Effect of Silica and Silane Coupling Agent on Mechanical Properties and Failure Modes of Blends of Plasticized Poly (Vinyl Chloride) and Copolyester Thermoplastic Elastomer

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Mechanical properties and failure modes of blends of plasticized poly (vinyl chloride) and copolyester thermoplastic elastomer have been studied with special reference to the effect of blend ratio, addition of silica filler and coupling agent. Incorporation of silica filler increases the hardness, modulus and tear strength of the blends. Tensile strength, elongation at break, impact strength and tensile set decrease with the addition of silica filler. Addition of small amount of coupling agent (1.5 phr) along with the filler reduces the viscosity of the system. This enables economic process-ability. Moreover, the coupling agent marginally increases the physical properties such as tear resistance, tensile strength, elongation at break and impact strength of the filled systems. The effect of silica on the crystallinity of the samples has been investigated by X-ray diffraction studies. In order to study the mechanism of failure, tensile and tear failure surfaces have been examined by scanning electron microscopy and it was found that the fractographs depend on the type of failure, blend ratio, presence of filler and coupling agent.

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INTRODUCTION

Thermoplastic elastomers are the class of polymeric materials which possess the elastomeric properties of rubber as well as the process-ability characteristics of thermoplastic. These materials can be

   i) polymers with stereo-regular structure and controlled extent of crystallinity

   ii) block copolymers with a hard thermoplastic segment and a soft rubbery segment

   iii) blends of rubbers and plastics.[1–6]

The copolyester elastomer (Hytrel 40 D) is reported[7] to have the thermoplastic rubbery nature due to its two phase domain structure with a crystalline phase serving as thermally reversible crosslinks and an amorphous phase contributing to the elastomeric character.

   Several studies have been reported[8–10] on blending commercial thermoplastic elastomers with different types of polymers so as to get optimum balance of physical and processing properties. Blends of hytrel with PVC have gained a lot of interest recently. The dynamic mechanical properties of hytrel-rigid PVC blends have been investigated by Hourston *et al.*[11] and Nishi *et al.*[12] In our earlier studies,[13–16] we have reported on the rheology, morphology, and mechanical properties and radiation resistance of plasticized PVC-hytrel blends. Correlation between morphology and properties has also been studied.[16]

   Fillers are generally incorporated in rubber compounds for reinforcement as well as for reducing the cost. In thermoplastic elastomer blends, fillers are mainly used to optimise processing characteristics, physical properties and economic factors. Since hytrel-PVC blends are used in a variety of applications in engineering and mechanical fields, the use of fillers are important to reduce the shrinkage and to increase the modulus and hardness. It has been reported[17–20] that addition of small amount of coupling agent enhances the polymer–filler interaction leading to better physical and processing properties. This paper reports the results of the studies on the effect of precipitated silica and (triethoxy silyl propyl) tetrasulphide (abbreviated as Si-69) coupling agent on the mechanical properties of blends of plasticized poly (vinyl chloride) (abbre-

viated as PVC) and copolyester thermoplastic elastomer (abbreviated as Hytrel 40 D). Failure modes of the blends has been studied by examining the fracture surfaces by scanning electron microscopy. Earlier studies indicated that useful information on failure mechanism could be obtained by scanning electron microscopic examination of the failure surfaces.[21-25]

EXPERIMENTAL

Materials used

Hytrel: Hytrel sample (grade 4055) was supplied as gift by E.I. Du Pont de Nemours and Company, U.S.A. The product is a random block copolymer of crystallizable tetramethylene terephthalate (4-GT) which forms the hard segments and poly (tetramethylene ether) glycol terephthalate (PTMEG/T) which comprises the soft segments.

PVC compound: The PVC compound was obtained as gift from the National Organic Chemical Industries, Bombay. It contains the following ingredients:-

Suspension grade PVC	—	100 (phr)
Dioctyl phthalate	—	60 (phr)
Barium-cadmium stabilizer	—	3 (phr)
Processing aid	—	1 (phr)

The compound, as prepared by the manufacturer, was used. The characterization data for both polymers are shown in Table I.

TABLE I

Characterization data for PVC and Hytrel samples used in blend preparation

Polymer	Density (g/cc)	Number average molecular weight (Mñ)	Molecular weight distribution (Mw̄/Mñ)
Hytrel 40 D	1.17	25 000–30 000	—
PVC	1.20	64 000	3

Precipitated silica: Precipitated silica (vulcasil-S) was obtained from Bata India Limited, Calcutta.

Coupling agent: Coupling agent (triethoxy silyl propyl) tetrasulphide was supplied by Degussa AG, Federal Republic of Germany.

Preparation of the blends

The formulations of the mixes used are given in Table II. For example, the mix H_{50}^s indicate 50:50, hytrel:PVC blend containing 30 phr silica and H_{50}^{sc} indicates the same composition along with the coupling agent. The corresponding unfilled blend is represented by H_{50}. The mixes were prepared in a Brabender Plasti-corder PLE-330 using a cam-type mixer with a rotor speed of 80 rpm and the mixer chamber temperature set at 180°C. In preparing the mixes, hytrel was added first, followed by PVC, silica and coupling agent. The ingredients were allowed to mix for 6 minutes. The mix was then taken out and sheeted out through a laboratory mill at 2 mm nip setting. The sheeted out stock was again mixed in the Plasti-corder at 180°C for one minute and then finally sheeted out in the mill so as to get uniform dispersion of the ingredients. The sheeted out material was compression moulded at 200°C for three minutes in specially designed moulds so that the mould with the sample inside could be cooled immediately after the moulding time keeping the sample still under compression.

Physical testing of the samples

Samples for tensile, tear, set and impact tests were punched along the mill grain direction from the moulded sheets of 15 cm × 15 cm × 0.2 cm size. The tensile testing of the samples was done at $25 \pm 2°C$ according to ASTM D 412-80 test method using dumb-bell shaped test pieces at a cross head speed of 500 mm/minute using Instron Universal Testing Machine (model 1195). The tear strength of the samples was determined according to ASTM D 624-81 test method using unnicked 90° angle test pieces. The tear test was carried out at the same conditions of temperature and crosshead speed as in the case of tensile testing. The energy at rupure in tear failure was

TABLE II

Formulations of the Mixes (Compositions are in parts per 100 parts of rubber by wt., phr)

					Mix No.[a]					
Ingredient	H_{100}^s	H_{100}^{sc}	H_{75}^s	H_{75}^{sc}	H_{50}^s	H_{50}^{sc}	H_{25}^s	H_{25}^{sc}	H_{0}^s	H_{0}^{sc}
Hytrel 40 D	100	100	75	75	50	50	25	25	—	—
PVC	—	—	25	25	50	50	75	75	100	100
Silica	30	30	30	30	30	30	30	30	30	30
Coupling agent	—	1.5	—	1.5	—	1.5	—	1.5	—	1.5

[a] The unfilled mixes in each series are represented by H_{100}, H_{75}, H_{50}, H_{25} and H_0 which contain 100, 75, 50, 25 and 0 weight percent of hytrel respectively.

calculated by the following equation.[26]

$$E = \frac{X \times L \times S}{10\,000}$$

where, E = energy in kg mm
$\quad\quad L$ = full scale load in kg.
$\quad\quad S$ = rate of sample extension in mm/min.
$\quad\quad X$ = integrator reading from Instron Testing Machine.

The hardness of the sample was measured and expressed in shore D units. The tensile set after failure was measured according to ASTM D 412-80. The tensile impact strength of the samples was determined according to DIN 53448 test method at $25 \pm 2°C$ using Ceast 6545/000 model Impact Tester. The energy required to break a test specimen was delivered by a single swing of a calibrated pendulum of the machine. The pendulum used could deliver a maximum energy of 25 Joules and the speed of travel was $3.7\,\text{m}\,\text{sec}^{-1}$.

X-ray diffraction studies

In order to study the effect of silica on the crystallinity of the samples, X-ray diffraction diagrams of both filled and unfilled samples were recorded with a Dron X-ray diffractometer using Zr-filltered molybdinum $K\alpha$ radiation.

Scanning electron microscopy (SEM) studies

The tensile and tear failure surfaces of H_0^s, H_{50}^s, H_{50}^{sc}, and H_{100}^s were examined by Philips 500 model scanning electron microscope. For comparison, the failure surfaces of corresponding unfilled samples (H_0, H_{50} and H_{100}) were also examined. The test samples for these observations were carefully cut out from the failed test pieces without touching the surfaces and then sputter coated with gold within 24 hrs of testing. The photomicrographs were taken along the direction of fracture propagation. The tilt was adjusted to zero degree in all cases. Figure 1 shows the details of the test specimen, failure surface and scan area of the tensile and tear samples.
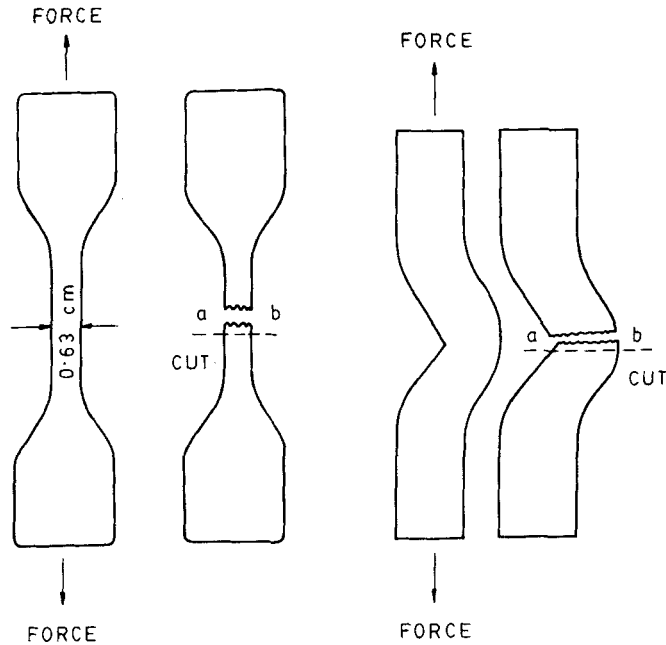
FIGURE 1 Samples for tensile and tear tests showing fracture surface and scan areas (a–b).

RESULTS AND DISCUSSION

Processing characteristics

The processing characteristics of the blends have been studied from Brabender Plastograph (Torque-Time Plot) given in Figure 2. It can be observed that in all cases the mixing torque falls rapidly upto about 3 min. of time and then levels off to give uniform values at the end of the mixing cycle indicating good level of mixing of the ingredients. Addition of silica filler increases the mixing torque and the uniform value of torque for filled samples is about three times that for unfilled samples. This is attributed to the increase in viscosity of the system. Similar to the unfilled mixes, the filled mixes also show higher viscosity at higher proportions of hytrel. Our
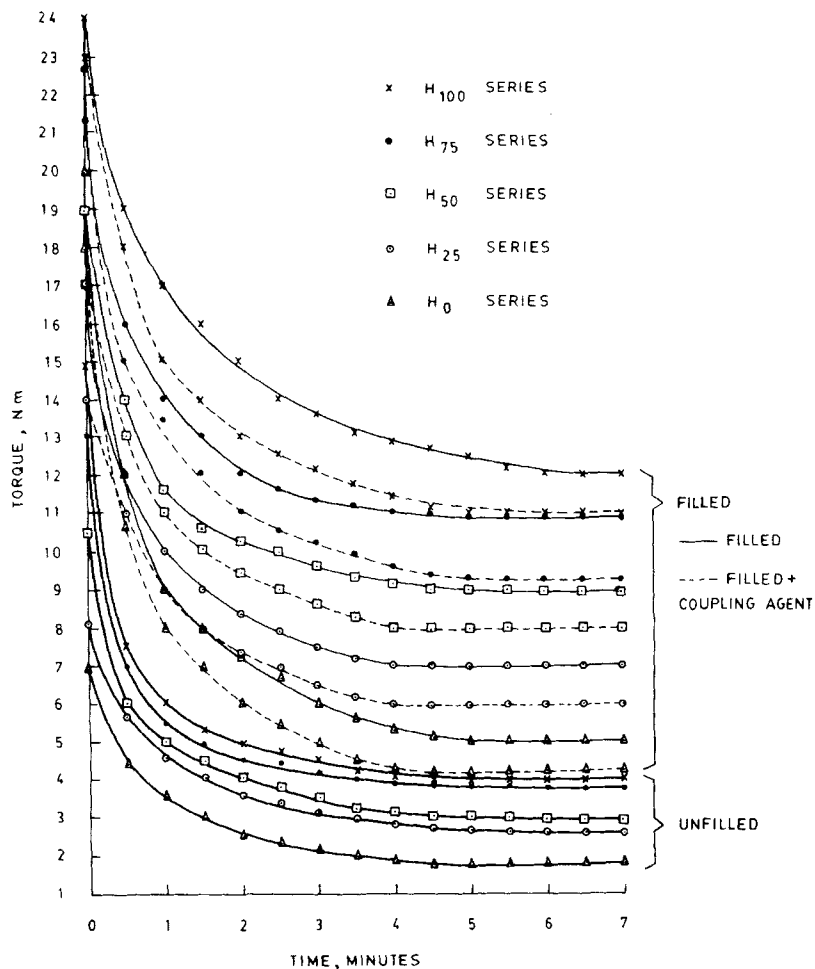
FIGURE 2 Plastographs showing the effect of silica and coupling agent on the viscosity of the mixes.

earlier studies[13] on the rheological behaviour of the system also indicated the increase of viscosity of the blends with increase of hytrel content. It can also be observed that addition of coupling agent lowers the mixing torque of the filled mixes due to the reduction in the viscosity of the system. The effect of coupling agent on reducing the viscosity of filled polymer composites has been

studied by many authors.[18–20] The decrease in viscosity is attributed to the lowering of the surface energy of the silica filler by the addition of coupling agent. Correspondingly, there occurs a reduction in agglomeration of silica particles and improvement in particle distribution leading to a decrease in the viscosity of the system.[19] Figure 2a shows the effect of weight percent of hytrel on the equilibrium stock temperature at the end of the mixing cycle. It can be seen that addition of silica filler increases the equilibrium mixing temperature. This is an expected trend in most of the filled composites. It can also be observed that in filled systems, the mixing temperature increases with the increasing proportion of the hytrel phase. This indicates that interaction of silica with the hytrel is more than PVC. Addition of coupling agent has no significant effect on the mixing temperature.

Effect of silica on the crystallinity of the blends

Figure 3 shows the X-ray diffraction diagrams of both filled as well as unfilled samples. It can be observed that Hytrel (H_{100}) shows maximum peak height indicating its crystalline nature. On decreasing the proportion of hytrel the peak height gradually decreases
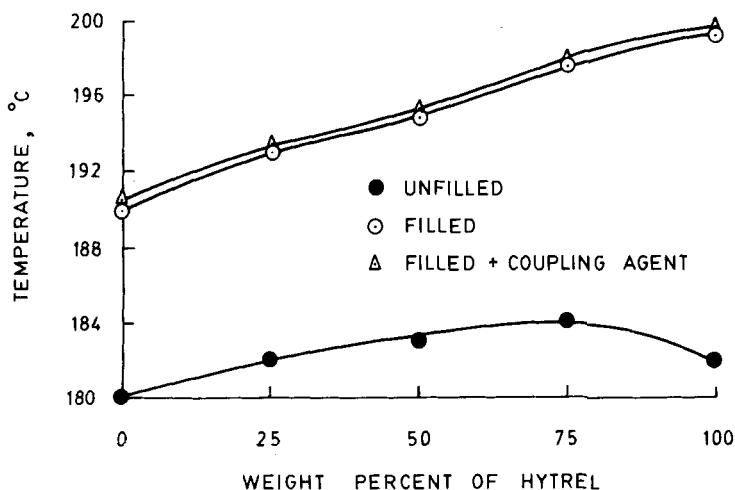

FIGURE 2a Effect of weight percentage of hytrel on equilibrium stock temperature.
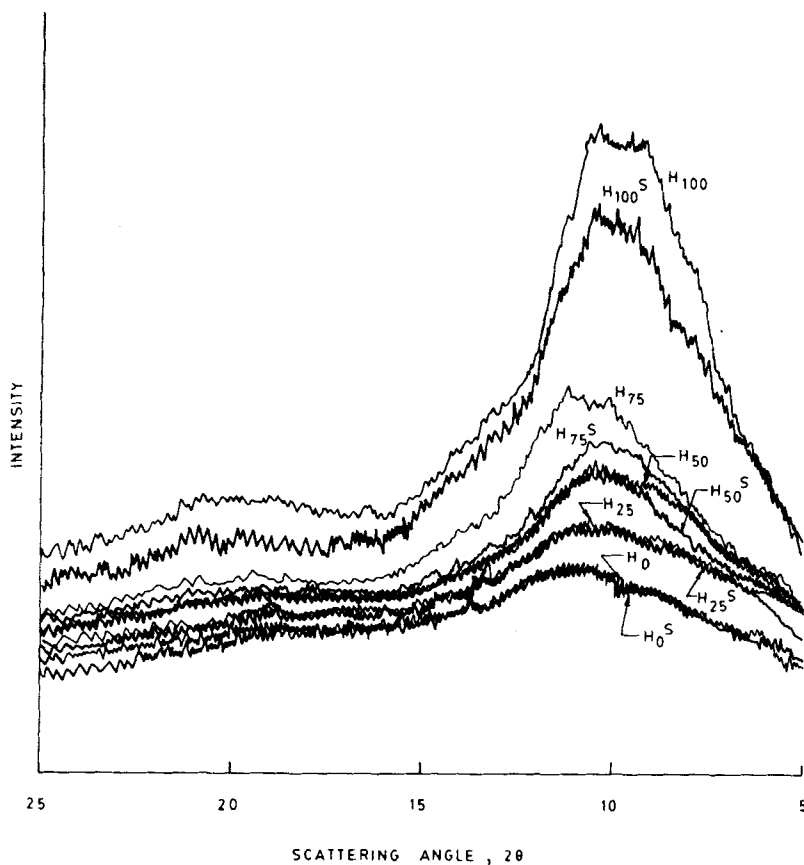
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FIGURE 3   X-ray diffraction diagram of both filled and unfilled samples.

showing the tendency towards the amorphous state. Addition of silica decreases the crystallinity of the high hytrel content ($\geq 75\%$) samples which is evident from the reduction in peak height. In low hytrel content samples ($\leq 50\%$), no change in peak height is observed on addition of silica. This is because, these blends are more amorphous in nature even in the unfilled state.

Mechanical properties

The results of our earlier studies[16] on hytrel-PVC blends have shown that the properties are dependent on the morphology of the

system, that is, the size, shape and distribution of the hytrel domains in the PVC matrix. It is also found that the hytrel particles have high level of compatibility with PVC phase.

Figure 4 shows the stress-strain curves of the filled samples. It can be seen that systems containing a higher proportion of hytrel ($\geq 75\%$) show high initial modulus with yielding at lower strains ($<100\%$). At higher strains ($>100\%$) they show a gradual increase in stress which is possibly due to the orientation of the hard segments of the hytrel phase in the direction of applied stress.[25] The stress-strain curves of H_{50}^s, H_{25}^s and H_0^s show increase in stress with strain without a definite yield point. Figure 5 shows the change in modulus of the samples with the weight percent of hytrel. The modulus of the filled samples show significant increase as compared to those of the unfilled samples and addition of coupling agent appears to have no influence on the modulus of the filled samples. It
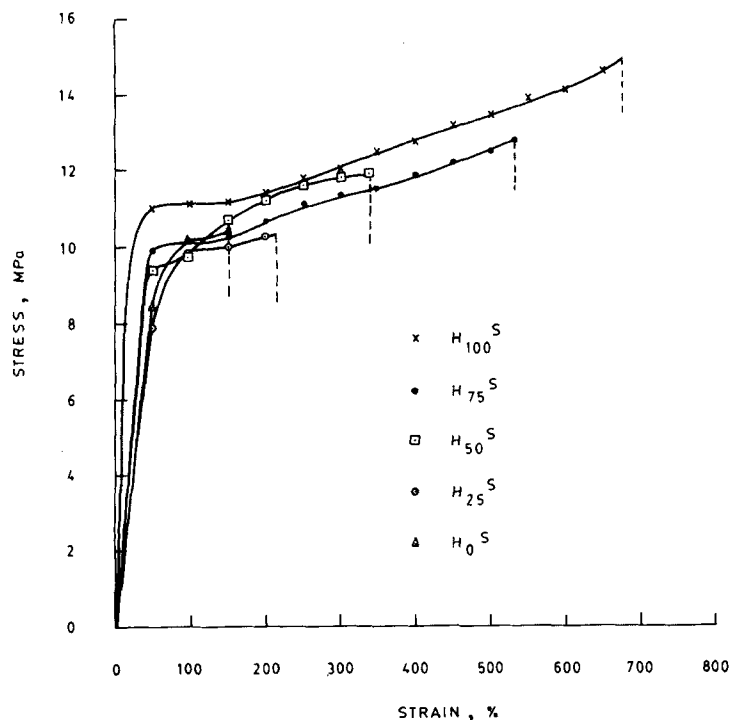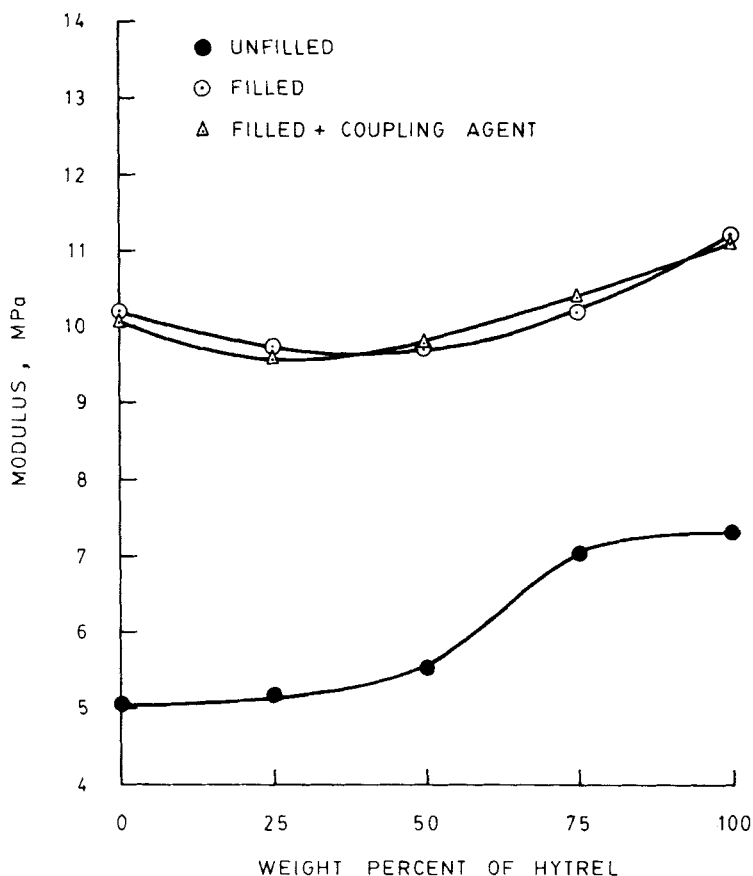

FIGURE 4   Stress-strain curves of the filled samples.

FIGURE 5   Effect of weight percent of hytrel on modulus.

can be see that in the case of filled mixes, the modulus slightly decreases initially followed by a slow rise at higher proportions of hytrel. The overall nature of the curves differ from those of the unfilled samples where modulus increase faster between 50 and 75% of hytrel and then levels off. The variation of tensile strength of the samples with weight percent of hytrel is given in Figure 6. All the curves show a similar trend where tensile strength first decreases upto 25% hytrel and then gradually increases with increase in hytrel content. This is because of the uniform stress distribution at higher
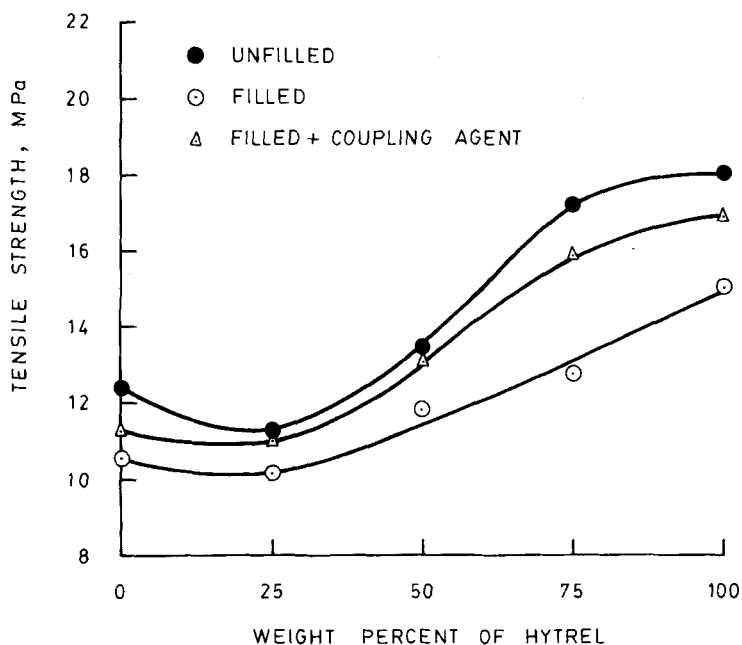
FIGURE 6   Effect of weight percent of hytrel on tensile strength.

hytrel content due to evenly distributed bigger elastomer particles as suggested in our earlier paper.[16] It can also be seen that the addition of filler reduces the tensile strenght of the samples. The decrease is more pronounced in systems containing higher proportions of hytrel. This may be associated with the reduction in crystallinity of the high hytrel content samples due to the presence of filler particles as revealed by X-ray diffraction studies (Figure 3). Addition of coupling agent increases the tensile strength of the filled stock and the maximum increase is at 75% hytrel content. This indicates that coupling agent has higher interaction with hytrel phase and the extent of interaction increased between 50 and 75% hytrel content by passing through a maximum at 75%. Figure 7 shows the elongation at break of the samples against composition. Addition of silica filler causes substantial reduction in elongation at break of the samples. This is an expected change in most of the filled composites where addition of filler reduces the segmental
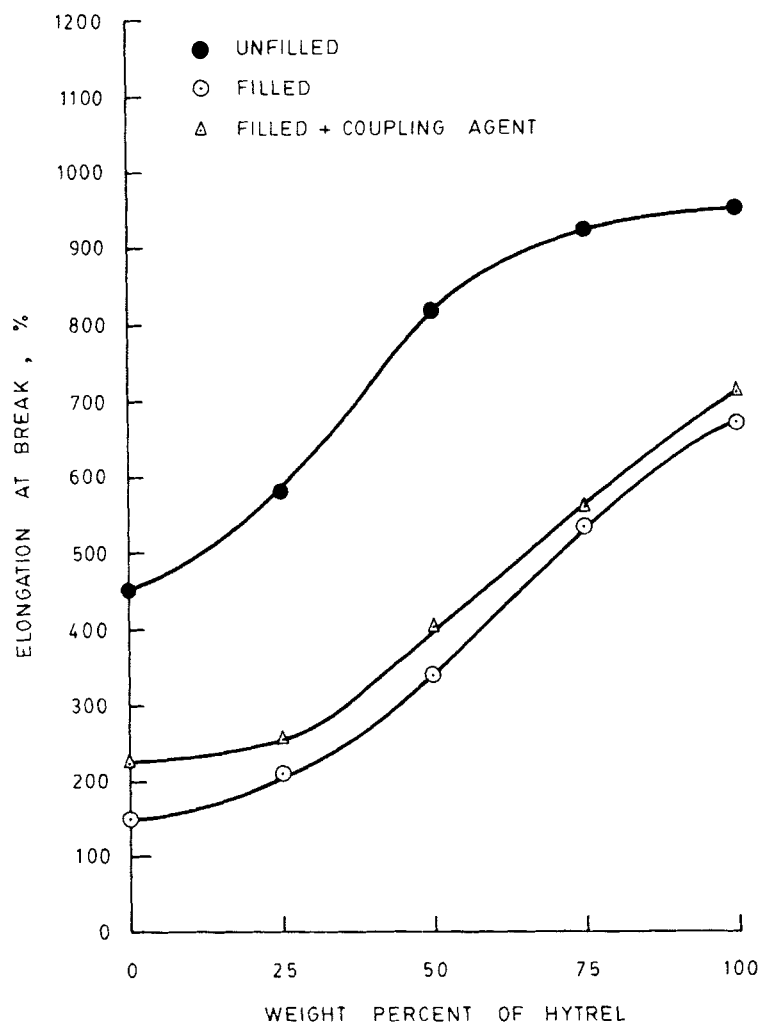
FIGURE 7   Effect of weight percent of hytrel on elongation at break.

mobility of the system. The coupling agent marginally increases the elongation at break of the samples.

The plot of tear strength versus blend composition is given in Figure 8. All the curves show an increasing value of tear strength with the increase of hytrel content. This is due to the fact that in tearing the elastomer phase which bridge the growing crack, stretch to very large strains before failing. Hence large amount of stress dissipation occurs.[27] This increases the tear strength of the matrix. Addition of silica enhances the tear strength of all the blends except
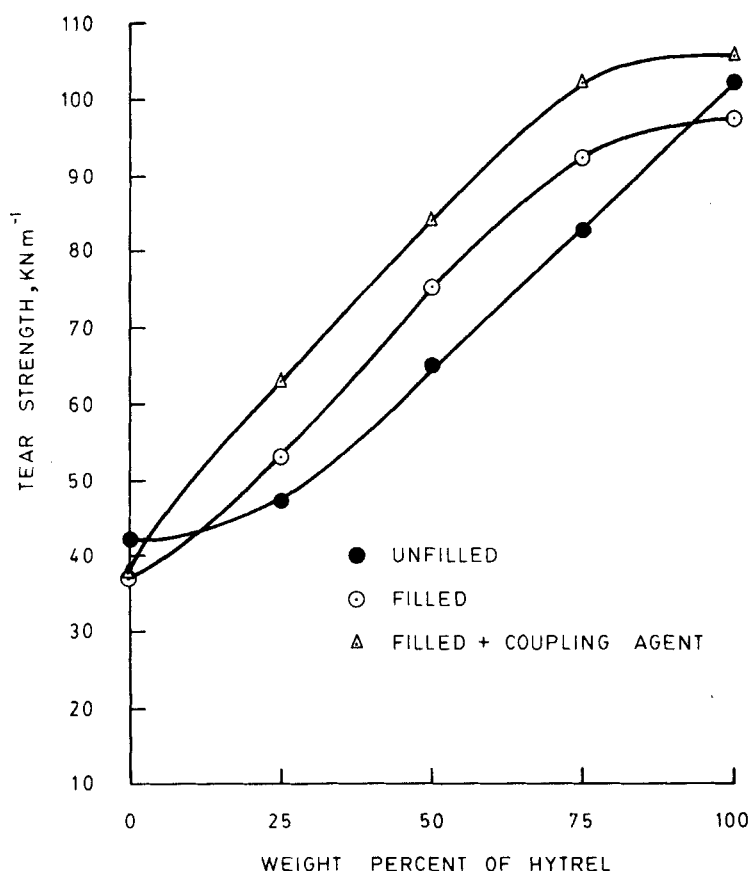
FIGURE 8   Effect of weight percent of hytrel on tear strength.

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the homopolymers. Coupling agent further increases the tear strength of the filled samples. This is associated with the improved interfacial adhesion between filler and polymer matrix. However, PVC does not show any change in tear strength on addition of coupling agent. This may be due to its lower affinity towards coupling agent. Figure 9 shows the influence of filler, coupling agent and percentage hytrel content on the hardness of the samples. Addition of filler increases the hardness of the samples considerably, whereas the coupling agent does not seem to have any effect on it. The increase in hytrel content increases the hardness value. The variation of tensile set after failure of the samples with the weight percent of hytrel is given in Figure 10. Addition of filler
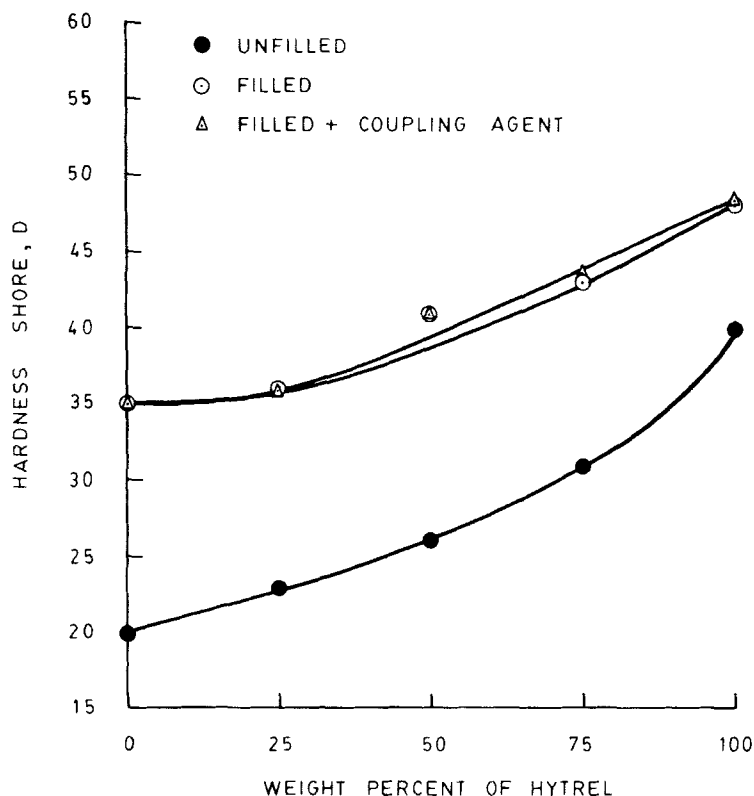
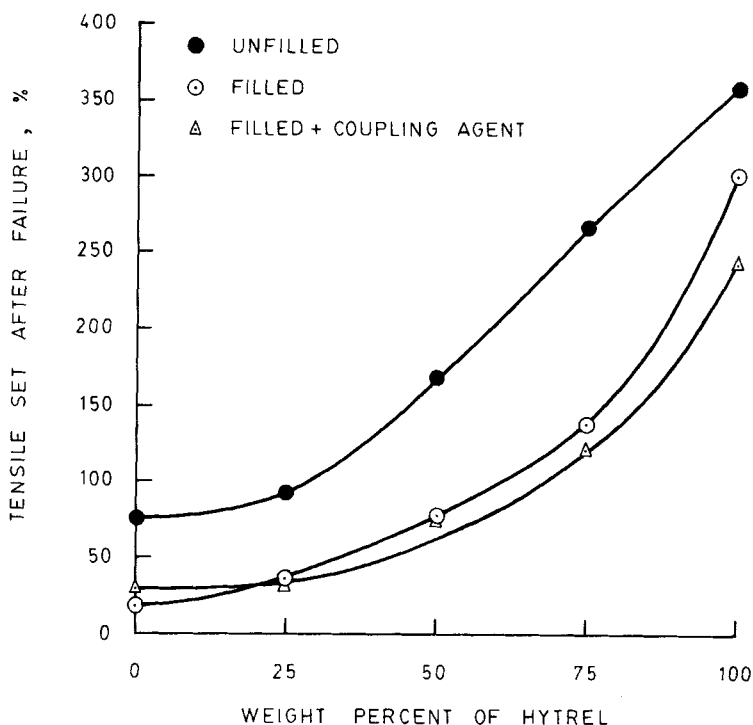FIGURE 9   Effect of weight percent of hytrel on hardness.

FIGURE 10   Effect of weight percent of hytrel on tensile set after failure.

reduces the tensile set after failure. Addition of coupling agent further reduces the set of blends containing higher proportion of hytrel. Impact properties of the blends are shown in Figure 11. All the curves show an increasing response with the increase of hytrel content. This is because as the hytrel content increases, the bigger and more elastomer particles stop the crack propagation by dissipating the applied impact stress.[28] Addition of filler reduces the ductile nature of the polymer matrix and hence the impact strength is decreased. Mixes containing coupling agent show marginal increase in impact strength as compared to the filled stock having no coupling agent. This may be associated with the improved interfacial adhesion between filler and polymer matrix as reported by Han and coworkers.[18]
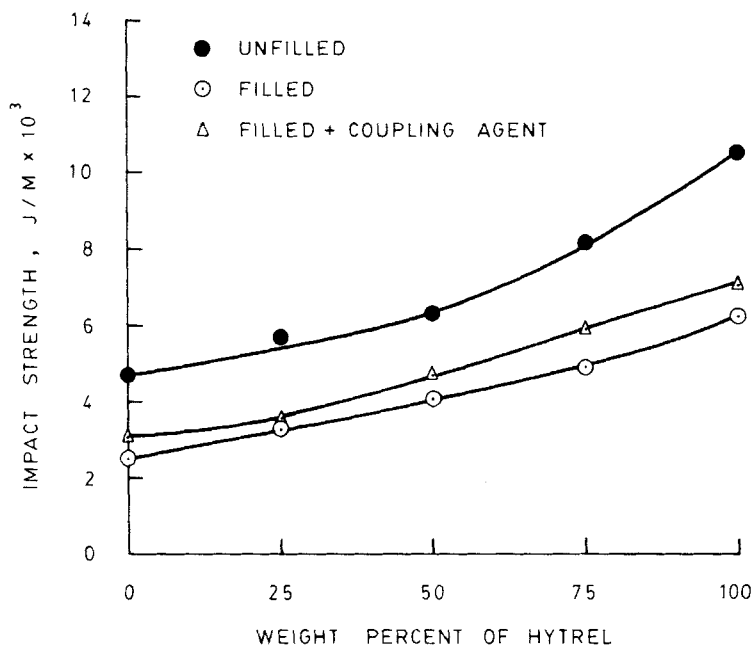
FIGURE 11   Effect of weight percent of hytrel on impact strength.

Figure 12 gives the tearing energy of the samples as a function of blend composition. In all cases the tearing energy increases till the blend composition exceeds 75% of hytrel followed by a slow decrease. Silica filled mixes show lower values of tearing energy at lower proportions of hytrel ($\leq 50\%$) as compared to the corresponding unfilled stocks. But at higher proportions of hytrel they show higher values of tearing energy. Addition of coupling agent enhances the tearing energy of the filled stock due to the improved interfacial adhesion between polymer and filler.

SEM studies

Tensile failure   Figure 13 gives the tensile failure surface of unfilled hytrel (H_{100}). It shows ductile type failure with high extent of plastic deformation as evidenced by the presence of long fibrils ($>10\,\mu$m length) on the fracture surface. Engel *et al.*[29] have suggested that
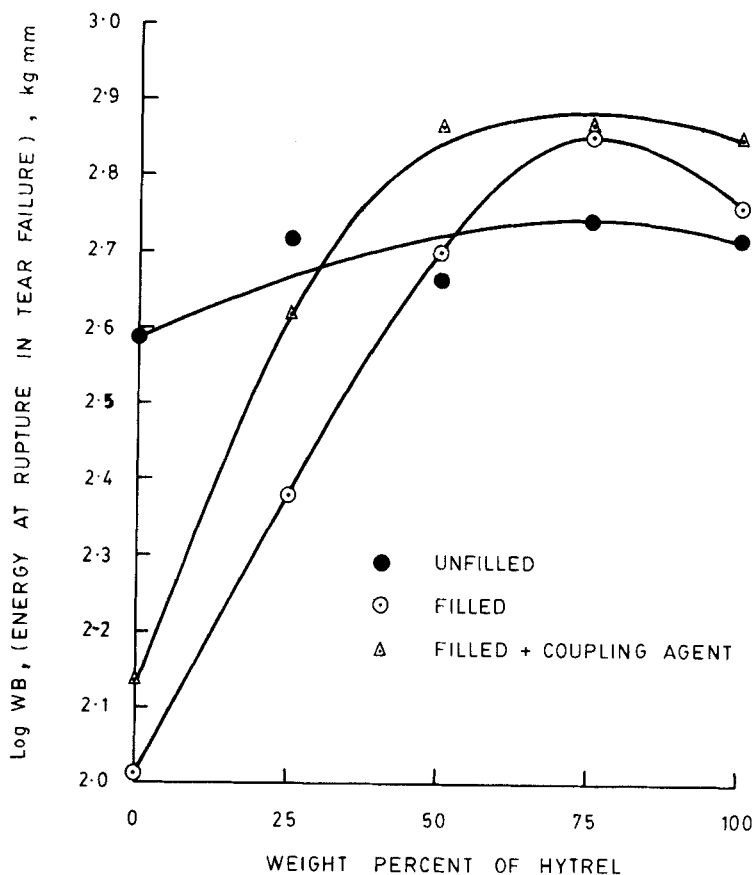
FIGURE 12   Effect of weight percent of hytrel on energy at rupture in tear failure.

fibril formation is a characteristic feature of ductile type failure. Moreover, in the present case the failure surface shows layer separation on the entire surface which is due to the shearing action between the hard and soft segments of the hytrel phase. The silica filled samples (Figure 14) shows no more fibrils on the fracture surface but exhibits fracture paths at different planes. The cavities on the surface are due to the dewetting of the silica particles.

Figure 15 gives the fracture surface of unfilled 50:50 blend (H_{50}). It shows a central stress path and layer separation. Small fibrils also
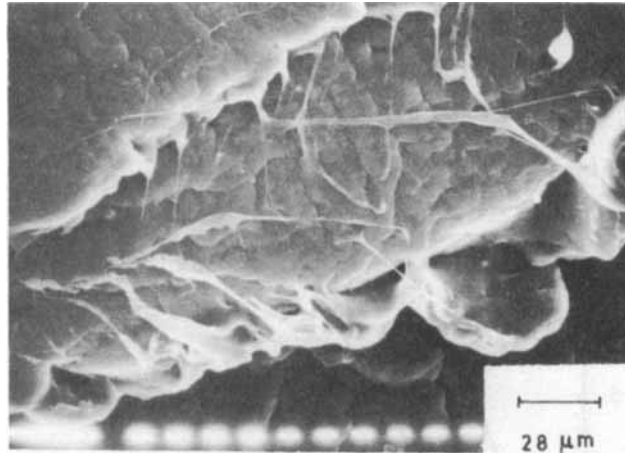
FIGURE 13   Tensile failure surface of H_{100} showing ductile failure.

can be seen on the fracture surface although it is not distinct as observed in unfilled hytrel (Figure 13). The corresponding silica filled composite (H_{50}^s) exhibits a different fracture topography (Figure 16). It shows a number of hollow cavities on the fracture surface. The cavities are associated with the dewetting of the silica
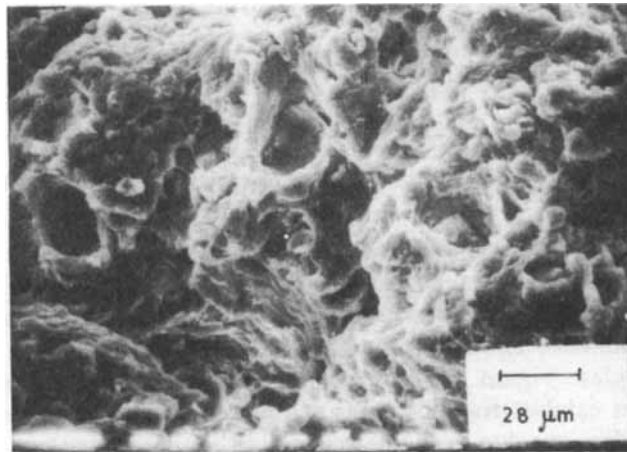

FIGURE 14   Tensile failure surface of H_{100}^s showing fracture paths in different planes.

FIGURE 15 Tensile failure surface of H_{50} showing ductile failure with a central stress path.

particle agglomerates due to poor polymer-filler interfacial adhesion. Addition of coupling agent improves the silica particle distribution and the interfacial adhesion with the polymer matrix. This is evident from the fracture surface of H_{50}^{sc} (Figure 17) which shows better adhesion of the silica particles with the polymer matrix. The fracture surface of unfilled PVC (Figure 18) shows
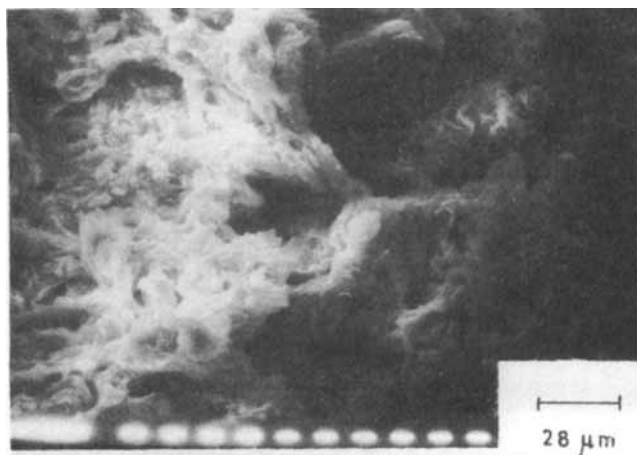

FIGURE 16 Tensile failure surface of H_{50}^{s} showing cavities on the fracture surface.
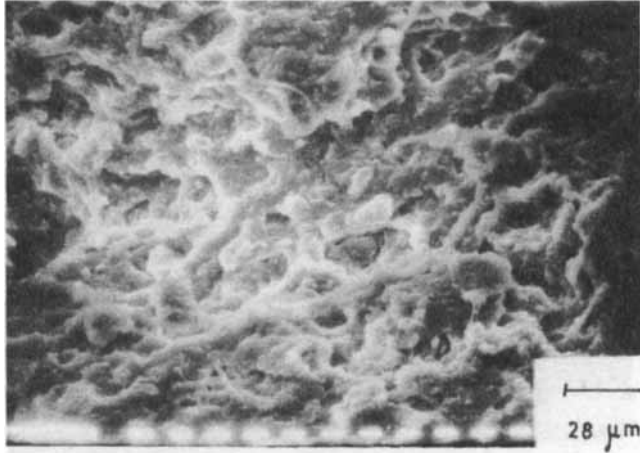
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FIGURE 17   Tensile failure surface of H_{50}^{sc} showing improved adhesion of the silica with the polymer matrix.

discontinuous fracture paths due to the shearing action between the amorphous and semicrystalline segments of the PVC.[25] Careful examination of the failure surface reveals small fibrils on the fracture paths, indicating its ductile nature. The corresponding silica filled mix (H_0^s) shows (Figure 19) poor polymer-filler interaction as evidenced by the presence of cavities and debonded silica particles on the failure surface.
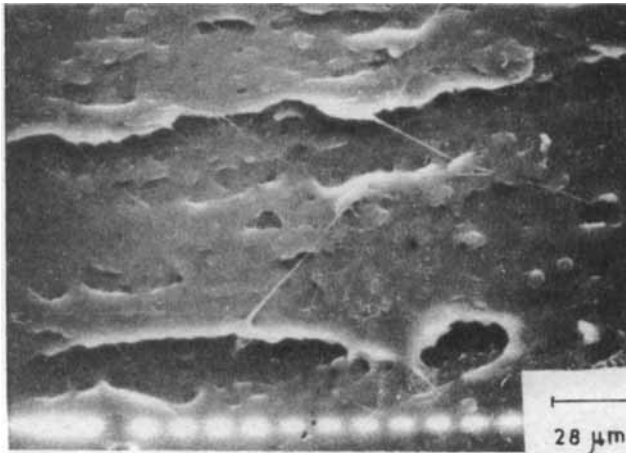

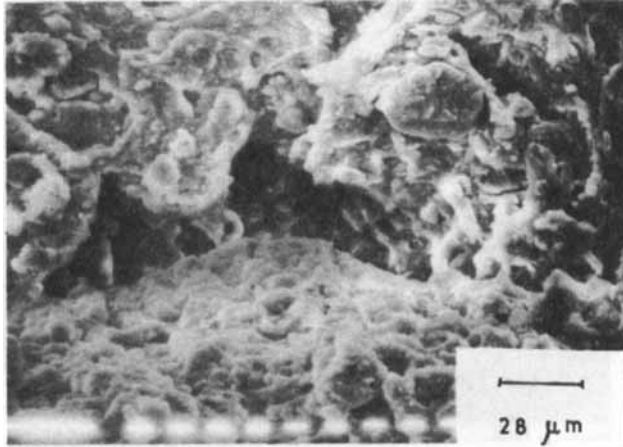FIGURE 18   Tensile failure surface of H_0 showing discontinuous fracture paths.

FIGURE 19   Tensile failure surface of H_0^s showing cavities and debonded silica particles.

Tear failure

The tear failure surface of unfilled hytrel (H_{100}) shows sinusoidal foldings and closely packed striations on the fracture paths (Figure 20). This is associated with the large amount of stress dissipation during the tear failure. The filled composite (H_{100}^s) exhibits a
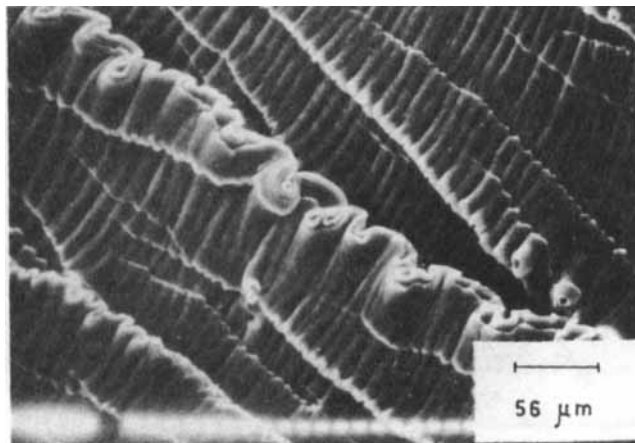

FIGURE 20   Tear failure surface H_{100} showing closely spaced folding and vertical striations.
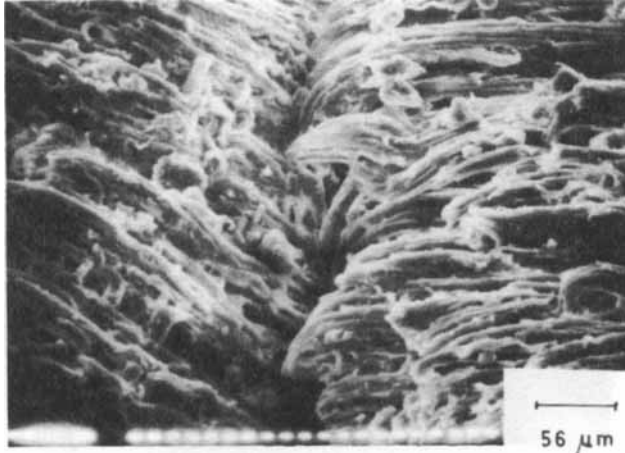
FIGURE 21   Tear failure surface of H_{100}^s showing pulled up matrix with a vertical channel and debonded silica particles.

different fracture topography (Figure 21). It shows pulled up materials projecting outwards with a vertical channel like formation. Unbonded silica particles also can been seen on the fracture surface. The tear failure surface of unfilled 50:50 blend (H_{50}) shows sinusoidal foldings and V-shaped tear paths (Figure 22). The frequency of foldings are less as compared to H_{100}. Addition of
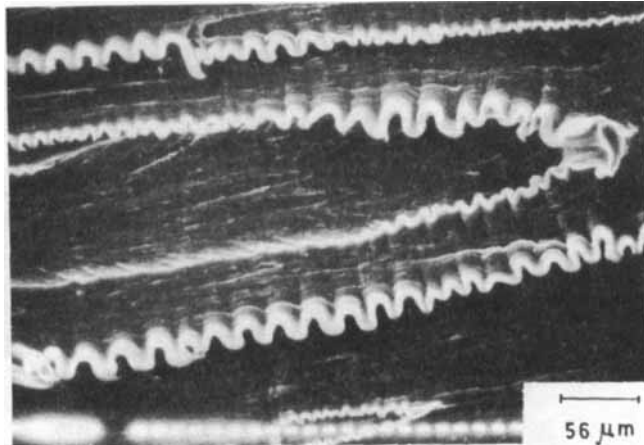

FIGURE 22   Tear failure surface of H_{50} showing sinusoidal tear paths.
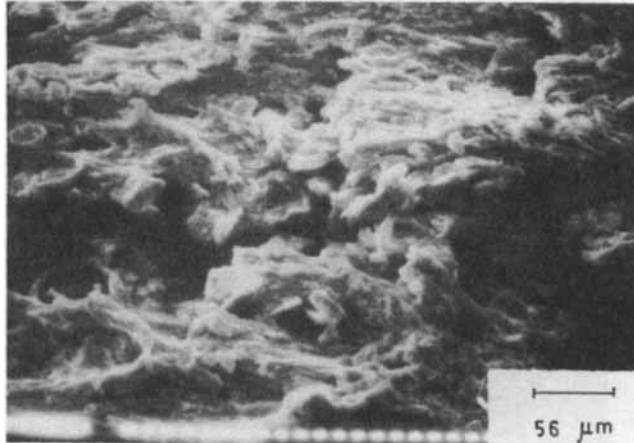
FIGURE 23 Tear failure surface of H_{50}^s showing cavity formation due to the dewetting of the silica particle agglomerates.

silica filler increases the tear strength of the blend which is evident from the tear failure surface of H_{50}^s (Figure 23) which shows a rough fracture mode.[30] Nevertheless, the surface shows cavities due to the dewetting of the filler particles. Sample containing coupling agent (Figure 24) shows no cavity formation due to the improved
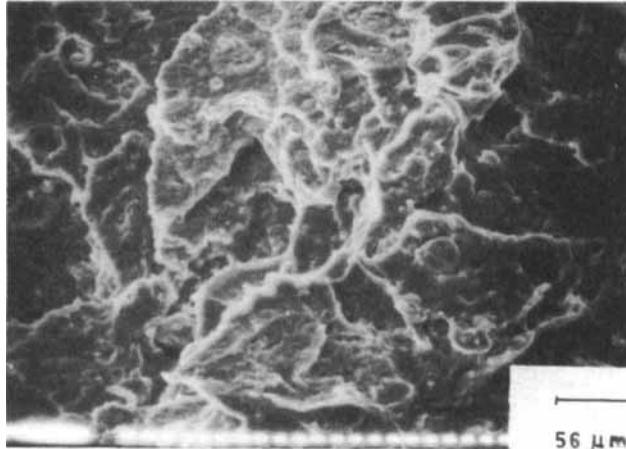

FIGURE 24 Tear failure surface of H_{50}^{sc} showing improved adhesion of silica with the polymer matrix.
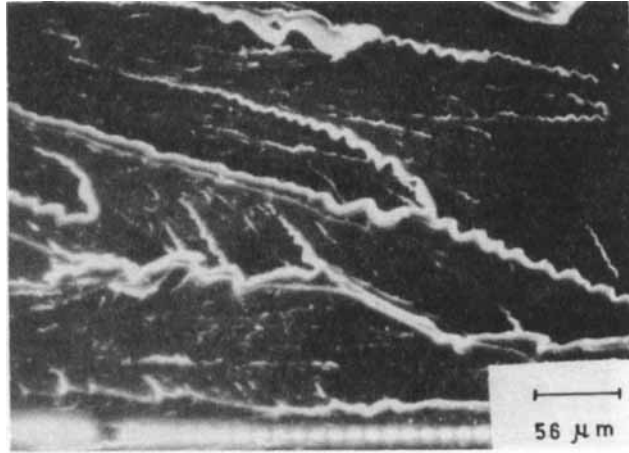
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FIGURE 25   Tear failure surface of H_0 showing wavy tear paths.

adhesion of the silica particles with the matrix. Physical measurements of tear strength also showed higher tear resistance of H_{50}^{sc} as compared to H_{50}^{s}. The failure surface of unfilled PVC (Figure 25) shows sinusoidal tear paths. The foldings are not prominent as observed in high hytrel content samples. Silica filled surface (Figure 26) shows weakly bonded silica particles projecting out on the
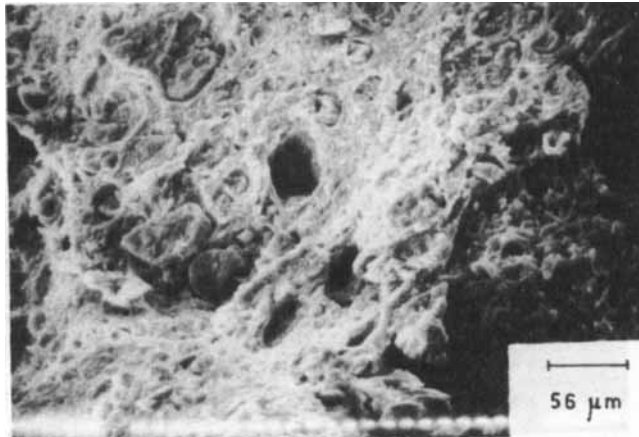

FIGURE 26   Tear failure surface of H_0^s showing debonded silica particles and cavities.

matrix. Formation of cavities due to the dewetting of silica particles also can be observed on the fracture surface.

CONCLUSIONS

Effect of silica and coupling agent on mechanical properties and failure topography of blends of plasticized PVC and copolyester thermoplastic elastomer have been studied. Silica filled blends show increased hardness, modulus, tear strength and set properties at the expense of tensile strength, elongation at break and impact strength. Addition of coupling agent promote interfacial adhesion between polymer and filler leading to an increase in tensile, tear and impact properties of the filled mixes. This effect is found more prominent at higher proportions of hytrel. The viscosity of the filled composites is lowered by the coupling agent so that significant reduction in energy needed for processing are possible. X-ray diffraction studies show that addition of silica reduces the crystallinity of high hytrel content samples. SEM studies on tensile failure surfaces show that addition of silica filler considerably changes the failure topography. The tear failure surfaces indicate characterisic features which could be correlated with the relative tear resistance of the samples. The SEM photomicrographs also reveal the level of adhesion of silica particles with the polymer matrix.

Acknowledgement

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