

Improving Mechanical Properties of Poly(vinyl chloride) by Doping with Organically Functionalized Reactive Nanosilica

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ABSTRACT: Nanosilica particles are functionalized by *in situ* surface-modification with trimethyl silane and vinyl silane. Resultant reactive nanosilica (coded as RNS) contains double bonds and possesses good compatibility with vinyl chloride (VC) and polyvinyl chloride (PVC). This makes it feasible for RNS to copolymerize with VC generating RNS/PVC composites via *in situ* suspension polymerization. As-prepared RNS/PVC composite resins are analyzed by means of FTIR. The tensile strength and impact strength of compression-molded RNS/PVC composites are measured and compared with that of compression-molded PVC composites doped with dispersible nano-SiO₂ particles (abridged as DNS) surface-modified with trimethyl silane alone. Moreover, the thermal stability of compression-molded RNS/PVC and DNS/PVC composites is evaluated by thermogravimetric analysis. It has been found that RNS/PVC composites possess greatly increased impact strength and tensile strength than PVC matrix, while DNS/PVC composites possess higher impact strength than PVC matrix but almost the same tensile strength as the PVC matrix. This implies that DNS is less effective than RNS in improving the mechanical strength of PVC matrix. Particularly, RNS/PVC composites prepared by *in situ* suspension polymerization have much higher mechanical strength than RNS/PVC composites prepared by melt-blending, even when their nanosilica content is only 1/10 of that of the melt-blended ones. Besides, *in situ* polymerized RNS/PVC and DNS/PVC composites have better thermal stability than melt-blended nanosilica/PVC composites. Hopefully, this strategy, may be extended to fabricating various novel high-performance polymer-matrix composites doped with organically functionalized nanoparticles like RNS.
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INTRODUCTION

Polyvinyl chloride (PVC), one of the major thermoplastics with low production cost as well as good insulation performance, chemical resistance, and flame retardance, is widely used in industry.^{1,2} However, pure PVC has poor impact resistance and thermal stability, which limits its application in engineering. These drawbacks, fortunately, could be well overcome by filling PVC with inorganic fillers such as CaCO₃,³ clay,⁴ talc,⁵ SiO₂,⁶ and carbon nanotube.⁷ Of various inorganic fillers, nanosilica with high surface activity and rigidity as well as good dimensional stability is of extraordinary interest. It has been found that nanosilica is able to improve the mechanical properties of melt-blended PVC to some extent.^{8,9} The comprehensive properties of melt-blended nanosilica/PVC composites, however, are still not good enough, largely because nanosilica, even after being modified with organic compound like polymer, can hardly be uniformly dispersed in PVC matrix, not to mention that PVC is vulnerable to decomposition in melt-blending

process. Therefore, it is imperative to improve further the dispersibility of nanosilica in PVC matrix by *in situ* surface-modification with organic modifiers, which possess good compatibility with PVC. In addition, it is essential to adopt novel approach like *in situ* polymerization to fabricate surface-capped nanosilica/PVC composites to inhibit decomposition of PVC during the fabrication process and minimize its damage to the mechanical properties of end-products.^{10–12}

Bearing those perspectives in mind, in the present research we fabricate reactive nanosilica (coded as RNS) by incorporating trimethyl silane and vinyl silane onto the surface of newly formed silica nanoparticles via *in situ* surface-modification. Resultant RNS possessing good compatibility with vinyl chloride (VC) and poly(vinyl chloride) is then allowed to copolymerize with VC generating RNS/PVC composites via *in situ* suspension polymerization. Hopefully, such a strategy helps to design and fabricate PVC-matrix composites with effectively improved mechanical strength, since functionalized RNS is able to chemically

combine with PVC matrix via covalent bond. Dispersible nanosilica (coded as DNS) functionalized by trimethyl silane alone is also prepared and incorporated into PVC matrix in the same manners for a comparative study. This paper reports the preparation, structure, mechanical properties and thermal stability of *in situ* polymerized RNS/PVC and DNS/PVC composites in relation to the properties of melt-blended RNS/PVC and DNS/PVC composites.

MATERIALS AND METHODS

Materials

Liquid sodium silicate was purchased from PQ Silicates Technology Company Limited (Tianjin, China). Hexamethyldisilazane (HMDS) supplied by Shanghai Hongxin Chemical Technology Company (Shanghai, China) and vinyltrimethoxyl silane (A-171) supplied by Nanjing Crompton Shuguang Organosilicon Company (Nanjing, China) were adopted as modifiers of nanosilica and used as-received. VC, compound initiator, terminator of polymerization, calcium stearate, and tribasic lead sulfate (TBLS) were supplied by Botian Chemical Company Limited (Tianjin, China). Suspension dispersants, partially hydrolyzed poly(vinyl alcohol) (PVA) and hydroxypropylmethyl cellulose (HPMC) were purchased from Shinetsu Chemical Industry Company of Japan. Analytical grade reagents tetrahydrofuran (THF), sulfuric acid, absolute ethanol, and carbon tetrachloride were used for synthesis and characterization. Deionized water prepared at our laboratory was used as a solvent.

Synthesis and Characterization of Organically Functionalized Nanosilica

A stoichiometric amount of sodium silicate was placed in a reactor and dissolved with deionized water. The sulfuric acid solution was dripped into the reactor under stirring at room temperature until the reaction solution turned turbid. Then the solution of modifier HMDS in absolute ethanol was dripped into the reactor, followed by the introduction of the solution of modifier A-171 in absolute ethanol from the same dripping funnel. Resultant suspension was heated to 50°C and stirred for 2 h thereat, where a certain amount of foam appeared on the surface of the aqueous solution while sulfuric acid was continuously dripped into the reactor to maintain a pH level of 3–4. After being stirred for additional 2 h at 70°C, the reaction solution was put into a separating funnel to generate a white floc on the top. The floc was collected by filtration and washed repeatedly with the mixed solvent of deionized water and ethanol (volume ratio 4 : 1). The filtered cake was dried to yield desired RNS. DNS was prepared in the same manner except that HMDS was adopted as the sole modifier.

A JEM-2010 transmission electron microscope (TEM) was performed to observe the microstructure of RNS and DNS, where the samples for TEM observation were obtained by placing a drop of the dispersion of RNS or DNS in ethanol onto Cu grid and drying in air. The specific surface area of RNS and DNS was measured by Brunauer-Emmett-Teller (B.E.T) method. A 721 spectrophotometer was performed to measure the light transmittance at 530 nm of RNS and DNS dispersions in liquid trichloroethylene possessing polarity similar to that of VC to estimate their dispersivity.

Synthesis of Nanosilica/PVC Composite Resins

Nanosilica/PVC composite resins were synthesized by *in situ* polymerization. First, a proper amount of DNS or RNS powders was

dispersed in the mixed solvent of ethanol and deionized water while the weight ratio of nanosilica/ethanol/water was kept at 1 : 3 : 5. Resultant mixture was then diluted with deionized water and emulsified on a high speed emulsifying machine for 20 min to achieve uniform dispersion of the nanosilica powders. Second, a 30 L stainless steel autoclave equipped with a stirrer consisting of two upend propellers and two incline propellers were loaded with 15 L of distilled water, 4 g of PVA, 1 g of HPMC, 5 g of sodium bicarbonate, and 7 mL of compound initiator; then the autoclave was sealed and loaded with 10 L of VC through the VC transportation system, followed by stirring at room temperature for 20 min before the reaction mixture was heated to 61°C to initiate polymerization at about 1.0 MPa. Third, the dispersion of DNS or RNS in the mixed solvent of ethanol and deionized water was added into the autoclave through a pump after about 1 h of polymerization reaction, where the reaction was terminated by adding terminator into the autoclave when the pressure dropped to 0.9 MPa. Finally, residual VC was removed from the reaction solution yielding raw nanosilica/PVC composite resins after centrifuging; and raw nanosilica/PVC composite resins were dried at 60°C for 12 h to yield desired nanosilica/PVC composite resins.

The above synthetic strategy is simple and can be conveniently industrialized, since it nearly does not need to modify traditional PVC polymerization technique.

Preparation of Nanosilica/PVC Composites by Compression Molding

A high-speed mixer was performed at 105°C to mix 200 g of RNS/PVC (or DNS/PVC) composite resin with 16 g of TBLS, 1.2 g of calcium stearate and 1.6 g of stearic acid for 10 min. Resultant mixture was milled at 175°C for 10 min using a twin-roller machine. As-milled PVC resin composites were compression molded at 185°C and 25 MPa using a vulcanizing machine to provide RNS/PVC (or DNS/PVC) composite plates with a size of 22 × 18 cm². Compression-molded specimens were finally cooled to room temperature in air yielding RNS/PVC (or DNS/PVC) composites as end-products for evaluation of mechanical properties and thermal stability.

For a comparative study, PVC resin was mixed with nanosilica particles, TBLS, calcium stearate, and stearic acid at the same ratio mentioned above to prepare melt-mixed nanosilica/PVC composites. Melt-mixed PVC composites composed of TBLS, calcium stearate and stearic acid but without nanosilica were also prepared in the same manner.

Analysis of Microstructure as well as Mechanical Properties and Thermal Stability of RNS/PVC Composites

The microstructure of nanosilica/PVC composites was analyzed using a JEM 100CX-II TEM (JEOL Company, Japan; accelerating voltage 22 kV). The fractured surfaces of PVC or nanosilica/PVC samples were coated with a gold-palladium film and then examined using a JSM-5600 scanning electron microscope (SEM, JEOL Company, Japan). Fourier transform infrared spectrometric (FTIR) analysis of nanosilica/PVC and nanosilica particulates extracted from the composites was conducted with an AVATAR360RT-IR spectrometer (KI was used for calibration). A proper amount of DNS/PVC or RNS/PVC composite resin was dissolved in THF and centrifuged at 3000 r/min to extract nanosilica particulates. After the supernatant liquid was removed, the remnant solid was washed with THF and centrifuged again. The above procedures were

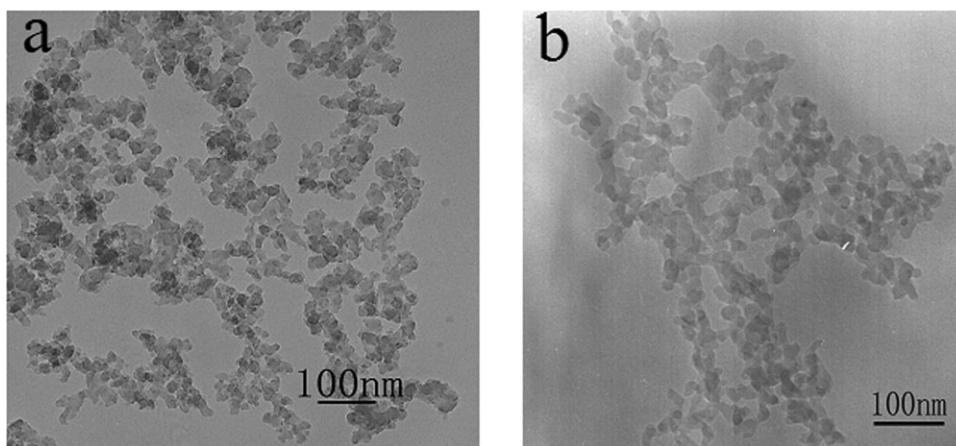


Figure 1. TEM images of RNS (a) and DNS (b).

repeated until no PVC was detected in the supernatant liquid by FTIR, and the final extracted DNS (coded as EDNS) or RNS (coded as ERNS) was dried in air before characterization.

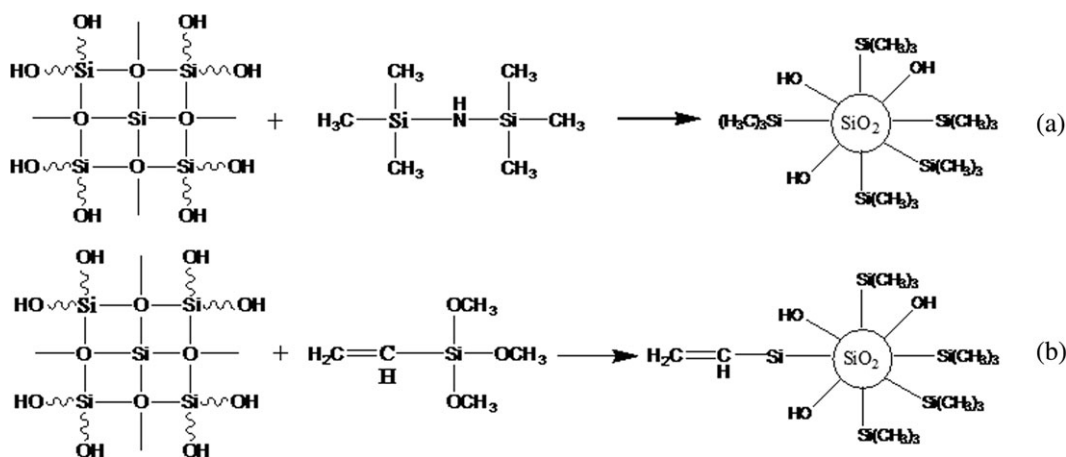
The thermal stability of DNS/PVC and RNS/PVC composite resins was evaluated using a Mettler Toledo TGA/SDTA851 thermobalance with which thermogravimetric analysis (TGA) in N_2 atmosphere was conducted at a heating rate of $10^\circ C/min$. The notched charpy impact strength of compression-molded PVC or nanosilica/PVC composites was measured using an XJJ-S impact-testing machine (Chengde Testing Machine Factory, China), where Chinese National Standard GB/T1043-93 was applied. The tensile strength of the compression-molded samples was determined using an LJ-500 testing machine (Wuzhong Minisize Testing Machine Factory, China), where Chinese National Standard GB/T 1041-92 was applied. All mechanical tests were done at an ambient temperature of about $23^\circ C$. The average of at least five repeat tests is reported in this article.

RESULTS AND DISCUSSION

TEM and FTIR Analyses of Organically Functionalized Nanosilica

Figure 1 shows the TEM images of RNS and DNS dispersed in ethanol. It is seen that both RNS and DNS particles with

net-like structures have a diameter of about 20 nm and seem to be well dispersed without obvious agglomeration. This indicates that surface-capping with trimethylsilane helps to prevent nanosilica from agglomeration. Scheme 1 schematically illustrates the formation mechanism of DNS and RNS. The *in situ* surface-modification process of nanosilica with trimethylsilane is a condensation-like polymerization process, where the hydrolyzate of silica precursor acts as an inorganic monomer and organic modifiers function as chain terminators yielding organically functionalized nanosilica hybrid.¹³ Briefly, sodium metasilicate is hydrolyzed in the presence of acid to form silicic acid. Silicic acid then takes part in condensation polymerization to form three-dimensional tetrahedral structure via Si—O bond leaving a large number of hydroxyls on the surface of silica nanoparticles. In the meantime, the organic modifiers added into the reaction system are also hydrolyzed; and as soon as the silica nanoparticles are formed, the —OH or —OCH₃ groups of the modifiers react with the —OH groups of nanosilica. Such a substitution of the active —OH group of silica by the organic chains leads to steric hindrance, thereby preventing nanosilica from further growing up or agglomerating. In this way, reactive nanosilica surface-capped with active organic compounds can be synthesized by properly controlling the reaction conditions



Scheme 1. Formation mechanism of nanosilica: (a) DNS and (b) RNS.

Table I. Light Transmittance of Organic Solvents Containing Different Dosages of Nanosilica

Type of nanosilica	Dosage (wt %)	Light transmittance (%)	
		CCl ₄	CHCl=CCl ₂
RNS	0.5	96.5	91.5
	1.0	92.3	88.0
DNS	0.5	92.5	90.0
	1.0	89.5	86.2
Unmodified SiO ₂	0.5	21.0%	20.0%
		Instant sedimentation	Instant sedimentation

while the size of the nanoparticles can be manipulated by adjusting the concentration of sodium metasilicate and the time to add the modifiers. To achieve high cost-efficiency and good dispersion of the surface-capped nanosilica, we suggest that 1.2 mol/L sodium silicate, 0.1 mol/L HMDS, and 0.04 mol/L A-171 be used for preparing RNS. DNS can be prepared under the same conditions except that only 0.1 mol/L HMDS is adopted as the sole organic modifier.

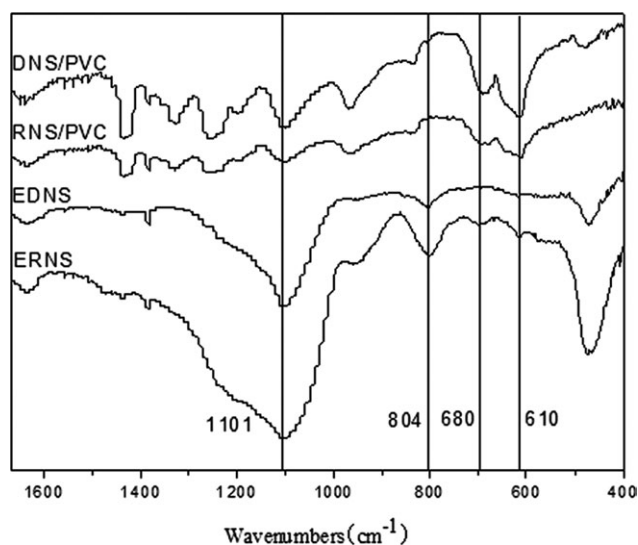
The dispersivity of organically functionalized RNS and DNS can be estimated by determining the light transmittance of their dispersions in proper solvents; because a higher light transmittance corresponds to better dispersivity of the nanoparticles (a liquid with LT above 80% virtually appears transparent). As seen in Table I, the dispersions of RNS in trichloroethylene and carbon tetrachloride solvents have a light transmittance from 88.0 to 96.5% depending on varying dosage, and those of DNS in the same solvents have slightly lowered light transmittance from 86.2 to 92.5%. Obviously different from RNS and DNS, the dispersion of unmodified SiO₂ in carbon tetrachloride and trichloroethylene has a light transmittance of as low as 20.0%, and the dispersed system in this case turns turbid along with instant sedimentation of the unmodified nanosilica. The above observations indicate that the surface modifiers can significantly improve the dispersivity of nanosilica in organic mediums, which should also be beneficial to enhancing the compatibility of nanosilica with organic compounds like VC monomer. This can be rationally anticipated if one notices that DNS consists of about 10% (mass fraction) of organic compounds (determined by TGA) while RNS consists of about 11% of organic compounds (determined by TGA); not to mention that RNS contains 0.44 mmol/g double bond segment while RNS and DNS have a large specific surface area of 242 m²/g and 257 m²/g, respectively.

Figure 2 shows the FTIR spectra of *in situ* polymerized nanosilica/PVC composite resins as well as EDNS and ERNS extracted from the composite resins. The characteristic absorbance bands at 804 and 1101 cm⁻¹ are assigned to the symmetric and asymmetrical stretching absorptions of Si—O bond in nanosilica. Those at 680 and 610 cm⁻¹ are assigned to the symmetric and asymmetrical stretching absorptions of C—Cl in PVC. These

FTIR data demonstrate that organic functionalized RNS and DNS species, thanks to their enhanced compatibility with PVC and high activity of double-bond-containing RNS, are strongly combined with PVC during the *in situ* polymerization process (PVC is not separated from the composite resins even after high-speed centrifugal processing). Interestingly, ERNS shows characteristic absorbance bands similar to those of RNS/PVC composite resin, but no absorption bands of PVC are detected in EDNS. This implies that RNS containing double bonds can participate in the polymerization of VC monomer and chemically combine with PVC molecules via covalent bonds. As a result, PVC chemically bonded with RNS cannot be separated by dissolving and extracting with THF. However, PVC molecules chemically adsorbed on the surface of DNS containing inactive organic groups can be easily removed by dissolving and extracting with THF, resulting in disappearance of the absorbance bands of PVC in EDNS. The TEM images of ERNS and EDNS shown in Figure 3 also give evidences to this supposition. Namely, the TEM image of EDNS is similar to that of DNS [Figure 1(b)]. ERNS particles, however, seem to be wrapped by a great deal of PVC chains, which is somewhat different from the TEM image of RNS [Figure 1(a)].

Analysis of Reactivity of RNS

Based on the TEM images of ERNS and EDNS, we can speculate that surface-capped nanosilicas are able to retain their original net-like structure and good dispersivity in VC disperse system or PVC matrix during *in situ* polymerization process. On one hand, PVC molecular chains gradually grow and fill into the net gaps of the nanosilicas. However, the nets of nanosilicas can be intertwined with PVC molecular chains resulting in enhanced interfacial adhesion. Besides, RNS particles containing active double bonds can copolymerize with VC to form PVC composite resin possessing three-dimensional network structure. When a single double bond of one RNS particle takes part in the copolymerization reaction, a molecular chain of PVC will be grafted onto RNS. When multiple double bonds of

**Figure 2.** FTIR spectra of DNS/PVC and RNS/PVC composite resins as well as EDNS and ERNS.

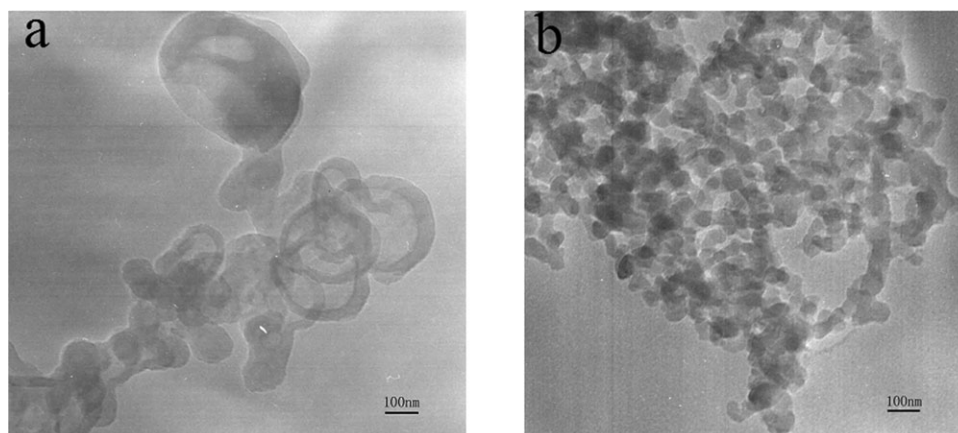


Figure 3. TEM images of (a) ERNS and (b) EDNS.

RNS particles are involved, one RNS particle will be linked with more molecular chains of PVC via covalent bond forming PVC-matrix composites with stable three-dimensional network structure (see Scheme 2).

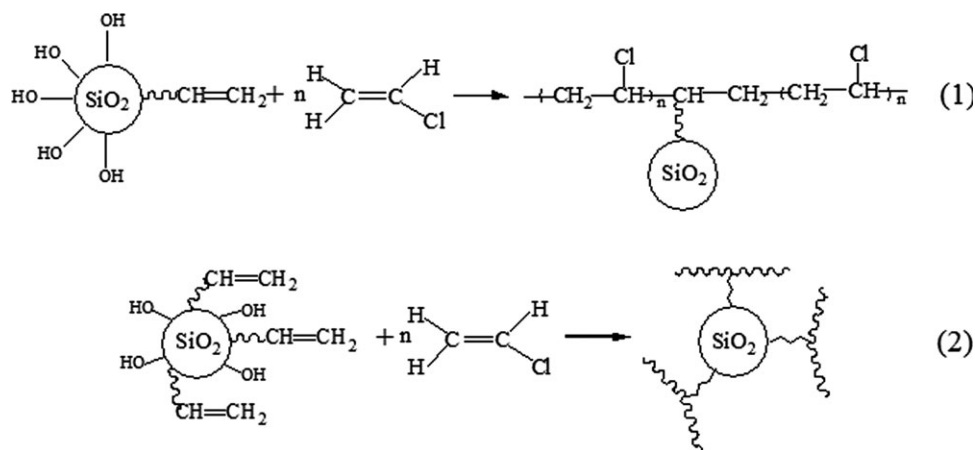
Thermal Stability of RNS/PVC and DNS/PVC Composite Resins

The TGA curves of PVC as well as DNS/PVC and RNS/PVC resins in nitrogen atmosphere are shown in Figure 4. The three materials all degrade thermally in a similar two-step manner. The first step degradation around 280°C is mainly due to the elimination of HCl from PVC molecules, and the second step degradation around 430°C is due to the decomposition of carbon chains in PVC.¹⁴ With the increase of nanosilica dosage, the thermal degradation onset temperature of DNS/PVC and RNS/PVC resins as well as the amount of resin residue after thermal degradation (see the local enlarged drawings in Figure 4) rises, which is more prominent at the first step degradation.

To better compare the thermal degradation behavior of DNS/PVC and RNS/PVC composite resins containing different fractions of DNS and RNS, we highlight the onset thermal degradation temperature (T_{onset}), the temperature corresponding to 10% weight loss ($T_{10\%}$) and the temperature corresponding to the maximum weight loss (T_{max}) vs. the mass fraction of DNS and

RNS in Figure 5, which is conducted based on magnifying relevant data points in Figure 4. It is seen that the T_{onset} , $T_{10\%}$, and T_{max} of both DNS/PVC and RNS/PVC resins rise with increasing mass fraction of DNS or RNS. Specifically, the incorporation of 1% DNS in PVC results in increase of T_{onset} , $T_{10\%}$, and T_{max} by 10, 12, and 10°C, respectively [Figure 5(A)]; but incorporation of 1% RNS leads to increase of T_{onset} , $T_{10\%}$, and T_{max} by 8, 10, and 7°C, respectively [Figure 5(B)]. This indicates that both DNS and RNS, even at a relatively low mass fraction of 1%, are able to improve effectively the thermal stability of PVC; and DNS seems to be advantageous over RNS in terms of the ability to increase the thermal stability of PVC. The reason may lie in that DNS and RNS particulates possessing a large specific surface area and reactive hydroxyls can absorb HCl released from PVC during thermal degradation, thereby retarding the thermal degradation of PVC molecules. In addition, RNS possesses species containing active double bond and is able to combine chemically with PVC via covalent bond, leaving less exposed hydroxyl on the surface as compared with DNS. As a result, RNS/PVC composite resin shows slightly lower thermal stability than DNS/PVC composite resin, due to weaker ability of RNS to absorb HCl released from PVC during thermal degradation.

Figure 6 shows the TGA curves of melt-blended DNS/PVC and RNS/PVC composites for a comparative study. Melt-blended



Scheme 2. Schematic drawings showing the copolymerization reaction of RNS and PVC molecules.

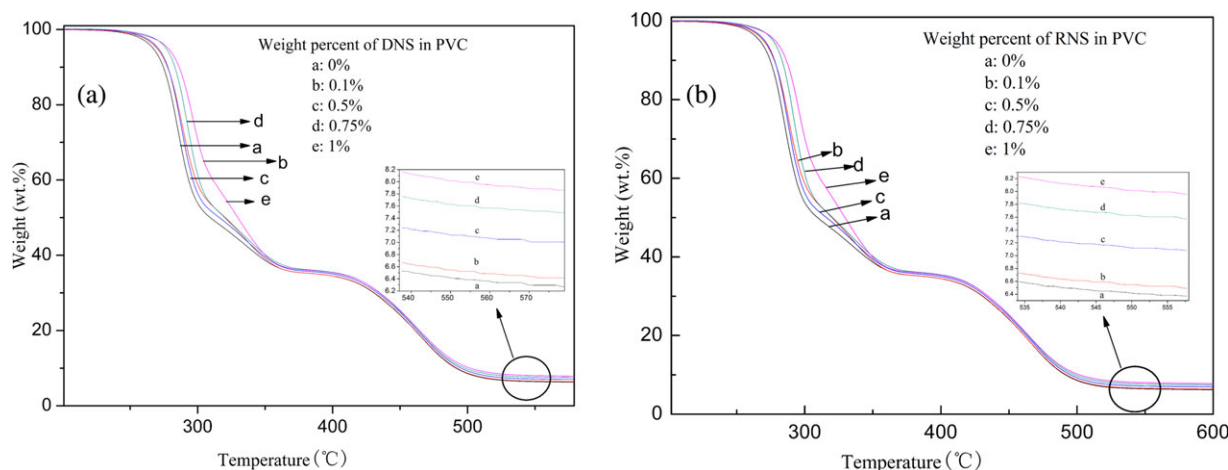


Figure 4. TGA curves of PVC as well as DNS/PVC (a) and RNS/PVC (b) resins with different nanosilica fractions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DNS/PVC and RNS/PVC composites, even with a maximum DNS and RNS mass fraction of 5%, sharply lose weight around 275°C. Considering the gradual weight loss of *in situ* polymerized DNS/PVC and RNS/PVC composite resins around 280°C (their maximum content of DNS or RNS is only 1%), we can speculate that *in situ* polymerization is indeed advantageous over melt-blending in strengthening the interfacial bonding between nanosilica filler and PVC matrix. In other words, *in situ* polymerized DNS/PVC and RNS/PVC composite resins with stronger nanosilica filler-PVC matrix interfacial bonding should possess better thermal stability and mechanical properties than melt-blended DNS/PVC and RNS/PVC composites.

Mechanical Properties of DNS/PVC and RNS/PVC Composites

Figure 7 shows the mechanical properties of *in situ* polymerized and melt-blended nanosilica/PVC composites vs. the mass fraction of DNS and RNS. The izod impact strength of melt-blended nanosilica/PVC composites increases with increasing dosage of DNS or RNS, and the melt-blended PVC composites

doped with 4% DNS or RNS possess the maximum izod impact strength which is higher than that of PVC matrix by 70%. However, the two kinds of functionalized nanosilica seem to have little effect on the tensile strength of melt-blended PVC composites. Besides, the mechanical properties of melt-blended DNS/PVC and RNS/PVC composites vary with filler mass fraction in a similar manner, which implies that the mechanical properties of melt-blended nanosilica/PVC composites are not affected by the surface structure of the nanosilica fillers. Nevertheless, *in situ* polymerized DNS/PVC and RNS/PVC composites show much different mechanical properties with varying mass fraction of DNS or RNS. The tensile strength of *in situ* polymerized DNS/PVC composites remains almost unchanged with the increase of DNS mass fraction, but that of *in situ* polymerized RNS/PVC composites mildly increases with increasing mass fraction of RNS. Moreover, the impact strength of *in situ* polymerized DNS/PVC composites apparently increases with increasing nanosilica content, and incorporation of even 0.1% DNS leads to a remarkable increase of the impact strength. The incorporation of 0.1% RNS also results in greatly increased

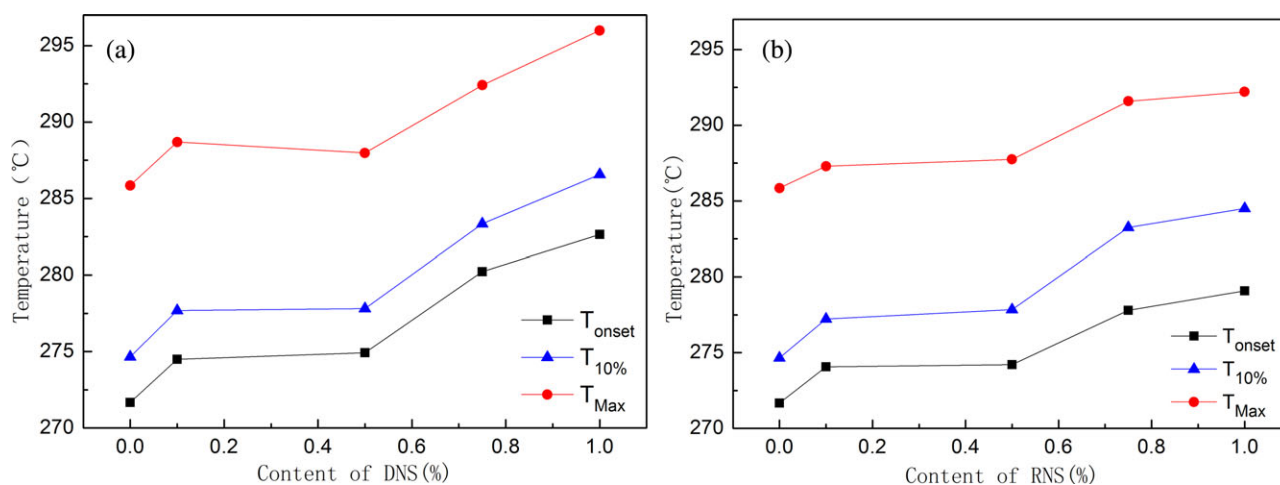


Figure 5. T_{onset} , $T_{10\%}$, and T_{max} of *in situ* polymerized DNS/PVC (a) and RNS/PVC (b) versus the mass fraction of DNS and RNS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

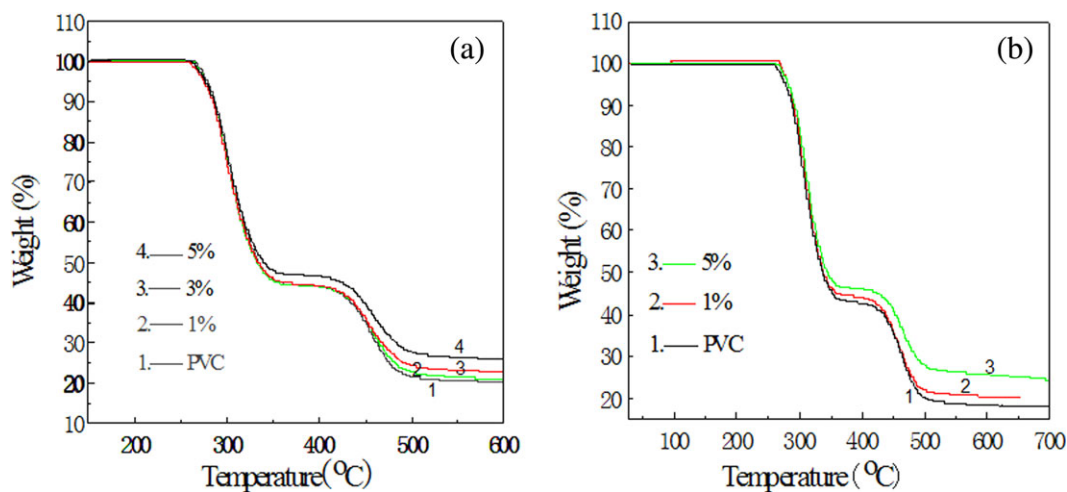


Figure 6. The TGA curves of PVC and melt-blended DNS/PVC (a) and RNS/PVC (b) with different mass fractions of nanosilica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

impact strength of *in situ* polymerized RNS/PVC composites; but further increase of RNS mass fraction only leads to slightly increased or even decreased impact strength of RNS/PVC, possibly due to its different surface structure from that of DNS.

What should be specially emphasized is that *in situ* polymerized nanosilica/PVC composites have much higher izod impact strength than melt-blended composites, even if their content of functionalized nanosilicas is only 1/10 of the nanosilicas content of the melt-blended ones. This means that *in situ* polymerization is indeed advantageous over melt-blending in fabricating nanosilica/PVC composites with improved mechanical properties.

Figure 8 shows SEM photographs of the impact-fractured surfaces of pure PVC and *in situ* polymerized nanosilica/PVC composites. It can be seen that the fractured surface of pure PVC is smooth and dominated by brittle fractures [Figure 8(a)]. However, the fractured surfaces of *in situ* polymerized DNS/PVC and RNS/PVC composites contain rough texture and layered thin slips [Figure 8(b,c)], implying increased toughness.

Moreover, some flower-like structures are visible in the magnified SEM images of the fractured surfaces of *in situ* polymerized DNS/PVC and RNS/PVC composites [Figure 8(b₁,c₁)], indicating presence of organically functionalized nanosilica. Interestingly, although the fractured surfaces of melt-blended DNS/PVC and RNS/PVC composites containing 4% of nanosilica also show similar visual texture (Figure 9), no flower-like structures are observed for them. This again demonstrates that *in situ* polymerization should be adopted to incorporate organically functionalized nanosilicas into PVC matrix to improve the mechanical properties of the polymeric composites more efficiently.

Analysis of Reinforcement Mechanism of Functionalized Nanosilica for PVC

Debonding of a large inorganic nanoparticle-polymer interface can absorb a large amount of energy upon fracture, which together with the toughening effect of inorganic particles results in increased toughness of PVC composites.¹⁵ During *in situ* polymerization process, newborn PVC chains tend to precipitate

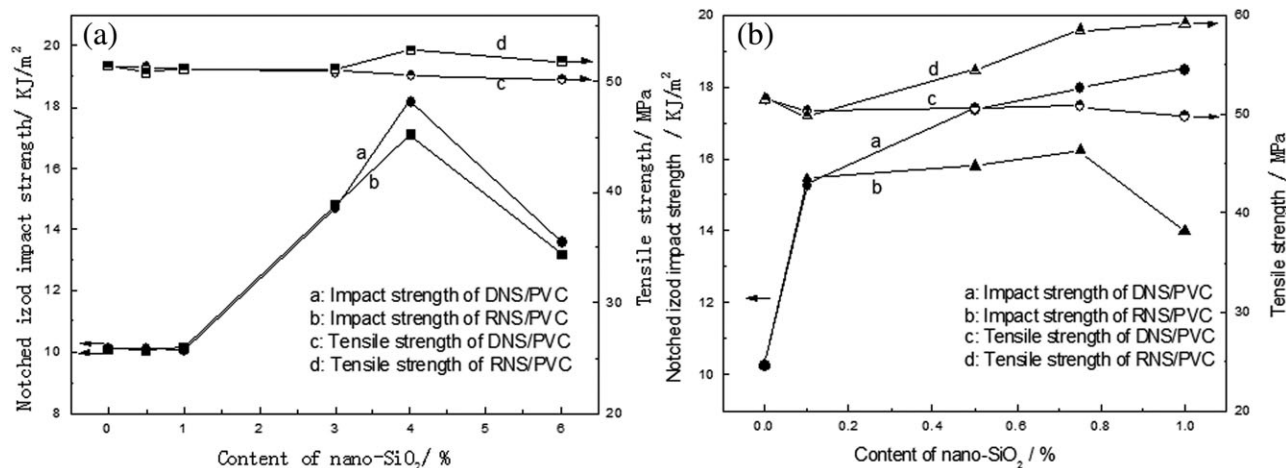


Figure 7. Notched izod impact strength and tensile strength of melt-blended nano-SiO₂/PVC composites (a) and *in situ* polymerized nano-SiO₂/PVC hybrids (b) versus the mass fraction of DNS or RNS.

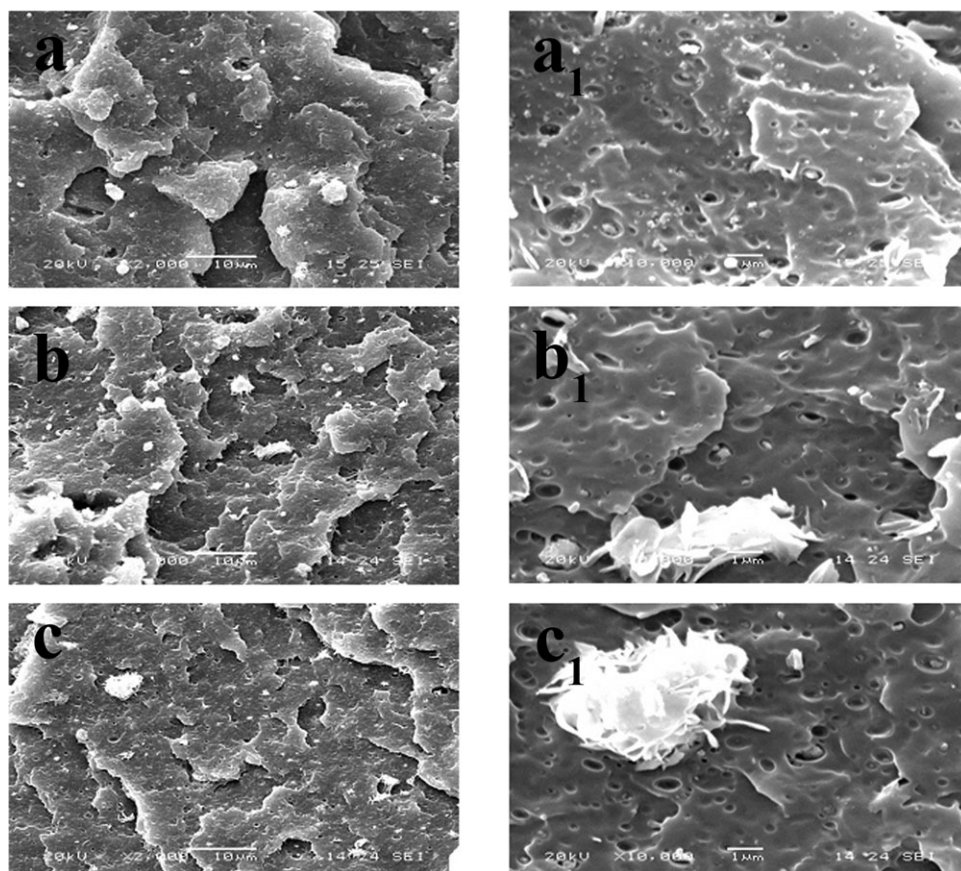


Figure 8. SEM images of fractured surfaces of PVC (a and a1) as well as *in situ* polymerized DNS/PVC (b and b1) and RNS/PVC (c and c1) composites.

on the surface of organically functionalized DNS and RNS particles possessing strong affinity to VC and PVC. The adhesion between the nanosilicas and PVC matrix can be strengthened when the net-like structure of the nanosilicas is entangled by PVC molecular chains, leading to improved mechanical strengths of *in situ* polymerized nanosilica/PVC composites. In melt-blended nanosilica/PVC composites, however, nanosilicas with net-like structure are hardly uniformly dispersed in PVC matrix and tend to agglomerate. As a result, incorporating DNS or RNS into PVC matrix results in only slight increase in the

impact strength of melt-blended nanosilica/PVC composites, unless a higher content of DNS or RNS (over 4%) is applied.

Furthermore, RNS containing reactive double bonds has good compatibility and stronger chemical affinity with PVC than DNS containing inactive carbon chains. The covalent linkage between RNS and PVC promotes the growth of local three-dimensional network structures (see Scheme 3), resulting in greatly improved tensile strength of *in situ* polymerized RNS/PVC composite. Such network structures can also function as

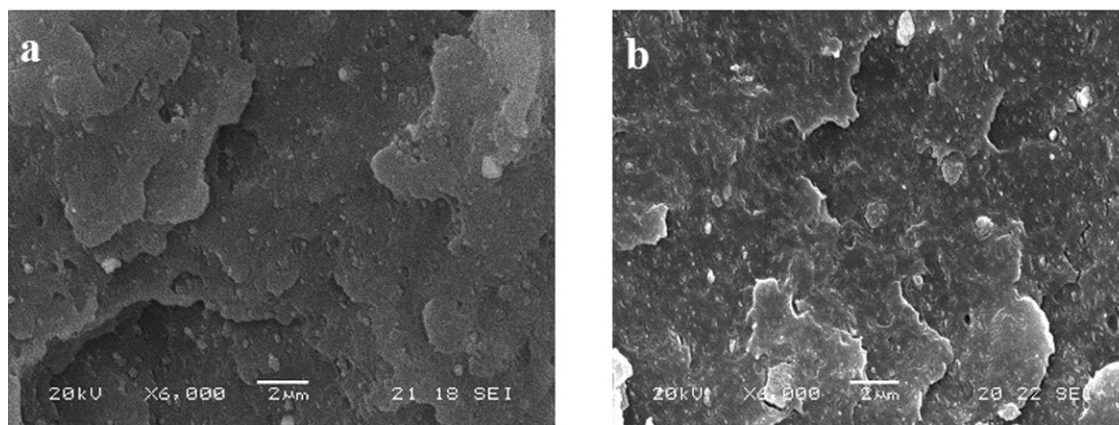
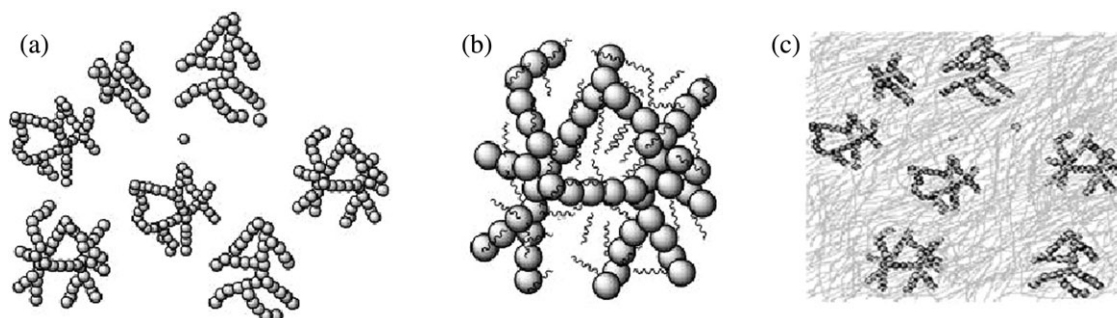


Figure 9. SEM images of the fractured surfaces of melt-blended DNS/PVC (a) and RNS/PVC (b) composites with 4 wt % nanosilica.



Scheme 3. Schematic diagram of (a) RNS particles, (b) RNS with grafted PVC chain, and (c): local net-work structure of *in situ* polymerized RNS/PVC composites.

movement units to absorb external impact energy, leading to improved toughness of PVC-matrix composites.

It is noteworthy that a large amount of such RNS/PVC network structure may retard the motion of PVC chain and endow thermoplastic PVC with some thermosetting capacity, leading to worsened mechanical processing behavior¹⁶ and declined toughness (as shown in Figure 7).

CONCLUSIONS

Reactive nanosilica particulates have been synthesized by bonding vinyl silane and trimethyl silane onto the surface of nascent nanosilica particles via *in situ* surface-modification. As-synthesized RNS has good dispersivity in VC and PVC and can copolymerize with VC through *in situ* suspension polymerization, generating RNS/PVC composites possessing local three-dimensional network structure. This makes it feasible to significantly improve the mechanical properties of PVC even by doping with a small amount of RNS. DNS particles functionalized by trimethyl silane alone in the same manner are less effective than RNS particles in terms of the ability to improve the mechanical properties of *in situ* polymerized PVC. This is possibly because RNS containing reactive double bond can form strong covalent bond with PVC matrix and thereby more efficiently strengthen the organic-inorganic interfacial interaction. Besides, organically functionalized DNS and RNS particulates show more prominent reinforcing effect in *in situ* polymerized PVC composites than in melt-blended PVC composites, possibly because they are easier to retain net-like structure and form stronger interfacial bonding with PVC matrix during *in situ* polymerization. Moreover, DNS and RNS particulates contain a large amount of hydroxyl groups and hence can absorb HCl released from thermally degraded PVC, resulting in better thermal stability of *in situ* polymerized nanosilica/PVC composites than the melt-blended ones.

The strategy reported here, hopefully, can be extended to developing other polyolefine-matrix composites, and it may find application in a wider scope when organic modifiers containing functional radicals such as amido, carboxyl, and epoxy are used for surface-capping of the inorganic nanoparticles.

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