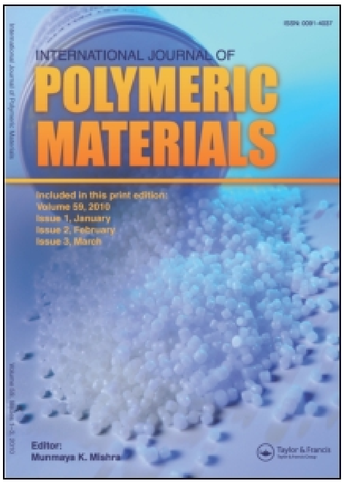

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# Tear and Wear Resistance of Silica Filled Thermoplastic Polypropylene—Natural Rubber Blend

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# Tear and Wear Resistance of Silica Filled Thermoplastic Polypropylene—Natural Rubber Blend

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The tear and wear resistance of silica filled thermoplastic polypropylene-natural rubber blend were found to increase with extent of dynamic crosslinking of the elastomer phase. Addition of silane coupling agent causes improvement in the failure properties of blends containing sulfur and sulfur-dicumyl peroxide [DCP] mixed vulcanizing systems and not in DCP containing blend. Scanning electron photomicrographs of the failure surfaces of the blends throw light on the mode of their failure.

## INTRODUCTION

Thermoplastic elastomers combine the excellent processing characteristics of the thermoplastic materials at higher temperatures and a wide range of physical properties of elastomers at service temperatures.[1–3]. The blends prepared by melt mixing of a crystalline thermoplastic material and an elastomer under high shearing action, have gained considerable attention due to the simple method of preparation and easy attainment of the desired physical properties by varying the blend ratios.[4] It has been further shown that addition of small quantities of crosslinking agent during the mixing operation improves the final properties without affecting the processing behaviour.[5–9] This process is known as dynamic crosslinking. The physical properties of the blend depend on the extent of dynamic crosslinking and on the presence of reinforcing carbon black filler particularly when the blend consists of higher proportion of rubber phase than the plastic phase.[10,11]

One of the major applications of the thermoplastic elastomers is in footwear wherein the use of fine particle silica at lower loadings has been reported to improve the physical properties and reduce the shrinkage of the thermoplastic elastomer blends.[12–13] The use of silane coupling agents in enhancing the physical properties of the silica and clay filled rubber vulcanizates has also been reported.[14–22] In this paper we report the results of our studies on the effects of dynamic crosslinking of the elastomer phase and use of bis [triethoxysilylpropyl] tetrasulfide, abbreviated as Si-69, on the tear and abrasion resistance of silica filled 70:30 natural rubber [NR]:polypropylene [PP] thermoplastic elastomer blend. In order to correlate the observations on strength properties, the failure surfaces of the test samples have been analysed by scanning electron microscopy [SEM].

## EXPERIMENTAL

### Preparation of the blends

Formulations of the mixes used are given in Table I. The blends containing no filler, those containing silica and those containing silica and coupling agent are denoted by the letters $A$, $B$ and $C$ respectively. The suffixes $U$, $D$, $M$ and $S$ denote blends without curing agent and those containing dicumyl peroxide [DCP], mixed cure [DCP and sulfur] and sulfur cure systems respectively. Thus, the blend $C_M$ denotes 70:30 NR:PP blend containing silica and coupling agent and having mixed cure system. Blends of NR and PP were prepared in a Brabender Plasti-corder model PLE 330, using a cam type mixer with a rotor speed of 80 rpm and mixer chamber temperature set at 180°C. PP was melted in the mixer for one minute and then NR was added and the mix was allowed to blend for four minutes. In the case of blends containing silica alone and that with coupling agent, master-batches of the ingredients in NR

TABLE I

Formulations of the blends

| Ingredients | A | B | C |
|---|---|---|---|
| Natural Rubber[a] | 70 | 70 | 70 |
| Polypropylene[b] | 30 | 30 | 30 |
| Silica[c] | — | 14 | 14 |
| Coupling Agent[d] | — | — | 0.70 |
| Curatives[e] | *UDMS* | *UDMS* | *UDMS* |

[a] Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala.

[b] Isotactic polypropylene, Koylene M0030, obtained from Indian Petrochemicals Corporation Limited, Vadodara, Gujarat.

[c] Precipitated Silica, Vulcasil S, obtained from Modi Rubber Limited, Modipuram.

[d] Si-69, Bis (Triethoxysilylpropyl) tetrasulfide, obtained from Modi Rubber Limited, Modipuram.

[e] *U*, Blends without any curative. *D*, Blends containing 1.0 phr 40% dicumyl peroxide, based on rubber phase only (DCP cure). *M*, Blends containing 1.0 phr 40% dicumyl peroxide and zinc oxide 5.0; stearic acid 2.0; CBS 1.0; TMTD 1.25 and sulfur 0.15 phr based on rubber phase only (mixed cure). *S*, Blends containing zinc oxide 5.0; stearic acid 2.0; CBS 2.0; TMTD 2.5 and sulfur 0.30 phr based on rubber phase only (sulfur cure).

were prepared first and then the masterbatch was blended with PP. At the end of five minutes curatives were added and the mixing was continued for three more minutes. The mix was taken out and sheeted through a laboratory mill at 2.00 mm nip setting. The sheeted material 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. In the case of mixed cure system, DCP was added after five minutes and allowed to blend for one minute. All the other ingredients were added after this step. The sheeted out stock 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 sample

Tear strength of the samples was determined as per ASTM D 624-81 test method, using unnicked 90° angle test pieces cut along the

TABLE II

Properties of the blends

| | Uncrosslinked | | | *D C P* Cure | | | Mixed Cure | | | Sulfur Cure | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Parameter | $A_U$ | $B_U$ | $C_U$ | $A_D$ | $B_D$ | $C_D$ | $A_M$ | $B_M$ | $C_M$ | $A_S$ | $B_S$ | $C_S$ |
| Brabender mixing torque, Nm | 10.0 | 9.5 | 9.5 | 16.0 | 19.0 | 17.5 | 18.5 | 18.0 | 21.5 | 22.5 | 32.0 | 32.0 |
| $V_r$ of swollen blend[a] | — | — | — | 0.1203<br>(0.0732) | 0.1166 | 0.1415 | 0.2097<br>(0.1358) | 0.1525 | 0.1874 | 0.2491<br>(0.1717) | 0.2030 | 0.2242 |
| Tear strength, kn/m | 22.1 | 27.2 | 24.0 | 27.2 | 41.4 | 42.4 | 38.0 | 42.2 | 60.6 | 44.4 | 48.8 | 66.0 |
| Abrasion loss, cc/h | 2.263 | 1.806 | 2.113 | 1.823 | 1.531 | 1.805 | 1.602 | 1.510 | 1.465 | 1.410 | 1.375 | 1.233 |

[a] Values in brackets correspond to 100% NR gum vulcanizates.

mill grain direction, at a crosshead speed of 500 mm per minute in Instron Universal Testing Machine [model 1195]. The abrasion test was carried out using Du Pont abrader on samples of dimension 2 cm square, 1 cm thick. The test results obtained are given in Table II. Figure 1 shows the force-tear charts of the silica filled blends with and without coupling agent tested at a crosshead speed of 500 mm per minute and chart speed of 50 mm per minute.

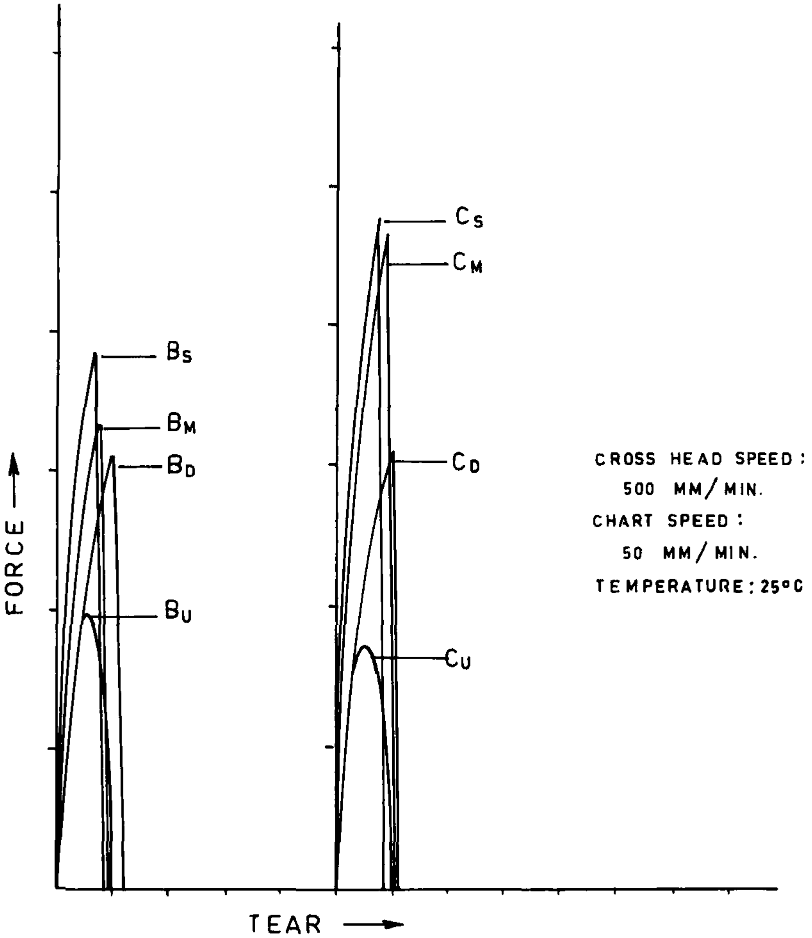

FIGURE 1 Force-tear curves for silica filled blends with and without coupling agent.

## Scanning electron microscopic studies

The SEM observations of the failure surfaces in tear and abrasion tests were made using Philips 500 model scanning electron microscope. The fracture surfaces of the test samples were carefully cut out from one of the failed test pieces without touching the surfaces and then sputter coated with gold within 24 hours of testing. The specimens were stored in a desiccator before and after gold coating until the SEM observations were made. Figure 2 shows the details of the test specimen and scan area of the failed surfaces.

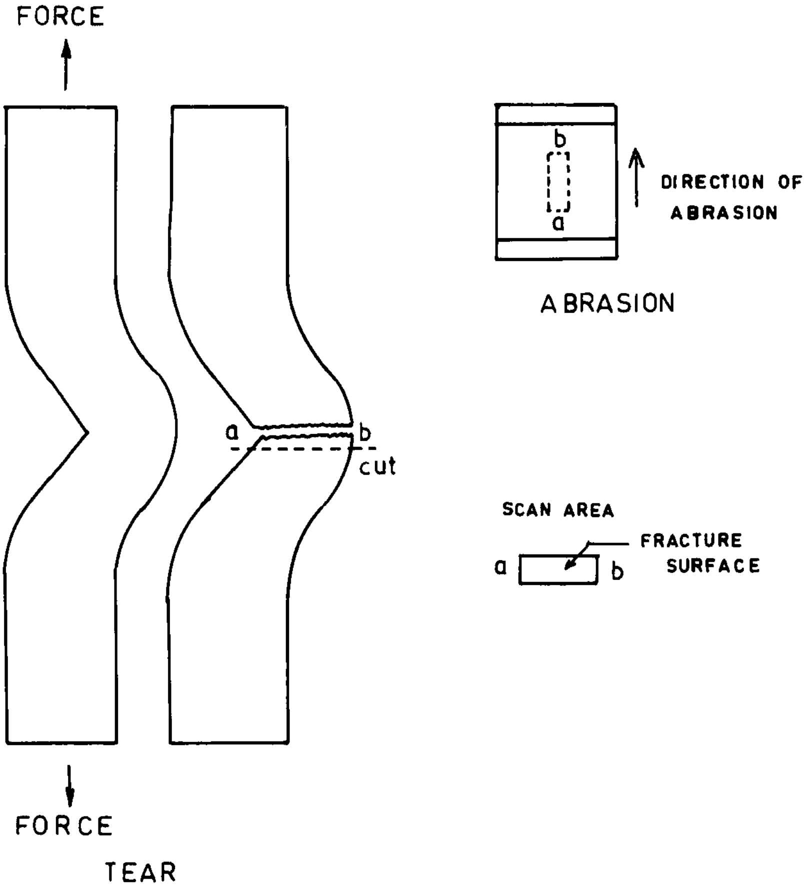

FIGURE 2 Samples for tear and abrasion tests, showing the fracture surface and scan area.

## RESULTS AND DISCUSSION

The physical properties of the thermoplastic elastomer blends depend mainly on factors like continuity of the phase, size of the dispersed particles and extent of dynamic cross-linking of the elastomer phase. At 70:30 NR:PP ratio, both NR and PP form continuous phases leading to an inter-penetrating two-phase system, looking like a sea sponge structure, due to higher proportion of the rubber phase and lower viscosity of the plastic phase.[23] The extent of crosslinking of the elastomer phase in the blends of present investigation was in the order, sulfur cure > mixed > DCP cure, as measured by $V_r$ values [volume fraction of rubber in the solvent swollen sample] of the natural rubber vulcanizates containing the same level of curatives and extent of curing as that in the blend. The $V_r$ values were 0.0732, 0.1358 and 0.1717 respectively for DCP, mixed and sulfur cured rubber vulcanizates and the corresponding values for the blends were 0.1203, 0.2097 and 0.2490 respectively for $A_D$, $A_M$ and $A_S$. The higher $V_r$ value of the blends compared with those of the rubber vulcanizates is due to the restriction imposed by the crystalline PP for swelling. The blends containing silica filler show lower $V_r$ values compared with those of the corresponding unfilled blends [Table II—$B_D < A_D$, $B_M < A_M$, $B_S < A_S$] due to the retarding effect of silica filler on rate of vulcanization of the rubber phase. The silica filled blends containing silane coupling agent show higher $V_r$ values compared with those of the corresponding silica filled blends without coupling agent [$C_D > B_D$, $C_M > B_M$, $C_S > B_S$]. This is due to the interaction of the coupling agent with the reactive groups on the silica filler and thereby reducing the retardation effect of the silica on the vulcanization rate. Similar observations had been reported earlier for silica filled EPDM and NR vulcanizates.[22,28,29] Among the different dynamically crosslinked blends containing silica filler, $B_M$ and $C_M$ which contain mixed cure system have lower Brabender mixing torque values. This shows better processing characteristics of the blends containing mixed cure system.

### Tear strength

The tear strength values of the 70:30 NR:PP blends given in Table II show that dynamic crosslinking of the elastomer phase improves the tear strength of the blends remarkably and that the increase is proportional to the extent of crosslinking. Tear strength is in the order $A_U > A_D > A_M > A_S$. Dynamic crosslinking of the elastomer phase increases the viscosity of the system as seen from the increase in Brabender mixing torque values [Table II]. At higher viscosity, better shearing action during blending leads to finer particle size and more uniform dispersion of the rubber phase in the PP matrix.[24] During tearing, the rubber particles which bridge the growing crack stretch to very large strains before failing. The tearing strain of a rubber particle increases as its size is reduced.[25] Thus the increase in tear strength with extent of crosslinking of the elastomer phase is due to smaller size and higher elongation of the crosslinked particles.

Addition of silica filler improves the tear strength of the blends and the effect is more prominent in uncrosslinked and DCP cured blends. Addition of silane coupling agent further enhances the tear strength of the blends containing mixed and sulfur curing systems. Figure 1 shows that addition of silane coupling agent adversely affects the tear energy of the uncrosslinked blend and does not affect the DCP cured blend, but increases the tear energy of the blends dynamically crosslinked by sulfur and sulfur plus DCP. The role of interfacial wetting and adhesion of the filler to the rubber phase through the coupling agent, in improving the tear strength, is

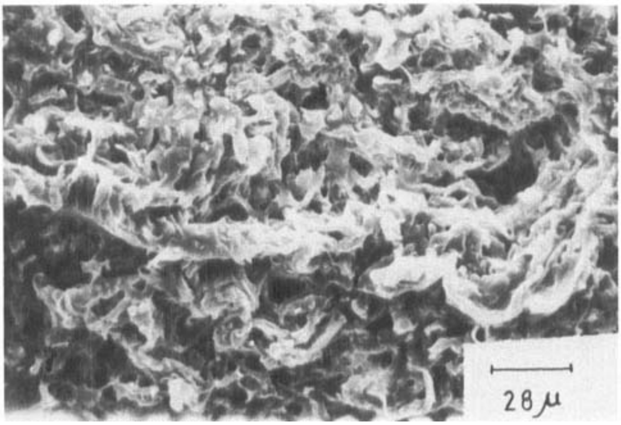

FIGURE 3 Tear fractograph of blend $C_U$—ductile failure, rough surface, with dimples and pores.

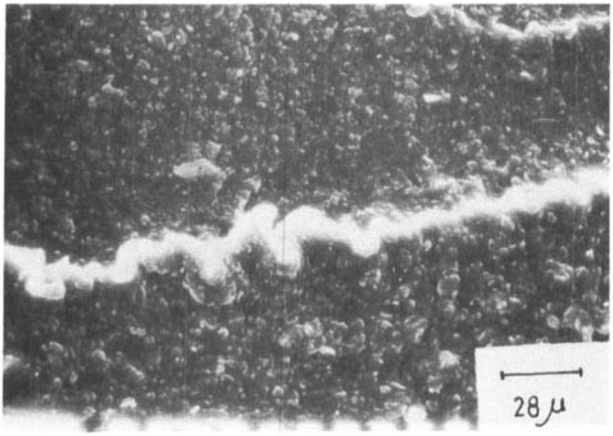

FIGURE 4. Tear fractograph of blend $C_D$—smooth surface and fracture path.

evident from the fact that the increase in tear strength of the DCP cured blend containing coupling agent is negligibly small due to lack of reactivity of the coupling agent in this cure system.[16] The blend without curing agent also shows no improvement in tear strength with the addition of Si-69.

The SEM observations of the tear fracture surfaces of the blends support these views. The tear fractograph of the uncrosslinked blend

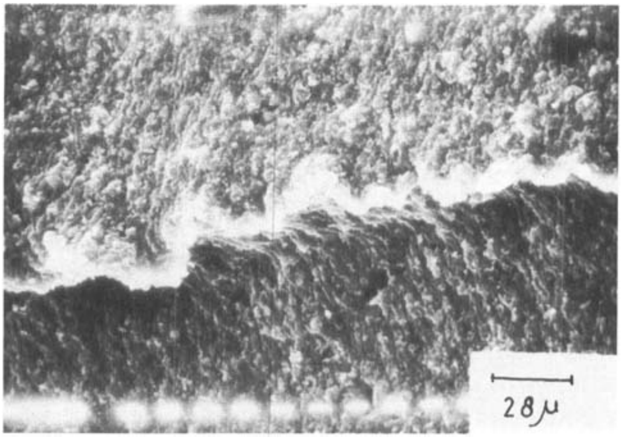

FIGURE 5. Tear fractograph of blend $C_M$—smooth surface and stretching of the matrix towards the fracture path.

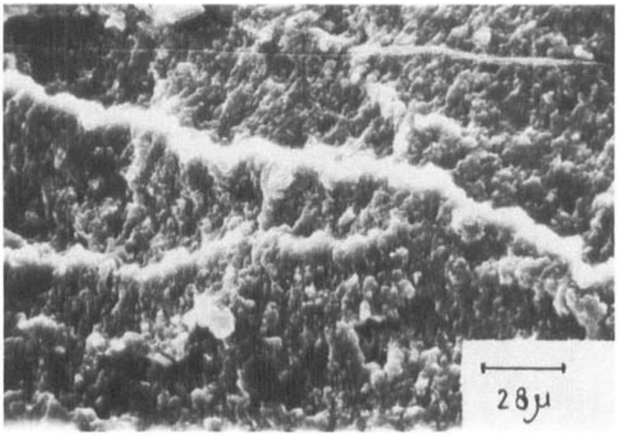

FIGURE 6. Tear fractograph of blend $C_S$—stretching of the matrix and subsidiary tear paths.

[$C_U$] shows rough surface and ductile failure with dimples and pores [Figure 3]. Dynamic crosslinking of the elastomer phase with DCP [blend $C_D$] reduced the deformation of the elastomer phase giving smooth fracture surface with fracture path [Figure 4]. The fracture surface of the blend $C_M$ is similar to $C_D$, but stretching of the matrix along the fracture path is visible due to better rubber-filler interaction [Figure 5]. The fracture surface of the sulfur cured blend containing silica and coupling agent [blend $C_S$] shows similar characteristics with subsidiary fracture paths. The stretching of the rubber phase along the fracture paths can also be observed in this case [Figure 6].

## Abrasion resistance

The abrasion resistance of the unfilled blends increases with increase in extent of dynamic crosslinking of the elastomer phase [$A_S > A_M > A_D > A_U$]. Silica filler improves the abrasion resistance of the NR–PP blends and the effect is more prominent in uncrosslinked and DCP cured blends [$B_U > A_U$, $B_D > A_D$, $B_M > A_M$, $B_S > A_S$]. Addition of silane coupling agent improves the abrasion resistance of the blends containing sulfur and sulfur-DCP mixed curing systems [$C_S > B_S$ and $C_M > B_M$]. In the uncrosslinked and DCP cured

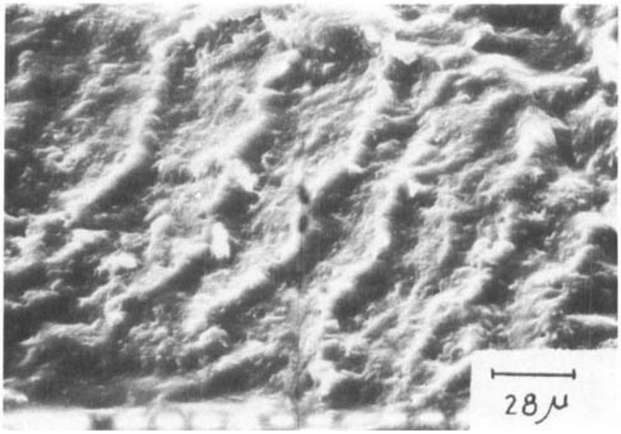

FIGURE 7. Abraded surface of blend $C_D$—thick and widely spaced ridges perpendicular to the direction of abrasion.

blends [$C_U$ and $C_D$] silane coupling agent adversely affects the abrasion resistance. These observations are similar to the trend in tear strength of these blends and may be explained in the following way. During abrasion, small particles are formed on the surface by microtearing of the matrix. The number and size of such particles and their removal from the matrix depend mainly on the tear

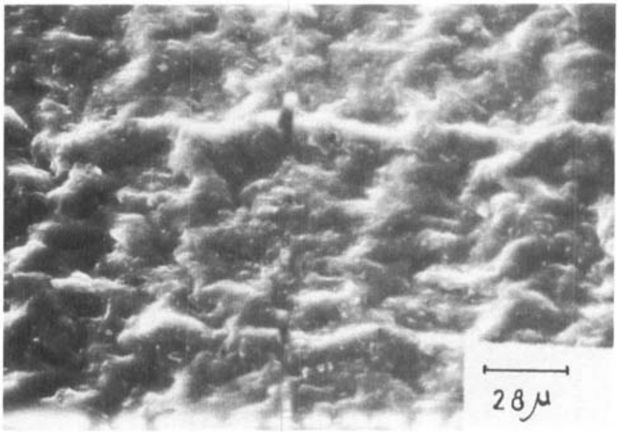

FIGURE 8. Abraded surface of blend $C_M$—small ridges interconnected by elongated rubber matrix.

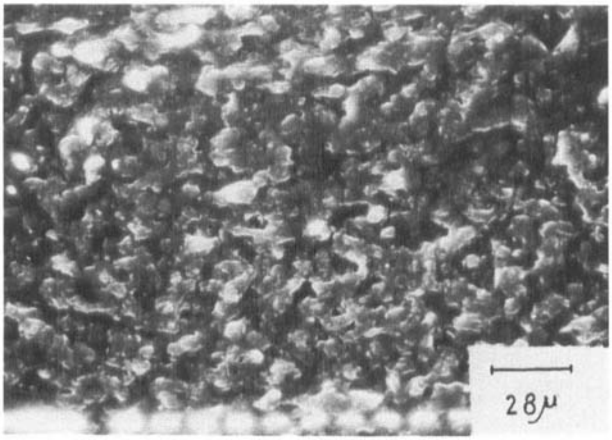

FIGURE 9. Abraded surface of blend $C_S$—without ridges.

strength of the matrix, apart from other factors like frictional force.[26] These particles coalesce to form ridges on the surface, aligned at right angle to the direction of abrasion.[27] Finer particles form finer ridges and the height and spacing of the ridges increase with the intensity of wear. The SEM photomicrograph of the abraded surface of the blend $C_D$ shows thick and widely spaced ridges [Figure 7] revealing the poor resistance to abrasion of the blend containing DCP cure system. In the case of blend $C_M$ the abraded surface shows small ridges interconnected by elongated rubber matrix [Figure 8]. The abraded surface of the blend $C_S$ shows no tendency towards ridge formation [Figure 9]. The abrasion resistance of the blends increase in the order, blend $C_S > C_M > C_D$. It can also be seen that the tear strength of these blends follow similar trend [Table II].

## CONCLUSIONS

The tear strength of the 70:30 natural rubber:polypropylene thermoplastic blend is increased by dynamic crosslinking of the elastomer phase and the increase is proportional to the extent of crosslinking. Addition of silica filler improves the tear strength of the blends and addition of bis[triethoxysilylpropyl] tetrasulfide, Si-69, further enhances the tear strength of the silica filled blends. Effect of silica filler is prominent in uncrosslinked and DCP-crosslinked systems. Effect of coupling agent is prominent in blends with sulfur and sulfur-DCP mixed vulcanizing systems. The abrasion resistance of different blends follow similar trend as the tear resistance.

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