

Co-poly(vinyl chloride-vinyl acetate-vinyl alcohol)-Silica Nanocomposites from Sol-Gel Process: Morphological, Mechanical, and Thermal Investigations

Uzma Nadeem,¹ Zahoor Ahmad,² Sonia Zulfiqar,³ Muhammad Ilyas Sarwar¹

¹Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

²Department of Chemistry, Faculty of Science, Kuwait University, Safat-13060, Kuwait

³Department of Physics, COMSATS Institute of Information Technology, Islamabad 44000, Pakistan

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ABSTRACT: Organic–inorganic nanocomposites consisting of co-poly(vinyl chloride-vinyl acetate-vinyl alcohol) and silica were prepared via sol–gel process. Two types of hybrids were prepared, one in which interactions between hydroxyl group present in the copolymer chain and silanol groups of silica network were developed. In the second set, extensive chemical bonding between the phases was achieved through the reaction of hydroxyl groups on the copolymer chains with 3-isocyanatopropyltriethoxysilane (ICTS). Hydrolysis and condensation of tetraethoxysilane and pendant ethoxy groups on the chain yielded inorganic network structure. Mechanical and thermal behaviors of the hybrid films were studied. Increase in Young's modulus, tensile strength, and toughness was observed up to

2.5 wt % silica content relative to the neat copolymer. The system in which ICTS was employed as binding agent, the tensile strength and toughness of hybrid films increased significantly as compared to the pure copolymer. Thermogravimetric analysis showed that these nanocomposite materials were stable up to 250°C. The glass transition temperature increases up to 2.5 wt % addition of silica in both the systems. Field emission scanning electron microscope results revealed uniform distribution of silica in the copolymer matrix. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: PVC-PVAc-PVA copolymer; silica; nanocomposites; mechanical/thermal properties; morphology

INTRODUCTION

The increasing demand of high performance materials has drawn considerable interest in the field of nanocomposite materials. For the preparation of these materials, polymers are generally reinforced either with fibers or with other inorganic particulate materials. In such hybrid materials, inorganic particles may not be homogeneously dispersed at the molecular level. The mechanical properties are expected to show improvements if the dispersion of reinforcement in the matrix is achieved at nano-level. So far, various techniques have been employed to produce these types of materials. Inorganic–organic nanocomposites prepared from the sol–gel process where the inorganic phases grown *in situ* are being actively pursued globally.^{1–9} The shift from the traditional blending of the reinforcing fillers into a polymeric matrix to the sol–gel process is due mostly to the subtle control over morphology of

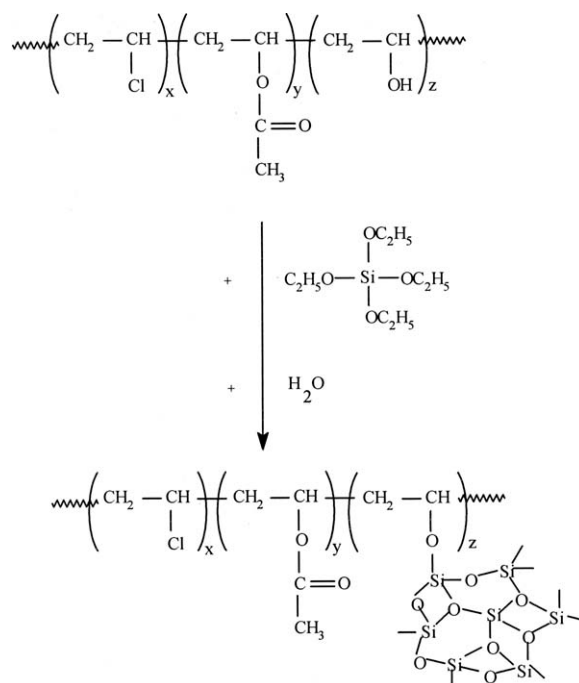
the growing inorganic phase in the polymer matrix by control of various reaction parameters like pH, concentration, temperature, etc. More importantly, unlike the traditional composites, which have macro-scale domain size varying from micrometer to millimeter scale, the inorganic–organic hybrids have domain sizes varying typically from 1 to 100 nm. Thus, the inorganic–organic hybrids are usually optically transparent, even though microphase separation may exist. The sol–gel process allows the *in situ* generation of inorganic network structures in the polymer matrices. The potential advantages of sol–gel process are the mild processing conditions and high homogeneity of resulting hybrid material. The inorganic network is produced in the presence of controlled amount of water and an acid or a base as catalyst. Under acidic conditions, the rate of hydrolysis is faster than the rate of condensation and diffused silica network structure is formed while under basic conditions, the rate of condensation reaction is faster and highly condensed silica network is produced.^{1,10}

Poly(vinyl alcohol)-silica composites prepared via sol–gel method has been evaluated.¹¹ Silica network connected with poly(vinyl alcohol) (PVA) matrix increased the ultimate tensile strength with

Correspondence to: M. I. Sarwar (ilyassarwar@hotmail.com).

increasing amount of silica content. Elongation of the hybrids decreased whereas the thermal stability was improved with silica content. The organic-inorganic transparent hybrid films based on PVA and alumina sols have also been reported.¹² Silica-based poly(vinyl acetate) hybrid composites were prepared by Jang et al.¹³ Two types of coupling agents, vinyltrimethoxysilane and 3-(trimethoxysilyl)propyl methacrylate were used to increase interfacial interactions in these hybrid materials. Addition of coupling agent gave homogeneous dispersion of silica network in the matrix with enhanced thermal stability of the hybrids. Various ceramic phases have been incorporated into polymeric matrices^{14,15} by sol-gel process including poly(methyl methacrylate),^{16,17} poly(vinyl acetate),^{18,19} poly(vinyl pyrrolidone),²⁰ poly(dimethyl siloxane),^{21,22} epoxy,²³ and polyimides.^{24,25} Extensive work has been carried out with thermally stable polymers such as aramids and polyimides using different types of coupling agents to enhance the compatibility between the disparate phases.²⁶⁻³³ The same authors have prepared PVC-titania and PVC-silica hybrid materials.^{34,35} The mechanical properties of such hybrids showed an increase in the Young's modulus, length at rupture, and toughness of the un-plasticized PVC. However, the stress at yields point and stress at rupture decreased with the addition of silica content. Previously, we have also reported PVC and co-poly(vinyl chloride-vinyl acetate-vinyl alcohol) reinforced with modified montmorillonite clay using solution intercalation technique. The mechanical properties and glass transition temperatures improved upon small loading of organoclay. Better reinforcement was achieved with copolymer clay composites than PVC-clay system because of the polar groups in the copolymer chains, which resulted in good interaction with the silicate sheets of the clay. The thermal stability and hardness of the composites also increased with the addition of organoclay.³⁶

In this attempt, two systems have been designed to reinforce the copolymer matrix with silica. In the first system, hydroxyl groups of copolymer chains were directly connected with silica network derived from tetraethoxysilane (TEOS) through sol-gel process while in the second system interfacial bonding between the two phases was established through 3-isocyanatopropyltriethoxysilane. The isocyanate groups of binding agent reacted with the hydroxyl groups on the polymer chain to produce pendant ethoxy groups on the chain. These ethoxy groups together with TEOS on hydrolysis and mutual condensation developed chemical bonding between silica network and copolymer chains. The hybrid films thus prepared using different amount of silica in the matrix were characterized for their morphology, mechanical, and thermal properties.



Scheme 1 Formation of PVC-PVAc-PVA copolymer-silica nanocomposites bonded through hydroxyl groups of copolymer chains.

EXPERIMENTAL

Materials

Co-poly(vinylchloride-vinylacetate-vinylalcohol) with an average $M_n = 27,000$, having a composition of vinylchloride, vinylacetate, and vinylalcohol, 90, 4, and 6 wt %, respectively, was obtained from Aldrich : (Taufkirchen/Germany), Merck: (Darmstadt/Germany). It was used after drying under vacuum at 50–52°C for 6 h. TEOS 98%, ICTS 95%, triethylamine, and benzophenone procured from Aldrich were used as received. Tetrahydrofuran (THF) 99% purchased from Merck was first distilled at constant boiling temperature, followed by the addition of anhydrous calcium oxide left overnight. After distillation, it was refluxed over sodium wire with benzophenone as indicator. The deep blue color of the solution confirmed the drying of THF which was used as solvent.

Synthesis of PVC-PVAc-PVA copolymer-silica nanocomposites (System I)

A stock solution of the copolymer was prepared by dissolving 10 g of polymer in 100 g of dried THF (as a solvent) with constant stirring for 24 h. Hybrids were prepared by mixing various concentrations of TEOS with an appropriate amount of copolymer solution. After complete mixing, hydrolysis and condensation was carried out with the subsequent addition of stoichiometric amounts of water solution in THF using triethylamine as catalyst with stirring for 12 h at room temperature and for 6 h at 40–45°C (Scheme 1).

Synthesis of PVC-PVAc-PVA copolymer-silica nanocomposites using ICTS as coupling agent (System II)

Interaction between the two phases was developed through coupling agent in the related second system. For this purpose, to the fresh stock solution of copolymer, a known amount of ICTS solution in THF was mixed and the reaction mixture was heated for 2 h at 55°C under complete anhydrous conditions. Then different amounts of TEOS were mixed with the copolymer solutions. The hydrolysis and condensation of ICTS and TEOS upon the addition of stoichiometric amount of water and catalyst was carried out for 12 h at ambient temperature and for 6 h at 40–45°C (Scheme 2).

Thin film preparation

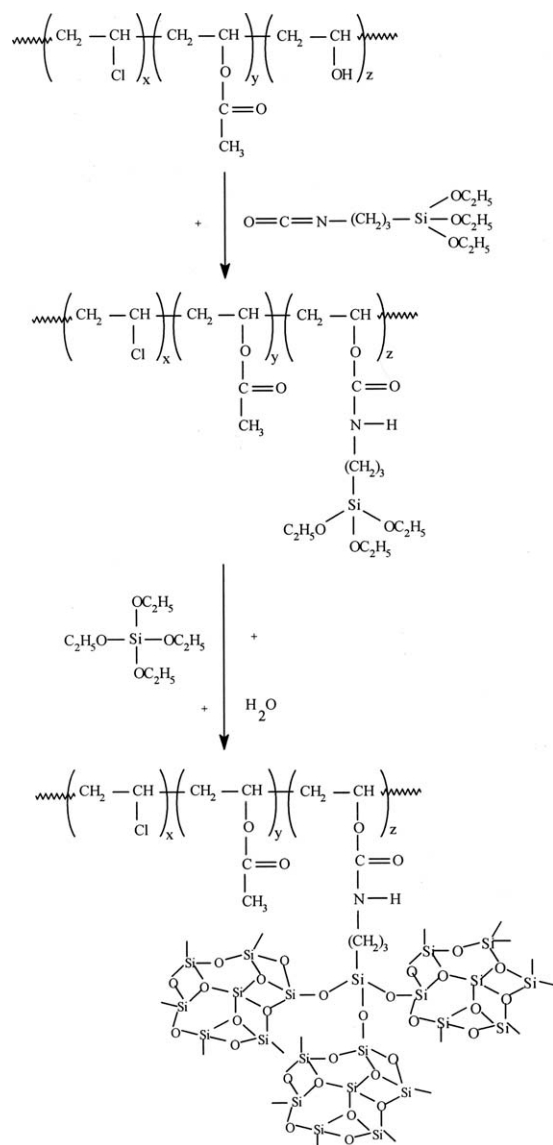
Thin films of pure copolymer and hybrid materials were cast by pouring the solutions into petri dishes placed on a leveled surface in an oven at 50°C for 6 h to evaporate the solvent. The films obtained were soaked in distilled water separately with occasional washing to remove the catalyst base added and then dried at 55°C under vacuum to a constant weight.

Measurements

Tensile properties of the hybrid films (rectangular strips) were measured according to DIN procedure 53455 having a crosshead speed of 0.1 cm min⁻¹ at 25°C using Testometric Universal Testing Machine M350/500 at room temperature. Average value obtained from five different samples for each concentration has been reported. Thermogravimetric analysis (TGA) on the hybrid samples was performed with TGA-7 Thermogravimetric Analyzer using 1–5 mg of the sample in Al₂O₃ crucible heated from 0 to 750°C at a heating rate of 10 °C min⁻¹ under air atmosphere. The glass transition temperature of nanocomposites was recorded by a METTLER TOLEDO DSC 822^e differential scanning calorimeter using 5–10 mg of sample encapsulated in aluminum pan and heated at a ramp rate of 10 °C min⁻¹ under nitrogen atmosphere. The morphology of copolymer-silica nanocomposites was investigated by JEOL JSM 7400F field emission scanning electron microscope (FESEM). The samples were fractured in liquid nitrogen prior to imaging.

RESULTS AND DISCUSSION

The pure polymer film was transparent while hybrid films with thickness in the range 0.01–0.020 cm were transparent up to 5 wt % silica content and light yellow in color. The films became semi-transparent and opaque with higher silica content. The stress-strain



Scheme 2 Formation of PVC-PVAc-PVA copolymer-silica nanocomposites using ICTS as binding agent

behavior of hybrid films was recorded at ambient temperature. The average engineering stress values of five samples in each case were reported. The pure sample was taken as a reference for both these studies. The thermal stability slightly increased with increase in the silica in the matrix. Scanning electron microscopy was employed to study the morphology of the fractured samples.

Optical properties

Copolymer and composite films having various amounts of silica were transparent and the % transmittance recorded (± 2) at 490, 530, and 600 nm for neat copolymer film with 0.10 ± 0.02 mm thickness were 78.7, 79.5, and 80.6, respectively. The maximum transmittance was found for the hybrid film

TABLE I
Transmittance Data of PVC-PVAc-PVA Copolymer-Silica Nanocomposites Bonded Through Hydroxyl Groups of Copolymer Chains

Sr. no.	SiO ₂ (%)	Film thickness (mm) ± 0.02	% Transmittance ± 2 at		
			490 nm	530 nm	600 nm
1	0.0	0.10	78.7	79.5	80.6
2	2.5	0.15	81.3	82.4	82.9
3	5.0	0.16	78.3	81.0	80.6
4	7.5	0.17	77.2	78.2	78.5
5	10.0	0.17	Opaque		
6	12.5	0.18	Opaque		

containing 2.5 wt % silica content in both the systems and beyond that it decreased gradually as shown in Tables I and II, respectively. Transparency of the films is related to the particle size of the ceramic phase, when this size of inorganic phase remained smaller than wavelength of light, films appeared to be transparent but at higher concentration of ceramic content, tendency toward particle growth increases. These particles agglomerate giving irregular distribution in the matrix with increased scattering and opaqueness.⁵⁻⁷ FESEM images further confirmed these observations.

Mechanical properties

The mechanical data for both systems are given in Tables III and IV (Figs. 1 and 2) respectively. Typical soft and tough behavior of the materials was observed from the stress-strain curves. Before the yield point, elastic behavior of the material is evident where the hybrids show reversible deformation with stress. Modulus for System I was found to increase up to 2.5 wt % silica as compared to pure copolymer and then decreased (Fig. 3). For System II modulus value found to decrease with increasing silica content relative to pure polymer (Fig. 3). Stress and strain at yield point decreased with increase in silica content relative to pure copolymer for both the systems. After yield point material shows viscous behavior due to slippage of chains and irreversible

TABLE II
Transmittance Data of PVC-PVAc-PVA Copolymer-Silica Nanocomposites Using ICTS as Binding Agent

Sr. no.	SiO ₂ (%)	Film thickness (mm) ± 0.02	% Transmittance ± 2 at		
			490 nm	530 nm	600 nm
1	0.0	0.10	78.7	79.5	80.6
2	2.5	0.16	83.3	84.2	84.7
3	5.0	0.16	80.2	81.3	82.3
4	7.5	0.18	79.0	80.6	81.4
5	10.0	0.19	Opaque		

deformation. For both systems, strain at rupture increases significantly for the composites attributing a chemical linkage between the phases. Increase in values of strain was greater in case of System I. Both the systems show an increase in value of stress at break point up to 2.5 wt % silica content. This is due to alignment of polymer chain and an increase in resistance to the applied load. Similar trend was not seen in any other concentration of both systems due to higher proportions of silica network in the nanocomposites. The addition of silica beyond 2.5 wt % reduced the mechanical properties of the hybrid materials because only a part of the silica network becomes chemically linked with copolymer chains due to limited number of OH group available. As the inorganic network became extensive, the tendency for particle-size growth increased, and their agglomeration made their distribution in the matrix irregular. These particles would then form clusters, thus making the inorganic structure porous and brittle, which would cause a decrease in the tensile strength and other associated mechanical properties of the hybrid material. The SEM micrographs supplement these observations as well.

The thickness of samples decreased continuously during stress-strain analysis and this decrease in thickness was significant that needed a correction to be applied to the values of engineering stress. The correction was applied by measuring thickness of the sample at rupture point of the stress-strain measurement in each case. The corrected value of stress is referred as the tensile strength of the sample. The

TABLE III
Mechanical Properties of PVC-PVAc-PVA Copolymer-Silica Nanocomposites Bonded Through Hydroxyl Groups of Copolymer Chains

SiO ₂ (%)	Stress at yield point (MPa)	Strain at yield point (%)	Engineering stress at rupture (MPa)	Strain at rupture (%)	Young's modulus (GPa) ± 0.02	Uncorrected toughness (MPa)	Tensile strength (MPa) ± 0.1	Corrected toughness (MPa) ± 0.20
0.0	71.5	5.85	53.3	9.51	2.60	4.81	63.9	5.22
2.5	64.2	4.42	52.0	150.50	2.72	72.50	96.2	130.50
5.0	48.9	4.92	37.8	145.93	2.10	53.07	66.9	91.87
7.5	42.5	4.92	31.0	90.70	1.70	28.56	52.9	47.19
10.0	36.9	4.03	27.6	46.44	1.26	13.54	37.3	17.13
12.5	32.9	4.03	25.5	40.24	1.25	10.57	26.0	5.98

TABLE IV
Mechanical Properties of PVC-PVAc-PVA Copolymer-Silica Nanocomposites Using ICTS as Binding Agent

SiO ₂ (%)	Stress at yield point (MPa)	Strain at yield point (%)	Engineering stress at rupture (MPa)	Strain at rupture (%)	Young's modulus (GPa) ± 0.02	Uncorrected toughness (MPa)	Tensile strength (MPa) ± 0.1	Corrected toughness (MPa) ± 0.20
0.0	71.5	5.85	53.3	9.51	2.60	4.81	63.9	5.22
2.5	59.8	5.23	59.1	135.50	2.53	68.37	105.1	121.54
5.0	55.7	4.77	45.8	106.15	2.15	46.78	77.3	76.40
7.5	47.3	4.22	37.5	109.90	2.10	39.03	54.9	54.56
10.0	42.5	4.97	28.1	43.37	1.10	12.98	42.4	18.49

values of engineering stress and tensile strength (corrected stress) for both the systems are given in Tables III and IV respectively. For System I, the value of tensile strength increases with silica content up to 2.5 wt % but beyond this limit a decreasing trend was observed. For System II the tensile strength increases up to 5 wt % silica content in the polymer matrix; however, beyond this concentration a decrease in this property was noticed. Introduction of silica within copolymer matrix reinforces the copolymer giving more tensile strength to the material. However, the increase in strength is large in case of System II than in System I. Because each ICTS molecule provides further three bonding sites for the silica network structure to bind to the polymer chains, thus, reinforcement in the copolymer was more as compared to System I. The value of tensile strength, however, decreases with further addition of silica. At high silica content, the particles tend to agglomerate resulting less interfacial interactions and with more phase separation. The relative increase in tensile strength of composite as compared to pure polymer was much more pronounced in System II, which may be due to strong urethane linkage relative to C—O—Si linkage between the polymer and silica network.

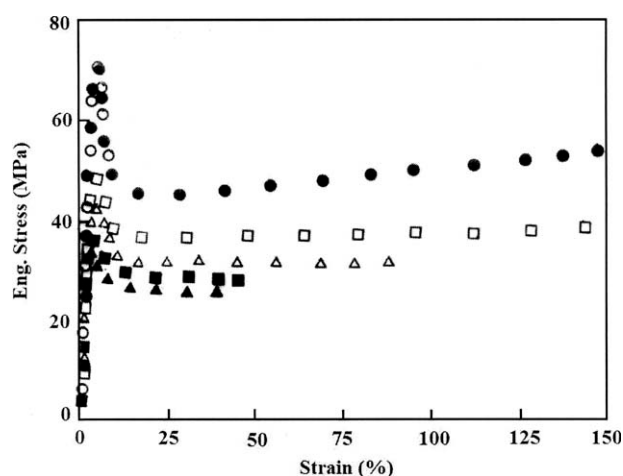


Figure 1 Stress-strain curves of copolymer-silica nanocomposites bonded through hydroxyl group of copolymer chain, silica wt % in matrix; 0 (○), 2.5 (●), 5 (□), 7.5 (△), 10 (■), 12.5 (▲).

Toughness was measured by integrating the area under stress-strain curves before and after corrections in the stress values for both the systems. These values indicate a significant increase in this particular property of hybrids than pure polymer as shown in Figure 4. The stress bearing property of inorganic condensed phase associated with relatively less free volume, whereas organic phase has large free volume and relatively less capable of bearing stress. The relative increase in toughness as compared to the pure polymer was much more pronounced in both the systems. It is attributed to the chemical bonding between the two phases.

The previously studied system of PVC-silica hybrid³⁵ in which two phases were unbonded although showed same trends for increase in the values of toughness but the reinforcement was relatively low. In the present study, the chemical bonding between the phases provided larger increase in the toughness, i.e., of the order 130 MPa for System I and 121 MPa for System II relative to pure copolymer (5 MPa) and unbonded PVC-silica system.³⁵ This shows that chemically bonded system have better stress transfer properties due to chemical linkage between disparate phases.

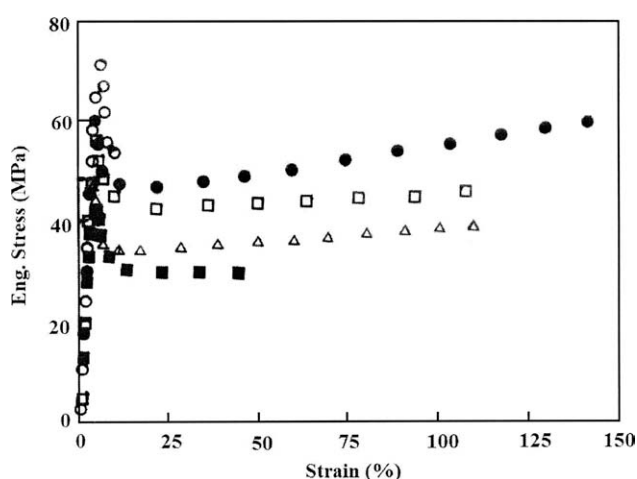


Figure 2 Stress-strain curves of copolymer-silica nanocomposites using ICTS as coupling agent, silica wt % in matrix; 0 (○), 2.5 (●), 5 (□), 7.5 (△), 10 (■).

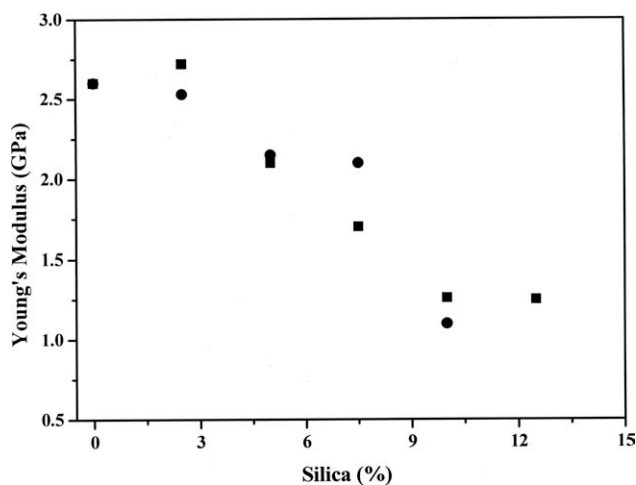


Figure 3 Variation of Young's modulus vs. silica content in copolymer-silica nanocomposites, (■) bonded through hydroxyl group (●) using ICTS as coupling agent.

Thermogravimetric analysis

Thermogravimetric analysis on the composite systems was carried out in air atmosphere in a temperature range 30–750°C. Thermograms for both systems are described in Figures 5 and 6, respectively. In both cases, the initial weight loss was probably assigned to the removal of water molecules produced from the conversion of uncondensed silica network structure. The organic matter started to decompose in the both the systems near 250°C. The first decomposition step (between 200 and 360°C) may be due to the dehydrochlorination of the organic polymer chains resulting in the formation of polymer sequences of different lengths. The second stage decomposition (between 360 and 500°C) may involve complex degradation mechanism. Thus the thermal stability of the materials was slightly

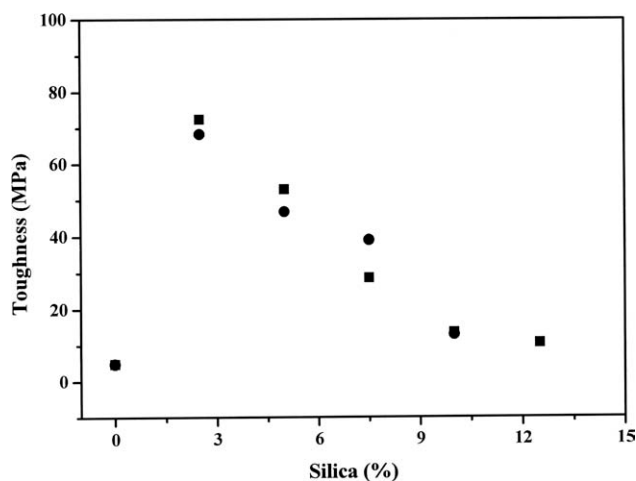


Figure 4 Variation of toughness vs. silica content in copolymer-silica nanocomposites, (■) bonded through hydroxyl group (●) using ICTS as coupling agent.

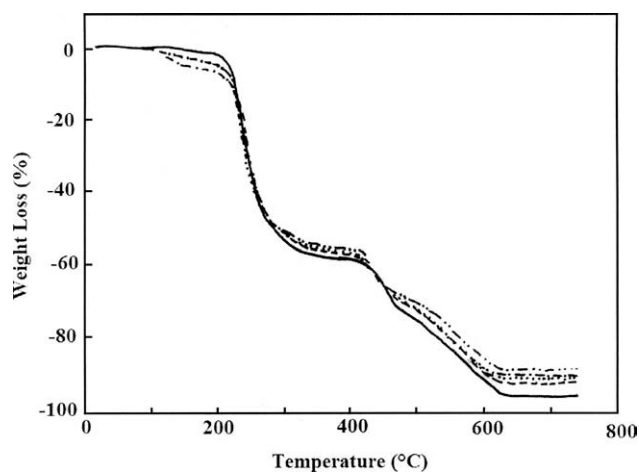


Figure 5 TGA curves of copolymer-silica nanocomposites bonded through hydroxyl group of copolymer chain, silica wt % in matrix; 0 (—), 2.5 (---), 5 (···), 7.5 (-·-·-), 10 (- - - -).

improved on the addition of the silica. The quantity of residue left above 700°C in both systems was found to be proportional to the inorganic content in the samples.

Differential scanning calorimetry

The glass transition temperatures (T_g) for copolymer-silica hybrids are presented in Figure 7. The results described a systematic increase in the T_g values with augmenting silica content in the copolymer matrix. The hybrid materials gave a maximum T_g value with 2.5 wt % silica in both the systems studied depicting interaction between two disparate phases relative to pure copolymer. Further addition of silica decreased the T_g value because entire silica may not linked with the copolymer chains resulting in poor interfacial interaction. Incorporation of silica reduced the segmental motion of the polymer chains

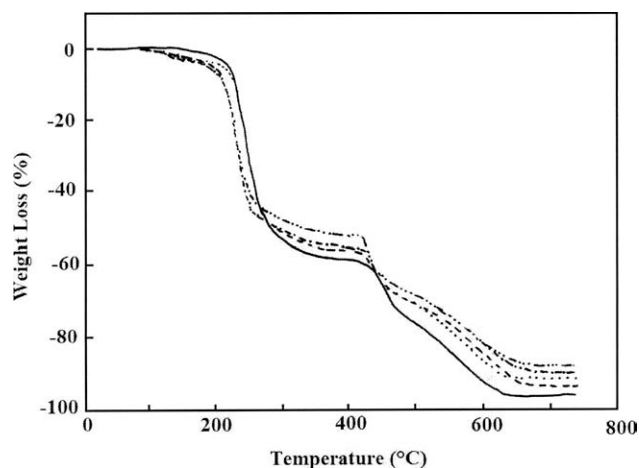


Figure 6 TGA curves of copolymer-silica nanocomposites using ICTS as coupling agent, silica wt % in matrix; 0 (—), 2.5 (---), 5 (···), 7.5 (-·-·-), 10 (- - - -).

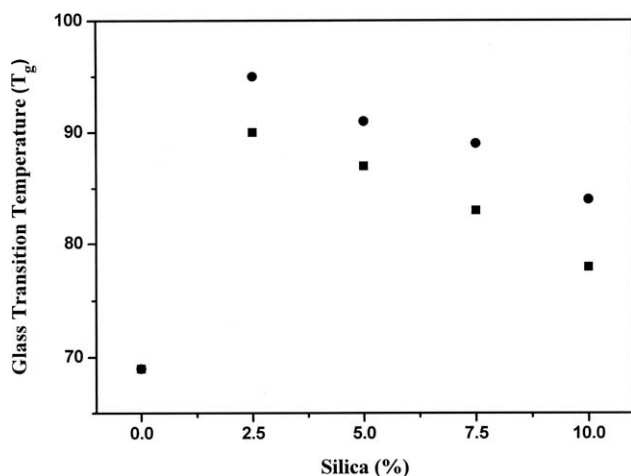


Figure 7 Variation in the glass transition temperatures vs silica content in copolymer-silica nanocomposites, (●) bonded through hydroxyl group (■) using ICTS as coupling agent.

and with augmenting amount of silica shifts the T_g toward high temperature. This suggested that more copolymer chains had linked with inorganic phase.

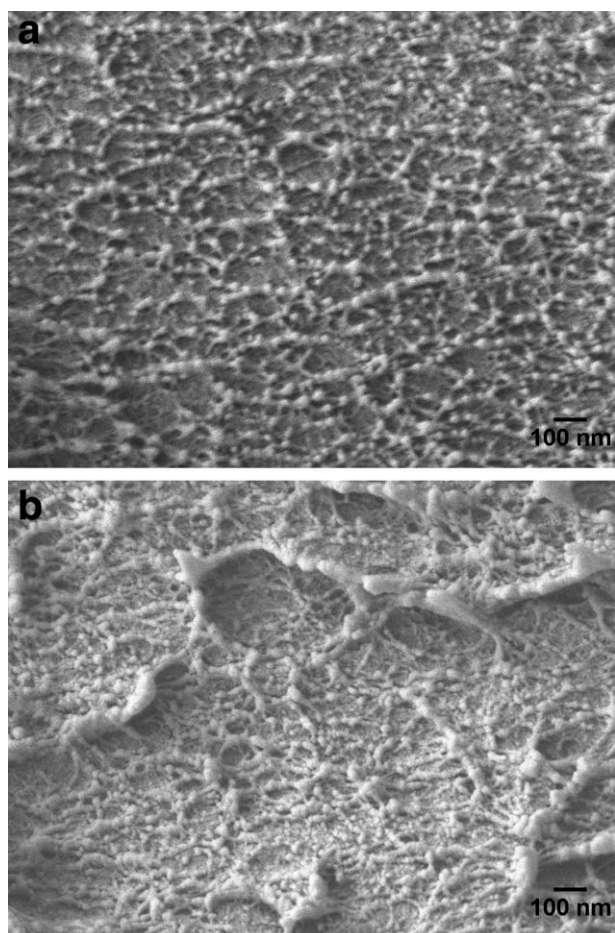


Figure 8 FESEM micrographs of copolymer-silica nanocomposites bonded through hydroxyl group (a) 2.5%, (b) 10%

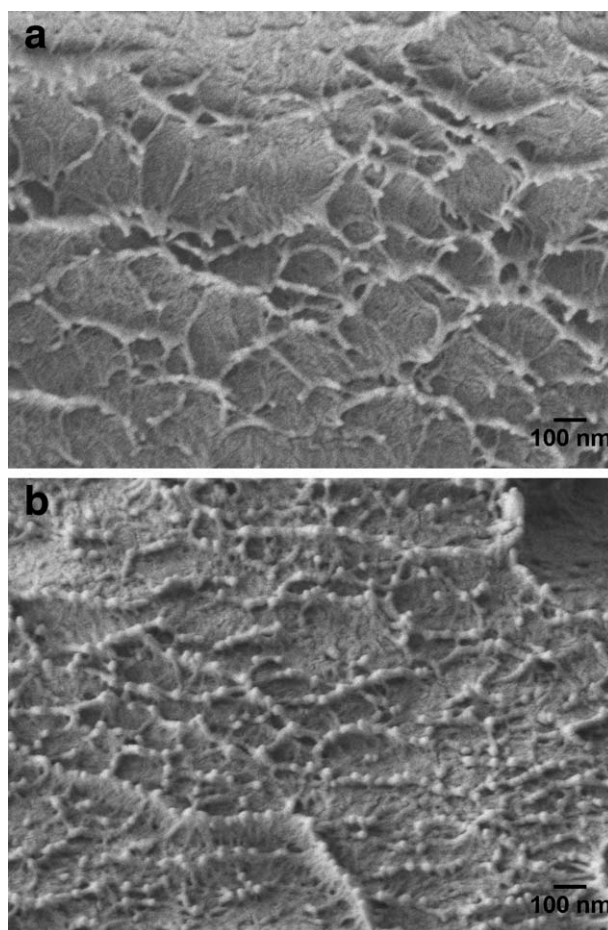


Figure 9 FESEM micrographs of copolymer-silica nanocomposites using ICTS as coupling agent (a) 2.5%, (b) 10%

Consequently, the motion of polymer chains was restricted, thus increasing the T_g values of composite materials. T_g 's of composites increased relative to pure copolymer. It may be explained due to mutual interaction of the two phases which suppresses the mobility of the polymer segments near the interface. T_g values are less pronounced in System II due to plasticization of the ICTS as compared with System I.

Field emission scanning electron microscopy

Morphological investigations were carried out on the fractured surface of copolymer-silica nanocomposite films. Composites bonded through hydroxyl groups containing 2.5 and 10 wt % silica are shown in Figure 8. The FESEM images indicate uniform distribution of silica network within the copolymer matrix, meaning that nanocomposite formation took place. These results show a fine dispersion of inorganic domain in the matrix. When the concentration of inorganic phase is increased (10 wt %), the average size of these silica particles and tendency toward agglomeration increases. The micrographs do indicate the presence of interconnected silica domains in

the continuous copolymer matrix, which demonstrates better compatibility between smaller silica nanoparticles and copolymer in the composite films. That is why the tensile strength of the composite film is improved for this system. Similarly, morphology of copolymer–silica hybrids obtained using ICTS as coupling agent with 2.5 and 10 wt % of silica in the matrix are represented in Figure 9. These hybrid films reveal that nanocomposites can be prepared using the same technique. The micrographs of this system clearly show a fine interconnected or co-continuous morphology. This phenomenon also indicates that the silica network has diffused network with a better interfacial cohesion that improves the efficiency of stress transfer mechanism between the two components. This better compatibility between the silica network and the copolymer in the composites result in improved tensile strength. An increase in the silica concentration (10 wt %) gives large domains that may deteriorate the mechanical properties of the composites.

CONCLUSIONS

PVC-PVAc-PVA copolymer and silica nanocomposites (bonding through hydroxy groups and ICTS) with greater toughness relative to the pure copolymer were successfully prepared using various amount of inorganic network through sol–gel process. These composites showed a toughness of 130.5 MPa for System I and 121.5 MPa for System II relative to pure copolymer which displayed a toughness of 5.22 MPa. These composites were thermally stable up to 250°C and further might be used to reinforce the virgin PVC. The shift in T_g values suggested the interaction between the two phases. The morphological investigations revealed a uniform distribution of silica network structure in the polymer matrix at the nanometer level.

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