Characterization and properties of hybrid composites prepared from poly(vinylidene fluoride–tetrafluoroethylene) and SiO$_2$

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Abstract

Organic–inorganic hybrids were prepared using poly(vinylidene fluoride–tetrafluoroethylene) (P(VDF–TFE)) and tetraethoxysilane (TEOS) via a sol–gel process, and their crystallization and mechanical properties including the morphological features, were investigated.

The hybrid films were transparent at TEOS contents up to 20 wt%. However, 30 wt% TEOS hybrid was less transparent due to formation of microvoids rather than pure polymer film. Crystallinity of P(VDF–TFE) in the hybrids increased with increasing TEOS content. This indicated that SiO$_2$ played the role of nucleating agent in the polymer crystallization. The crystal structure of P(VDF–TFE) in the hybrids was found to be β-phase according to X-ray diffraction measurements. No aggregation of SiO$_2$ networks in the hybrids was observed in small angle X-ray scattering measurements.

The hybrid films, as well as pure P(VDF–TFE) film, showed clear yielding phenomena in stress–strain relation. The yield strength, yield strain, and tensile modulus of the hybrids increased with increasing TEOS content up to 20 wt%, but decreased abruptly at 30 wt% TEOS. It is interesting that the breaking elongation of the samples was the highest at 10 wt% TEOS, two times higher than that of pure P(VDF–TFE) film. Consequently, the transparent hybrid films could be obtained without any loss in either crystallinity of P(VDF–TFE) or mechanical properties. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: P(VDF–TFE)–SiO$_2$ hybrids; Crystallization; Mechanical properties

1. Introduction

In recent years, preparation of hybrid organic–inorganic composites [1–5] has attracted much attention because such hybrids may show controllable properties such as optical, electrical and mechanical behaviors by combining the properties of both organic polymer and inorganic compound [6–9]. Hybrids are prepared usually through a sol–gel process by incorporating organic polymers with alkoxysilanes, mainly tetramethoxysilane or tetraethoxysilane (TEOS). By properly controlling the reaction conditions of hydrolysis and condensation of TEOS in the presence of a preformed organic polymer, it is possible to obtain optically transparent hybrids with improved properties compared with the original compounds. The organic polymer can enhance the toughness of brittle inorganic materials, whereas, the inorganic network can increase the scratch resistance and hardness of plastics. The polymers having functional organic groups may be introduced also into the inorganic networks for applications of the hybrids in many fields such as biomaterials, membranes, coatings, optics and electronics.

Poly(vinylidene fluoride) (PVDF) and its copolymers with other fluorocarbons [10] are well known to have ferroelectric, piezoelectric, and pyroelectric properties and crystallize easily on cooling from the melt. Their combination with SiO$_2$ may result in a large diversity of electro-active and mechanical properties. Hybrids of PVDF with SiO$_2$ have been investigated for application in electronic devices having a charge storage effect and electro-active stability [11] since better electronic properties can be created without losing the crystallization characteristics of polymers. Preparation and characteristics of hybrids of PVDF copolymers and SiO$_2$ have been also reported [12]. It was found recently in our laboratory that, in comparison to PVDF–SiO$_2$ hybrids, the hybrids prepared from poly(vinylidene fluoride–tetrafluoroethylene) (P(VDF–TFE)) have superior characteristics in mechanical properties as well as in crystallinity.

In this study, the crystallization and mechanical properties as well as morphological features of P(VDF–TFE)–SiO$_2$ hybrids produced via the sol–gel process are investigated.

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* Corresponding author. Tel.: +82-2-450-3513; fax: +82-2-457-8895.
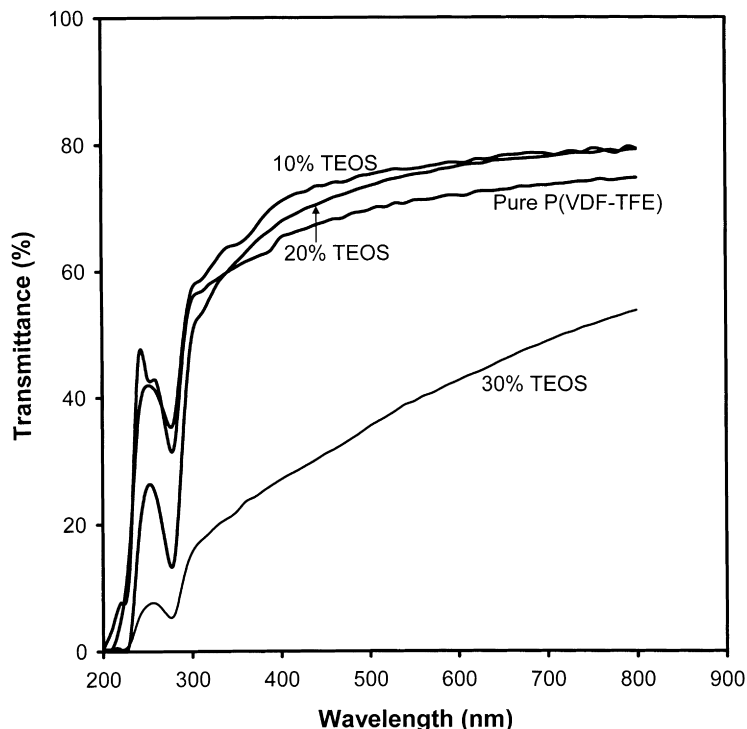*E-mail address:* jwcho@kkucc.konkuk.ac.kr (J. W. Cho).

Fig. 1. UV/VIS spectra of pure P(VDF–TFE) film and P(VDF–TFE)–SiO$_2$ hybrid films.

2. Experimental

Polymer used in this study was P(VDF–TFE) (Daikin Kogyo, 80/20 mol% VDF/TFE). It was dissolved in tetrahydrofuran at room temperature with a concentration of 10 wt% and was stirred constantly to ensure homogeneity. A homogeneous TEOS mixture was also prepared using deionized water, hydrochloric acid, ethanol, and TEOS in a molar ratio of 2/0.01/7/1. Four different volumes of TEOS solution were added carefully to the 10 wt% P(VDF–TFE) solution while stirring to obtain four mixtures with different weight percentage of P(VDF–TFE)/TEOS (100/0, 90/10, 80/20, and 70/30), which were then stirred at 40°C for 2 h. The resulting homogeneous solutions were transferred to a closed Petri dish and were allowed to stand at 60°C for 24 h for gelation. Finally, the gelled samples were obtained and then slowly dried at room temperature for more than 2 weeks.

Fourier transform infrared (FT-IR) and UV–visible (UV/VIS) spectra of films were obtained using Jasco FT-IR 300E and Shimazu 160A UV/VIS spectroscopies, respectively. FT-IR measurements were performed with an attenuated total reflectance method. The surface characteristics of the composite films were examined with a scanning electronic microscopy (SEM), Alpha-25A. Differential scanning calorimetry (DSC) scans were obtained with a TA DSC 2010 under nitrogen flow at a heating rate of 10°C/min. X-ray diffraction measurements were carried out with Rigaku Rinter 2100 Series, using Cu K$_\alpha$ radiation. Small angle X-ray scattering (SAXS) measurements were

performed using Bruker SAXS with general area detector diffraction over a range of $2\theta = 0.5$ to $5.0°$. Thermogravimetric analysis (TGA) measurements were carried out using a TA TGA 2050 instrument with a heating rate of 10°C/min from room temperature to 600°C under nitrogen gas atmosphere. Tensile stress versus strain evaluations were carried out at room temperature using an Instron 4468 tensile tester operating at a strain rate of 1 in./min. Each tensile sample was tested five times to provide assurance of good data reproducibility.

3. Results and discussion

The incorporation of SiO$_2$ into P(VDF–TFE) matrices produced composite films with different optical characteristics. The composite film with thickness of 0.075 mm was transparent at TEOS content levels up to 20 wt%. However, the composites was translucent when the TEOS content was 30 wt%. Fig. 1 shows the UV/VIS spectra measured for various samples. The transmittance of composite films at TEOS levels up to 20 wt% was at least above 65 % over a range of 400–800 nm, and had better optical transparency than that of pure P(VDF–TFE) film. However, the composite film at 30 wt% TEOS showed a transmittance from 25 to 50% over 400–800 nm range. This optical transmittance may be used as an initial criterion for the formation of a homogeneous phase of both inorganic and organic components. However, the translucency of composite film at 30 wt% TEOS should be ascribed to the presence of
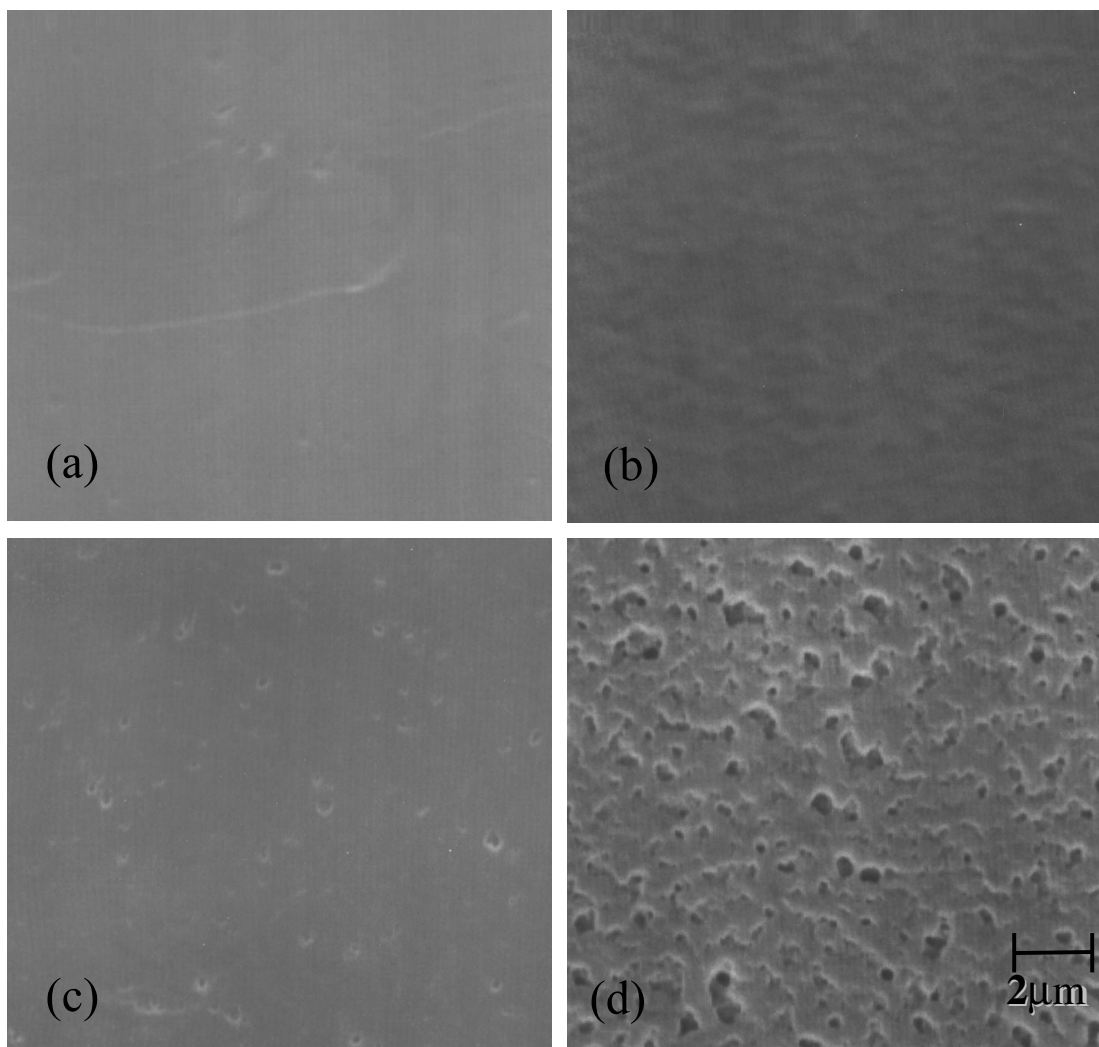
Fig. 2. SEM pictures of samples: (a) pure P(VDF–TFE); (b) 10 wt% TEOS; (c) 20 wt% TEOS; and (d) 30 wt% TEOS.

microvoids formed within the sample during the sol–gel reaction, not to the phase separation into polymer chains and SiO$_2$ networks. As shown in Fig. 2(d), the voids were observed in the sample of 30 wt% TEOS.

Fig. 3 shows the FT-IR spectra of composite films along with the pure polymer film. The pure SiO$_2$ shows the characteristic bands [13,14] at 794 cm^{-1} (symmetric Si–O–Si stretching), 1078 cm^{-1} (asymmetric Si–O–Si stretching), and 943 cm^{-1} (Si–OH stretching). Typical pure P(VDF–TFE) bands [15] are at 508 cm^{-1} (CF$_2$ bending), 838 cm^{-1} (CH$_2$ rocking), and 879 cm^{-1} (CF$_2$ symmetric stretching). In the spectra of composite films, both characteristic FT-IR bands for SiO$_2$ and P(VDF–TFE) are present, indicating that hybridization was done via sol–gel reaction. However, the amounts of SiO$_2$ formed after the sol–gel reaction may not be corresponded necessarily to the added amounts of TEOS. In order to determine the amounts of SiO$_2$ preserved in each sample, TGA measurements were performed.

Fig. 4(a) shows a major weight loss of composite films at onset temperature of about 450°C, which is attributed to the

decomposition of the polymer. Pure SiO$_2$ film does not present any abrupt decrease in weight and only a slight decrease at approximately 100°C appears due to the removal of the loss of absorbed water [16]. In the case of hybird films, the weight retained after decomposition is dependent on the polymer content as shown in Fig. 4(b). That is, the weight residue of composites at 550°C increases with increasing TEOS content. Based on this, the amounts of SiO$_2$ formed in the composites can be determined. The calculated results are listed in Table 1.

Fig. 5 shows the DSC endothermic curves for the pure P(VDF–TFE) film as well as the composite films. The corresponding thermal data are listed in Table 1. The single melting temperature of the polymer near 125°C appeared clearly in all the samples. The melting temperature of P(VDF–TFE) crystallites in the hybrids was similar to that of pure P(VDF–TFE), which in turn, implies that the existence of the silica network had little significant effect on crystal stability of P(VDF–TFE). However, the corresponding heat of fusion of P(VDF–TFE) in hybrids increased with
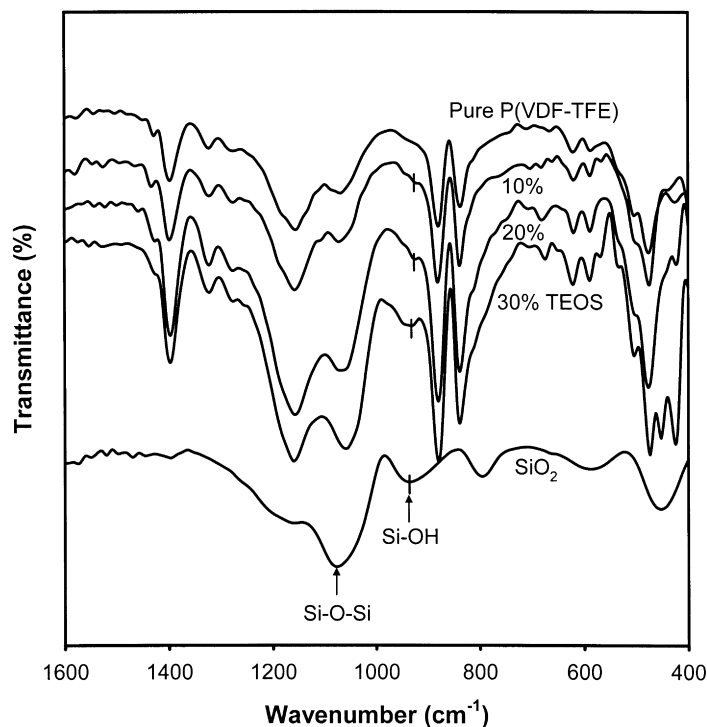
Fig. 3. FT-IR spectra of P(VDF–TFE)–SiO₂ hybrid films.

increasing TEOS content. Here, it should be emphasized that this heat of fusion is not an actual one due to pure P(VDF–TFE) weight alone, but the value obtained for the total weight including both polymer and SiO₂. Considering the pure weight of the polymer only, the actual heat of fusion should be calculated from the measured heat of fusion and the weight fraction of SiO₂, which is known from the TGA results. That is, the crystallinity (X) can be determined from the following equation:

$$X = \Delta H_m/(\Phi \Delta H_m^0) \qquad (1)$$

where Φ is the P(VDF–TFE) content in hybrids by weight fraction, and ΔH_m and ΔH_m^0 are the experimental heat of fusion and the equilibrium heat of fusion for complete P(VDF–TFE) crystals, respectively. 104 J/g for PVDF [17] was also used as ΔH_m^0 in this study. The results obtained were plotted in Fig. 6. It is interesting that the crystallinity increased linearly with the addition of TEOS. It indicates that the presence of SiO₂ had a favorable effect on the extent of P(VDF–TFE) crystallization in hybrids.

That is, the SiO₂ networks acted as a kind of nucleating agent in polymer crystallization. Such similar phenomenon has been reported in crystalline polymer blends or composites [18,19].

According to X-ray diffraction measurements shown in Fig. 7, the crystal structure of composite films did not change even with the formation of SiO₂ networks. Pure P(VDF–TFE) film showed diffraction peaks at around $2\theta =$ 19.9, 35.5, and 40.8° according to the existence of form I crystals of ferroelectric all *trans* phase [20,21]. The composite films showed the same X-ray diffraction patterns for all TEOS contents, indicating that the presence of SiO₂ did not change the crystal structure of P(VDF–TFE). Further, more no significant change in lattice space was observed. Small angle X-ray spectra in Fig. 8 showed that no intensity peak, which would be indicative of spatially correlated domains is apparent. It indicates that there never existed any aggregation of SiO₂ networks within the composite films. This leads to the conclusion that SiO₂ networks are uniformly dispersed into P(VDF–TFE) molecules without any molecular aggregation. Consequently, the transparency of

Table 1
Actual weight fraction of SiO₂ formed after sol–gel reaction and melting temperature and heat of fusion of P(VDF-TFE) in the hybrids

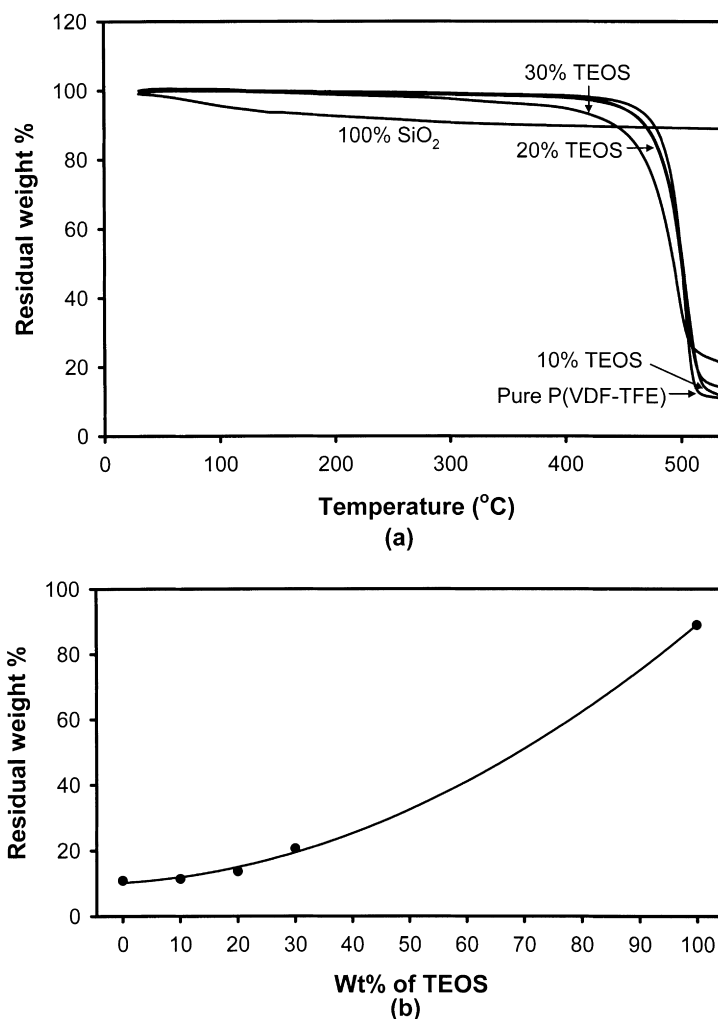| Wt% of TEOS	Wt fraction of SiO₂ (Φ)	Melting temperature(°C)	Heat of fusion (ΔH_m, J/g)
0	0	123.9	37.9
10	0.0054	123.8	39.9
20	0.0289	124.9	44.6
30	0.0982	123.9	48.3

Fig. 4. (a) TGA curves. (b) Residual weight percent of samples at 550°C.

composite films seems to originate in the homogeneous distribution of P(VDF–TFE) molecules and SiO$_2$ networks.

Fig. 9 describes the stress–strain results obtained on the hybrid films as well as for pure P(VDF–TFE) film. A yielding phenomenon was observed clearly and the maximum stress appeared at the yield point for all the samples. The yield stress and yield strain tended to increase slightly as TEOS content increased up to 20 wt%, but then decreased sharply when 30 wt% TEOS was incorporated (Fig. 10). In fact, the film at 30 wt% TEOS ruptured just beyond the yield point due to the presence of voids. The effect of TEOS content on the tensile modulus was also similar to that on yielding stress, which is shown in Fig. 11. This mechanical behavior of hybrid films indicates the reinforcing effect in strength through the homogeneous dispersion of the micro SiO$_2$ particles in the polymer matrix. An abrupt reduction of mechanical properties such as yield stress, yield strain, and tensile modulus is believed to result from the presence of voids in the sample as described previously. On the other hand, the film of 10 wt% TEOS exhibited an excellent breaking elongation despite of its relatively high modulus,

which was two times higher than that of pure P(VDF–TFE) film as shown in Fig. 12. This is different from the dependence of yield stress and tensile modulus on the TEOS content. Similar phenomena have been reported in the poly-silicate-based hybrids having the interpenetrating networks or the confining effect of the network on the polymer chains [22] In this study, it may be due to some interaction at the interfacial region between polymer phase and SiO$_2$ networks. That is, the maximum breaking elongation at 10 wt% TEOS is a result attributed to the competition between the interfacial interaction and the stiffening effect of the SiO$_2$ networks. Consequently, 20 wt% TEOS content might be the optimum composition for the high elongation of the P(VDF–TFE)–SiO$_2$ hybrids.

4. Conclusions

By preparing and investigating P(VDF–TFE)–SiO$_2$ hybrid films with various TEOS contents, the following conclusions could be drawn. Transparent P(VDF–TFE)–SiO$_2$
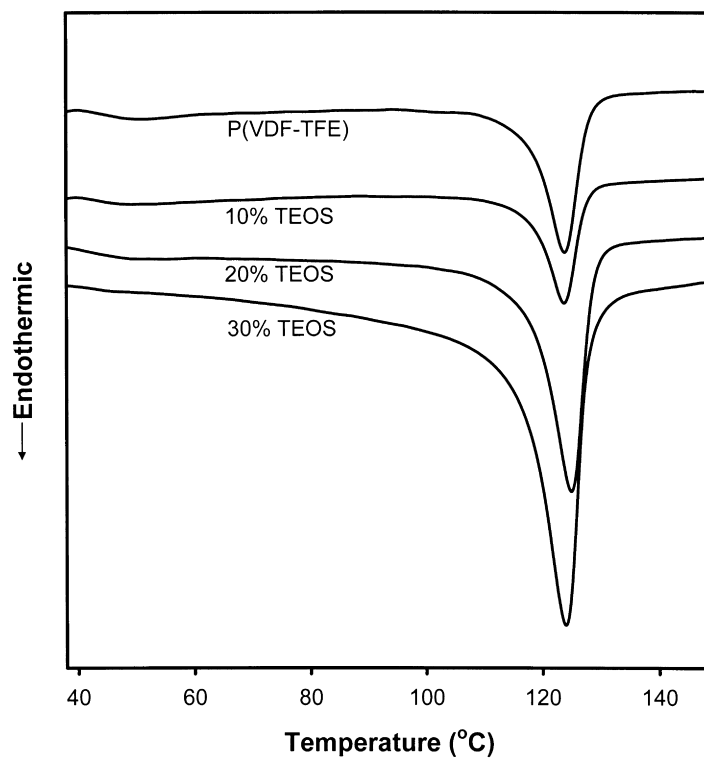
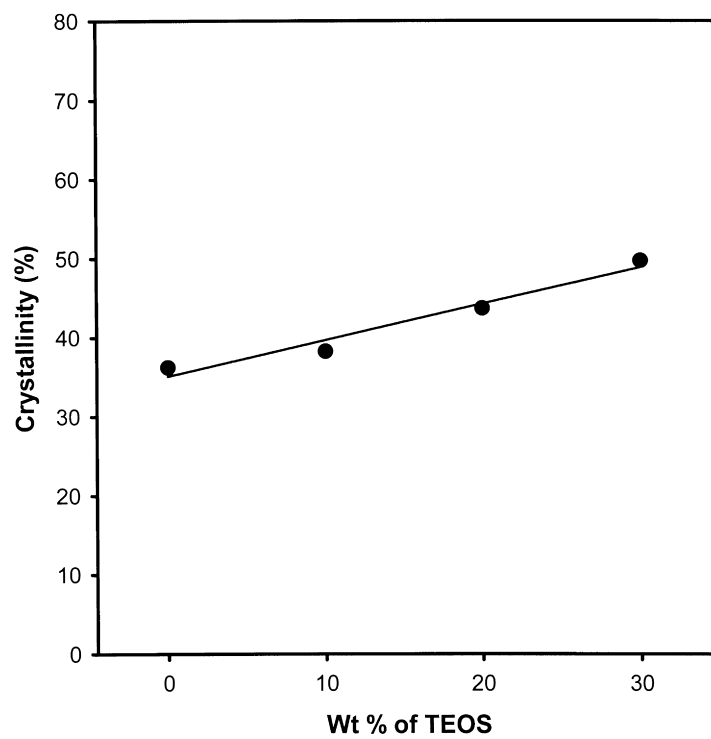Fig. 5. DSC thermograms of pure P(VDF–TFE) and P(VDF–TFE)–SiO$_2$ hybrid films.

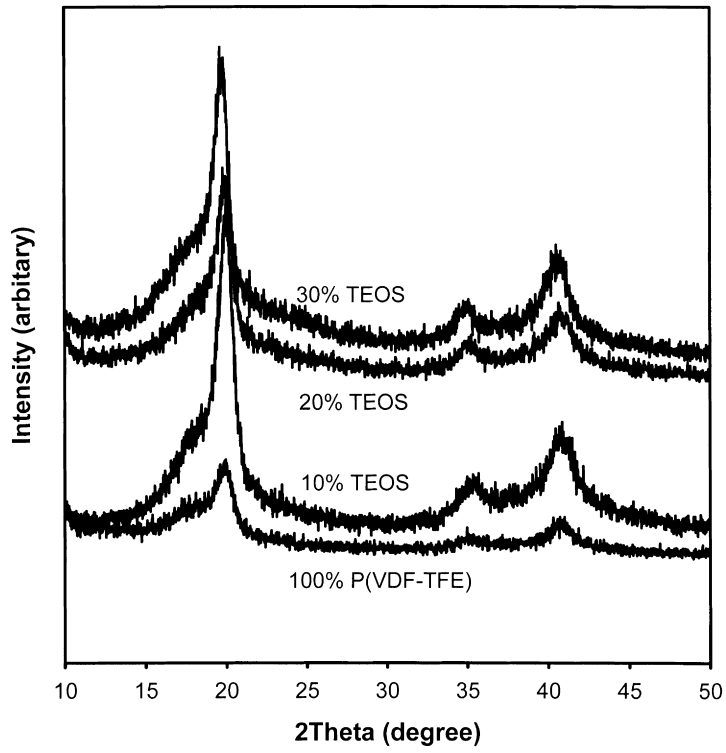Fig. 6. Effect of wt% of TEOS on the crystallinity of P(VDF-TFE)–SiO$_2$ hybrid films.

Fig. 7. X-ray diffractograms of pure P(VDF-TFE) and P(VDF-TFE)–SiO$_2$ hybrid films.
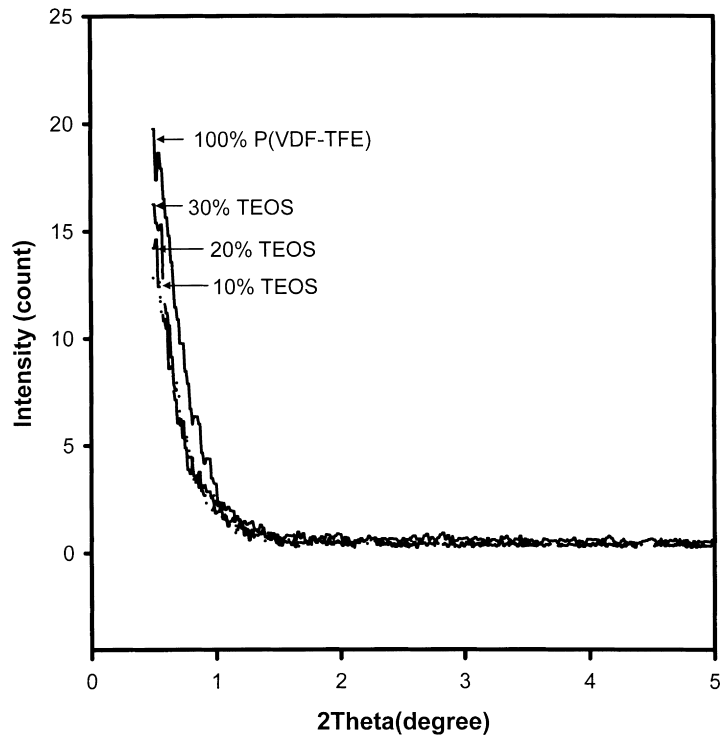

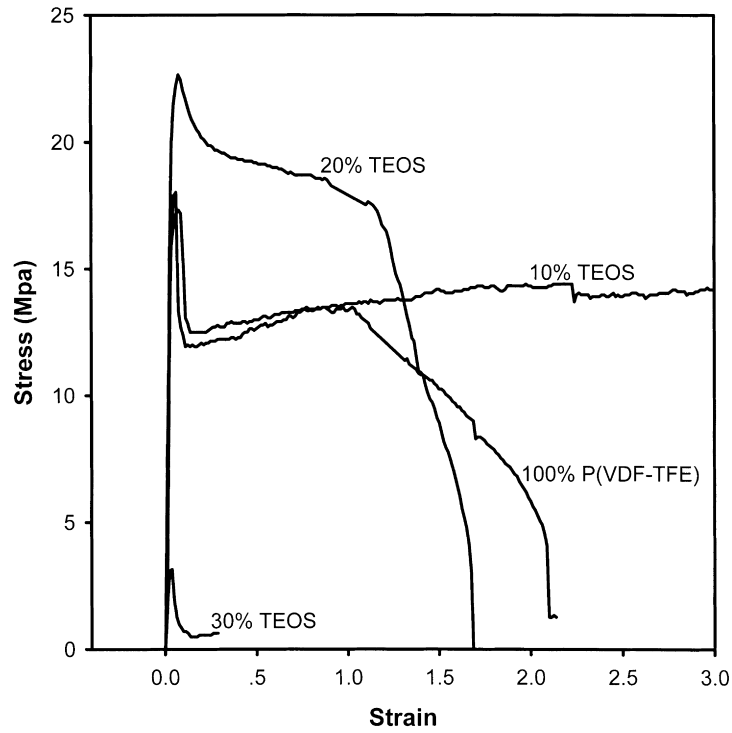Fig. 8. SAXS curves of pure P(VDF-TFE) and P(VDF-TFE)–SiO$_2$ hybrid films.

Fig. 9. Stress–strain curves of pure P(VDF-TFE) and P(VDF-TFE)–SiO$_2$ hybrid films.

hybrid films could be obtained at TEOS contents up to 20 wt%. The presence of SiO$_2$ networks had a favorable effect on the crystallinity of P(VDF–TFE) in hybrids, which in turn played a role as a kind of nucleating agent. All the hybrid samples had a crystal structure of β-phase P(–TFE) in X-ray diffraction measurements. The yield strength, yield strain, and tensile modulus of samples increased with increasing TEOS content up to
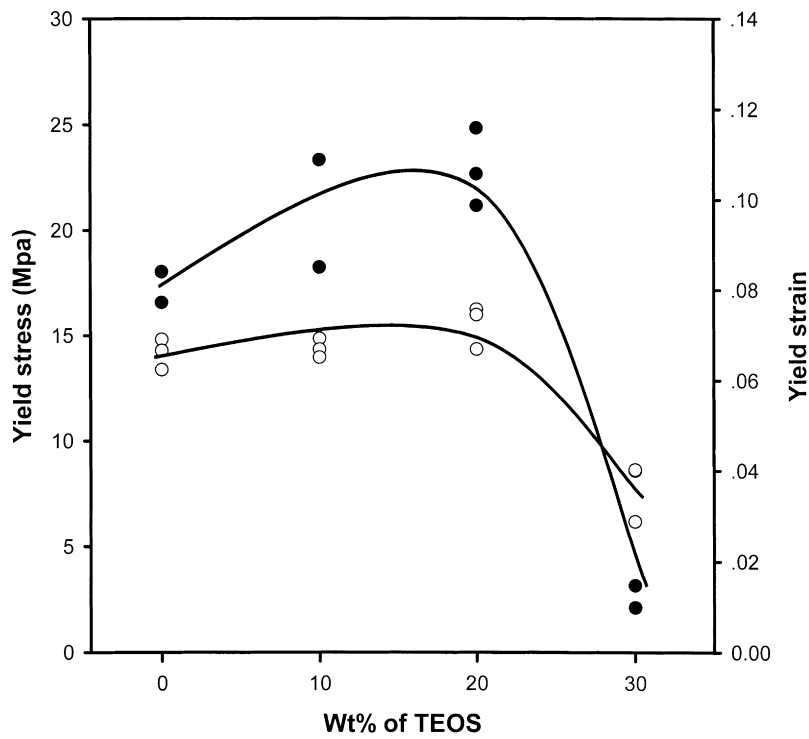

Fig. 10. Effect of wt% of TEOS on the yield stress(●) and yield strain(○) of P(VDF-TFE)–SiO$_2$ hybrid films.
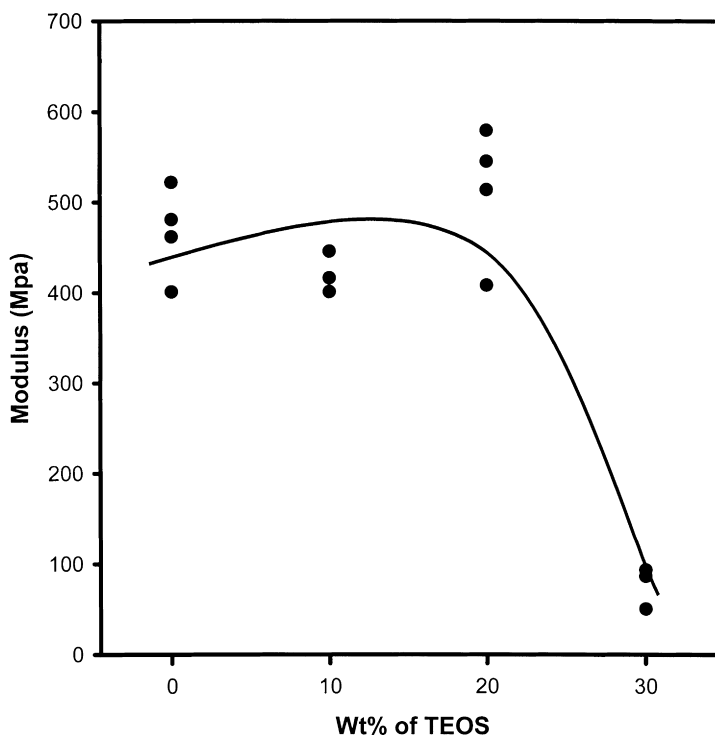
Fig. 11. Effect of wt% of TEOS on the tensile modulus of P(VDF-TFE)–SiO$_2$ hybrid films.

20 wt%, but, decreased abruptly at 30 wt% TEOS. It was interesting that the breaking elongation of samples was the highest at 20 wt% TEOS, which was two times higher than that of pure P(VDF–TFE) film. Conse- quently, via a sol–gel process, transparent hybrid films could be obtained without any loss in both crystallinity of P(VDF–TFE) and mechanical properties via a sol– gel process.
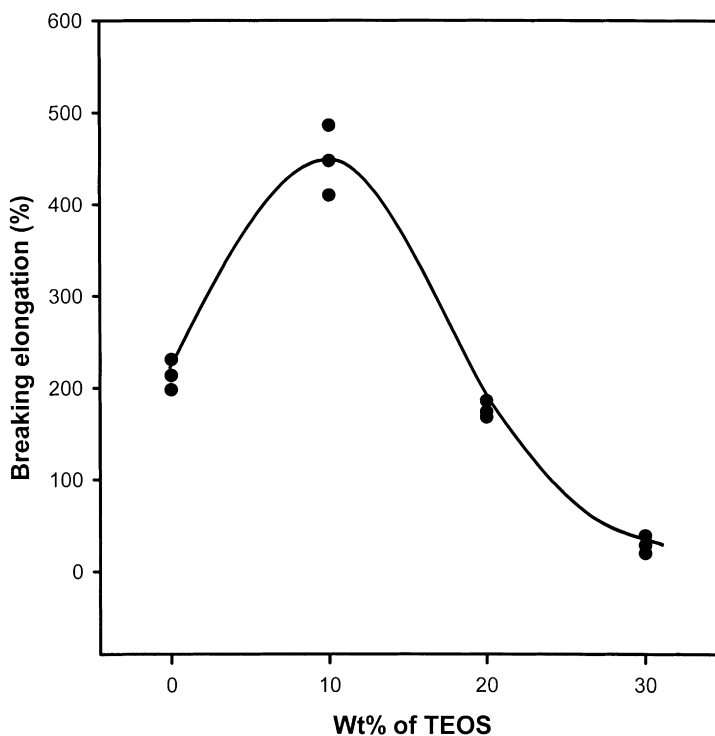

Fig. 12. Effect of wt% of TEOS on the breaking elongation of P(VDF-TFE)–SiO$_2$ hybrid films.

Acknowledgements

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