Ageing Behavior of Natural Rubber – Hydrogenated Nitrile Rubber Blend Containing Dichlorocarbene Modified Natural Rubber as Compatibiliser

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Abstract

Hydrogenated nitrile rubber (HNBR) could be blended with natural rubber (NR) to improve its ageing resistance without affecting drastically the dynamic properties. The polarity difference between the polymers is reduced by incorporation of small quantities of dichlorocarbene modified NR (DCNR) which is formed during the alkaline hydrolysis of chloroform in presence of NR . The compatibilising action of DCNR is due to its dipole interaction with the –CN group of the acrylonitrile segments in HNBR as revealed from a shift in the characteristic IR absorption peak. This modified form of NR enables the formation of a more uniformly mixed blend of NR and HNBR resulting in more cross links as revealed from an increase in rheometric torque. In blends, the NR matrix cross links to a same extent as pure NR, while the level of cross-linking of HNBR matrix is lower than that obtained for the pure HNBR. However in the presence of DCNR there is the formation of interfacial cross-links as evaluated from selective solvent swelling. During ageing at a comparatively lower temperature the NR matrix of the blend undergoes cross-linking reactions while at high temperatures it undergoes scission reactions. The scission reactions taking place in the NR matrix are reduced in presence of compatibiliser as observed from the application of two-network theory for samples subjected to high temperature stress relaxation. A reduction in chain scission reactions at high temperature results in better ageing characteristics of the compatibilised blends.

Introduction

Natural rubber continues its significance in rubber industry due to its excellent dynamic properties. However it has very poor resistance to ageing in presence of air, ozone, fuels and oils. Attempts have always been made to improve the behavior of NR with respect to its ageing characteristics by compounding or by blending with rubbers that are inherently resistant to ageing. Hydrogenated nitrile rubber, a comparatively new elastomer [1-2] which is being used extensively in automobile applications as a substitute for NBR[3] has a combination of high temperature, aggressive fluid and oil resistances. It would be possible to improve the ageing behavior of NR by blending it with HNBR. Blends of HNBR with NR could be used in outdoor applications due to the combination of properties like heat resistance, oil resistance and ozone resistance along with low compression set, as NR is a versatile and cheap raw material with excellent dynamic properties combined with very good low temperature flexibility. Generally blends of NR with other polar or less unsaturated elastomers have inferior properties than the blend constituents. This is mainly due to incompatibility between the polymers and cure rate mismatch during vulcanization. The cure incompatibility arising from cure rate mismatch during vulcanization is reduced by following certain mixing procedures, judicious choice of curatives and by techniques of light vulcanization of one of the phases prior to processing [4-5]. The polymer incompatibility is generally reduced by incorporating small quantities (5-10 phr) of a polymer having segments closely related to individual elastomers, called compatibilisers, in the blend. It has been observed earlier that modified forms of NR acted as compatabiliser in blends of NR with other synthetic rubbers.[6]

This paper discusses the blending of NR with HNBR so as to improve the properties of NR with respect to aging and the improvement in polymer compatibility by addition of a modified form of NR. An attempt is made to understand the changes in molecular level network structure that occur in the individual matrices of NR/HNBR blends by selective solvent swelling of the aged and unpaged samples. The net cross linking and scission reactions occurring in the blend are evaluated by two-network theory [7]. This theory has been used in studying the role of modified NR in controlling the scission and cross-linking reactions.

Experimental

NR used was of ISNR 5 grade obtained from PCRF, Rubber Board, Kottayam, India. HNBR used was Zetpol 2010 grade of Nippon Zeon Co Japan. The dichlorocarbene modified NR used was of 15 % chlorine content. It was prepared in the laboratory by the alkaline hydrolysis of chloroform on NR using phase transfer catalyst according to the method suggested by Makosza and Wawrzyniewicz and developed by Joshi et al [8-9]. 50/50 blend of HNBR/NR was prepared on a laboratory size two roll mill at a friction ratio of 1:1.25. The rubbers were masticated separately and then mixed together before addition of compounding ingredients. Cure characteristics were studied using a Monsanto rheometer R 100 at 150 ^{0}C according to ASTM D 2705. The samples were vulcanized to their optimum cure time in a hydraulic press at 150^{0}C and pressure of 45 kg per cm^2 on the mould. The tensile properties and tear resistance of samples were tested with Zwick Universal testing machine (Model 1474) at temperature of 25 ^{0}C and crosshead speed of 500mm/min according to ASTM D 412-80 and ASTM D 624-8 respectively. All other physical properties were determined according to the respective ASTM standards.

IR spectra of blends were recorded with a Schimadzu –8101 M Fourier transform infrared spectrophotometer using a pyrolysate of sample. The scission and cross linking reactions occurring during vulcanization and ageing for the individual matrices were studied by selective solvent swelling of the unaged and aged samples. The samples subjected to ageing for 70^{0}C for 5 days, 120^{0}C for 5 days and the unaged samples were tested for selective swelling of the individual matrices by immersion in the solvent to equilibrium swelling time which was taken as 48 hours. The solvents used were methyl ethyl ketone and n-heptane. The weight of solvent absorbed per gram of the sample was calculated from measurement of swollen weight.

The stress relaxation of the blends was studied using Zwick Universal testing machine (Model 1474) at 130^{0}C. The calculation of permanent set during stress relaxation was from the scission and cross linking reactions that take place during intermittent and continuous stress relaxation as reported by Andrews et al.[7]

Results and Discussion

1. IR Spectroscopic studies

The compatibilising action of DCNR could be due to its dipole interaction with blend constituents. Such interactions are known to affect the characteristic IR absorption peaks as reported earlier [10-11] As observed from IR spectra of pyrolyzates,.HNBR shows characteristic IR absorption at 2237 cm $^{-1}$ for –CN group. Pure NR/HNBR blend shows an IR absorption at 2237 cm $^{-1}$ while this is shifted to 2240cm $^{-1}$ for the compatibilised blend. This is due to the possible dipole interaction between the - Cl of dichlorocarbene modified NR and -CN group of acrylonitrile segments in HNBR.. Such interactions have been reported earlier for blends of NR/NBR in presence of chlorine containing polymer.[6]

2. Cure characteristics

The formulations of the mixes are given in Table 1. The cure characteristics are given in Table 2. Pure HNBR shows a comparatively high scorch time and rheometric torque. The 50/50 NR/HNBR blend has a lower scorch time and rheometric torque as compared with NR and HNBR. The level of cross linking in either HNBR or NR phase is not up to the levels obtained for the pure

NR and HNBR mixes which could be due to the unequal migration of curatives in the separate NR and HNBR phases. The blend containing 7 parts of DCNR records a higher rheometric torque, showing the formation of additional cross-links in the presence of compatibiliser. Interactions leading to chemical reactions between chlorine containing polymers and HNBR without the aid of vulcanizing agents resulting in an increase of rheometric torque has been reported earlier[12]. In presence of dichlorocarbene modified NR the mixing is more homogeneous and the curatives are possibly more evenly distributed resulting in the formation of interfacial cross-links.

3 Selective solvent swelling

During swelling by n-heptane the NR matrix of the blend swells highly while the HNBR phase swells lightly and the tendency is reversed during swelling by methyl ethyl ketone. The swelling characteristics of unaged and aged pure NR, HNBR, blend and compatibilised blend in both MEK and n heptane are shown in Table 3. The per cent volume of normal heptane absorbed by pure NR, HNBR, blend and compatabilised blend is shown in Fig 1.The weight of normal heptane absorbed by NR matrix of the unaged blend(shown as 30^{0}C in the figure) is the additive average of the weight of solvent absorbed by NR and HNBR. Thus the level of cross-linking of the NR phase in the blend is to the same level as observed for the pure NR vulcanisate. The weight of solvent absorbed by the blend in the presence of compatibiliser is less than the additive average (shown by dotted line in the figure). The weight of solvent absorbed by samples aged at 70^{0}C for five days and 120^{0}C for five days is also lower for the compatibilised blend showing the presence of interfacial bonds. It is clear that there is restriction of swelling of NR phase by the lightly swollen HNBR phase and this shows the formation of interfacial cross-links. The restriction of solvent swelling by formation of interfacial bonds have been reported earlier [13-14]. In the case of HNBR matrix of the blend the weight of MEK absorbed is higher than the additive average of weight of MEK absorbed by pure HNBR and NR. Thus the HNBR matrix in the blend is not vulcanized to the same level as pure HNBR. However there are interfacial bonds formed as there is restriction to penetration of HNBR phase by MEK in presence of compatabiliser. Thus it is due to the lower cross linking of the HNBR phase that a lower rheometric torque is registered for the blends in comparison with either NR and HNBR. The higher rheometric torque recorded for the compatibilised blend should be due to the formation of interfacial bonds.

NR matrix of the blend undergoes cross linking reaction during ageing at low temperatures and scission reactions during ageing at high temperature as seen from a reduced swelling of the samples aged at 70°C for five days and 120°C for five days and a higher swelling of the samples aged at 150^{0}C for one day. HNBR phase is less sensitive to cross link formation during ageing due to the observation that the weight of MEK absorbed by aged samples remained almost same. Weight of solvent absorbed by blend containing compatibiliser is lower for the aged and unaged samples.

4. Stress relaxation characteristics

The net cross-linking and chain scission reactions occurring during ageing is obtained from intermittent and continuous stress relaxation studies. The stress relaxation characteristics and permanent set obtained at a temperature of 130^{0}C are shown in Figures 2and 3. The experimental values of permanent set obtained for blends agree with the calculated values and hence they obey the two-network theory of ageing.[7] The continuous and intermittent stress relaxations of the blends at 130^{0}C are shown in Figure 4. The change in modulus for the intermittent stress relaxation is very less at 130 ^{0}C, due to the better ageing characteristics of HNBR.. It has been observed earlier that the relaxed modulus of HNBR was less sensitive to temperature changes and showed a slight increase at high temperature of 140^{0}C.[15] The intermittent and continuous stress relaxation showed a higher value for compatibilised blends revealing a lower level of chain scission for the compatibilised blend as compared to the pure blends during ageing. Probably interfacial bonds helped in having a lower stress relaxation for the compatibilised blend.

5. Physical properties

Physical properties of the blends are shown in Table 4. Modulus, tensile strength, tear strength and hardness of the blend increased with incorporation of 7 parts of dichlorocarbene modified NR Dynamic properties of the blend like compression set and heat build-up decreased whereas, resilience increased in presence of modified NR. However these properties are inferior to the pure components. This could be due to the low level of cross links formed in the HNBR matrix in the blends.

6. Ageing characteristics

The retention of the tensile properties is shown in Figure 5. As known already HNBR has excellent ageing characteristics [16] compared to NR. After ageing the blend showed very poor ageing behavior. However the blend containing 7 parts of DCNR showed a comparatively higher percent retension of modulus and tensile strength compared to pure blend . The better aging properties of the compatibilised blend should be due to the enhanced homogeneity during mixing and the formation of interfacial cross links that resulted in a lower level of scission reactions during ageing.

Conclusion

Dichlorocarbene modified NR acted as compatibiliser in blends of NR/HNBR due to the possible interaction between chlorine of modified NR and –CN of HNBR. The state of cure achieved for the HNBR matrix in pure blend was lower than that in pure HNBR and this could be improved by the incorporation of dichlorocarbene modified NR into the blend. As a result of enhanced level of mixing in the presence of compatibiliser interfacial bonds were formed during vulcanization. The formation of interfacial bonds resulted in a lesser amount of chain scission reactions during high temperature ageing resulting in better aging resistance for compatibilised blends.

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Table 1 Formulations of the mixes

Ingredients	HNBR	NR	NH	NHC7
HNBR	100	-	50	50
NR	-	100	50	50
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
TMTD[1]	1.5	3.0	1.5	1.5
MBT[2]	0.5	0.2	0.5	0.5
Sulphur	0.5	0.2	0.5	0.5
DCNR[3]	-	-	-	0.7

[1] Tetramethylthiuram disulphide

[2] Mercaptobenzothiazole

[3] Dichlorocarbene modified natural rubber

Table 2 Cure characteristics of the mixes at 150 ^{0} C

Mix	Torque min,dN. m	Torque max,dN. m	Optimum cure time at 150^{0} C,minutes	Scorch time at 150^{0}C, minutes
NR	3	45.0	7.5	3,25
HNBR	11	60.0	25.0	7.5
NH	5	36.0	6.25	1.5
NHC7	5	39.5	9.00	1.6

Table 3 Weight of solvent absorbed during selective solvent swelling by aged and unaged samples of NR, HNBR, NH and NHC7

Solvent	n-heptane (wt. of solvent absorbed/g of rubber)				MEK (wt. of solvent absorbed/g of rubber)			
Ageing condition (^{0}C/days)	150/1	120/5	70/5	unaged	150/1	120/5	70/5	unaged
NR	3.92	1.5	1.6	2.6	0.56	0.51	0.49	0.51
HNBR	0.23	0.20	0.21	0.22	2.40	2.20	2.22	2.81
NH	1.27	0.51	0.84	1.42	2.30	2.40	2.40	2.18
NHC7	1.05	0.48	0.80	1.30	2.13	2.30	2.32	2.17

Table 4 Physical properties of the gum vulcanizates

Parameters	NR	HNBR	NH	NHC7
Tensile strength, MPa	18.0	21.1	10.6	12.3
Modulus,100%, MPa	0.85	1.10	0.93	1.13
Modulus 300 %, MPa	1.83	1.45	1.5	1.58
Elongation at break, %	725	720	740	690
Tear strength, kN/m	20.8	16.9	20.5	23.9
Hardness, Shore A	37	49	44	45
Resilience , %	72	65	69	70
Compression set, %(22 h 70 ^{0} C)	8.3	30.1	46.2	39.0

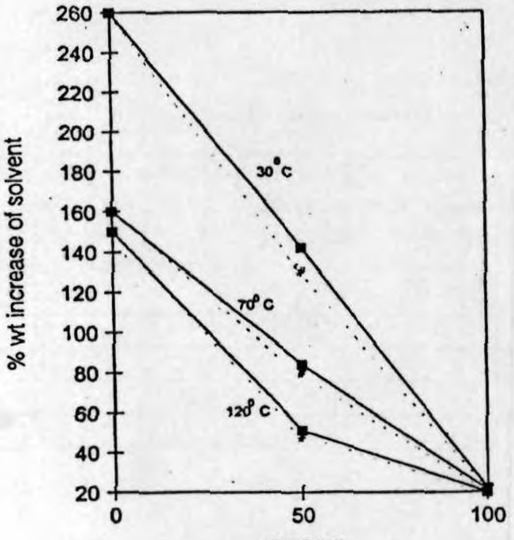

Fig 1. Solvent swelling of the unaged and aged NH(shown by solid line) and NHC7(showed by dotted line) samples .

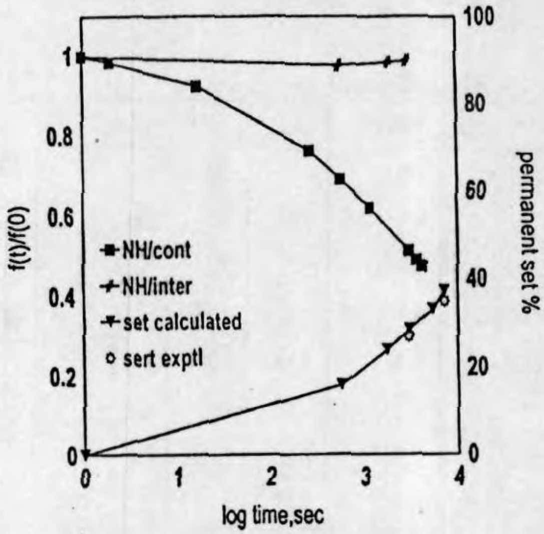

Fig2 Intermitent and continuos stress relaxation along with calculated and experimental permanent set for pure HNBR/NR blend at 130 C

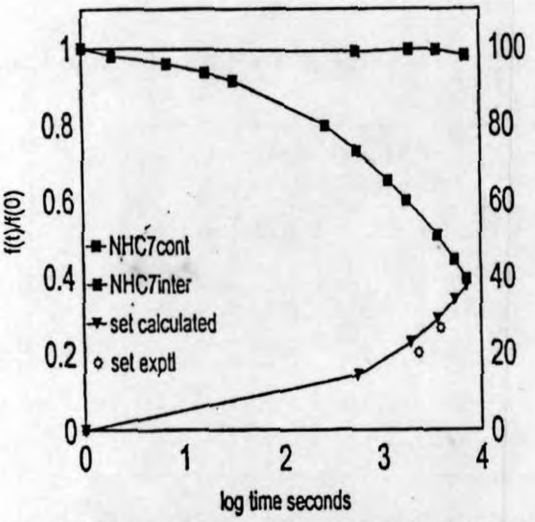

Fig3 Intermitentand continuos stress relaxation along with calculated and experimental permanent set for compatabilised HNBR/NR blend at 130 C

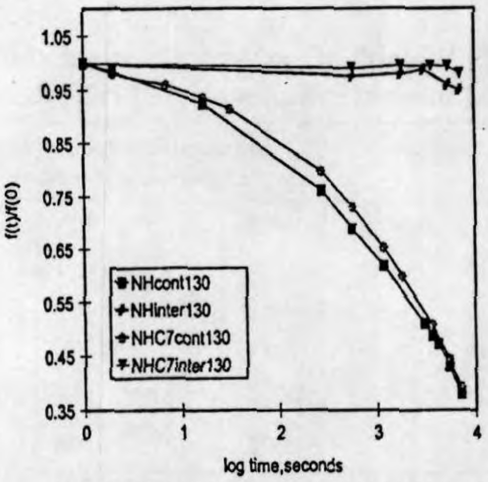

Fig.4 Intermittent and continuous stress relaxation of pure and compatabilised NR/HNBR blends at 130 C

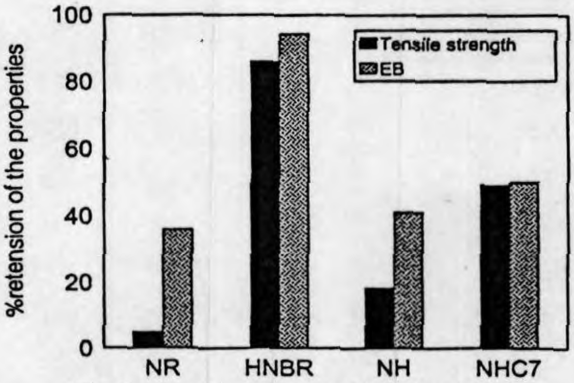

Fig.5 Percent retension of tensile strength and elongation at break for samples aged at 120 C°for five days