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### PVC-Silica Sol-gel Hybrids: Effect of Interphase Bonding by Aminopropyltrimethoxysilane on Thermal and Mechanical Properties

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## PVC–Silica Sol-gel Hybrids: Effect of Interphase Bonding by Aminopropyltrimethoxysilane on Thermal and Mechanical Properties

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*Two types of hybrid materials from Poly(vinyl chloride) (PVC) using different amounts of silica have been prepared by the sol-gel technique. The hybrids without inter-phase bonding were prepared by the in-situ generation of silica network from tetraethoxysilane (TEOS) in the PVC matrix. The inter-phase bonding in the hybrid material was achieved by the reaction of aminopropyltrimethoxysilane (APTMS) with the PVC chain and then carrying out sol-gel process in presence of TEOS. Morphology of the silica particles produced in-situ in the hybrid films was studied by Scanning Electron Microscopy. The inter-phase bonding considerably reduced the silica particle size making their distribution more uniform in the matrix as compared to the unbonded hybrids. Dynamical mechanical thermal analysis was carried out to measure the glass transition temperature from the maxima of  $\tan \delta$  curves. The storage modulus and the glass transition temperature of the resulting hybrids were found to increase whereas the thermal coefficient of expansion was considerably reduced with the inclusion of aminosilane in the sol-gel hybrids.*

**Keywords:** aminosilane, composites, inter-phase bonding, PVC, silica, sol-gel process

### INTRODUCTION

PVC is one of the most versatile plastic materials used in the world today. Being the second largest among the polymers produced, it has

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a wide range of diverse industrial and domestic applications. It is being used in the form of blends [1], composites [2–3], and copolymers [4–5] to suit a variety of applications both in the rigid and flexible forms. The PVC, however, is very susceptible to thermal degradation, which imposes some limitations on its service temperature. The rigid PVC has a heat distortion temperature around 80°C, thus causing inappropriate modulus and creep compliance values above this temperature [6]. Many electrical/electronic appliances require suitable mechanical properties at relatively high temperatures. Two different methods have been used to solve this problem. One is based on blend technology [1, 7–8] where PVC is mixed with other miscible or semi-miscible polymer that has a higher heat distortion temperature. The second option is cross-linking it with organic or inorganic polymers having a three-dimensional structure. Materials like organo-clay [9] and organo-silanes [10] also have been successfully employed to produce hybrid materials. These hybrids, usually called ceramers [11], may combine the advantageous properties of both the polymer and its ceramic counterpart. Organic polymers give flexibility to the inorganic components and the metal oxides impart rigidity and strength to the polymeric components. Ceramers generally have higher heat resistance, better mechanical properties, and lower coefficient of thermal expansion [12–17] as compared to the pure polymer component.

Incorporation of silica network into the polymer matrix has been carried out via various routes; however, to get a homogeneous composite material, the inorganic oxide should be uniformly dispersed in the polymer matrix. The sol-gel process [18–20] is a convenient route to introduce ceramic network in the polymer matrix. The mechanical properties of the composite material are improved with increased interfacial interaction [21–23].

PVC has been modified by cross-linking it with various functionalized silanes to improve the mechanical and thermal properties. Kelnar and Schatz [24–25] grafted amino- and mercaptoalkyltrialkoxysilanes with plasticized and un-plasticized PVC in water and in air at 20–140°C. In both media, the cross-linking occurred faster for plasticized PVC grafted with aminosilanes. For mercaptosilanes, a marked dependence of the cross-linking rate on the silane structure was found and this rate was slow with 5-mercaptopentyltriethoxysilane as compared to 3-mercaptopropyltrimethoxysilane. Practically no cross-linking occurred in un-plasticized PVC below  $T_g$ . PVC grafted with mercaptosilanes showed improved strength parameters at elevated temperatures.

The properties of the PVC resin have been modified by Jorn et al. [26] using a copolymer of vinyl chloride and glycidyl-methacrylate (GMA). The grafting of a mercaptoalkyltrialkoxysilane with the copolymer

and its subsequent hydrolytic cross-linking was successful by steaming at 120°C whereas no cross-linking was possible with PVC homopolymer. The silane grafted and cross-linked samples were found to have better thermal stability than the pure PVC.

Gilbert et al. [27] produced plasticized PVC films with increased porosity by generating *in situ* the silica network from TEOS via sol-gel processing. Tetrahydrofuran (THF), was used as co-solvent, and  $\alpha$ -glycidylxypropyl-trimethoxysilane as a coupling agent. The films produced were transparent, with moderate mechanical properties. The film with 20 wt.% silica showed a 45% increase in water vapor permeability. Gilbert and Rodriguez-Fernandez [28–29] showed that rigid or plasticized PVC can also be grafted with aminopropyltrimethoxysilane during extrusion process, which can then be further cross linked by hydrolytic mechanism. To achieve a high cross-linking speed, the extruded PVC had to be placed in warm water or in a steam-heated vessel. The effects of catalyst concentration, moisture concentration, the immersion time and temperature on the rate and degree of cross-linking were investigated.

Ahmad et al. [30] prepared hybrid PVC material by *in situ* generation of titania network from tetrapropylorthotitanate using THF as solvent. Homogeneous and semi-transparent films were obtained by casting and solvent evaporation. Mechanical properties of these films with up to 15 wt% titania contents were studied. The results showed an increase in the Young's modulus, length at rupture, and toughness of the un-plasticized PVC. However, the tensile strength and stress at break point decreased with the addition of titania contents. The same workers reported [31] micro-composites from PVC by *in situ* generation of silica network from TEOS using various catalysts. Mechanical properties of these films were studied and related with the morphology of the resulting hybrids.

In the present work we have prepared PVC-silica hybrid by the hydrolysis/condensation of tetraethoxysilane (TEOS) in the matrix. The inter-phase bonding in the hybrid material was developed by using aminopropyltrimethoxysilane (APTMO). Morphology of the silica particles in the hybrid films was studied by scanning electron microscopy. Thermal mechanical properties of some of these hybrids have been studied and related with composition and the inter-phase bonding in the hybrid material.

## EXPERIMENTAL

### Materials Used

AR-grade PVC was obtained from Aldrich in the form of fine powder and was dissolved in peroxide-free tetrahydrofuran (THF) and then

precipitated out using methanol. It was washed repeatedly and then dried under vacuum at 70°C till a constant weight was obtained. The number and weight average molecular weights of the PVC were 64,000 and 200,000, respectively, with inherent viscosity 1.02. The THF, 99.5% pure was received from Loba Chemie. It was distilled over sodium wire before use. The tetraethoxysilane (TEOS), 98%, and 3-aminopropyltrimethoxysilane (APT MOS), 97% pure were received from Aldrich and used as such

## Preparation of the Hybrid Films

PVC-silica composites in the form of thin films with silica contents ranging from 5 to 20 wt% were prepared. The stock solution of PVC in THF was prepared by dissolving 20 g of PVC in 180 g of THF. In a set of five 50-ml conical flasks specific amount of PVC solution was placed and a calculated amount of TEOS was added and mixed thoroughly by stirring for 1 h. Stoichiometric amount of water ( $H_2O$ : TEOS in mol ratio 1:2), in the form of 0.001 N HCl aqueous solution, was added to carry out hydrolysis and condensation of TEOS where HCl acted as a catalyst in the sol-gel process. Stirring of the reaction mixture continued for 6 h at 60°C. The hybrid films were obtained by evaporating the solvent overnight at room temperature. The films were then dried under vacuum at 75°C for 18 h and then at 100°C for 5 h.

For the chemically bonded system a calculated amount of APT MOS was first mixed with the polymer solution and stirred for 3 h so as to react with PVC at 60°C. Addition of TEOS to this reaction mixture was carried out to achieve various concentrations (5–20 wt%) of silica in the matrix. Of the total silica present in the matrix only 2.5% were derived from APT MOS whereas 97.5% were from TEOS because higher proportions of APT MOS resulted in earlier gelation in the reaction mixture. The sol-gel process was carried out as described earlier. The films were then dried under vacuum at 75°C for 18 h and then at 100°C for 5 h.

## Characterization

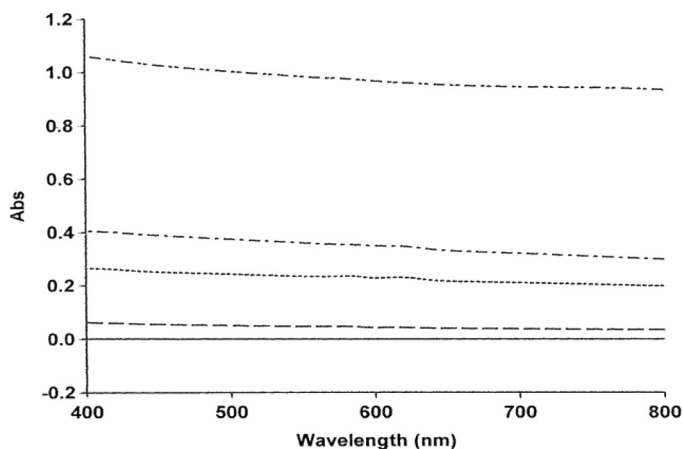
The chemically bonded and unbonded hybrid films with various silica loadings were characterized using different techniques as described in the following.

UV-visible spectroscopic analysis was carried out on Varian Cary 5. The absorption was measured in the 400–800 nm range. The morphology of the hybrid films was studied using scanning electron microscopy (SEM) conducted on a JSM-630 electron microscope operated at 20 kv.

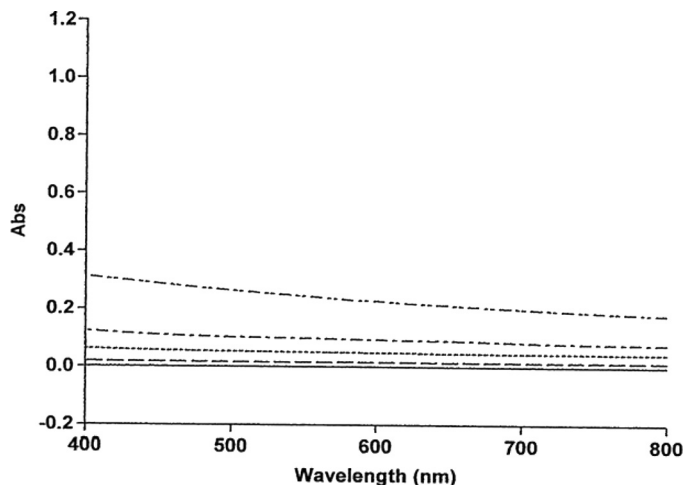
The brittle fractured films were sputter-coated with gold by means of Balzer's SCD 050 sputter-coater before analysis. Dynamic mechanical thermal analysis (DMTA), to measure the storage modulus and  $\tan \delta$ , was carried out under the tension mode in the temperature range of 45°C to 110°C with a heating rate of 2°C/min using a frequency of 2 Hz under inert atmosphere. The temperature where the maxima of  $\tan \delta$  curve occurred was taken as the glass transition temperature for the hybrid material. The linear coefficient of thermal expansion was measured from the thermal mechanical analysis carried out on Shimadzu TMA-60 at a heating rate of 10°C/min with an applied load of 2.00 g under inert atmosphere.

## RESULTS AND DISCUSSION

The PVC hybrid films obtained had thickness ranging from 0.055 to 0.065 mm. The transparency was measured through UV-visible spectrometer and these results for the unbonded and bonded hybrids are presented in Figures 1 and 2, respectively. The pure PVC films were completely transparent in this range showing zero absorption. With the increase in silica loading in the matrix the absorption increased and transparency of the films decreased. The increase in absorption was much more for similar increase in the silica contents in case of higher loadings, that is, 15 to 20 wt% of silica (Table 1). The NMR studies on similar organic-inorganic hybrids [32–33] have shown that



**FIGURE 1** UV-visible spectra for the unbonded PVC-silica hybrids. Silica wt%; 0 (—), 5 (— —), 10 (---), 15 (- . -), 20 (- . . -).



**FIGURE 2** UV-visible spectra for the bonded PVC–silica hybrids. Silica wt%; 0 (—), 5 (— —), 10 (— — —), 15 (- . - .), 20 (- . . .).

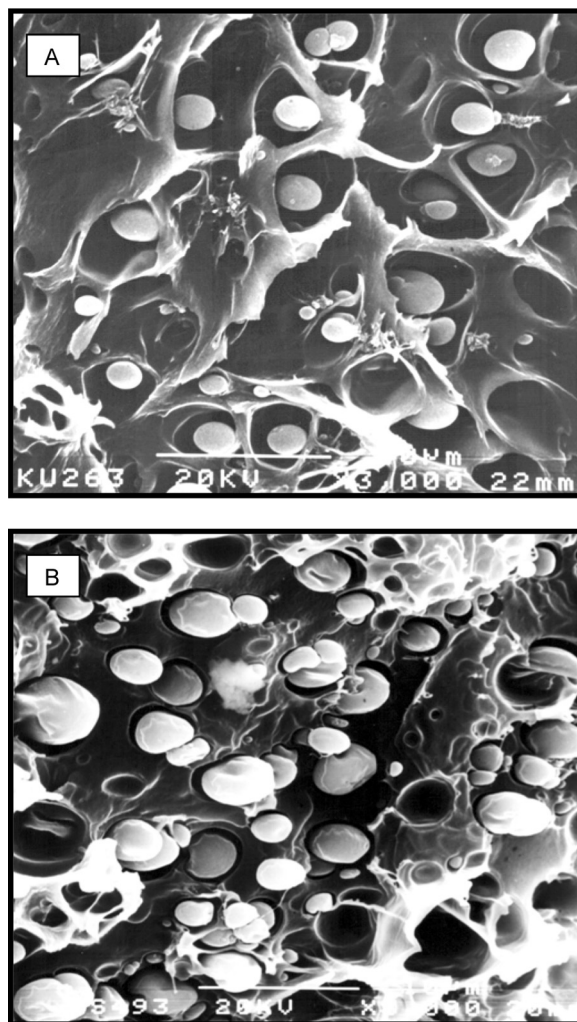
silica network in the sol-gel hybrids exists in various forms such as fully condensed network, mono-hydroxy, di-hydroxy, and tri-hydroxy silica. As the amount of silica in the matrix is increased the proportion of fully condensed network increase significantly. The increased cross-linking results in the growth and agglomeration of silica particles. The absorption in case of 20 wt% silica loading was therefore much higher and these films were opaque and white in color. The hybrid films where small amount of APTMOS was used as binding agent showed a drastic decrease in the absorption. In these films the presence of APTMOS distributed the silica network uniformly in the matrix thus reducing the tendency of the silica phase to aggregate.

**TABLE 1** UV-visible Absorbance for the Unbonded and Bonded PVC–silica Hybrids

SiO <sub>2</sub> %	Unbonded system, absorbance at			Bonded system, absorbance at		
	400 nm	600 nm	800 nm	400 nm	600 nm	800 nm
0	0	0	0	0	0	0
5	0.063	0.049	0.035	0.033	0.016	0.015
10	0.262	0.234	0.198	0.064	0.053	0.055
15	0.397	0.348	0.298	0.124	0.094	0.083
20	1.05	0.966	0.937	0.310	0.229	0.186

In this system the film with  $\leq 10$  wt% silica content were found to be fairly transparent.

Scanning electron micrographs of the unbonded hybrid films containing 10 and 20 wt% silica are given in Figure 3. As can be seen from the micrographs there is a gross phase separation of silica particles



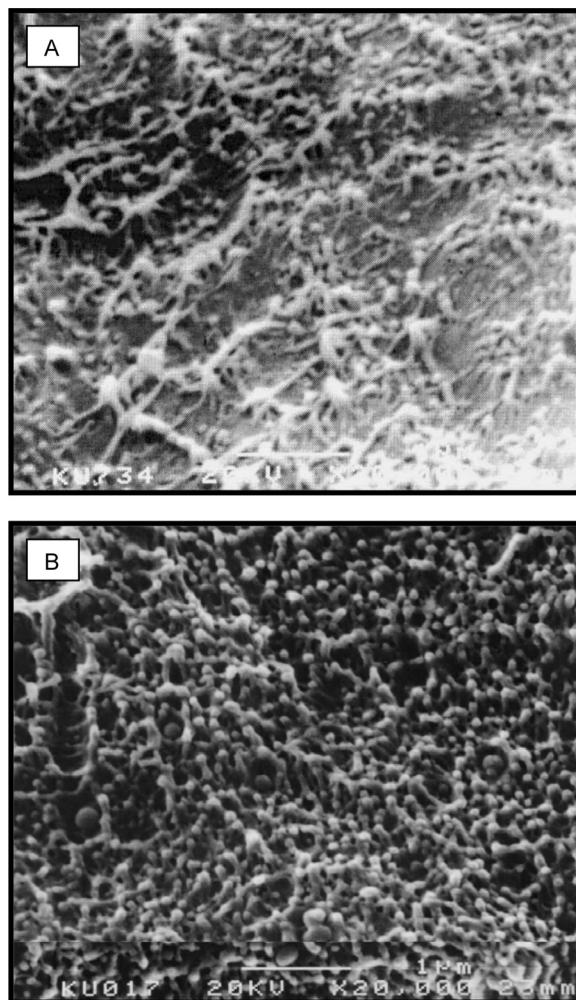
**FIGURE 3** Scanning Electron Micrographs for the unbonded PVC-silica hybrids prepared by *in situ* hydrolysis and condensation of silica. Silica wt%; 10 (A), 20 (B).



with the diameter of the particles ranging from 3–5  $\mu\text{m}$  in case of unbonded hybrids with 10 wt% silica. Such particle distribution is an evidence of phase separation by spinodal decomposition. As the silica concentration is increased from 10 to 20 wt% the average diameter of the silica particles increased from 4 to 8  $\mu\text{m}$  with a larger distribution in size.

Scanning electron micrographs of the bonded hybrid films with 10 and 20 wt% silica in the matrix are shown in Figure 4. As seen from these micrographs the silica particle size is considerably reduced and is in the range 100–200 nm with a fairly narrow size-distribution. The hybrid film with 10 wt% silica shows a combination of linear and nonlinear network whereas in case of 20% the particles are spherical, showing a nonlinear growth although no significant increase in size is visible with the higher silica loading in the matrix. A homogenous distribution with small particle size can be attributed to the chemical reaction [29] of  $\text{NH}_2$  groups of APTMOS with the Cl atoms on PVC chain to produce HCl (Scheme 1). The increased binding of the silane and its further condensation with the alkoxo groups of TEOS in the sol-gel process reduces the agglomeration tendency of the similar phase making its distribution uniform in the matrix and thus retarding the gross phase separation of silica from the matrix. This also explains the increased transparency observed for similar silica loading in case of bonded hybrids as compared to the unbonded system through the UV-visible spectroscopic studies.

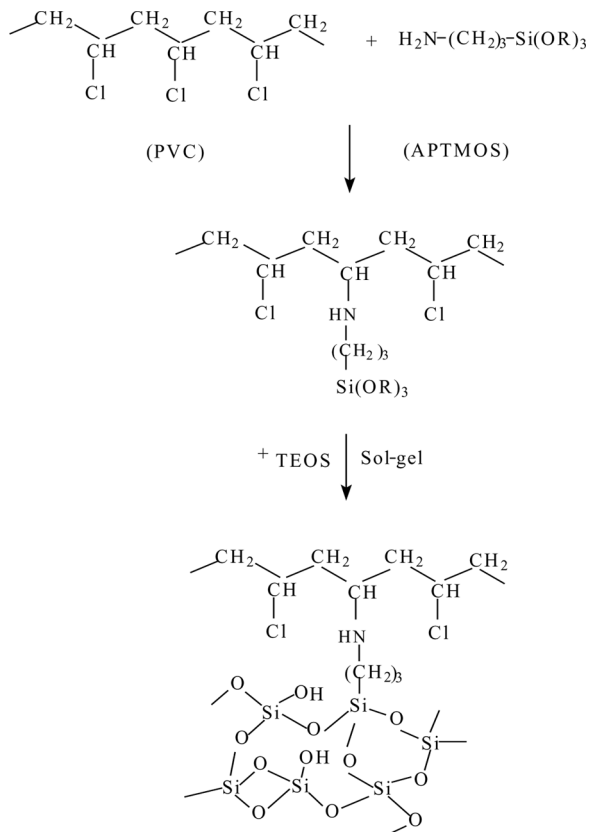
The variation of loss modulus ( $\tan \delta$ ) with temperature for PVC pure and its hybrids with various silica contents is presented in Figures 5 and 6. The visco-elastic properties of the hybrids are given in Table 2. A comparison of the peak height of the pure PVC with that of its hybrids with silica shows that the magnitude of  $\tan \delta$  decreases with increasing the amount of silica. Inclusion of three-dimensional silica network in the matrix thus reduces its viscous behavior at higher temperature. The  $T_g$  associated with  $\alpha$ -relaxation measured from the maxima of the curve, however, is not altered in the case of unbonded system, a typical behavior of inert fillers because the polymer chains have no interaction with the silica particles. On the other hand, for the bonded hybrids the maxima of the  $\tan \delta$  curves are shifted toward higher temperature and an increase of about 8°C in  $T_g$  was observed (Figure 7) with increasing silica content up to 20 wt%. This suggests that polymer molecules are adsorbed/reacted on the silica surface and as a result their mobility is restricted. This was further evident from the higher damping in the  $\tan \delta$  values against the pure matrix (Figure 6). This large reduction in the  $\tan \delta$  curves and increase in  $T_g$  for the bonded hybrids (Table 2) can be



**FIGURE 4** Scanning Electron Micrographs for the bonded PVC-silica hybrids prepared by *in situ* hydrolysis and condensation of silica. Silica wt%; 10 (A), 20 (B).

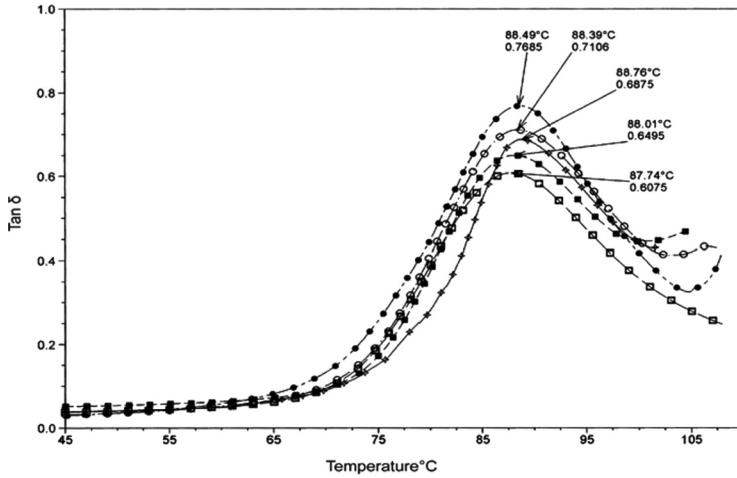
attributed to the improved interaction between the organic and inorganic phases because of the reaction of amino groups of APTMOS with the Cl of the matrix chain.

The variation of storage modulus versus temperature for the PVC and its hybrids is shown in Figures 8 and 9. The values of storage moduli measured at 45°C show that these values increase with inclusion of



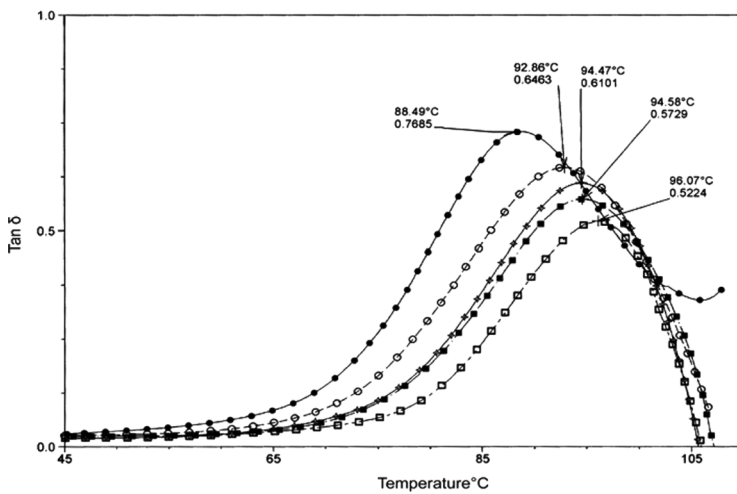
**SCHEME 1** Reaction scheme for the preparation of chemically bonded PVC-silica hybrids.

silica. The increase is more in case of bonded system. The modulus decreases sharply with increase in temperature in case of pure matrix. In case of unbonded hybrids the storage modulus is retained at higher temperatures as compared to the pure PVC matrix. However, when the authors have used APTMOS to bond the polymer chain with the silica network the original higher values are not retained to the same extent as in case of unbonded system. It seems that the reaction of APTMOS with PVC produces HCl as by-product that affects the stability of the PVC. It has already been shown [34–36] that the presence of HCl can auto-catalyze the dehydrochlorination in PVC, which can degrade the polymer at higher temperature. So some degrading effect due to APTMOS might also be evident in case of bonded hybrids.



**FIGURE 5** Temperature variation of  $\text{Tan } \delta$  for the unbonded PVC-silica hybrids. Silica wt%; 0 (●), 5 (○), 10 (◇), 15 (■), 20 (□).

The thermal mechanical analysis on pure PVC film and those with 20 wt% silica in case of both bonded and unbonded hybrids is given in Figure 10. In case of pure PVC the TMA curve shows a slight kink and then a sharp decrease above 100°C as the polymer begins to soften.

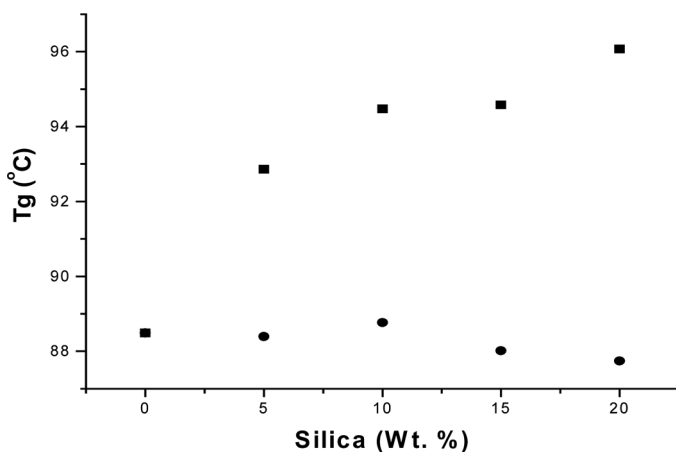


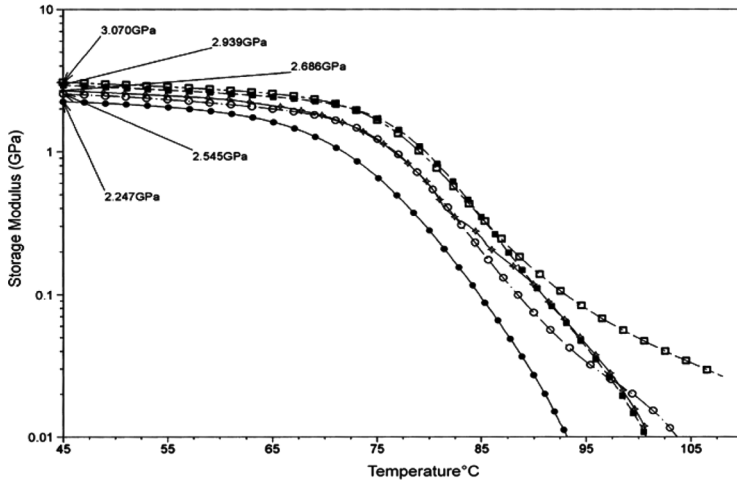
**FIGURE 6** Temperature variation of  $\text{Tan } \delta$  for the bonded PVC-silica hybrids. Silica wt%; 0 (●), 5 (○), 10 (◇), 15 (■), 20 (□).

**TABLE 2** Visco-Elastic Properties of PVC–Silica Hybrids

SiO <sub>2</sub> %	Storage modulus (GPa) at 45°C		T <sub>g</sub> (°C)		Tan δ	
	Unbonded	Bonded	Unbonded	Bonded	Unbonded	Bonded
0	2.247	2.247	88.49	88.49	0.7685	0.7685
5	2.545	2.731	88.39	92.86	0.7106	0.6463
10	2.686	2.875	88.76	94.47	0.6875	0.6101
15	2.939	3.009	88.01	94.58	0.6495	0.5729
20	3.070	3.196	87.74	96.07	0.6075	0.5224

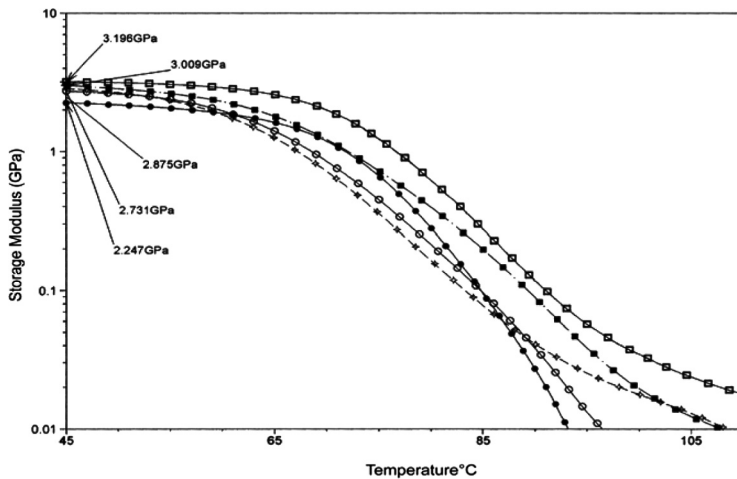
Above 150°C as the polymer degrades and cross-linking takes place, the curve then shows a steep rise. The average coefficient of thermal expansion (CTE) values calculated from the slope of the curve in the temperature range from ambient to 100°C was 71.65 ppm/°C, which agree with the literature for PVC with similar molecular weight [37]. The TMA curve for the unbonded hybrid with 20 wt% silica is linear with no steep drop around 100°C. This shows that the non-linear silica network has increased the softening point of the polymer. The average value of CTE measured was 68.54 ppm/°C. In case of bonded system with similar silica loading the value of CTE was 38.21 ppm/°C. The large reduction in the CTE value in case of bonded hybrids containing

**FIGURE 7** Variation of glass transition temperature with silica content in PVC–silica hybrids: unbonded (●), bonded (■).

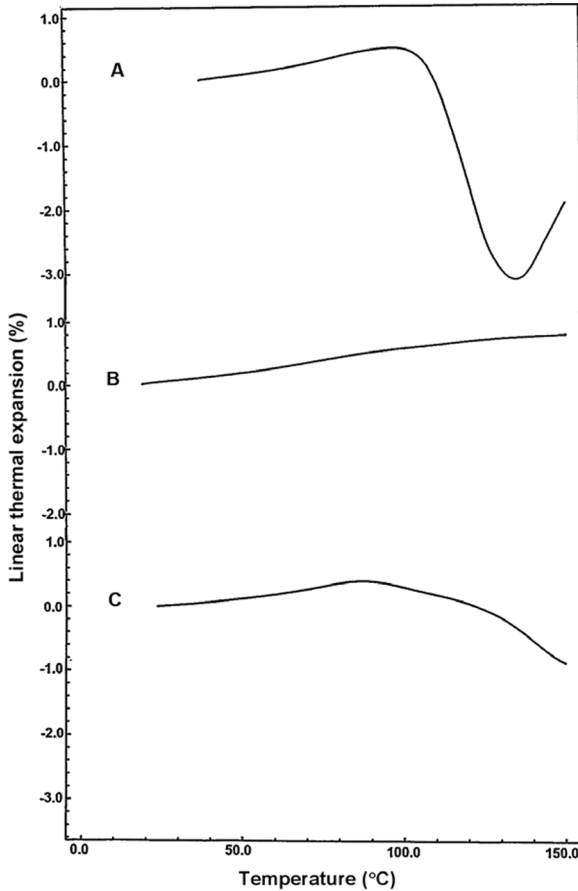


**FIGURE 8** Temperature variation of storage modulus for the unbonded PVC-silica hybrids. Silica wt%; 0 (●), 5 (○), 10 (◇), 15 (■), 20 (□).

APTMOs can be attributed to the chemical bonding between the PVC and silica phases because CTE is very sensitive to the inter-phase bonding. However, as already mentioned, the presence of APTMOs may also have a slight degrading effect on the polymer itself. That is



**FIGURE 9** Temperature variation of storage modulus for the bonded PVC-silica hybrids. Silica wt%; 0 (●), 5 (○), 10 (◇), 15 (■), 20 (□).



**FIGURE 10** Thermal mechanical analysis: A (Pure PVC), B (PVC-silica hybrids: with 20% silica, unbonded), C (PVC-silica hybrids with 20% silica, bonded).

why the TMA curve drops down at higher temperature in case of bonded hybrid film.

## CONCLUSIONS

The Interphase bonding in PVC-silica hybrids using aminopropyltri-methoxysilane have considerably reduced the silica particles produced by the sol-gel process in the matrix. This has improved the transparency of the hybrid films and reduced considerably the coefficient of thermal expansion value for such films.

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