Die Angewandte Makromolekulare Chemie 153 (1987) 153 – 163 (Nr. 2507)

Department of Polymer Science & Rubber Technology, Cochin University of Science & Technology, Cochin-682 022, India

Blends of Polychloroprene and Polyvinylchloride*

K. E. George, Rani Joseph, and D. Joseph Francis

(Received 12 December 1986)

SUMMARY:

Blends of polychloroprene rubber and plasticized polyvinylchloride have been prepared in various compositions and their properties evaluated. The properties of the blends show that they can be used to replace polychloroprene in many applications.

ZUSAMMENFASSUNG:

Aus Polychloropren und Polyvinylchlorid wurden Blends in verschiedenen Zusammensetzungen hergestellt und ihre Eigenschaften bestimmt. Die Eigenschaften der Blends zeigen, daß sie Polychloropren in vielen Anwendungen ersetzen können.

Introduction

Polychloroprene rubber (CR) and polyvinyl chloride (PVC) both posses excellent oil resistance, chemical resistance, weather resistance, and nonflammability. PVC is generally used as a cheap plastic material whereas CR is used as a comparatively high priced special rubber. Hence, blends of CR and PVC could be advantageously used to replace CR in many applications. Blends of CR and PVC require a host of additives like curatives for CR and stabilizers for PVC. However, it has recently been shown that magnesium oxide/zinc oxide combination, conventional curative for CR, in presence of stearic acid could act as an efficient stabilizer for plasticized PVC' and that tribasic lead sulphate (TBLS), conventional stabilizer for PVC, could be an efficient curative for CR². These additives were hence used in a dual role in this study.

* Presented in part at the International Conference on Rubber and Rubberlike Materials, November 6-8, 1986, Jamshedpur, India.

© 1987 Hüthig & Wepf Verlag, Basel

0003-3146/87/\$03.00

K. E. George, R. Joseph, and D. J. Francis

Experimental

Modification of CR with PVC

When the amount of CR was generally in excess of PVC, the blend was cured similar to that of pure CR. MgO/ZnO combination in presence of stearic acid was used both as the curative for CR and stabilizer for PVC. Blending of CR and plasticized PVC was done on a Brabender Plasticorder model PL 3S at 150° C for two min using roller type rotors at a speed of 30 rpm. MgO, ZnO, and stearic acid required for stabilizing PVC were added at this stage. However, MgO, ZnO, stearic acid, and ethylene thiourea (NA-22) required for the vulcanization of CR were added later on a laboratory mixing mill at near ambient temperature (30° C). The cure curves of the mixtures were then taken on a Monsanto rheometer model R-100. The mixtures were then vulcanized up to the respective optimum cure times on a steam heated laboratory press at 150° C. The formulations of the mixtures are shown in Tab. 1 and the cure curves in Fig. 1.

Mixture	Α	В	С	D	Е	F	G
CR ^a	100	90	80	70	60	50	40
PVC ^b	ines <u>n p</u> i	10	20	30	40	50	60
Dioctyl phthalate (50% of PVC)	cial <u>m</u> iè replace	5	10	15	20	25	30
MgO (4% of CR + 4% of PVC)	4	4	4	4	4	4 4	4
ZnO (5% of CR + 4% of PVC)	5.0	4.9	4.8	4.7	4.6	4.5	4.4
Stearic acid (2% of CR + 3% of PVC)	2.0	2.1	2.2	2.3	2.4	2.5	2.6
NA-22 (0.5% of CR)	0.5	0.45	0.4	0.35	0.3	0.25	0.2

Tab. 1. Modification of CR with PVC, formulations of the mixtures.

^a W type: Mooney viscosity (ML 1 + 4 at 100 °C): 82; delivered by DuPont, USA.
^b Suspension polymer; K value: 65; delivered by NOCIL, India.

Tensile properties of the blends were determined as per ASTM D 412-80 test method at 20 °C using dumb-bell shaped test pieces at a crosshead speed of 500 mm/min on a Zwick Universal Testing Machine. Hardness of the vulcanizates was determined according to ASTM 2240 (1968) and expressed in Shore A units. Compression set was determined according to ASTM D 395-69 under constant deflection.

Blends of Polychloroprene and Polyvinylchloride

The resistance to swelling of the vulcanizates was determined by allowing circular specimens of 1 cm diameter (approx. 40 mg) to stand in excess of chloroform for 48 h at 30 °C and then measuring the percentage change in weight. The ageing resistance was determined by keeping the vulcanizates at 100 °C for 48 h in an air oven and then measuring the retention of these properties.

SEM observations of the tensile failure surfaces were made using a Phillips 500 model scanning electron microscope. The fracture surfaces were carefully cut out from failed test pieces without touching the surfaces and then sputter coated with gold within 24 h of testing. In order to avoid contamination, the specimens were stored in a dessicator before and after gold coating till the SEM observations were made.

Modification of PVC with CR

When the amount of PVC was generally in excess of CR, the CR phase was dynamically crosslinked at the time of blending and then the blend was sheeted out similar to that of pure PVC. TBLS was used both as the curative for CR and stabilizer for PVC since this procedure involved higher tempeatures. Blending of CR and plasticized PVC was done on the Brabender Plasticorder employing the same mixing parameters as before, but at 190 °C. The blending was continued till the dynamic crosslinking of the CR phase was over as observed from the torque — time curve of the Brabender plasticorder. Then the blend was sheeted out by pressing for two minutes

Mixture	F'	G'	H	I de la	J	K
PVCa	50	60	70	80	90	100
CR ^b	50	40	30	20	10	_
Dioctyl phthalate (50% of PVC)	25	30	35	40	45	50
TBLS (same as the loading of MgO and ZnO in Tab. 1)	8.5	8.4	8.3	8.2	8.1	8.0
Stearic acid (2% of CR + 3% of PVC)	2.5	2.6	2.7	2.8	2.9	3.0
NA-22 (0.5% of CR)	0.25	0.20	0.15	0.10	0.05	10.0 390
PBN (1% of CR + 1% of PVC)	rque <mark>f</mark> lee er melt)	ioi <mark>p</mark> rintri Invol edit	The paxi y due to	ontept. obviousi	a PYC o of PVC,	i segri stinos

Tab. 2. Modification of PVC with CR, formulations of the mixtures.

^a Suspension polymer; K value: 65.

W type; Mooney viscosity (ML 1 + 4 at 100 °C): 82.

551 an that of CR. This might indicate that the constituents of the blend are not fully compatible. The tensile strength goes to a minimum and then starts

K. E. George, R. Joseph, and D. J. Francis

at 190 °C on a laboratory hydraulic press. An antioxidant, phenyl- β -naphthylamine (PBN), was also added for this study because the blending and moulding were done at 190 °C. The formulations used for the study are shown in Tab. 2. The tensile properties of the blends were determined as before.



Fig. 1. Cure curves of the mixtures (reference: Tab. 1).

Results and Discussion

Modification of CR with PVC

The cure curves (Fig. 1) of the mixtures show that the presence of PVC does not affect the curing of CR. The scorch safety improves with an increase in PVC content. The maximum torque decreases with increasing amounts of PVC, obviously due to the lower melt viscosity of plasticized PVC compared to that of CR. The cure curves further show that there is no scorching of the mixtures during blending.

The tensile strength of the blends (Fig. 2) decreases with an increase in PVC content, even though the tensile strength of plasticized PVC is higher than that of CR. This might indicate that the constituents of the blend are not fully compatible. The tensile strength goes to a minimum and then starts increasing only after the PVC content is about 50% of the total polymer. To

Blends of Polychloroprene and Polyvinylchloride



Fig. 2. Variation of tensile strength with PVC content: (\bigcirc) before ageing, (\bullet) after ageing.

understand this phenomenon the SEM photographs of the tensile fracture surface of pure CR, 30% PVC blend, and 60% PVC blend were taken (Figs. 3, 4, and 5). These figures suggest that the PVC phase becomes continuous only when the PVC content is fairly high. This might imply that the composition at which tensile strength of the blends starts increasing is the one at which the PVC phase becomes continuous.

The variation in tensile strength of the blends with ageing (Fig. 2) is interesting. The retention in tensile strength improves with an increase in PVC content and finally the aged samples take over the values of the original samples when the PVC content is above 50%. This behaviour shows that the PVC phase is comparatively unaffected by the ageing conducted at 100 °C. Even though there was no intention of crosslinking the PVC phase in this study, there could occur a low degree of crosslinking in the PVC phase in the presence of ZnO³. The increase in tensile strength with ageing of the samples with higher PVC content might be due to a slight increase in this crosslink density in the PVC phase.

The variation of elongation at break with PVC content (Fig. 6) is more or less similar to that of the tensile strength. The retention of this property with ageing is also found to improve with an increase in PVC content. The modu-

751 VC content. However, there is a marked improvement in the values with

where we have not start a set of the start of the

K. E. George, R. Joseph, and D. J. Francis



Fig. 3. SEM photograph of the tensile fracture surface of CR (\times 133).



Fig. 4. SEM photograph of the tensile fracture surface of 30% PVC blend (×133).



Fig. 5. SEM photograph of the tensile fracture surface of 60% PVC blend (×133).

lus and hardness of the blends improve with increasing PVC content (Figs. 7, 8). This is due to the higher modulus and hardness of PVC compared to CR and is expected. These values further increase with ageing due to the increase in crosslink density of the matrix with ageing.

The deterioration of the set property with increasing PVC content (Fig. 9) is also expected due to the decrease in rubbery properties with an increase in PVC content. However, there is a marked improvement in the values with ageing. The resistance to swelling seems to improve with increasing PVC content as seen by the swelling behaviour of the blends in chloroform

Blends of Polychloroprene and Polyvinylchloride



Fig. 6. Elongation at break versus PVC content: (0) before ageing, (•) after ageing.







K. E. George, R. Joseph, and D. J. Francis

Fig. 8. Hardness versus PVC content: (0) before ageing, (•) after ageing.



Fig. 9. Compression set versus PVC content: (O) before ageing, (•) after ageing.

Blends of Polychloroprene and Polyvinylchloride



Fig. 10. Resistance to swelling in chloroform versus PVC content: (0) before ageing, (•) after ageing.



Fig. 11. Tensile strength versus blend composition.

K. E. George, R. Joseph, and D. J. Francis

(Fig. 10). The resistance improves further with ageing due to the increase in the crosslink density. However, the blends are not suitable for prolonged contact with solvents since there is a chance of the plasticizer getting extracted.

Modification of PVC with CR

Blends F' and G' with the same polymer compositions of blends F and G are found to show more or less similar physical properties. This suggests that this method of preparing CR/PVC blend could actually supplement the previous method and could be employed when the amount of PVC is higher. The tensile strength of the blends prepared through the two different routes was combined in Fig. 11. The large deviation in tensile strength from the



Fig. 12. Elongation at break versus blend composition.

Blends of Polychloroprene and Polyvinylchloride

predicted relationship indicates the incompatibility of the polymers. Fig. 12 shows a combined curve of the elongation at break which also has a similar trend.

Conclusion

Blends of polychloroprene rubber and plasticized polyvinylchloride are found to possess many advantages compared to polychloroprene such as better ageing resistance, higher modulus and hardness, better solvent resistance, and lower cost. They can successfully replace polychloroprene in many applications.

¹ K. E. George, R. Joseph, D. J. Francis, Plast. Rubber. Process. Appl. 5 (1985) 179

² R. Joseph, K. E. George, D. J. Francis, Angew. Makromol. Chem. 148 (1987) 19

³ V. Duchacek, A. Kuta, J. Appl. Polym. Sci. 27 (1982) 1549