynamic volume of the polymer chain. As a result, the viscosity of the blending solution decreases. Recently, Mackay et al. observed a similar non-Einstein-like decrease in viscosity for linear polystyrene/nano particle blend system.²² It was explained that the free volume as well as certain configuration changes of the linear polymer give rise to the viscosity decrease.

Morphologies

TEM photographs of VC-AN nanocomposite are given in Figure 2. As for the VC-AN nanocomposite with untreated SiO₂, [Fig. 2(a)] the nano particles are not so well dispersed in the matrix. Some agglomerations are shown. In the case of UV-light-treated SiO₂, the nano particles are dispersed well in the copolymer matrix than

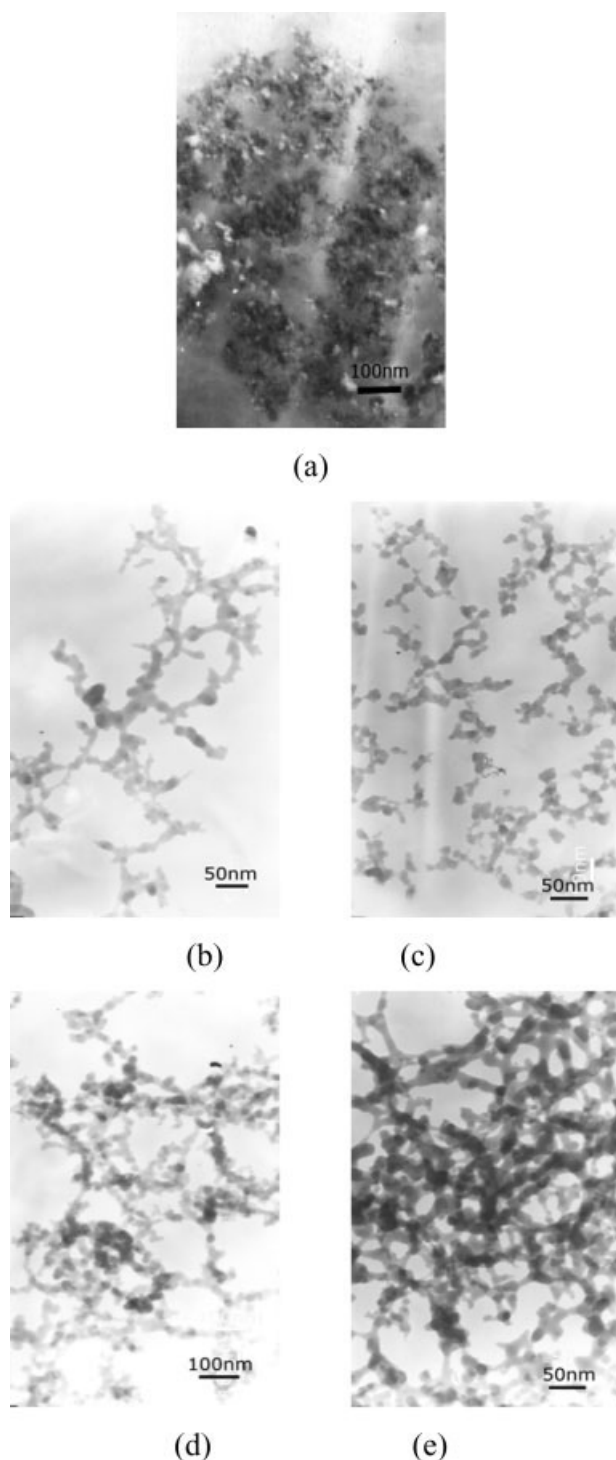


Figure 2. TEM micrographs of nanocomposites with SiO₂ not treated by UV-light (a) and with UV-treated SiO₂ (b–e). The silica content for the nanocomposites with untreated SiO₂ is 2.0 wt % and for the nanocomposites with UV-treated SiO₂ are 2.1 wt % (b), 5.0 wt % (c), 10.7 wt % (d), and 13.4 wt % (e).

untreated nano particles. UV-light treatment can activate the surface of particles and form some adhesive points on the surface.²³ As a result, the nano particles become more adhesive on the matrix polymer and disperse well in it. However, for the UV-light-treated nano particles, when the SiO₂ content become high, some aggregation also appears. (see Figs. 2(d) and 2(e) for the nanocomposites with SiO₂ content of 10.7 and 13.4 wt %).

Thermal Properties

Figure 3 shows the DSC curves of the matrix copolymer and nanocomposites. Curve 1 is the result obtained for the matrix copolymer. With increasing temperature, the curve displays an endothermic peak at 51.4 °C. According to Hwang and Liu's report,²⁴ it is corresponding to the destruction of the crystals formed by AN segment in copolymer chain. With the incorporation of nano silica particles, the endothermic peak area is gradually reduced, and finally disappears when nano silica content is over 10 wt %. It suggests that the nano silica destroys the order within the crystalline domains of AN segment, and the packing of the AN segment tends to be amorphous.

TGA curves of the VC–AN matrix copolymer (curve 1) and nanocomposites with various nano particle contents are shown in Figure 4. All the nanocomposite samples with different silica loading exhibit similar behavior—a slight weight loss around 100 °C corresponding to the weight loss of solvent, an ~20–30% weight loss corre-

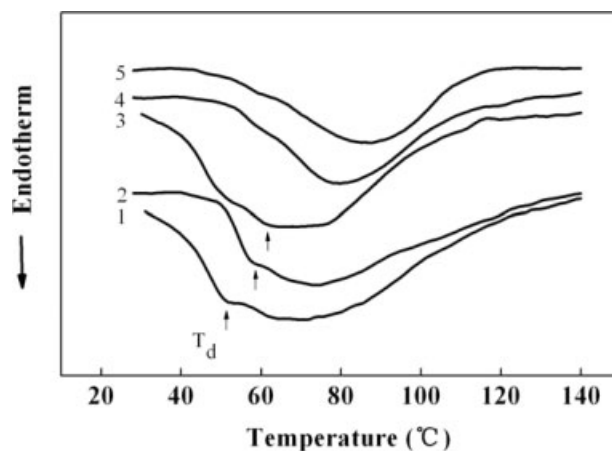


Figure 3. DSC thermograms for nanocomposites with SiO₂ content of 0 wt % (1), 2.1 wt % (2), 6.7 wt % (3), 10.7 wt % (4), and 14.9 wt % (5).

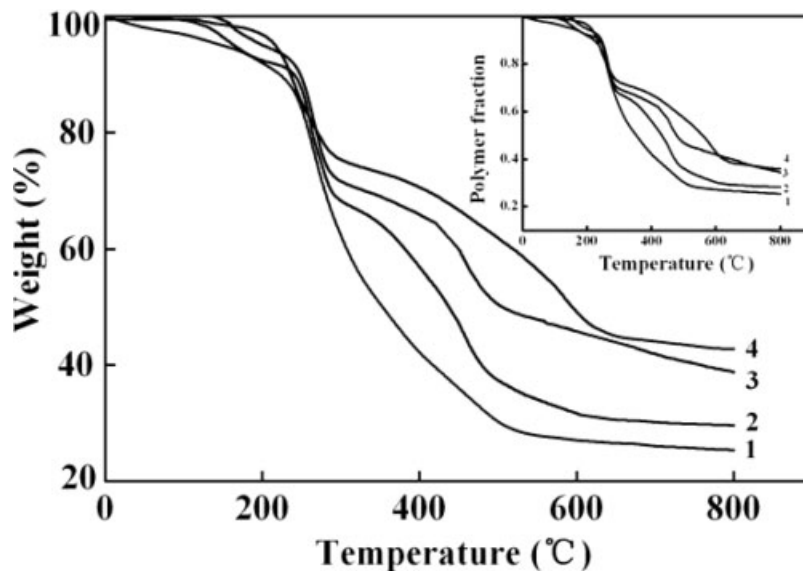


Figure 4. Thermal gravimetric curves for nanocomposites with SiO₂ content of 0 wt % (1), 2.1 wt % (2), 6.7 wt % (3), and 10.7 wt % (4). Shown in inset is a plot where the data were replotted as polymer fraction against temperature.

sponding to the dehydrochlorination of the PVC segments in the copolymer, and a final significant weight loss down to final ash corresponding to the degradation of the copolymer backbone. That is to say, the two large shoulders in the thermal degradation curve correspond to the degradation of the materials in two steps, the dehydrochlorination of the PVC segments and the copolymer backbone degradation.

Table 1 summarizes the TGA data for copolymer and nanocomposites. The data include the temperature indicating the onset of the degradation when 10% weight is lost; the temperature at which 50% weight is lost, a measure of the course of the degradation; and the fraction not volatile labeled as char remaining. The onset of decomposition for the copolymer/nano SiO₂ composite is shifted toward higher temperature with increasing SiO₂ content, indicating an enhancement of the thermal stability of the material.

The enhanced thermal stability can also be noted from the inset plot in Figure 4 where the data were replotted as polymer fraction against temperature. As it can be seen, in the decomposition temperature region, the remaining polymer fraction becomes appreciably higher when the nano SiO₂ particles are incorporated. With such a plot, the simple dilution effect on the thermal stability due to the introduction of nano SiO₂ particles is ruled out. The promotion of the thermal stability can be explained that network forms in the nanocomposites through polymer/nano particle interactions. The interactions between the copolymer chains and nano particles can be ion-induced dipole force.²⁵ On the other hand, the CN groups in the copolymer chains can form H-bonds with the OH groups on the silica surface.²⁶ It could also provide strong interaction between the polymer and silica particles. Thus, a network could be formed through

Table 1. TGA Data for the VC-AN Copolymer Nanocomposites

Nano Content (wt %)	Temperature at Which 10% Weight Lost (°C)	Temperature at Which 50% Weight Lost (°C)	Char Remaining from Polymer Fraction (wt %)
0	228	283	25.0
2.1	236	302	27.5
6.7	238	326	32.3
10.7	243	404	32.1

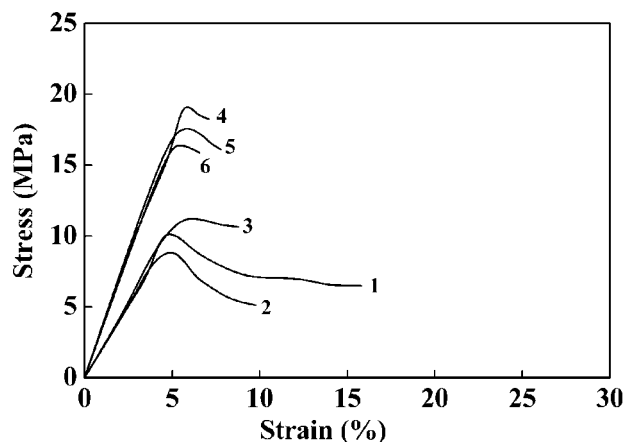


Figure 5. Stress–strain curves of VC–AN copolymer nanocomposites with SiO₂ content of 0 wt % (1), 2.1 wt % (2), 5.0 wt % (3), 6.7 wt % (4), 10.7 wt % (5), and 13.4 wt % (6).

the fixation between the polymer chains and inorganic particle surface,²⁷ and result in an enhanced thermal stability. Such effects have been reported for polystyrene,^{28,29} polypropylene,³⁰ and polymethyl methacrylate nanocomposites,³¹ respectively. In all these cases the polymer chain/particles network is formed via particle–polymer interactions. It makes the matrix polymer become more stable under heating.

Mechanical Properties

Typical stress–strain curves for the nanocomposites with various compositions are shown in

Figure 5. Both the VC–AN copolymer and its nanocomposites show toughness rupture properties. With the introduction of the nano silica, the extension to failure decreases, that is to say the brittleness of the materials increases after the nano inorganic additive is introduced into the matrix. Figure 6 gives the measurement results of the tensile strength and the Young's modulus of the nanocomposites. As it can be seen, the strength and modulus increase with increasing nano SiO₂ content and then decrease when the nano particle loading is over than 7 wt %. At about 7 wt % of silica loading, the film samples exhibit optimal strength and modulus, which are two times higher than that of matrix VC–AN copolymer. The enhanced mechanical properties could be attributed to the formation of network through interactions between polymer chains and SiO₂ particles.^{6,32} The deterioration of the mechanical properties of the nanocomposites with more nano particles incorporated is believed to be the effect of the aggregation of nano particles caused by the overdose nano additive as it can be seen from Figures 2(d) and 2(e).

CONCLUSIONS

In the present work, the VC–AN copolymer/silica nanocomposites were prepared via solution blending. The flowing behavior of this solution was studied to give useful information to pre-

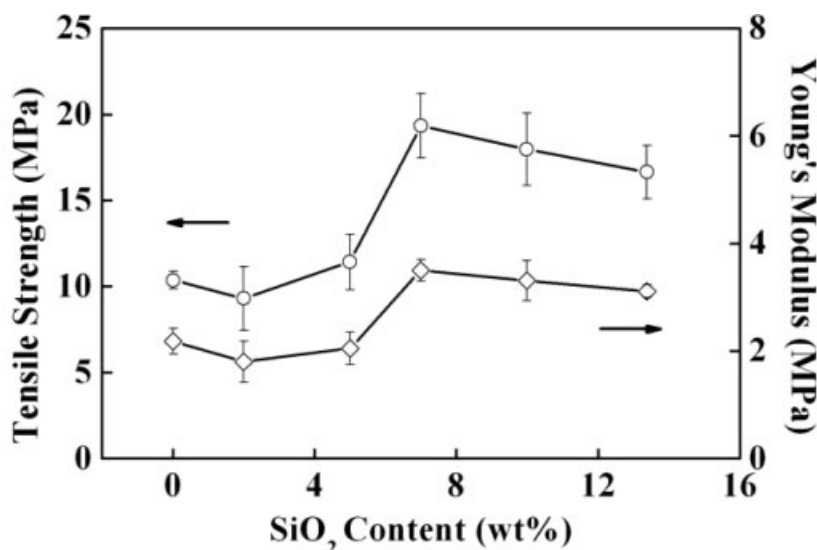


Figure 6. Influence of nano SiO₂ content on tensile strength (○) and Young's modulus (◇) of nanocomposites.

pare the nanocomposite films. Studies on the influence of the nano silica on the thermal and mechanical properties were carried out. A feasible method, solution blending, to prepare nanocomposites is provided, in case of the matrix polymer and nano material having common solvent. The polymer solution has relatively low viscosity, which leads to a better mixing and combination of nano particles and polymer. Besides the effect of the nanometer scale dispersion of the nano particle in the polymer matrix, the interactions between the copolymer chains and the nano particles could play an important role in determining various properties of VC-AN copolymer/SiO₂ system. The interactions can be the hydrogen bonding between the CN groups in copolymer chain and the OH groups on the silica surface and also ion-induced dipole force. Through such interactions, polymer chain/nano particles network could form, which could contribute greatly to the enhance the thermal stability and the mechanical property. However, excessively adding nano particle could result in aggregation. As a consequence, the mechanical properties could deteriorate. In the VC-AN copolymer/silica solution, the interactions between the nano particles and copolymer chain may change the chain conformation and reduce the hydrodynamic volume of the polymer chain, resulting in a decrease in viscosity with adding small amount of nano particles. The results obtained throughout the experiments are summarized as follows:

1. It was found from the rheology studies that the flow behavior of the copolymer/nano silica solution shows insensitivity to the increase of the shear rate, and the solution viscosity decreases with adding small amount of nano particles. According to the TEM studies of the film cast from the blending solution, the nano SiO₂ treated by the UV-light could be dispersed well in the VC-AN copolymer matrix.
2. The nano silica destroys the order of the polyacrylonitrile chain packing in the copolymer. It shows smaller or no endothermic peak around 51.4 °C in DSC curves of nanocomposites. TGA data confirm that the inorganic nano silica make the nanocomposites much more stable than the matrix copolymer when resisting the heat.
3. The VC-AN copolymer nanocomposites show an enhanced strength and Young's modulus. The elongations at break were

found to decrease with adding nano SiO₂ particles.

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