Flow Behaviour of Polyblends of Crosslinkable Polyethylene and Silicone Elastomer with and without Silane Coupling Agent

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Synopsis

Flow behaviour of melt-mixed blends of crosslinkable polyethylene (XLPE) and silicone elastomer with and without vinyl silane are studied over the entire composition range. Viscosity and extrudate swelling have been studied as a function of shear rate and processing temperature. The effect of shearing and temperature have pronounced effect as is observed from the data of shear modulus, stored elastic energy, relaxation time, etc. Extrudate surface morphology is studied by scanning electron microscopy. A structure consisting of cross-linked microgelled silicone elastomer dispersed in continuous XLPE matrix is proposed.

INTRODUCTION

The technique of blending of two or more polymers to produce a balanced combination of properties for specific end-use requirements is a very active area in the field of polymer processing. Flow behaviour of polymeric fluids within a duct is the heart of all extrusion processes. Thus, viscosity of individual components plays a decisive role in the flow and forming of compounds. Several attempts have been made to predict the complicated rheological behaviour of polymer blends in view of its relevance to processing.[1–8] To understand varieties of response during flow, a classification of polymer blends based on the deviation of rheological properties from the mixing rule has been introduced.[9] However, a definite equation to characterise multiphase flow is yet to be established. Recently, Utracki[10] has reviewed rheology of multiphase flows.

The minor phase in an immiscible polymer blend is deformable and may give rise to a wide range of sizes and shapes during processing. This, in turn affects the blend morphology of the system. The melt rheology of a system is particularly sensitive to morphology.[11,12] We have reported the rheology and morphology of the blend of crosslinkable polyethylene (XLPE) and EPDM of different E : P ratio following a model developed by the authors.[13,14]

Here, we have studied the flow behaviour of polyblends of XLPE and silicone elastomer in presence and absence of silane coupling agent by capillary rheometry. The technique is chosen as it is relatively simple and closely resembles most commercial extrusion processes. The effects of shearing on melt-viscosity, flow activation energy, extrudate swell as well as other rheological parameters related to extrudate morphology have been reported.

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EXPERIMENTALS

Blend formulations are given in Table I. Crosslinkable polyethylene was of XLPE-11 variety from IEL Ltd., India. Silicone elastomer was of Silopren HV6/600U type from Bayer, West Germany. Vinyl triacetoxy silane (Z-6075) was from Dow Corning, USA. Melt mixing was carried out at 110°C and at 60 rpm in a Brabender Plasticorder following the procedure as before.[15,16] Gottfart rheograph 2001 was used for rheological measurements. The rheograph 2001 was a high pressure capillary rheometer with microprocessor. The barrel temperature of which was controlled by three electronic temperature controllers. Seven shear rates and three temperatures were selected for the study of rheological parameters. Non-Newtonian index (n) and consistency index (k) were determined from shear stress and shear rate data by regression analysis.

Activation energy of flow was determined from the change in viscosity with temperature as a function of shear rate. Extrudate samples were used to determine the swelling ratio (α) with the help of a microscope fitted with a micrometer. Viscoelastic parameters like stored elastic energy (W), recoverable deformation (γ_m), shear modulus (G), relaxation time (t_R), modified weissenbery number (W'_N) were determined as earlier.[14]

Morphology and melt fracture of the extrudates were studied with the help of SEM (Cam Scan-2000 and E 5200 Auto Sputter Coater).

RESULTS AND DISCUSSION

Effect of Shear Rate and Processing Temperature on Viscosity

The variation of apparent viscosity with shear rates for various blends are shown in Figures 1 and 2 at 140 and 150°C. The viscosity of all blends decrease with increasing shear rate over the processing temperatures studied. At low shear rate regions viscosity differences are higher but come closer at the shear rate increases for both temperatures studied. This decrease may be attributed to disentanglement of chains at high shear region associated with increase in temperature. However the addition of silane coupling agent has marked effect on the viscosity profile throughout the entire shear rate studied.

At 140°C the silane coupling agent decreases the viscosity of the blends at the low shear rate region (curves A, F and B, G). But at high shear rate region

TABLE I
Blend Formulations

Blend nos.	A	B	C	D	E	F	G
Crosslinkable polyethylene (XLPE-11)	90	70	50	30	10	90	70
Silicone elastomer (Silopren HV6/600U)	10	30	50	70	90	10	30
Silane coupling agent (Z-6075)	—	—	—	—	—	1.0	1.0

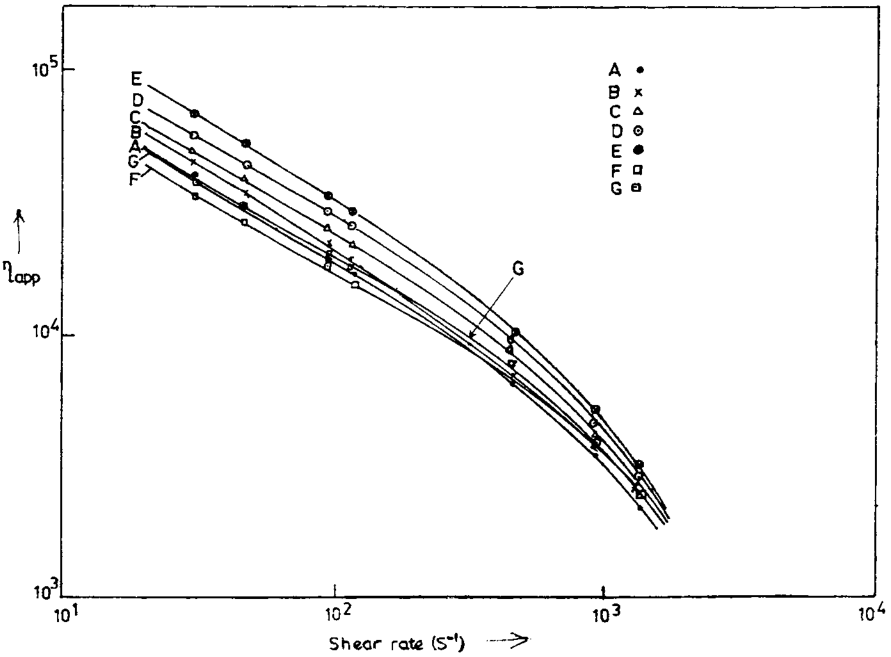

Fig. 1. Variation of apparent viscosity with shear rate for the blends at 140°C.

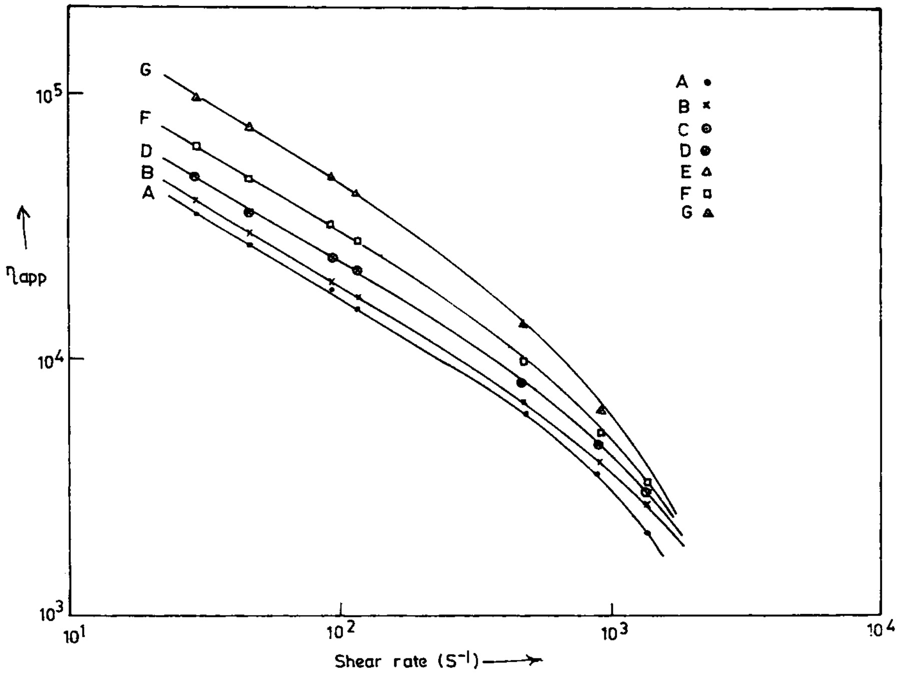

Fig. 2. Variation of apparent viscosity with shear rate for the blends at 150°C.

the presence of silane coupling agent increases the viscosity. The shear rate at which the silane coupling agent reverses its activity depends on the blend ratio. For the high XLPE/Silicone ratio blends the increased viscosity is observed due to presence of coupling agent, at comparatively higher shear rate (curves A and F) than for low XLPE/Silicone ratio of blends (curves B and G) where crossover occur at low shear rate. The difference in viscosity of blends F and G at 140°C is initially appreciable but as shear rate increases the difference gradually diminishes and finally merges at higher shear region. Whereas at higher temperature (150°C) viscosity difference is comparatively higher at low shear rate than that at 140°C and difference narrows as shear rate increases but never merge as is the case at 140°C. Moreover at any particular shear rate viscosities of blends F and G are higher at 150°C than at 140°C which may be due to the effective role played by silane coupling agent at higher temperature. When vinyl silane is added to the same composition, viscosity increases rapidly at 150°C which can be due to crosslinking between the neighbouring chains at the high temperature of extrusion. However at low temperature the shear induced crosslinking is responsible for increased viscosity after certain shear rate.

Effect of Blend Composition and Coupling on the Power Law Indices

Non-Newtonian index (n) and consistency index (k) as determined by regression analysis for all the blends and temperatures studied are shown in Table II. As observed 'n' increases slightly from blend A to B but then decreases as the XLPE/Silicone ratio decreases. This decreases may be due to increasing crosslinks amounting to more gel content[17] with the increasing silicone content. Again, the addition of silane coupling agent (F and G) to the same composition (A and D) at lower temperatures (130° and 140°C) increase 'n' values but an appreciable decrease in 'n' values are observed at 150°C. In presence of coupling agent when the silicone content increases 'n' value decreases. This decrease is probably a clear manifestation of shear induced crosslinking in presence of vinyl silane which is further decreased with more silicone content in the blend as observed in blend G. 'k' values are decreased as temperature is increased. However at higher temperature (150°C) with the addition of silane coupling agent 'k' values are increased.

TABLE II

Values of Non-Newtonian Index (n) and Consistency Index (k) at 130, 140, and 150°C

Blend nos.	n	$K \times 10^{-5}$
A	0.268(140), 0.297(150)	5.07(140), 4.02(150)
B	0.274(130), 0.272(140), 0.315(150)	5.96(130), 5.54(140), 4.06(150)
C	0.255(140)	6.68(140)
D	0.225(130), 0.241(140), 0.296(150)	9.91(130), 8.26(140), 5.44(150)
E	0.218(140)	10.56(140)
F	0.397(140), 0.231(150)	2.47(140), 9.38(150)
G	0.299(130), 0.335(140), 0.155(150)	5.12(130), 3.91(140), 19.59(150)

The value in the parentheses indicates the processing temperature in °C.

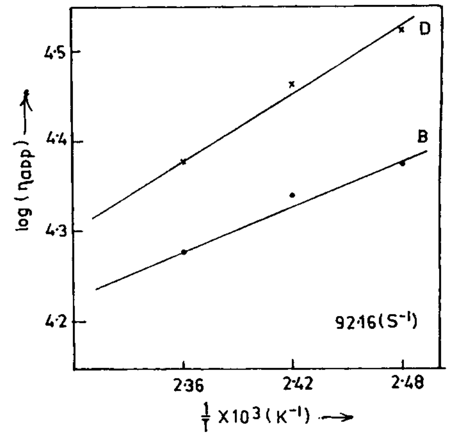

Fig. 3. Variation of viscosity with temperature at 92.16 (s^{-1}) shear rate.

Effect of Blend Composition and Coupling Agent on Flow Activation Energies

A representative example of the change of viscosity with the processing temperature has been shown in Figure 3 at a particular shear rate. The plot of viscosity versus T^{-1} is linear and confirms the Arhenius type of behaviour, the slope of which gives the flow activation energy at that rate. Flow activation energies of blends B and D at all the shear rate studied are shown in Table III. After the addition of coupling agent (blend G), the plot did not follow linearity and so flow activation energy could not be calculated. As observed from Table III, with increase in silicone elastomer flow activation energy increases. Initially in shear rate increases the flow activation energy but then decreases at high shear rate region. A lower flow activation energy is exhibited by the high chain flexibility.[18]

Effect of Blend Composition and Coupling Agent on the Swelling Ratio

Extrudate swell behaviour as a function of shear rate at 140°C has been shown in Figure 4 for all the blends. Initially with increasing shear rate, swelling ratio increases, reaches a maximum then decreases and flattens in mid-shear

TABLE III
Flow Activation Energy of Blends B and D at all Shear Rates

	Flow activation energy, kJ/mol					
Shear rates (s^{-1})	29.65	46.08	92.16	115.2	460.8	921.6
Blend nos.						
B	3.58	3.63	4.83	4.38	2.96	2.14
D	4.84	5.41	5.75	4.38	4.18	1.67

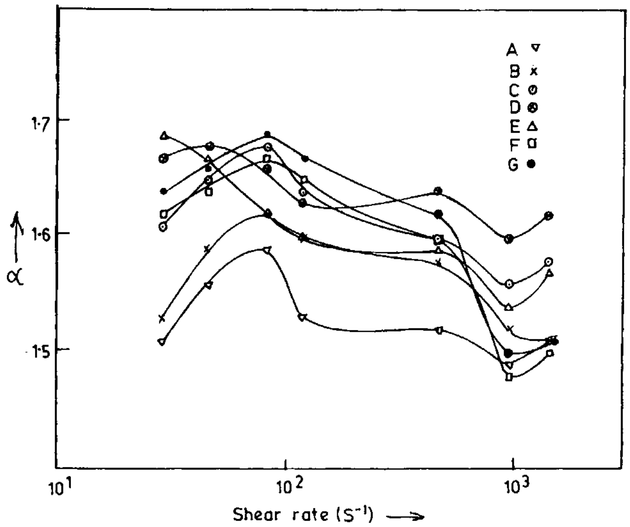

Fig. 4. Variation of extrudate swell with shear rate at 140°C.

region and finally at high shear again shoots up. This trends is true for blends A, B, C, and D. But in case of blend E, swelling ratio decreases with increasing shear rate, attains a minimum and then slowly increases in the mid-shear region and at high shear again increases rapidly. As the silicone content in the blend increases, swelling ratio increases for all the blends. The addition of coupling agent to the same composition rapidly increases the swelling ratio at low shear rate region but shows the same up-down pattern as without it. As the extrusion temperature is increased to 150°C swelling decreases. This may be caused by viscous heating, which is true for all the blends studied.

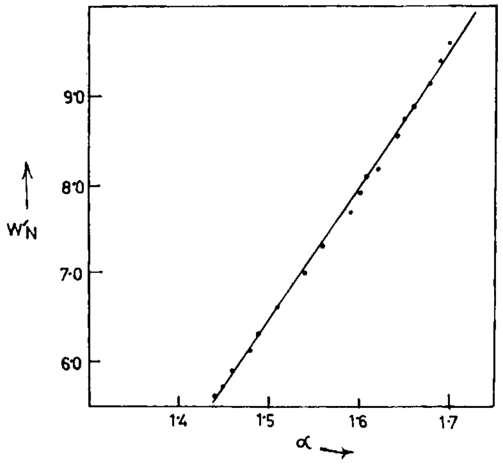

Fig. 5. Variation of Weissenberg number with extrudate swell.

Effect of Blend Composition and Coupling Agent on Rheological Parameters

The shear rate at wall (γ_w), stored elastic energy (W), shear modulus (G) and relaxation time (t_R) for all the blends studied at 130°, 140°, and 150°C are shown in Table IV, V, and VI, respectively. The variation of modified Weissenberg number (W'_N) is a monotonically increasing function of α and is shown in Figure 5. The recoverable deformation (γ_m) is plotted against the extrudate swell (α) at all three processing temperatures and is shown in Figure 6, which also follow a straight line pattern.

In absence of coupling agent W increases with the increase in shear rates for all the blends. Also at the shear rate increases the relaxation time decreases. However, at still higher wall shear rate (around 2200 s^{-1}) slight decreases in W has been observed. As the temperature is increased to 140°C W increases but at 150°C W decreases which may be due to the decrease in melt elasticity of blends at higher temperature. In presence of coupling agent at 150°C a marked increase in W is observed which clearly confirms the assumption of shear induced crosslinking at the said temperature. Increase of silicone content in the blend further decreases the melt elasticity. Shear modulus of blends follow the same pattern as stored elastic energy. t_R decreases with increasing shear rate for all the blends. As temperature is increased to 140°C, t_R slightly decrease but at 150°C an appreciable decrease in relaxation time is recorded. However, with the addition of coupling agent at 150°C, t_R increases.

TABLE IV
Values of γ_w, W, G, and t_R for the Blends at 130°C

Blend	γ_w (s^{-1})	W (10^5 J/m^3)	G (10^5 N/m^2)	t_R (s)
B	49.29	8.35	4.46	0.702
	76.60	11.09	4.77	0.413
	153.20	15.15	5.69	0.181
	191.51	17.01	6.61	0.109
	766.03	22.70	10.11	0.027
	1532.07	23.77	12.69	0.015
	2297.45	21.46	13.40	0.015
D	55.18	14.41	4.92	1.900
	85.76	17.97	5.59	0.918
	171.52	22.74	8.01	0.229
	214.4	22.14	8.60	0.198
	857.6	31.29	12.57	0.038
	1715.2	31.19	13.14	0.032
	2572.05	29.41	13.10	0.038
G	46.94	9.52	3.58	0.604
	72.96	11.66	4.11	0.353
	145.92	15.08	4.99	0.172
	182.4	16.39	5.96	0.106
	729.6	23.87	9.27	0.026
	1459.2	25.55	12.67	0.012
	2188.16	23.98	12.81	0.013

TABLE V

Values of γ_w, W, G, and t_R for the Blends at 140°C

Blends	γ_w (s^{-1})	W (10^5 J/m^3)	G (10^5 N/m^2)	t_R (s)
1	2	3	4	5
A	49.89	6.29	4.09	0.685
	77.54	8.36	4.46	0.378
	155.09	11.29	5.40	0.160
	193.86	11.09	6.65	0.099
	775.45	16.97	10.18	0.020
	1550.90	17.22	12.17	0.013
	2325.68	16.62	10.81	0.018
B	49.49	7.40	4.44	0.637
	76.91	9.67	4.62	0.404
	153.82	13.43	5.78	0.154
	192.28	14.05	6.48	0.111
	769.13	20.08	9.96	0.025
	1538.25	20.71	12.93	0.013
	2306.72	18.94	12.31	0.016
C	51.30	9.43	4.20	1.039
	79.73	12.37	4.80	0.501
	159.47	16.95	5.97	0.185
	199.34	16.96	6.81	0.133
	797.36	23.33	10.76	0.027
	1594.73	23.38	12.48	0.018
	2391.40	23.33	11.57	0.022
D	52.99	12.31	4.48	1.393
	82.36	14.71	5.18	0.722
	164.72	19.33	7.26	0.197
	205.90	20.37	8.46	0.122
	823.60	28.11	11.29	0.035
	1647.21	28.30	13.06	0.023
	2470.11	27.57	11.85	0.032
E	56.24	15.30	5.22	1.974
	87.40	17.49	6.36	0.892
	174.80	20.75	8.92	0.255
	218.51	21.87	10.09	0.165
	874.04	29.58	14.14	0.037
	1748.08	28.17	16.25	0.027
	2621.36	27.42	14.10	0.043
F	40.90	6.48	2.78	0.253
	63.57	8.25	3.31	0.155
	127.15	11.78	4.28	0.075
	158.94	12.26	4.76	0.060
	635.57	18.30	8.44	0.016
	1271.55	18.38	13.56	0.007
	1906.77	19.56	13.25	0.007
G	44.36	7.69	3.09	0.491
	68.94	9.75	3.66	0.276
	137.89	14.06	4.80	0.112
	172.37	14.46	5.26	0.091
	689.48	22.81	9.81	0.016
	1378.96	22.05	14.94	0.007
	2067.84	20.03	13.02	0.010

TABLE VI
Values of γ_w, W, G, and t_R for the Blends at 150°C

Blend	γ_w (s^{-1})	W (10^5 J/m^3)	G (10^5 N/m^2)	t_R (s)
1	2	3	4	5
A	47.19	4.92	3.97	0.466
	73.34	6.50	4.59	0.244
	146.69	9.20	5.74	0.099
	183.37	8.77	6.47	0.081
	733.47	13.13	11.07	0.015
	1466.95	14.97	13.22	0.009
	2199.80	13.02	12.66	0.011
B	45.77	5.96	4.04	0.391
	71.13	7.75	4.47	0.238
	142.26	10.80	5.35	0.113
	177.82	11.44	6.11	0.081
	711.31	15.96	9.96	0.020
	1422.62	18.10	12.79	0.010
	2133.32	20.06	13.59	0.008
D	47.28	9.00	4.15	0.569
	73.47	12.21	4.17	0.393
	146.95	16.42	5.43	0.154
	183.69	17.21	6.47	0.099
	734.79	25.18	9.78	0.025
	1469.57	28.19	12.12	0.014
	2203.73	28.05	11.66	0.015
F	54.32	8.87	7.48	1.082
	84.43	11.12	8.57	0.517
	168.86	14.01	11.81	0.149
	211.07	13.98	13.58	0.103
	844.30	18.24	20.63	0.021
	1688.60	17.83	22.45	0.018
	2532.17	16.50	23.26	0.018
G	70.06	14.25	11.48	5.016
	108.88	17.92	12.67	1.863
	217.76	25.69	16.04	0.579
	272.20	26.06	17.66	0.390
	1088.82	32.18	24.80	0.061
	2177.65	28.31	23.87	0.101
	3265.53	22.92	22.28	0.232

Extrudate Morphology of Blends

Physical appearance of the extrudates of the different blends are shown in Figure 7 as a function of shear rate and temperature. As the shear rate is increased for blend A (extrudates 1 and 2) the extrudate swell slightly decreases with increasing round wrinkles on the surface. With increasing temperature (150°C) at the same higher shear rate extrudate swell further decreases with

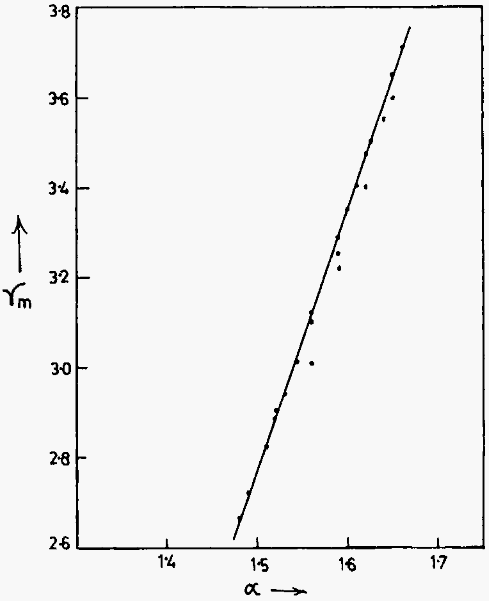

Fig. 6. Variation of recoverable deformation with extrudate swell.

similar surface irregularities. The above pattern is true for blend C (extrudates 4 and 5) at 140°C. But as XLPE/Silicone ratio decreases (blend E, extrudates 6 and 7) melt fracture appears from intermediate to high shear rate region. The addition of silane coupling agent to the same composition (blend F) increases extrudate swell but melt fracture disappears (extrudates 8 and 9). As the temperature is increased to 150°C, extrudate swell decreases and shark

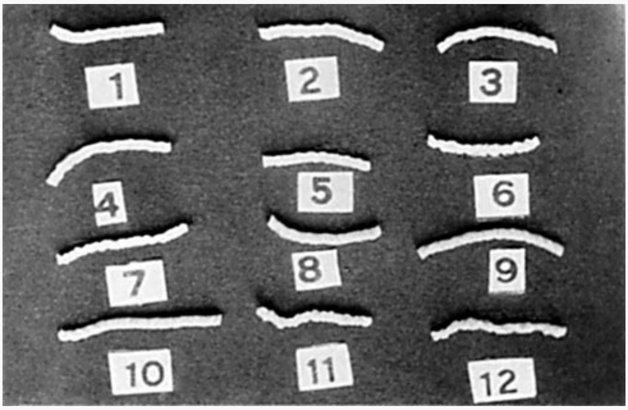

Fig. 7. Photographs of the extrudates: 1.—blend A at 46.08 s^{-1} and 140°C, 2.—blend A at 115.2 s^{-1} and 140°C, 3.—blend A at 115.2 s^{-1} and 150°C, 4.—blend C at 46.08 s^{-1} and 140°C, 5.—blend C at 921.6 s^{-1} and 140°C, 6.—blend E at 92.16 s^{-1} and 140°C, 7.—blend E at 460.8 s^{-1} and 140°C, 8.—blend F at 92.16 s^{-1} and 140°C, 9.—blend F at 921.6 s^{-1} and 140°C, 10.—blend G at 921.6 s^{-1} and 140°C, 11.—blend F at 92.16 s^{-1} and 150°C, 12.—blend F at 921.6 s^{-1} and 150°C.

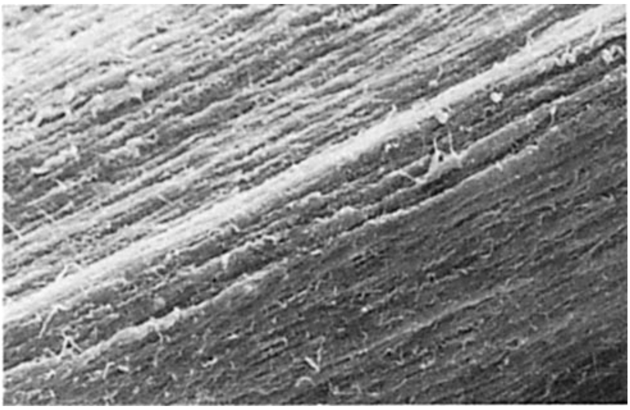

Fig. 8. SEM photograph of the extrudate (blend A at 46.08 s^{-1} and 140°C) at 500×.

skin behaviour predominates (extrudates 11 and 12). However at lower temperature (140°C) a smooth extrudate (blend G, extrudate 10) results.

Extrudate surface morphologies are studied by SEM and are shown in Figures 8, 9, 10, and 11. All micrographs show typical morphological feature as the shear rate and composition are changed. A continuous layers of resin (blend A) are observed at low shear rate as shown in Fig. 8. As shear rate is increased continuity of flow in the direction of extrusion is disturbed (Fig. 9) but XLPE remains as the continuous phase. As the silicone content increases (blend B), silicone particles appear as dispersed in continuous XLPE matrix (Fig. 10). Addition of coupling agent to the same composition (Blend B) reveal variation in topography such as scraps, microridges on the surface of the extrudates. However, XLPE still maintains its phase continuity (Fig. 11).

It appears that at the low temperature of extrusion the shear induced crosslinking caused by viscous heating effect is operative in presence of silane coupling agent. Whereas at higher temperature the usual heat induced crosslinking

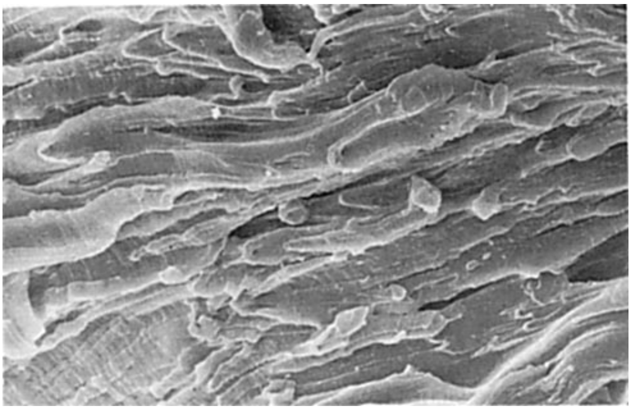

Fig. 9. SEM photograph of the extrudate (blend A at 115.2 s^{-1} and 140°C) at 500×.

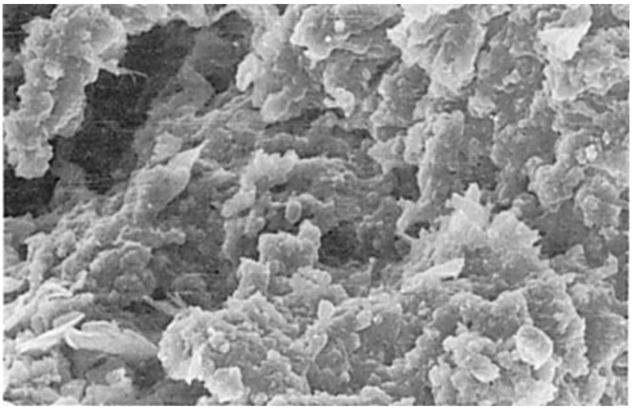

Fig. 10. SEM photograph of the extrudate (blend B at 115.2 s^{-1} and 140°C) at 500×.

through vinyl functionality of the silane coupling agent play a predominant role. However plasticizing action of the coupling agent affect the flow behaviour at lower shear role and at lower temperature of processing.

CONCLUSIONS

Heat and shear induced crosslinking affects the flow behaviour and morphology of the blend extrudates to an appreciable extent. Viscosity change is observed in presence of coupling agent at higher temperature which is further reflected on the rheological parameters of the blends studied. Increase in viscosity with the increasing dosage of silicone elastomer probably suggest the presence of elastomer in gelled state, as fillers, as dispersed phase in XLPE matrix.

Fig. 11. SEM photograph of the extrudate (blend G at 115.2 s^{-1} and 140°C) at 500×.

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