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The effect of PF resin-zinc oxide system as curative for soft thermoplastic NR:PP blends

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Dynamic crosslinking has been suggested as a method for improving the properties of thermoplastic elastomers prepared by melt blending (refs. 1-4). The production of thermoplastic elastomeric blends from natural rubber (NR) and polypropylene (PP) has been described by Elliot and Tinker (ref. 5). The use of phenol-formaldehyde (PF) resin and zinc oxide as curatives for hard blends of NR and PP has been studied by Mathew and Tinker (ref. 6). This article is a study on the use of a phenol-formaldehyde resin/zinc oxide system as a curative for thermoplastic elastomers prepared from a 60/40 NR/PP blend. The main objectives of the present work are:

- To study the effect of different dosages of PF resin/zinc oxide system on the physical properties of NR/PP blends and to compare the same with those of the blends crosslinked using conventional systems such as dicumyl peroxide and mixed curatives.
- To study the effect of the different curing systems on the melt flow properties of the blends.

Experimental

Materials

The NR used was ISNR-5 grade block rubber. The characteristics of this rubber are given in table 1. The PP used was isotactic polypropylene. The properties of the PP are given in table 2. PF resin (SP 1045) and dicumyl peroxide (containing 40% active ingredient) and other compounding ingredients were of commercial grades.

Blending

The blending and further mixing were carried out in a KO MK3 Shaw intermix. The rotor speed was set at 80 rpm. The chamber was preheated to 120°C. The chamber temperature was further raised to 150°C by operating the intermix with NR as feed material. Meanwhile, the requisite quantity of PP was preheated to 150°C in an air oven. The ram pressure was maintained at 3 bar. The mixing cycle was:

- 0 min. - NR and PP
- 3 min. - crosslinking agents
- 6 min. - dump

The dump temperature was 175 ± 10°C. The blends were passed through a laboratory mixing mill at 2 mm nip and the sheets, after cooling, were granulated. The granules were used for molding test pieces and for melt flow studies. Test specimens for the various mechanical properties were compression molded at a temperature of 190°C.

Physical properties

Tensile test was carried out on a Zwick Universal Testing Machine (UTM, Model 1474) using a crosshead speed of 500 mm/minute at 25 ± 2°C.

The other mechanical properties such as hardness, tension set, compression set and ozone resistance were performed in accordance with the corresponding ASTM test methods. Abrasion loss was tested as per DIN 1319-section B. Rebound resilience was measured using a Dunlop Tripsometer as per BS 903, Part A8. Stress relaxation under tension mode was tested by stretching the specimen to 100% elongation at room temperature (25 ± 2°C) and at a crosshead speed of 500 mm/min.

Melt rheology

The melt flow index (MFI) was tested using a Ceast Modular Flow Index, Model 6542/000, according to ASTM-D 1238 Method A. Rheological studies were carried out using a capillary rheometer 1400-790B attached to a Zwick UTM Model 1474. The sample for testing was placed inside the barrel, kept at a temperature of 200°C. The sample was forced down the capillary using a plunger. The melt height in the barrel before extrusion was kept constant in all the cases. The melt was extruded through the capillary at preselected speeds of the crosshead. Forces corresponding to specific crosshead speeds were recorded. The shear stress at the wall ($\tau\omega$) and the shear rate at wall ($\dot{\gamma}\omega$) were calculated based on the following equations.

$$\tau\omega = \frac{F}{4A_p\,(l_c/d_c)}$$

$$\dot{\gamma}\omega = \frac{3n'+1}{4\,n'} \times \frac{32.Q}{d_c^3}$$

where F = force applied at a particular shear rate
A_p = cross sectional area of plunger
l_c = length of capillary
d_c = diameter of capillary

Table 1 - specification and actual values of ISNR-5

Sample no.	*Parameters*	*Actual value*	*Limit*
1.	Dirt content (% by mass, max)	0.0095	0.05
2.	Volatile matter (% by mass, max)	0.29	0.80
3.	Ash (% by mass, max)	0.24	0.60
4.	Nitrogen content (% by mass, max)	0.45	0.60
5.	Initial plasticity (Po min)	54	30
6.	Plasticity retention index (PRI, min)	76	60

Table 2 - properties of Koylene M0030

Sample no.	*Property*	*Test method*	*Value*
1.	Melt flow index (g/10 mts)	ASTM D 1238	10
2.	Melting point (°C)	-	165-170
3.	Vicat softening point (°C)	ASTM D 1525	152
4.	Brittle point (°C)	ASTM D 746	5
5.	Density at 23°C (g/cm^3)	ASTM D 1505	0.905
6.	Hardness Rockwell (R. scale)	ASTM D 785/B	72

Q = volumetric flow rate

n' = flow behavior index defined as d log $\tau\omega$/d log $\dot{\gamma}\omega.a$

$\dot{\gamma}\omega.a$ = apparent shear rate at the wall

n' was determined by regression analysis of the value of $\tau\omega$ and $\dot{\gamma}\omega.a$ obtained from the experimental data. The shear viscosity η was calculated as:

$$\eta = \tau\omega/\dot{\gamma}\omega$$

The following assumptions were made for the analysis of the experimental data from capillary studies.

- the flow is parallel to the axis
- the velocity of any fluid element is a function of radius only
- the fluid is incompressible
- the fluid velocity is zero at the wall
- all energy is consumed within the capillary and the flow is isothermal
- the end correction factor is negligible as the l_c/d_c ratio of the capillary is 40.

Results and discussion

The formulations of the blends are given in table 3. A 60:40 ratio of NR:PP was selected based on the reported fact that they are flexible and elastic enough (tension set less than 50%) to be considered elastomeric and were reprocessable as thermoplastic materials (ref. 7). The test results are presented in tables 4-6.

Processing characteristics

Melt flow index - The melt flow index and the flow behavior index (n') are given in table 4. The results clearly show that the MFI of the blends is significantly affected by the additives. The DCP system is found to cause the minimum effect. The mixed curing system reduces the MFI to a very low value. The resin curing system prevented melt flow of the blend under the test conditions.

The reduction in MFI is brought about by various factors. One of these is the crosslinking of the rubber phase. Another factor is the enhanced interfacial interaction of the two phases. Both these factors are believed to be operating in the case of DCP and mixed crosslinking systems. The DCP in both these systems may cause degradation of PP and thus help in increasing the flow rate of the blend. In the case of PF resin there is a drastic reduction in melt flow. Though crosslinking of the rubber phase and increased interfacial bonding could be influencing melt flow index, these alone cannot explain such a drastic reduction in MFI. It is possible that the PF resin may get crosslinked at the time of melt blending. Since PF resin is thermosetting, it remains as fine dispersions in the molten polymer matrix, restricting its flow through the capillary. The presence of zinc oxide in these samples also may be contributing to the restricted flow.

Table 3 - composition of the blends

Components	Composition of the samples 1	2	3	4	5	6	7
NR	60	60	60	60	60	60	60
PP	40	40	40	40	40	40	40
DCP	-	3	0.6	-	-	-	-
ZnO	-	-	3.0	2	3	1	-
St. acid	-	-	1.2	-	-	-	-
CBS	-	-	0.6	-	-	-	-
TMTD	-	-	0.75	-	-	-	-
Sulfur	-	-	0.09	-	-	-	-
SP 1045	-	-	-	4	6	2	4
Sn C12	-	-	-	-	-	-	1

Table 4 - processing characteristics

Sample no.	Properties	1	2	3	4	5	6	7
1.	MFI g/10 mts (200°C and 2.16 kg load)	3.7	1.25	0.055	No material flow			
2.	Flow behavior index n'	0.34	0.34	0.23	0.25	0.21	0.18	0.20

It may be noted that both shear rate and shear stress experienced during the MFI test are much lower than those usually encountered in processes such as injection molding and extrusion. Also, the low L/D ratio of the die makes the data subject to an unassessed end correction. The differences in the MFI may not be reflected in the injection molding

Figure 1 - log-log plot of viscosity vs. shear for samples 1, 2 and 3

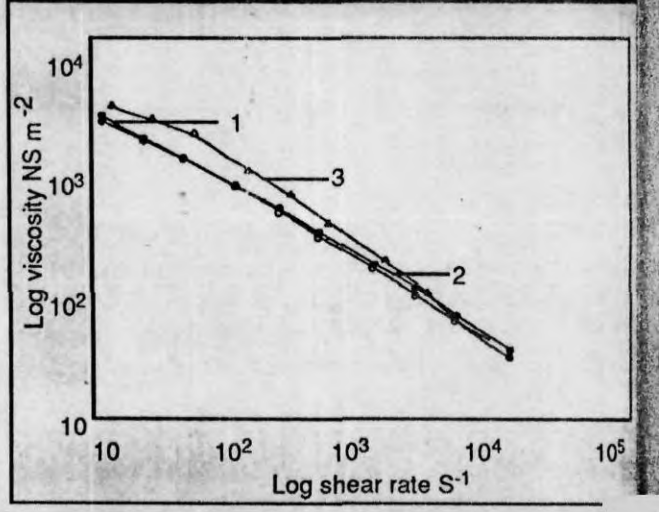
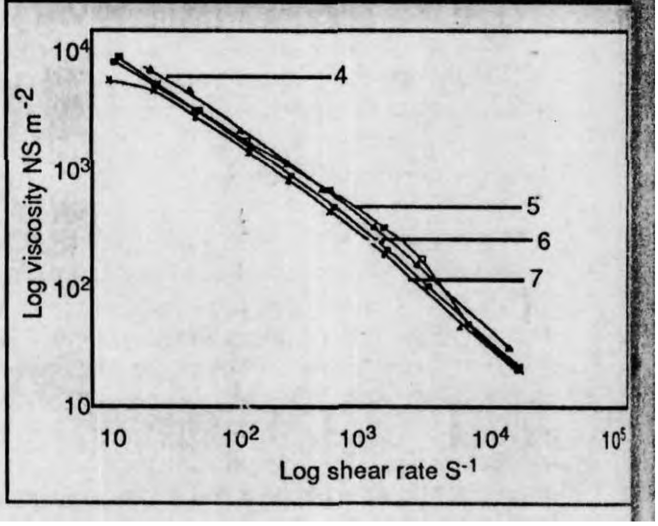


Figure 2 - log-log plot of viscosity vs. shear rate for samples 4, 5, 6 and 7



behavior of these blends. Actually, it was found that even under compression molding conditions, the flow of all the blends was quite satisfactory and defect free moldings could be produced in all cases.

Rheological properties - The flow behavior index, n', given in table 4, shows that all the blends are pseudoplastic. The pseudoplasticity is observed to be more or less similar for the blends 3 to 7, which contain mixed and resin curing systems. The pseudoplasticity is comparatively less for the blends 1 and 2. All the blends are found to exhibit Power law behavior, though the value of n' changes from 0.18 to 0.34.

The effect of both shear rate and shear stress on viscosity of the blends is shown in figures 1-5. It may be observed that the viscosity decreases rapidly with the increase in shear stress. Log-log plots of viscosity against shear rate (figures 1 and 2) show that an increase in shear rate also decreases the viscosity of the polymer melt. At higher shear rates the effects are more or less similar for all the samples. Thus it can be observed that the flow properties of the resin cured blends are quite comparable with those cured with either peroxide or mixed curing systems. The flow properties, as evidenced by the rheological behavior of the blends, are similar in nature at the processing conditions. The processability of a rubber-plastic blend into a finished product is a function of its melt rheology. The results indicate that shear rate should be kept high to ensure adequate flow of the melt. The high melt viscosity at low shear rate is expected to provide high melt integrity and permit the retention of shapes of extrudates or blow moldings. The low viscosity of the melt at high shear stress and shear rate facilitates rapid and complete mold filling during injection molding. When the mold is filled the shear rate decreases rapidly causing a rapid increase in viscosity, and it enables rapid ejection of the molded part and reduces the molding cycle time.

Figure 3 - log-log plot of viscosity vs. shear stress for samples 1 and 2

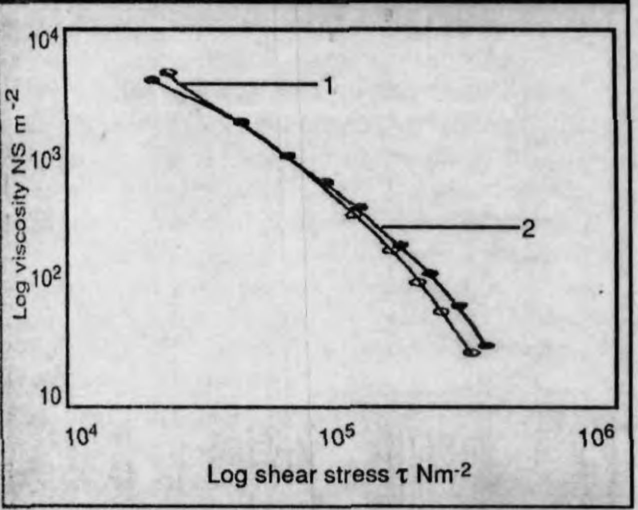
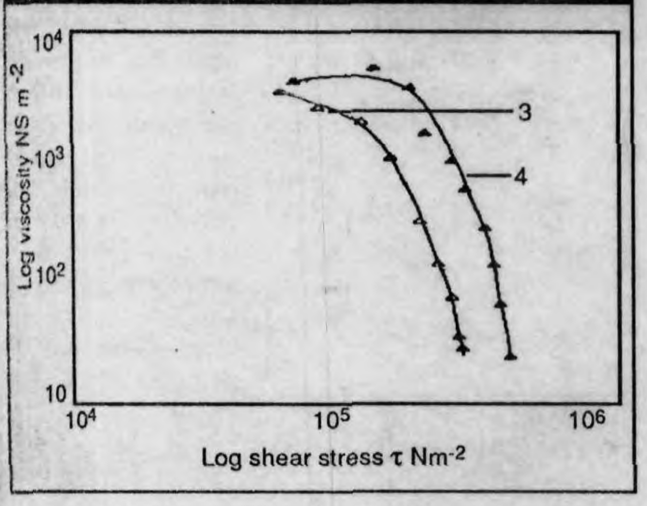


Figure 4 - log-log plot of viscosity vs. shear stress for samples 3 and 4



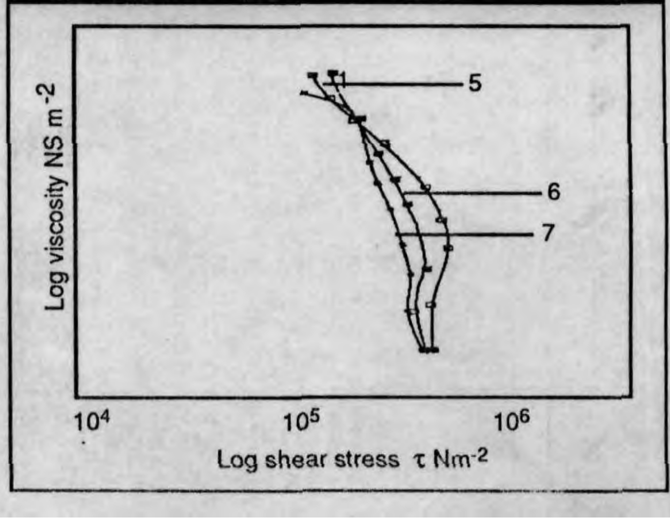
Physical properties

The results of physical testing are given in table 5. Modulus at 100% elongation is maximum for the resin cured blends. It is also found to increase with the dosage of the curative. Both modulus and tensile strength are improved by cross-linking, except in the case of the DCP cured blends. The reduction in modulus and tensile strength, in the case of DCP cured blends, is probably due to the molecular degradation of PP at the processing temperature in the presence of the peroxide. The mixed cure system is found to give the highest tensile strength, whereas the blend containing four parts per hundred polymer (pphp) of the resin and two pphp of zinc oxide gives the maximum tensile strength among the resin-cured blends. Higher and lower dosages of resin/ZnO are observed to give lower tensile strength.

The improvement in modulus and tensile properties as a result of the additives is primarily due to dynamic vulcanization.

Coran (ref. 7) has defined dynamic vulcanization as the process of vulcanizing rubber during its intimate melt mixing with a nonvulcanizing thermoplastic polymer. This process results in the formation of a particulate vulcanized rubber phase of stable domain morphology during further melt processing. In the case of phenolic resin, it is further possible that the resin can technologically compatibilize the

Figure 5 - log-log plot of viscosity vs. shear stress for samples 5, 6 and 7



blend of PP and NR. This could be the result of the formation of a block copolymer, formed by a reaction which requires the presence of chain end unsaturation in the PP molecules. Thus the improved compatibility between NR and PP through block copolymer formation is believed to be another reason for the improvement in tensile properties, brought about by the resin/ZnO system.

Elongation at break (EB) is an index of the rubberiness of the blends. The additives improve EB, the maximum improvement being observed for blend 3, which employed the mixed cure system. The resin cure system is better than DCP and among the resin/ZnO system the highest EB was exhibited by blend 4, indicating that four pphp of resin and two pphp of zinc oxide would be the optimum dosage.

The elastic character of polymeric materials is indicated best by tension set. The results show the superiority of the mixed and resin/ZnO cure systems in imparting higher elasticity to the blends.

In the case of the resin/ZnO system, the minimum set value was obtained when the dosage was maximum. The dosage which was found optimum with respect to tensile and other properties was having a set value comparable to that exhibited by the mixed curing system. The set for the DCP-cured blend was found to be the same as that of the uncured blend. This may be due to the strain induced molecular rearrangement of the blend. The data on stress relaxation also confirm the above observation. The compression set values at constant stress, determined at room temperature, are also generally in agreement with the tension set results, except in the case of the DCP-cured blend, which shows the least compression set. This may be due to the fact that the applied stress is insufficient to cause breakage of carbon-carbon bonds, formed during the crosslinking reaction and to cause reformation as in the case of the tension set experiment.

The additives in general are found to improve tear resistance of the blends. In this case, the resin system is found to be comparable with the other systems studied, although a higher dosage was observed to improve tear resistance. Tear resistance of blend 5 is higher than that of blend 4, though its tensile strength is lower.

Hardness values of the blends depend primarily on the blend ratio of NR and PP, and the additives do not have any significant effect. Hardness also is observed to increase with the dosage of the additives, though only marginally.

Abrasion resistance of the blend is improved significantly by curing. The DCP and mixed curing systems show better resistance when compared with the resin/ZnO system. The abrasion resistance value depends also on the dosage of the curing agent. The specific gravity of the blends are affected only marginally by the curing system.

Aging and ozone resistance

Results of the aging and ozone resistance test are tabulated in table 6. The retention of modulus and tensile strength observed in the case of the resin/ZnO system is comparable to that of the mixed curing system. Retention of tensile strength in the case of the resin system is better than that in the case of DCP. In mix 5, which contains the maximum dosage of the resin, modulus and tensile strength are found to increase significantly upon aging. Interestingly, the retention of tensile strength in the case of the samples cured with stannous chloride-activated resin is appreciably l than that of even the control. Retention of EB also is comparable in the case of the resin/ZnO and mixed cure systems, while it is much lower in the case of the DCP and the stannous chloride-activated resin cure system. This leads to the inference that PF resin activated with zinc oxide could effectively function as a curing system for NR:PP blends.

As is evident from table 6, all the samples were found to be highly resistant to ozone, although the blends contain 60 parts NR. During the melt blending process and the subsequent molding operations the PP phase being lower in viscosity (at the melt temperature) is reported to form the continuous phase (ref. 8). As a result, in the final molded specimen the NR phase is protected by the saturated PP, making the blend highly resistant to ozone.

A surface bloom was observed in all cases except in those containing zinc oxide. The mixed curing system showed the maximum blooming, followed by the stannous chloride activated resin system, DCP and uncrossli blend in that order. The bloom may be caused by degradation of PP at the surface. It is well known that DCP induces degradation of PP and hence the appearance of bloom in the DCP cured sample is not surprising (ref. 9). In the case of the mixed curing system, possibly, the other curatives and their reaction products which are having only limited solubility in the polymer blend are also believed to bloom to the surface.

Table 5 - physical properties

Sample no.	*Properties*	*1*	*2*	*3*	*4*	*5*	*6*	*7*
1.	Modulus at 100% elongation	6.00	4.45	8.80	8.45	9.10	7.40	8.75
2.	Tensile strength (N/mm^2)	6.23	4.92	18.30	14.35	11.7	10.6	13.4
3.	Elongation at break (%)	130	152	378	250	167	200	275
4.	Tear resistance (N/mm)	54.6	85.4	84.6	85.7	103.4	83.2	88
5.	Hardness (Shore A)	83.5	86.0	85.0	89.0	90.0	88.5	91.5
6.	Abrasion loss (mm^3) DIN-load 5 N	146	68.6	78.4	83.1	81.7	130.4	92.1
7.	Specific gravity	0.92	0.92	0.94	0.93	0.94	0.93	0.925
8.	Tension set (%) at 25 ± 2°C	36	36	12	12	8	20	24
9.	Compression set (%) at 25 ± 2°C	20	3.6	6.8	6.9	5.6	18	6.3
10.	Stress relaxation at 100% elongation after 10^4 secs	79.78	80.21	62.6	65.12	61.59	-	-
11.	Rebound resilience % (Dunlop tipsometer)	32.63	36.81	40.07	40.29	42.59	37.35	35.24

Conclusions

The following conclusions ar

Table 6 - aging and ozone resistance

Sample no.	Properties	1	2	3	4	5	6	7
	Before aging							
1.	Modulus at 100% elongation (N/mm^2)	6.0	4.45	8.80	8.45	9.10	7.40	8.75
2.	Tensile strength (N/mm^2)	6.23	4.92	18.30	14.35	11.70	10.60	13.4
3.	Elongation at break (%)	130	152	378	250	167	200	275
	After aging							
4.	Modulus at 100% elongation (N/mm^2)	-	-	9.80	9.37	10.7	8.26	6.44
	% retention	-	-	111.36	110.89	117.58	111.62	73.6
5.	Tensile strength (N/mm^2)	4.77	4.27	19.59	14.45	14.03	10.22	7.22
	% retention	76.6	86.8	107	101	120	96.4	53.9
6.	Elongation at break (%)	57.0	71.0	370	248	185	179.0	149
	% retention	43.8	46.7	97.9	99.2	111	89.5	54.2
7.	Ozone resistance	No cracking observed even after 7 days						

drawn from the study. The melt viscosity of the blends is less dependent on the presence of crosslinks in the rubber phase at higher shear rates. The flow behavior index for the samples employing the resin/ZnO curing system is comparable to that of the samples employing a conventional curing system.

The melt viscosity of the blends is highly shear sensitive, making the blends suitable for injection molding. A combination of SP 1045 and ZnO was found to be an effective cure system for the dynamic vulcanization of thermoplastic NR-PP blends. The mechanical properties of the samples employing the above system were found to be either superior or comparable to those with the conventional curing systems.

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