Properties of PVC-titania hybrid materials prepared by the sol-gel process

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Abstract

Hybrid materials from Polyvinyl chloride (PVC) and titania were prepared using sol-gel technique. In-situ generation of titania network in the PVC matrix was carried out by introducing required amounts of tetrapropylorthotitanate (TPOT) followed by hydrolysis/condensation of TPOT in the matrix. Homogeneous and semi-transparent films were obtained by casting and solvent evaporation. Mechanical properties of these films 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 unplasticised PVC. However, the tensile strength and stress at break point decreased with the addition of titania contents. Thermal stability of the material was studied using dehydrochlorination (DHCl) technique and thermogravimetric analysis. The PVC samples with small amount of titania were found to be more stable as compared with the pure PVC.

Introduction

The demand for materials with unique combinations of properties has led to the recent efforts in modification of known polymers via incorporation of a variety of additives. The sol-gel process has been consistently employed to produce microsized inorganic network to prepare ceramers, ceramics, and various glass systems [1–6]. The in-situ hydrolysis and polycondensation of metal alkoxide establishes three-dimensional highly cross-linked inorganic network homogeneously distributed in the polymeric matrix. The size of the inorganic network produced depends on various factors such as solvent, pH, temperature, etc. Ahmad and Mark have studied in-situ formation of silica and titania as reinforcing agents in various organic polymer networks [7–12].

Tsuji et al [13] have synthesized PVC-titania composites having titania particles of the order of 10μm in powdered PVC. They observed an immense increase in the impact strength and Young's modulus of the unplasticised PVC. Control of the particle size and orientation during in-situ hydrolysis of titanium alkoxide has also been studied by Burdon et al [14] using the solubility parameters of various polymers, titanium alkoxides and solvents. Transparent PVC films having titania particle size less than 0.1μm have

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been reported. The inorganic network not only provided toughness to the material but also retarded photo-degradation of PVC thus improving the weatherabilty of the material. Andrady and co-workers [15] have observed the effect of titania on controlling the degradation of PVC. They found that both photoyellowing and photobleaching are wavelength dependent phenomenon in the range of 280–500nm, this thus can increase the useful life of the PVC.

Although PVC is an important thermoplastic but it has low thermal, thermo-oxidative and photostability [16–18]. Its degradation results in the formation of polyene linkages with the evolution of HCl [19,20]. Thermal degradation has been studied by using different techniques such as UV-visible spectroscopy [21–23], conductometry [24,25], thermogravimetry [26], mass spectroscopy and thermal volatilisation analysis [27]. The most commonly methods are conductometry and thermogravimetry.

In the present work, we report the preparation of micro-composites of PVC with titania produced by the sol-gel process. Thermal stability and the mechanical properties of these composites have been studied.

Experimental

Material and sample preparation

PVC having molecular weight 100,000±100 (obtained as a fine powder from BDH) was dried at 30°C in the vacuum oven for an overnight. TPOT (obtained from Gelest) was used as received. Peroxide free AR-grade tetrahydrofuran (THF), (obtained from E. Merck) was used as such.

Different stoichiometric quantities of TPOT were mixed with PVC in the presence of THF for about 2 hrs. For the hydrolysis of TPOT, calculated amount of HCl solution in water as catalyst was used and the solutions were stirred for another 6 hrs. Semi-transparent films of uniform thickness were obtained by casting the measured amount of reaction mixture into petri dishes and allowing the solvent to evaporate. Films of pure PVC and composites containing different percentages of titania were washed repeatedly with distilled water and then dried at 60°C under vacuum for 72 hrs before use. Mechanical properties of the composites films were measured at room temperature using an Instron Universal Testing instrument model 4467 UK.

Samples of PVC and PVC-titania composites were degraded at 180±1°C under N_2 atmosphere having flow rate 20 cm^3/min. N_2 carried away the HCl produced during degradation, which was passed through a cell containing 130ml conductivity water placed in thermostat at 25±0.1°C. Conductivity measurements were carried out using Orion Research Conductivity Meter Model 101. The detailed experimental procedure for the degradation studies has been explained elsewhere [28,29]. Thermal degradation was also studied by thermogravimetric technique using Seiko Instrument SSC/5200 thermogravimetric analyzer. The known weight of sample was taken in crucible and heated from room temperature to 500°C at heating rate of 5°C/min. The N_2 gas flow rate was maintained at 100 cm^3/min.

Results and discussion

Although on macro scale pure PVC and titanium alkoxide are incompatible, it was possible to mix the TPOT and PVC using THF as solvent. Fast reaction of a TPOT
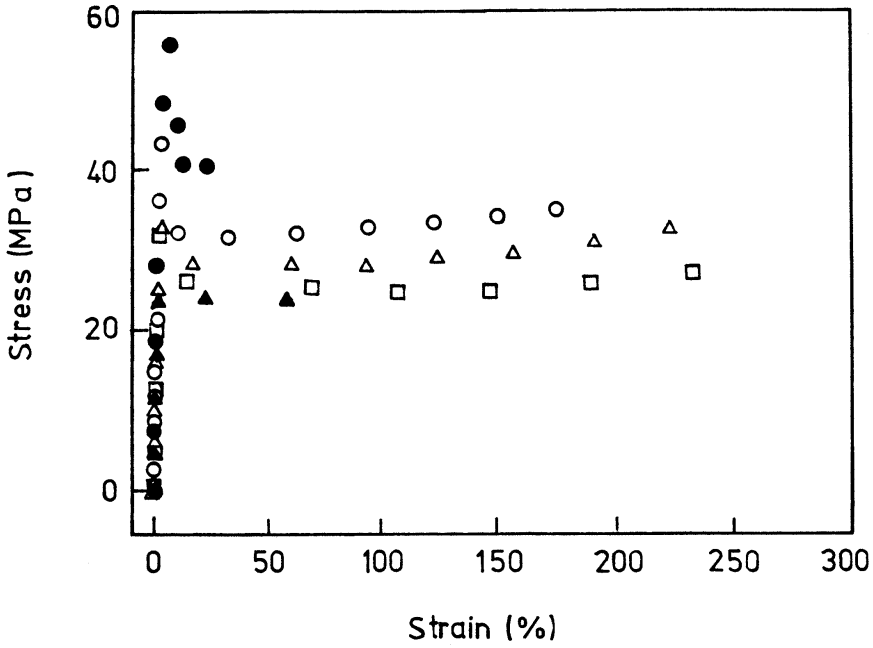
Figure 1: Stress-strain curves of PVC-titania composites,titania
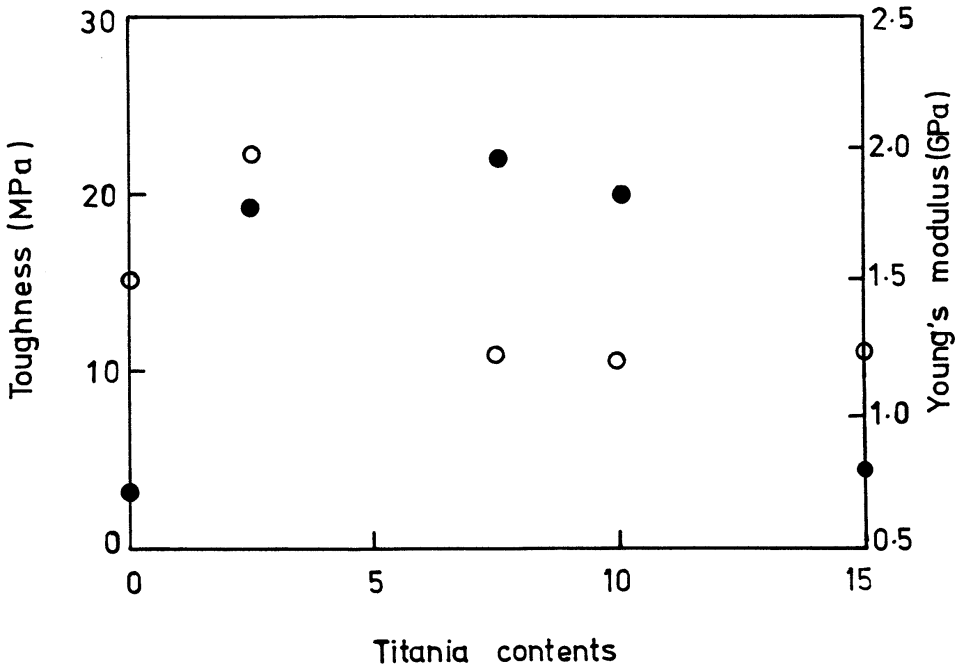Wt % in PVC; (●)0, (O)2.5,(△)7.5, (□)10, (▲)15

Figure 2: Variation of toughness (●) and young's modulus (O) vs titania
contents in PVC-titania composites

particularly the condensation reaction leads to an increase in the particle size of TiO_2 and thus causes the precipitation of inorganic phase in the organic matrix [30–34]. To overcome this difficulty, different experimental runs were carried out to optimize the reaction conditions such as, the amount of solvent, temperature and concentration of catalyst which are the key factors in controlling the reaction kinetics and resulting inorganic structure in the sol-gel process. After extensive experimental work, the optimum conditions i.e. temperature $10\pm2°C$, amount of solvent, 91.74 % THF in reaction mixture and concentration of catalyst 2 % solution in distilled water were adjusted. Under these conditions it was possible to obtain composites of PVC-titania having titania contents 0–15 wt. % without any precipitation. The films containing 2.5 wt. % titania (thickness ranging from 0.155–0.255 mm), were semi-transparent and light yellow in color. The transparency tends to decrease with increased titania contents. Film containing 15 wt. % titania were whitish and non-transparent. The transmittance measured by Schmidzu spectrophotometer model UV-250-02 for the film having thickness 0.155 mm with 2.5 wt. % titania in the range 490–600 nm was 49.1 %. Whereas that of the sample containing 15 wt. % titania with thickness 0.160 mm was 0.0 %.

Stress-strain curves obtained for PVC pure and four different PVC-titania composites having titania contents ranging from 2.5–15 wt. % are shown in Fig. 1. For the pure PVC the value of stress at yield point was 55.60 MPa and the stress at break point was 40.40 MPa. The tensile modulus that calculated from the initial slope of the curve was 1.51 GPa. The Young's modulus values obtained from the stress-strain curve for PVC-titania composites were found to increase initially with increase in the inorganic contents. The maximum value recorded was 1.99 GPa for the composites containing 2.5 wt. % titania. The variation in the Young's modulus vs titania contents is shown in Fig. 2, which shows that the value of Young's modulus decreases after 2.5 wt. % increase in titania contents in the PVC matrix. The initial increase in the Young's modulus seems due to small particle size and more interphase interaction between the organic and inorganic structure. As the amount of titania is increased there is an increasing tendency towards particle agglomeration. As the particle size grow, the surface interaction between the two phases becomes less which results stress transfer problem and increase in the brittleness of the sample. The strain at yield point for pure PVC occurred at 6 % (Table 1). The stress at yield point and the tensile strength showed a significant decrease with increase in titania contents. The value of length at break, however, revealed a considerable increase (Table 1) which was more than 10 times as compared to the value of pure PVC.

Table I: Stress-strain Analysis of PVC-titania Composites

Experiment No.	Titania in PVC Wt. %	Tensile Strength MPa	Strain at Yield Point %	Stress at Rupture MPa	Length at Rupture %	Young's Modulus GPa
1	0.0	55.60	6.00	40.40	21.50	1.51
2	2.5	49.90	4.20	34.90	174.70	1.99
3	7.5	32.60	2.10	33.50	223.20	1.25
4	10.0	33.00	3.60	27.30	232.40	1.22
5	15.0	23.70	2.70	23.80	56.60	1.25

Toughness of these composites was measured from the area under the respective stress-strain curve. The variation of toughness against titania contents is shown in Fig. 2. It was found that the toughness of the pure PVC (3.30 MPa) showed seven times improvement (22.12 MPa) with the addition of 7.5 wt. % of titania. This value, however, decreased with further addition of titania and the sample containing 15 wt. % titania had a value of 4.50 MPa. The inorganic component is present in the form of diffused network. However, as the amount of titania is increased, this diffused network has a tendency to grow in size and cross-link, which results in the growth of titania particles. Further addition of titania make these particles to grow more which yields to the phase separation with 20 to 25 wt. % titania in the polymer matrix. When the inorganic network is present in very small amount there is greater surface interaction between the inorganic and organic phase. The diffused network of titania provides high strain value at the break and thus provides toughness to the polymer but the complete high cross-linking network provides rigidity and brittleness to the material.

DHCl of samples containing different proportions of titania was carried out and change in conductance with time was measured. Fig. 3 shows percent HCl loss with time for PVC and PVC-titania composites having titania in the range of 0.3–4 wt. %. With pure PVC an induction period of 12 minutes was recorded and percent HCl loss after 5 hrs was found to be 5.5915 %. In case of PVC-titania composites there was an increase in induction period and decrease in percent a HCl loss as compared to pure PVC. Induction period was 20 minutes for PVC having 0.3 wt. % titania. The stabilization seems due to the reaction of allylic chlorine in PVC chain with the uncondensed inorganic network. This network structure in the chain then act as a 'catch or block' thus hindering the zip elimination [19,35] of HCl causing degradation in PVC. However the increased amount of titania was
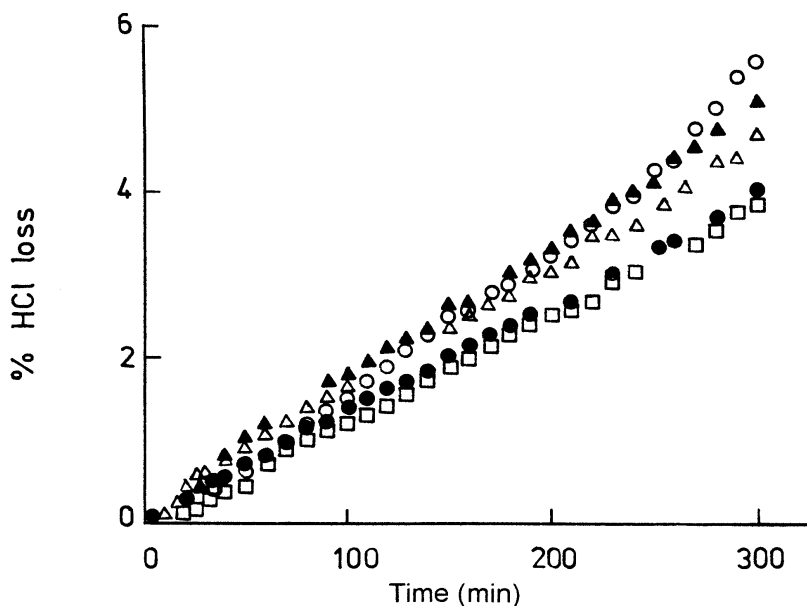

Figure 3: DHCl studies of PVC-titania composites at 180±°C, (o) PVC, (□) PVC+0.3%TiO$_2$, (●) PVC+2%TiO$_2$, (Δ) PVC+3%TiO$_2$, (▲) PVC+4%Ti

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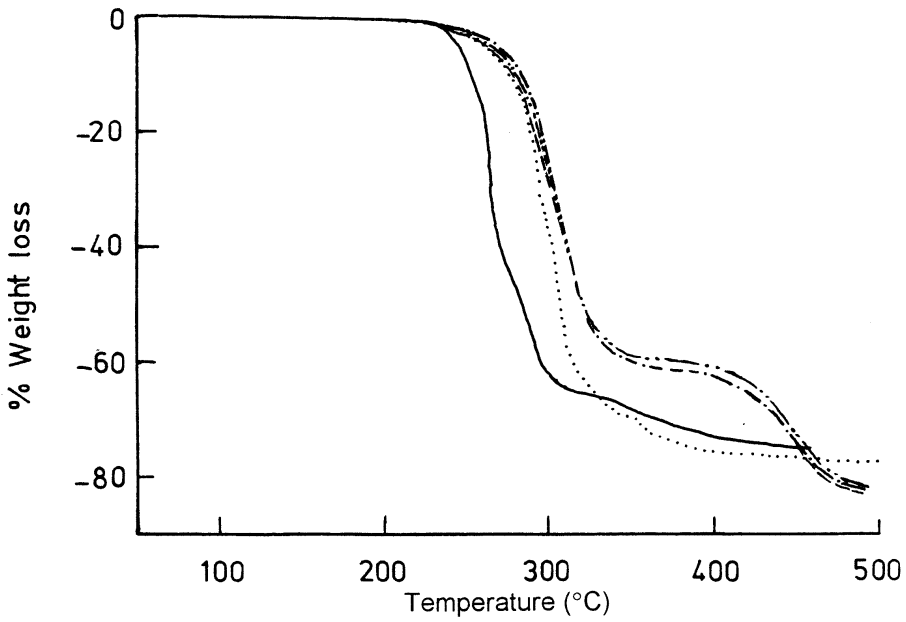

Figure 4: TGA curves for PVC and PVC-titania composites, titania wt. % in PVC; 0 (———), 0.3 (·······), 2 (– – – –), 3 (–·–·–), 4 (–··—)
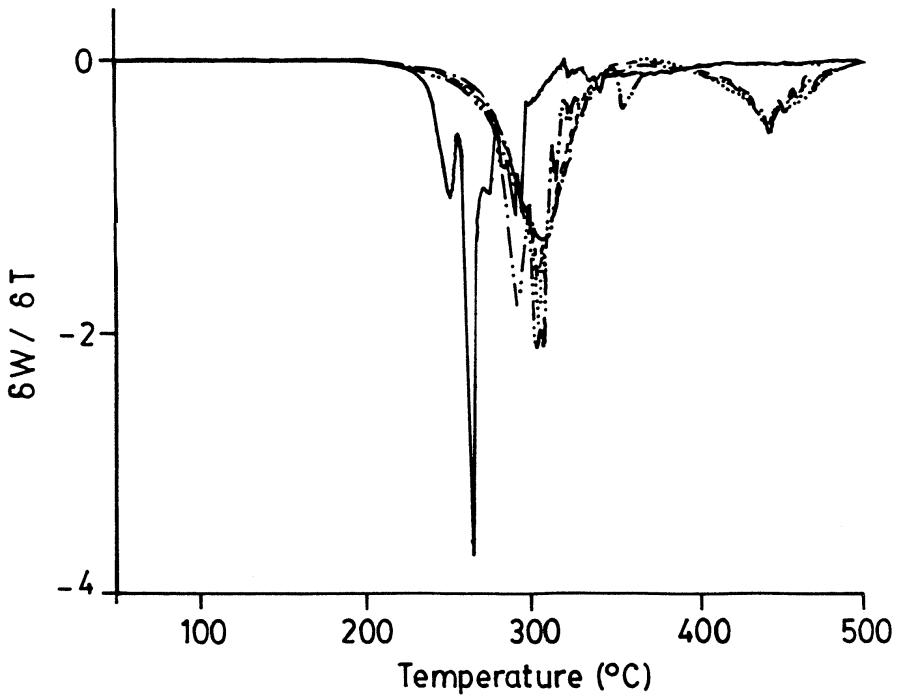
Figure 5: DTGA curves for PVC and PVC-titania composites, titania wt. % in PVC; 0 (———), 0.3 (·······), 2 (– – – –), 3 (–·–·–), 4 (–··—)

not effective in reducing the dehydrochlorination rate in PVC during isothermal heating. The reduced miscibility among phases causing aggregation of titania network, may increase self condensation or crosslinking within titania network at higher temperature and reduce the interaction of allylic chlorine with uncondensed titania which may bring dehydrochlorination rate at higher concentration of titania closer to pure PVC.

Non-oxidative degradation of PVC and PVC-titania composites was also studied using thermogravimetric technique and the thermograms are shown in Fig. 4. The weight loss in case of pure PVC occurred much earlier than the PVC titania composites. The inflection temperature (Ts) measured from the DTGA curve (Fig.5) increased from 265°C for pure PVC to 306°C for composites having 0.3 wt. % titania and then decreased slightly with the higher contents, i.e., Ts for samples having 2, 3, and 4 wt. % titania were 305, 303 and 290°C respectively. Fig. 4 also indicates an increase in percent wt. loss at temperature higher than 360°C in case of PVC-titania composites as compared to pure PVC. The degradation of PVC involves a primary process, which involves dehydrochlorination and a secondary process that occurs above 360°C involving the formation of volatile alkyl aromatics and condensed ring aromatic hydrocarbons [36]. Due to the presence of titania in PVC matrix the primary process is slowed down as explained earlier, but volatilization of aromatic hydrocarbons produced from the secondary process occuring in the temperature range 360–500°C is increased. The weight loss at higher temperature in PVC composites seems due to more porous nature of the composites than pure PVC due to presence of titania in the matrix.

Conclusions

PVC-titania composites with greater toughness as compared to the pure PVC can be prepared using an optimum amount of inorganic network through the sol-gel process. Thermal degradation analysis of these composites reveals that the primary process in PVC degradation is delayed in the presence of small amount of titania network thus rendering greater thermal stability to the matrix.

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