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Hybrid filler system for nitrile rubber vulcanizates

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Relative efficiency of different types of fillers e.g., phenolic resin, carbon black and carbon black plus phenolic resin hybrid system in nitrile rubber vulcanizates for improvement of physico-mechanical properties, resistance to swelling in oil/fuel and thermal stability has been studied. The hybrid system was always found to offer maximum benefit in strength and dynamic mechanical properties coupled with higher percent of (a) retention of physical properties due to aging and (b) swelling resistance in oil or fuel. Both thermogravimetric analysis (TGA) as well as thermomechanical analysis (TMA) reflect much better thermal stability for the combined filler system compared to the vulcanizates containing either phenolic resin or carbon black. © *2001 Kluwer Academic Publishers*

1. Introduction

Acrylonitrile-co-butadiene rubber (NBR), for its oil and fuel resistances, is extensively used in automobiles, aircraft, tank and other military applications as seals, gaskets, 'O'-rings etc. However, rubber composition based on NBR poses problems due to inferior tack, limited high temperature stability as well as poor shelf life. British resin products limited has developed a range of synthetic phenolic resins to reinforce both synthetic and natural rubbers [1]. These resins are hardened under the influence of heat and in the presence of aldehyde donors like hexamethylene tetramine (Hexamine), though in the uncured state they exhibit thermoplasticity. Giller [2] and Chow and Steiner [3] reported that phenolic resin (novolac type) and hexamine, when incorporated in the rubber, cure in the normal way during vulcanization to increase hardness of the vulcanizate. Murke [4] studied the stabilization of NBR latex with cresol-formaldehyde condensate and observed that the coagulum compounded and vulcanized gave a product with good elasticity and thermal stability. Thorough studies were also carried out with NBR and phenolic resins based on cashew-nut shell oil [5]. Use of these resins as reinforcing agents for NBR compounds in the hardness range of 60 to 90 Shore A has been reported by Smedley [6]. Novolac type of phenolic resins with hexamine have been commonly used as reinforcing filler as well as cross linking agent in NBR for seals, valves and gasket applications. Addition of phenolic resins has also been found to provide superior resistance to abrasion, heat as well as improved tackiness for the gum compounds compared to carbon black. The chemistry of phenol-formaldehyde resin vulcanization of ethylene propylene diene monomer (EPDM) rubber, for the evidence of methylene crosslinks has been studied by Duin & Souphanthong [7]. Further, dual phase filler morphology using carbon black-silica and their surface chemistry characterization through electron spectroscopy for chemical analysis (ESCA) and fourier transform infrared spectroscopy (FTIR) were reported by Murphy *et al.* [8, 9]. Sirisinha *et al.* [10] reported the nature of distribution of different grades of carbon black in polybutadiene rubber- NBR blends and their effect on dynamic mechanical properties. Literature on carbon black filled NBR vulcanizates are vastly populated and has not been reviewed again. However, a detailed study on the reinforcement characteristics, swelling properties and thermal stability, especially at elevated temperatures, using a combination of phenolic resin plus carbon black is still lacking which has been undertaken here.

2. Experimental

The formulations of the mixes are given in Table I. Mixing was carried out in a two-roll rubber mixing mill. Mixes were vulcanized for 30 min at 150°C in a hydraulic press.

Physico-mechanical and swelling properties are given in Table II. Tensile testing was done as per ASTM method D 412-51T using dumb-bell specimens. This test also enables us to obtain elongation at break and modulus values of the vulcanizates. Shore A type durometer was employed to find out the hardness of the vulcanizates as per ASTM method D 676-52T. The compression set at constant strain (25%) for 22 h at 70°C has been reported as per ASTM D 395-61, method B. Tear strength of the vulcanizate was determined using un-notched 90 degree angled tear test piece (die C) as per ASTM method D 624-48. Samples of 10 mm diameter, 2.5 mm thickness and weight 0.3 g (approx.) were cut from the central portion of the moulded sheet and allowed to swell in various oils and fuels at 35°C in a thermostatically controlled water

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TABLE I Formulation of mixes

Ingredients	Mix Nos. A	B	C	D
Nitrile Rubber[a]	100	100	100	100
Zinc oxide	15	15	15	15
Stearic acid	1.5	1.5	1.5	1.5
Phenolic resin[b]	-----	50	-----	20
Carbon black[c]	-----	-----	50	50
Hexamine[d]	-----	5	-----	2
Sulfur	0.3	0.3	0.3	0.3
MBTS	1	1	1	1
TMT	3	3	3	3

[a] NBR, Perbunan 3307, Bayer A.G., Germany.

[b] PR 202, Rubber reinforcing resin, M/S Hard Castle Wand Ltd., Mumbai, India.

[c] SRF carbon black (N 705), obtained from Phillips Carbon Black Ltd., Durgapur, India.

[d] Hexamethylene tetramine, BDH, U.K.

Other ingredients are of pure AR grade.

TABLE II Physico-mechanical and swelling properties of the vulcanizates

Property	Vulcanizate Nos. A	B	C	D
Tensile strength, MPa	2.28	5.32	15.29	18.85
Modulus at 100% elongation, MPa	.09	5.18	2.02	4.09
Elongation at break, %	300	125	450	325
Tear strength, N/cm	1.22	4.21	5.86	4.86
Hardness, Shore A	40	85	55	75
Compression set, %	12.0	15.6	4.0	10.0
Volume swelling, (%):				
A. X-oil (High viscosity mineral oil)	2.12	1.65	0.09	0.11
B. Ox-38 (Ester type oil)	0.24	0.73	0.00	−0.05
C. Iso-octane : Toluene 70 : 30 (Fuel)	0.83	0.72	0.52	0.31
D. ATF (Turbine fuel)	1.77	1.59	1.32	0.73

TABLE III Percent retention of physical properties of the vulcanizates after aging

Properties	Vulcanizate Nos. A	C	D
Tensile strength	61	45	85
Elongation at break	68	65	96
Tear strength	84	52	108

bath. Swollen samples were taken out after 72 h, blotted with filter paper and weighed quickly in stoppered weighing bottle. Triplicate readings were taken for each sample and percentage of oil/fuel swelling was calculated. The accelerated aging test in a heat oven (ASTM designation 537-67) was carried out at 100 ± 2°C for 72 h. The samples were allowed to rest at room temperature for 24 h before evaluation of physical properties and the percentage change in these properties are reported in Table III.

TA Instrument's (USA) TMA module 2970 with controller 3100 under static load of 10 g rate of heating 10°C/min was utilized for determination of thermomechanical properties of the vulcanizates in nitrogen atmosphere. Thermogravimetric analysis was done in the firm's TGA module 2100 under nitrogen gas flow, heating rate 20°C/min and in the temperature range of 0 to 600°C. Du Pont's DMA module 983 was utilized for evaluation of dynamic mechanical properties of the vulcanizates at a heating rate of 10°C/min and in the resonant frequency mode.

The fractured surfaces of the tensile test specimens were carefully cut without touching the surface. The surfaces, subsequently sputter coated with gold, were studied under a JEOL 35 CF Scanning Electron Microscope (SEM) for fracture topography.

3. Results and discussion

The phenolic resin used is a low melting solid (m.p. 40–50°C) and is also compatible with NBR. Thus the resin is absorbed by the NBR during mixing. An excess of resin compared to normal dose of plasticizer, e.g., dioctyl phthalate or dioctyl adipate used conventionally for NBR of less than 20 parts per hundred parts of rubber, probably caused formation of a separate resin phase of highly viscous material within the rubber matrix. Further in presence of hexamine which liberates NH_3 and HCHO during molding, the resin gets crosslinked [1]. Applied load during tensile testing of the vulcanizate of mix B was, therefore, partially shared by the resin matrix and it showed better strength properties than the unfilled vulcanizate of mix A (Table II). For the same reason mentioned as above, a lower elongation at break coupled with an increase in the compression set and hardness values for mix B were obtained compared to mix A. The extent of enhancement in physico-mechanical properties in case of mix B, however, is less than those of carbon black filled vulcanizate of mix C. Efficacy of carbon black as a reinforcing filler is superior than phenolic resin. It has also been observed that the carbon black together with phenolic resin in mix D can act in synergism and also produced maximum benefit in the physical properties. Phenolic resin, because of its thermoplasticity at processing temperature, augmented the strength properties of carbon black filled vulcanizate by improving the dispersion of the filler. In addition to this, novolac being polar and chemically reactive was absorbed on the surface of carbon black and subsequent wetting of carbon black improved polymer-filler interaction. Extent of volume swelling in various types of oil and fuel media showed superiority of the hybrid filler system (mix D) compared to others.

Fig. 1 is the SEM photomicrograph of the tensile fractured surface of mix A. A smooth surface with many bright spots indicating presence of rubber chemicals e.g., zinc oxide, stearic acid etc. marked the topography. Addition of phenolic resin alone (mix B) caused rapid increase in hardness and a substantial drop of the elongation at break value compared to mix A. These are also reflected in the features observed in the SEM photomicrograph in Fig. 2. The brittleness of the vulcanizate and failure in separate planes are clearly visible. These justify our assumption of formation of a separate

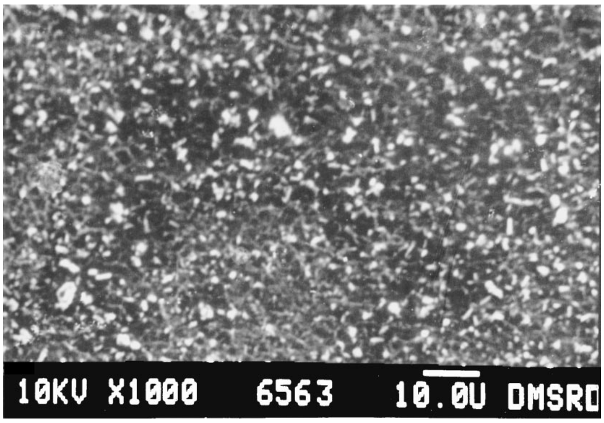

Figure 1 SEM photograph of the vulcanizate of mix A.

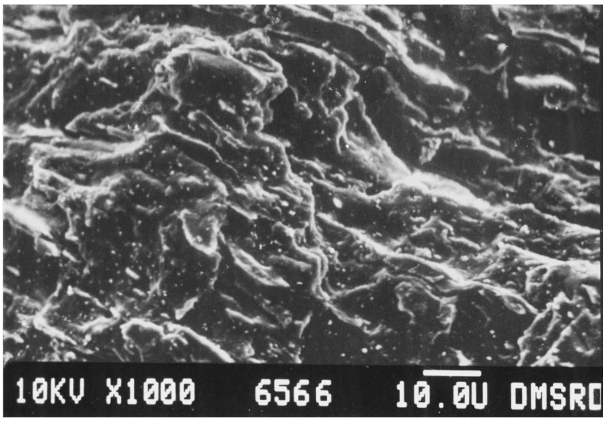

Figure 2 SEM photograph of phenolic resin filled vulcanizate of mix B.

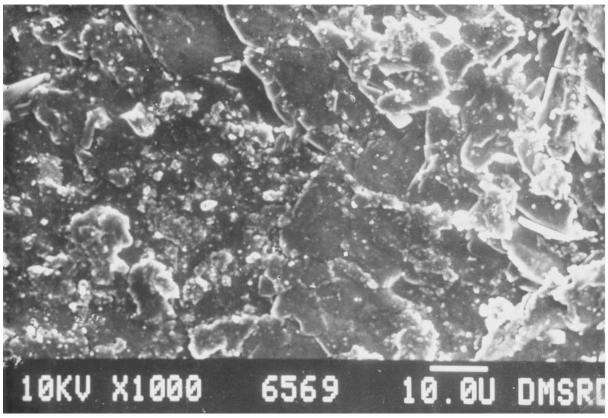

Figure 3 SEM photograph of carbon black filled vulcanizate of mix C.

resin phase, closely adhered to the rubber matrix and taking part in sharing the applied stresses.

Fig. 3 is the SEM photomicrograph of the tensile failed surface of mix C. The fracture surface shows rough fracture zone and presence of short fracture fronts. SEM studies reported earlier by Setua *et al.* [11–13] on different carbon black filled rubber vulcanizates and rubber-rubber blends showed the occurence of similar features which are indicative of higher tensile strength properties.

Figure 4 SEM photograph of carbon black + phenolic resin filled vulcanizate of mix D.

Coarsening of the fracture surface is further escalated while using the hybrid filler system into NBR (Fig. 4). Neither the brittle failure (Fig. 2) nor the tiny fracture fronts (Fig. 3), as exist in cases of only resin (mix B) and carbon black (mix C) systems respectively, were evident. Presence of resin improved the wettability of the carbon black filler particles, which resulted in an uniform distribution of carbon black agglomerates over the entire fracture surface. The observation supports for the maximum reinforcement properties of the vulcanizate of mix D.

Percentage retention of strength properties of the vulcanizates of mixes A, C and D due to heat aging at 100°C for 72 h are reported in Table III. Use of phenolic resin-hexamine in combination with carbon black was found to be advantageous when prolonged exposure to heat is concerned. The detrimental influence of heat was more than equalized by the protective influence of phenolic resin.

TGA plots for the vulcanizates of mixes A, C, D are shown in Fig. 5. Mix D showed better heat stability compared to mixes A and C. Structural integrity and compactness of mix D were also evident in the TMA plots (Fig. 6). In-situ resin curing with hexamine as well as improved surface properties of carbon black generated better reinforcement and lower susceptibility towards dimensional changes on heating of this vulcanizate.

A more conclusive information on the resin influence can be obtained from the measurement of viscoelastic properties of the vulcanizates as measured in dynamic methods e.g., storage modulus E' (Fig. 7), loss modulus E'' (Fig. 8) and loss tangent ($\tan\delta$, Fig. 9) vs. temperature. In Fig. 7, E' was found to be maximum when carbon black and resin-hexamine used in combination (mix D) and the observation is equivalent to those obtained for hardness and modulus of the vulcanizate compared to mixes A or C (Table II). Fig. 8 shows the plots of E'' vs. temperature of the vulcanizates of mix A, C & D. In all cases the peak maxima represents the glass transition temperature (Tg). Tg of the unfilled mix A (at -9°C) was found to be shifted to -5°C for carbon black filled mix C. However, the presence of hybrid system in mix D showed the occurrance of Tg at $+3^\circ$C. Similar to the decreasing trend of E'' from mixes A, C & D, Fig. 9 which represents the $\tan\delta$ (ratio of E''/E') vs temperature plots shows progressive reduction of the peak maxima of the tan δ values.

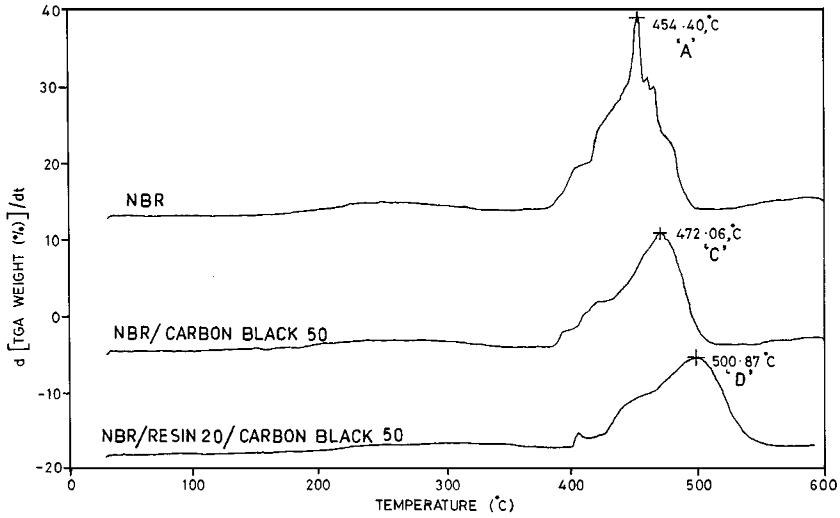

Figure 5 TGA plots of (A) unfilled, (C) carbon black and (D) carbon black + phenolic resin filled vulcanizates.

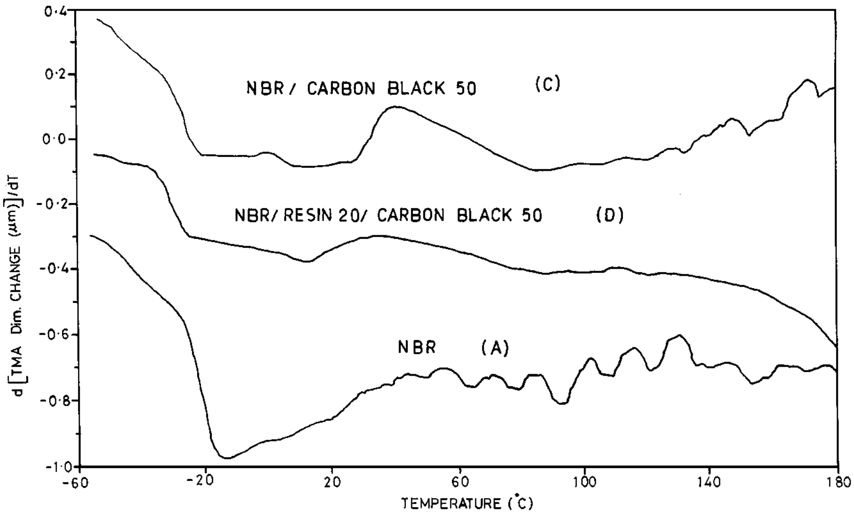

Figure 6 TMA plots of (A) unfilled, (C) carbon black and (D) carbon black + phenolic resin filled vulcanizates.

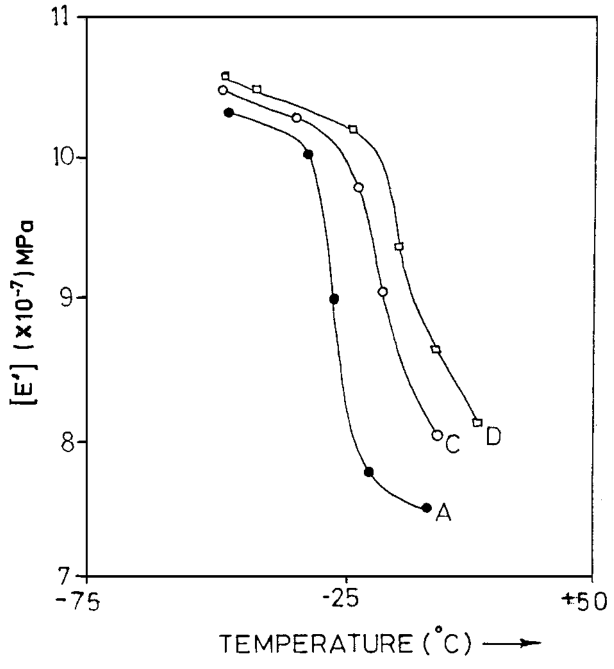

Figure 7 Storage modulus (E') vs. temperature plots of (A) unfilled, (C) carbon black and (D) carbon black + phenolic resin filled vulcanizates.

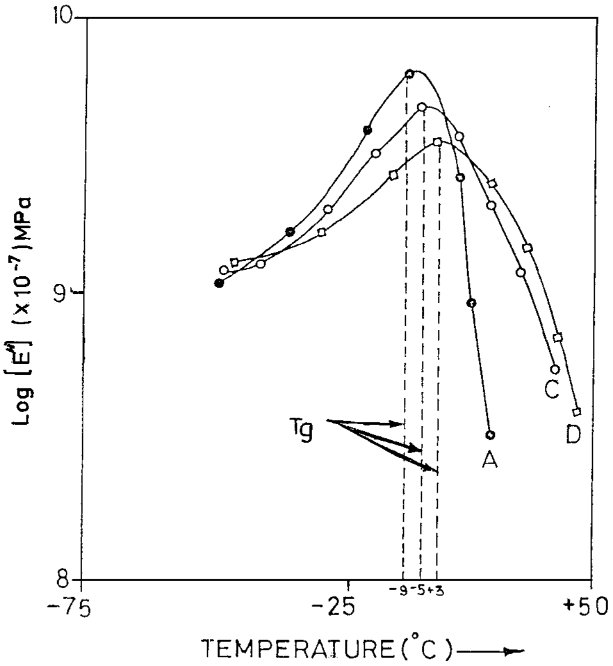

Figure 8 Logarithm of loss modulus (E'') vs. temperature plots of (A) unfilled, (C) carbon black and (D) carbon black + phenolic resin filled vulcanizates.

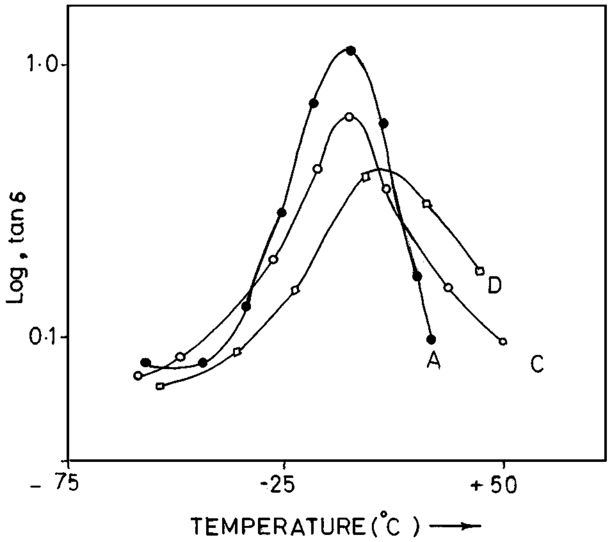

Figure 9 Logarithm of tan δ vs. temperature plots of (A) unfilled, (C) carbon black and (D) carbon black + phenolic resin filled vulcanizates.

4. Conclusion

1. Novolac type of phenolic resin in combination with carbon black in nitrile rubber vulcanizates has been found to improve the oil/fuel resistances, physico-mechanical properties as well as thermal stability.

2. Phenolic resin acts in synergism with carbon black and leads to better structural integrity, damping and extended service life for the vulcanizates.

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