CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

The details of the materials used and
experimental techniques adopted in the present
investigation are given in this chapter

2.1 Materials

2.1.1 Acrylonitrile butadiene rubber (NBR)

The generic term nitrile rubber refers to copolymers of an unsaturated nitrile and a diene. Commercially, acrylonitrile and butadiene are used almost exclusively. Nitrile rubbers are produced by emulsion polymerisation. The acrylonitrile content varies from 18–50%, with a median value of about 32% by weight.

Acrylonitrile butadiene rubber (Aparene N 553 NS) used in this study was supplied gratis by Gujarat Apar Polymers Ltd., Mumbai. The basic characteristics of NBR are given in Table 2.1.

Table 2.1.   Basic characteristics of NBR

Characteristics	
Bound acrylonitrile (%)	34.000
Mooney viscosity (ML_{1-4} 100°C)	40.000
Intrinsic viscosity (dl/g)	1.527
Antioxidant (%)	1.400
Volatile matter (%)	0.130
Organic acid (%)	0.250
Soap (%)	0.004

2.1.2 Poly(ethylene–co–vinyl acetate) (EVA)

Poly(ethylene–co–vinyl acetate) (EVA) with 18% vinyl acetate content (Pilene–1802) was procured from Polyolefins Industries Ltd., Chennai. The basic characteristics of EVA are given in Table 2.2.

Table 2.2. Basic characteristics of EVA

Characteristics	
Vinyl acetate (%)	18.00
Melt flow index (g/10 min)	2.00
Intrinsic viscosity (dl/g)	0.17
Density (g/cc)	0.94
Vicat softening point (°C)	59.00

2.1.3 Chemicals

The rubber chemicals such as dicumyl peroxide (40% active), zinc oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS) and sulphur were of commercial grade. Propane–2–thiol was supplied by Merck India Ltd., Mumbai.

2.1.4 Fillers and solvents

The black fillers such as high abrasion furnace black (HAF) and semi reinforcing furnace black (SRF) were of commercial grade. The white fillers such as silica and clay were purchased locally.

Toluene, cyclohexanone, carbon tetrachloride, chloroform, dichloromethane and n–heptane were of reagent grade and supplied by Merck India Ltd., Mumbai.

2.2 Preparation of the blends

Blends of NBR/EVA were prepared on a two roll mixing mill having a friction ratio 1:1.4. The blends are designated as N_X (X = 0, 10, ..., 100), where the

value of X indicates the weight percentage of NBR in the blend. The uncrosslinked blends were compression moulded at 150°C. The blends were crosslinked using three crosslinking systems, viz., dicumyl peroxide (DCP), sulphur (S) and a mixed system (DCP + S) and are indicated as P, S and M respectively. The compounds containing dicumyl peroxide are designated as N_0P, $N_{30}P$, $N_{50}P$, etc. The peroxide cured 50/50:NBR/EVA blend ($N_{50}P$) was selected for investigating the effect of fillers. The different fillers used such as high abrasion furnace black (HAF), semi-reinforcing furnace black (SRF), silica and clay are designated as BH, BS, S and C, respectively. The loading is indicated by prefixing numbers. Thus, 10 BH indicates 10 phr HAF loaded system, 20 BH indicates 20 phr HAF loaded system and so on. The compounding recipe of the blends are given in Table 2.3. The compounded blends were then compression moulded at 160°C for optimum cure.

Table 2.3   Compounding recipe for NBR/EVA blends

Ingredients (phr)[a]	Peroxide system (P)	Sulphur system (S)	Mixed system (M)	10 S	10 C	10 BS	20 BS	30 BS	10 BH	20 BH	30 BH
Polymer	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	-	5.0	5.0	-	-	-	-	-	-	-	-
Stearic acid	-	1.5	1.5	-	-	-	-	-	-	-	-
MBTS[b]	-	1.5	1.5	-	-	-	-	-	-	-	-
Sulphur	-	1.5	1.5	-	-	-	-	-	-	-	-
DCP[c]	4.0	-	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Silica	-	-	-	10	-	-	-	-	-	-	-
Clay	-	-	-	-	10	-	-	-	-	-	-
SRF[d]	-	-	-	-	-	10	20	30	-	-	-
HAF[e]	-	-	-	-	-	-	-	-	10	20	30

[a]parts per hundred rubber by weight; [b]mercaptobenzo thiazyl disulphide; [c]dicumyl peroxide; [d]semi-reinforcing furnace black; [e]high abrasion furnace black.

2.3   Characterisation of the blends

2.3.1   Mechanical properties

(a)   Tensile strength, modulus and elongation at break

Tensile testing of the sample was done at 25 ± 2°C according to ASTM D412-87 test method using dumb–bell shaped test pieces at a crosshead speed of 500 mm/min on an Instron Universal Testing Machine (Model 1121). The test pieces were punched out from the moulded sheets using a die. The thickness of the dumb–bell specimens was measured using a micrometer having accuracy of 0.1 mm. The load–elongation curves were recorded on a strip chart recorder. The Young's modulus was determined from the linear portion of the stress–strain curve. The failure properties were calculated using the equations,

$$\text{Tensile strength} = \frac{\text{Load at failure (N)}}{\text{Area of cross section (mm}^2)} \qquad (2.1)$$

$$\text{Ultimate elongation (\%)} = \frac{\text{Displacement at failure}}{\text{Effective gauge length}} \times 100 \qquad (2.2)$$

For mechanical property measurements, a minimum of five specimens per sample were tested and an average of these values are reported.

(b)   Tear strength

The tear strength of the samples was determined using unnicked 90° angle test pieces according to ASTM D624-81 test method. The instrument and the experimental conditions are the same as in the case of tensile testing. The tear strength was calculated using the equation:

$$\text{Tear strength} = \frac{\text{Load at failure (N)}}{\text{Thickness (mm)}} \qquad (2.3)$$

(c)   Hardness

The hardness of the samples was measured using durometer according to ASTM D2240–86 test method and is expressed in shore A units.

2.3.2   Optical microscopic studies

Thin films of the blends were casted after dissolving the blends in chloroform. The morphological studies of the blends were carried out by observing the films under an optical microscope.

2.3.3   Scanning electron microscopic (SEM) studies

(a)   Morphology

Moulded samples of the uncrosslinked blend were fractured cryogenically using liquid nitrogen. This was done to avoid any possible deformation of the phases. For studying the morphology of the blends, NBR from EVA rich blends was extracted using toluene and EVA from NBR rich blends was extracted using carbon tetrachloride. In the case of 50/50 blend NBR was extracted. The cryogenically fractured edge of the sample was kept immersed in the solvent for about 48 h at ambient temperature for the preferential extraction of one of the phases. The samples were dried in an air oven at $40 \pm 1°C$ for 24 h. The dried samples were preserved in a desiccator for SEM studies. The solvent extracted samples were sputter coated with Au/Pd alloy and SEM observations were made using JEOL–JSM–T330A scanning electron microscope.

(b)   Fractography

After testing the tensile and tear specimens up to failure, the fractured surfaces were sputter coated with Au/Pd alloy. SEM observations of the tear failure

surfaces of the uncrosslinked blends, tensile and tear failure surfaces of the crosslinked and filled systems were also carried out to analyse the failure mechanism

2.3.4 X-ray studies

In order to estimate out the degree of crystallinity, X-ray diffraction patterns of the samples were recorded with an X-ray diffractometer using Ni-filtered CuK_α radiation from a Philips X-ray generator. The angular range was 5 to 40° (2θ). Samples of the same thickness and the same area were exposed to the X-ray source. The operating voltage and the current of the tube were kept at 40 kV and 20 mA respectively throughout the course of investigation.

2.3.5 Cure characteristics

The cure behaviour of the blends was determined using a Monsanto Rheometer at 160°C. The cure time, scorch time, maximum torque and cure rate index were determined from the rheographs.

2.3.6 Polysulphidic linkage estimation

Samples, each weighing approximately 0.2 g were treated with a solution of propane-2-thiol (0.4 M) in n-heptane for 2 h at room temperature under nitrogen atmosphere. The samples were then washed with petroleum ether (b.p. $40–60^\circ$C) and dried. The polysulphidic crosslinks were obtained by the difference between the values of total crosslink concentration (measured by volume swelling method) before and after the treatment.[1,2]

2.3.7 Crosslink density determination

(a) From tensile measurements

The crosslink density (ν) of the samples was calculated from the tensile measurements using the equation,[3]

$$v = \frac{F}{2A_0\rho_p RT\left(\alpha - \frac{1}{\alpha^2}\right)}$$ (2.4)

where F represents the load; A_0, cross sectional area of the sample; ρ_p, density of the polymer; R, gas constant; T, the absolute temperature; and α, the extension ratio.

(b) From swelling method

The crosslink density of the unaged and aged samples was determined by the swelling method. The samples were allowed to swell in cyclohexanone and the equilibrium uptake is noted. The molecular weight between the crosslinks (M_c) is calculated using the equation,

$$M_c = \frac{\rho_p V_s \phi^{1/3}}{\ln(1-\phi) + \phi + \chi\phi^2}$$ (2.5)

where ρ_p — Density of polymer

V_s — Molar volume of solvent

ϕ — Volume fraction of polymer in the swollen mass

χ — Interaction parameter

ϕ and χ are given by the following equations,

$$\phi = \frac{w_1 \rho_1}{\left(w_1 \rho_1 + w_2 \rho_2\right)}$$ (2.6)

where w_1 – Weight of polymer

ρ_1 – Density of polymer

w_2 – Weight of solvent at equilibrium

ρ_2 – Density of solvent

$$\chi = 0.34 + \frac{V_s}{RT}(\delta_A - \delta_B)^2 \tag{2.7}$$

where V_s – Molar volume of solvent

δ_A, δ_B – Solubility parameter of solvent and polymer

From the molecular weight between crosslinks, the crosslink density, ν is calculated using the equation,

$$\nu = 1/2M_c \tag{2.8}$$

2.3.8 Melt flow studies

(a) Rheological measurements

The shear viscosity of the blends was determined using an Instron Capillary Rheometer—Model 3211. The capillary having an l/d ratio of 20.27 and an angle of entry of 90° was used. The sample was placed inside the barrel of the extrusion assembly and forced down to the capillary with a plunger attached to the moving crosshead. The experiment was done at 90°C. After a warming up period of 5 min the melt was extruded through the capillary at preselected crosshead speeds which varied from 0.6 to 200 mm min⁻¹. The force corresponding to specific plunger speeds was noted from a recorder assembly. The force and crosshead speed were converted into shear stress (τ_w) and apparent shear rate ($\dot{\gamma}_{w.a}$) at the wall using equations,

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \tag{2.9}$$

where F represents the force; A_p, the area of the plunger; l_c and d_c, the length and diameter of the capillary respectively.

$$\dot{\gamma}_{w,a} = \frac{2d_b^2}{15d_c^3} V_{xh} \qquad (2.10)$$

where V_{xh} is the crosshead speed; d_b, the diameter of the barrel; and n', the flow behaviour index.

From the apparent shear rate ($\dot{\gamma}_{w,a}$) values, the true shear rate at the wall ($\dot{\gamma}_w$) was calculated using the following equation which includes the Rabinowitch correction.

$$\dot{\gamma}_w = \frac{(3n'+1)}{4n'} \dot{\gamma}_{w,a} = \frac{(3n'+1)}{4n'} \frac{8V}{d_c} \qquad (2.11)$$

where

$$V = \frac{V_{xh}}{60} \left[\frac{d_b}{d_c} \right]^2 \qquad (2.12)$$

n' is defined as

$$n' = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{w,a})} \qquad (2.13)$$

The flow behaviour index (n') was obtained by regression analysis based on the values of τ_w and $\dot{\gamma}_{w,a}$ obtained from the experimental data. The shear viscosity, η was calculated using the equation,

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \qquad (2.14)$$

(b) Die swell

The extrudates were carefully collected as they emerged from the capillary die; adequate care was taken to avoid effects of draw-down and contraction on

cooling. The diameter of the extrudate (d_e) was measured and the die swell was calculated as the ratio of the diameter of the extrudate to that of the capillary (d_e/d_c).

(c)   Extrudate morphology

The morphology of the uncrosslinked blend was studied by solvent etching technique. For this, cryogenically fractured extrudates of EVA rich blend (N_{30}) and the 50/50 blend (N_{50}) were kept immersed in toluene for about 48 h for preferential extraction of NBR phase. Carbon tetrachloride was used for the preferential extraction of EVA from NBR rich blend (N_{70}). The samples were then dried in an air oven and the extracted surface was examined using scanning electron microscope.

(d)   Extrudate deformation

The extrudates of the blends at different shear rates were collected and observations were made on the extrudate deformation behaviour.

2.3.9   Dynamic mechanical analysis

The dynamic mechanical properties of NBR, EVA and NBR/EVA blends were measured using a dynamic mechanical thermal analyser (Polymer Laboratories DMTA MK-II). The instrument measures dynamic moduli (both storage and loss moduli) and the damping of the specimen under an oscillatory load as a function of temperature. The experiments were conducted at a dynamic strain of 0.325% and at frequencies, 0.1, 1, 10, 50 and 100 Hz. Liquid nitrogen was used to achieve subambient temperature and a programmed heating rate of 1°C min^{-1} was given. Mechanical loss factor tan δ and dynamic moduli (E′ and E″) were calculated with a microcomputer. Samples of dimension 70 x 10 x 2.5 mm were prepared for testing. The storage modulus E′ and the loss modulus E″ are obtained from E* and δ using the following equations.

$$E'' = E^* \sin \delta \qquad (2.15)$$

$$E' = E^* \cos \delta \qquad (2.16)$$

where E^* is the dynamic complex modulus.

The loss tangent is given as

$$\tan \delta = E''/E' \qquad (2.17)$$

2.3.10 Diffusion experiments

Diffusion experiments were carried out using both crosslinked and filled systems. Circular samples (diameter $\approx$ 2 cm) were punched out from the moulded sheets by means of a sharp edged die. The thickness of the samples was measured using a micrometer. Samples were immersed in the solvent taken in test bottles. The samples were withdrawn periodically from the solvent and the solvent adhering to the surface was rubbed off. The samples were weighed on a highly sensitive electronic balance of accuracy 0.1 mg and then replaced in the test bottle. This process was continued till equilibrium was reached. To minimise the error due to the evaporation of solvent from the sample, the time for weighing was kept to a minimum of 30s in all the experiments. For the experiments above room temperature, the samples were kept in a thermostatically controlled air oven. The mole per cent uptake (Q_t), of the solvent by 100 g of the polymer was plotted against square root of time and the results were analysed. When equilibrium was reached, Q_t was taken as Q_∞, i.e. mole per cent uptake at infinite time.

2.3.11 Thermal analyses

(a) Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out on a delta series–TGA 7 analyser in nitrogen atmosphere. Samples were scanned from 30–750°C at a heating rate of 10°C/min.

(b) Differential scanning calorimetry (DSC)

The thermal behaviour of the blends was studied using a DSC Mettler thermal analyser. The samples were inserted into the apparatus at room temperature and immediately heated to 200°C at a rate of 40°C min^{-1} and kept for 1 min at this temperature in order to remove the volatile impurities. The samples were quenched to –80°C and then heated to 250°C at a heating rate of 5°C min^{-1} in nitrogen atmosphere. The glass transition temperature of each sample was taken as the midpoint of the step in the scan. The peak from DSC curve was considered as the melting point.

(c) Ageing characteristics

Test samples were heated at 50 and 100°C in an air circulating oven for 72 h. After cooling and conditioning at room temperature, the dimensions of each specimen were measured. The tensile properties of these samples were determined according to ASTM D412-87 using an Instron Universal Testing Machine (Model 1121) at a crosshead speed of 500 mm/min. The oil resistance of these blends was also studied. The samples were dipped in the oil for 7 days at ambient conditions and the percentage uptake was estimated.

2.4   References

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