Summary

The details of the materials and experimental techniques used for the present investigation are discussed in this chapter. An account of the characteristics of the materials, formulations of the mixes and sample preparation procedures is given. The experimental procedures for sorption, pervaporation, vapour sorption and gas transport through the EVA matrix have been described. Other characterisation methods (x-ray diffraction analysis, transmission electron micrographs, scanning electron microscopy and mechanical property measurements) used to complement the observations from the transport studies are also given.
2.1. Materials

2.1.1. Poly (ethylene-co-vinyl acetate) (EVA)

Poly(ethylene-co-vinyl acetate) is a random copolymer of ethylene and vinyl acetate, which is commonly referred to as EVA copolymer or simply EVA. The character of EVA varies strikingly with change in vinyl acetate (VA) content. At very low proportions of VA, the copolymer resembles low density polyethylene (LDPE) but exhibits the physical properties and processing behaviour of a tough thermoplastic. EVA with high VA content (20 to 40% by weight) are less crystalline and hence have more transparency and flexibility. The wide range of properties, depending on the VA content, extends the application profile from plastics to rubber like elastic products.

2.1.1.1. Chemical structure

EVA is a random copolymer with a long ethylene chain and pendant acetate groups. It is represented by the following structure (Figure 2.1).

![Chemical structure of EVA](image)

**Figure 2.1:** Structure of Poly (ethylene-co-vinyl acetate)
The amount of VA in the copolymer controls its character. At low VA content it has a plastic nature. Increase in the VA content results in increased flexibility. The crystallinity decreases and it becomes more rubber like or elastic in nature. The presence of acetate groups also gives polarity to the polymer that reflects in its solubility, adhesion and filler intake properties.

2.1.1.2. Properties of EVA

Physical properties

(1) Vinyl acetate content: The VA content has a very important effect on the crystallinity and polarity of the copolymer. As the VA content increases, due to the relative bulkiness of the acetoxy side chain, the close packing of polymer chains becomes difficult and the ability of the polymer to form crystalline regions, often referred to as crystallites, decreases. Hence as the VA content increases, the crystallinity decreases.

Another overriding effect of VA content results from the polar nature of the acetoxy side chain. Thus, as the VA content increases so does the polarity of the copolymer. An increase in polarity gives rise to a number of interesting properties such as compatibility with other polymers, increased adhesion, printability and electrical properties.

An increasing VA content can increase the flexibility, transparency, tackiness, filler retention, shock resistance etc. and decrease the hardness, stiffness, melting point, chemical resistance etc.
(2) **Melt flow index**: Melt flow index (MFI) is a direct indication of the average molecular weight of the EVA copolymer. As the melt flow index increases the flowability of the melt increases but viscosity of the melt, toughness, impact strength and stress cracking strength decrease.

(3) **Crystalline melting point**: The crystalline melting point ($T_m$) of the EVA ranges between 70 and 150°C. The value decreases with increase in VA content. Short term heating above service temperature without mechanical strength is possible right upto the crystalline melting point. Physical or chemical crosslinking can bring about an increase in thermal stability under load.

(4) **Thermal conductivity**: In comparison with their homopolymers, LDPE or high density poly ethylene (HDPE), EVA shows lower thermal conductivity.

(5) **Electrical properties**: EVA copolymer does not have the same dielectric properties compared to LDPE due to the polarity of the VA group.

(6) **Creep properties**: At low VA content, say upto 20%, the creep or cold flow behaviour of EVA is similar to that of LDPE. But as VA content increases, resistance to creep decreases.

**Chemical properties**

(1) **Water absorption**: EVA absorbs small quantities of moisture due to its polar nature. The water absorption increases with increase in VA content.
(2) **Chemical resistance** : Unstressed samples of EVA show excellent resistance to strong alkalis, brine solution, detergents and non-oxidising media but have poor resistance to hydrocarbons and chlorinated solvents due to the low crystallinity (higher degree of branching) and its polar nature. The resistance deteriorates with increase in VA content.

(3) **Solubility** : EVA copolymer is soluble in aliphatic, aromatic and chlorinated solvents. The solubility in all solvents is minimal at room temperature but higher VA content grades can be dissolved in warm solvents.

(4) **Resistance to stress cracking** : EVA copolymers are highly resistant to stress cracking even in the presence of polar organic solvents or surface active agents like detergents. The resistance to stress cracking increases with increase in VA content.

(5) **Gas and vapour permeability** : EVA is permeable to gases and vapours such as \( \text{CO}_2 \), \( \text{O}_2 \), water vapour etc. Because of its lower crystallinity, EVA is more permeable to these gases than LDPE. Permeability increases with increase in VA content.

(6) **Weathering** : Exposure to UV radiations, in the presence of atmospheric oxygen slowly degrades unprotected EVA.
2.1.1.3. Applications of EVA

Due to great versatility of EVA copolymers it could find a wide range of applications. The properties of EVA such as their intrinsic flexibility, toughness chemical resistance, environmental stress cracking resistance (ESCR), easier processing and ozone resistance give them an advantage over other polymers. EVA offers a cost advantage over rubber and poly vinyl chloride (PVC) compounds due to low density. EVA is superior to LDPE due to its properties like ESCR, low softening temperature, better UV resistance etc.

EVA has advantage over PVC and elastomers with outstanding low temperature flexibility, retention of flexibility over long periods, better chemical resistance, better UV and ozone resistance, better ESCR, high processability etc.

EVA is compatible with a wide range of fillers, waxes, resins, and other thermo plastics and hence widely used in hot melt and other blend applications. It is also ideal for packaging and storing food stuffs since they are devoid of plasticisers.

The products that require greater flexibility at low temperature such as freezer doors, gaskets, boots, ice cube trays can be made. Medico-pharmaceutical applications such as anesthetic facemask, contact lens holders, orthodontia products and disposable feeding bottle teats can be made. EVA copolymers are widely used in the manufacture of various
types of films which require flexibility, toughness and optical properties, films for fresh meat packaging, horticultural films, cling films and disposable surgical gloves can be manufactured. The basic characteristics of EVA are given in Table 2.1.

**Table 2.1 : Characteristics of EVA**

<table>
<thead>
<tr>
<th>Material</th>
<th>Properties</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene-co-vinyl acetate) Pilene 1802.</td>
<td>Melt flow index(g/10 min) 2.00</td>
<td>PIL, Madras</td>
</tr>
<tr>
<td></td>
<td>Density (g cc(^{-1})) 0.937</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vicat softening Point (°C) 59.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vinyl acetate (wt%) 18.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Intrinsic viscosity (dl g(^{-1})) 0.170</td>
<td></td>
</tr>
</tbody>
</table>

**2.1.2. Vulcanizing aents**

The vulcanizing agents used for crosslinking the EVA matrix were dicumyl peroxide (DCP) (40 % active) and benzoyl peroxide (BP). All the chemicals used were of commercial grade.

**2.1.3. Nano filler**

The nano clay used is closite Na\(^+\), (a natural montmorillonite) manufactured by Southern Clay Products, USA. The properties of nano clay are given in Table 2.2.
Table 2.2 : Properties of nano clay

<table>
<thead>
<tr>
<th>Cation exchange capacity</th>
<th>92.6 m eq/100g day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>10% less than</td>
<td>2 μ</td>
</tr>
<tr>
<td>50% less than</td>
<td>6 μ</td>
</tr>
<tr>
<td>90% less than</td>
<td>13 μ</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.86 g/cc</td>
</tr>
<tr>
<td>Colour</td>
<td>Off white</td>
</tr>
<tr>
<td>Organic modifier</td>
<td>None</td>
</tr>
</tbody>
</table>

2.1.4. Solvents

The solvents used in the present work such as aromatic hydrocarbons (benzene, toluene and xylene), aliphatic hydrocarbons (n-pentane, n-hexane, and n-heptane) chlorinated hydrocarbons (dichloromethane, chloroform and carbon tetrachloride), acetone, ethanol and methanol were obtained from E-Merck (India) Ltd., Mumbai, India. They were of reagent grade (99% pure) and were distilled twice before use to ensure purity. Relevant data are given in Table 2.3.
Table 2.3: Characteristics of solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point (°C)</th>
<th>Density at 25°C (g/cc)</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>56.24</td>
<td>0.791</td>
<td>58</td>
</tr>
<tr>
<td>Benzene</td>
<td>80.1</td>
<td>0.874</td>
<td>78.11</td>
</tr>
<tr>
<td>Toluene</td>
<td>110.6</td>
<td>0.867</td>
<td>92.14</td>
</tr>
<tr>
<td>Xylene</td>
<td>138.3</td>
<td>0.86</td>
<td>106.17</td>
</tr>
<tr>
<td>Pentane</td>
<td>36</td>
<td>0.626</td>
<td>72</td>
</tr>
<tr>
<td>Hexane</td>
<td>68.9</td>
<td>0.659</td>
<td>86.18</td>
</tr>
<tr>
<td>Heptane</td>
<td>98.4</td>
<td>0.684</td>
<td>100.2</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>76.5</td>
<td>1.594</td>
<td>153.8</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61.7</td>
<td>1.492</td>
<td>119.3</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>40.5</td>
<td>1.325</td>
<td>84.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.3</td>
<td>0.783</td>
<td>46</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.5</td>
<td>0.793</td>
<td>32</td>
</tr>
</tbody>
</table>

2.2. Experimental techniques

2.2.1. Preparation of membranes

EVA membranes were prepared on a two roll mixing mill (150mm x 30mm) with a nip gap of 1.3mm and a friction ratio of 1:1.4. The nip gap, mill speed ratio, time of mixing and temperature of rollers were kept same for all mixes. The formulations of the mixes are given in Tables 2.4, 2.5 and 2.6 respectively.
Table 2.4: Formulation of EVA/DCP mixes

<table>
<thead>
<tr>
<th>Amount of the polymer (kg)</th>
<th>Amount of DCP (kg)</th>
<th>No. of moles of DCP</th>
<th>Representation of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>D₀</td>
</tr>
<tr>
<td>0.1</td>
<td>0.001</td>
<td>0.0015</td>
<td>D₁</td>
</tr>
<tr>
<td>0.1</td>
<td>0.002</td>
<td>0.003</td>
<td>D₂</td>
</tr>
<tr>
<td>0.1</td>
<td>0.004</td>
<td>0.006</td>
<td>D₄</td>
</tr>
<tr>
<td>0.1</td>
<td>0.006</td>
<td>0.009</td>
<td>D₆</td>
</tr>
<tr>
<td>0.1</td>
<td>0.008</td>
<td>0.012</td>
<td>D₈</td>
</tr>
</tbody>
</table>

Table 2.5: Formulation of EVA/ BP mixes

<table>
<thead>
<tr>
<th>Weight of the polymer (kg)</th>
<th>Weight of BP (kg)</th>
<th>Number of moles BP</th>
<th>Representation of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.001</td>
<td>0.004</td>
<td>B₁</td>
</tr>
<tr>
<td>0.1</td>
<td>0.002</td>
<td>0.008</td>
<td>B₂</td>
</tr>
<tr>
<td>0.1</td>
<td>0.004</td>
<td>0.016</td>
<td>B₄</td>
</tr>
<tr>
<td>0.1</td>
<td>0.006</td>
<td>0.025</td>
<td>B₆</td>
</tr>
<tr>
<td>0.1</td>
<td>0.008</td>
<td>0.033</td>
<td>B₈</td>
</tr>
</tbody>
</table>

Table 2.6: Formulation of EVA/nano clay composites

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>F₀</th>
<th>F₃</th>
<th>F₅</th>
<th>F₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA (kg)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>DCP (kg)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Closite Na⁺ (kg)</td>
<td>0</td>
<td>0.003</td>
<td>0.005</td>
<td>0.007</td>
</tr>
</tbody>
</table>
2.2.2. **Time for optimum cure**

The optimum cure time ($t_{90}$) was determined by using a Geottfert Rheometer at a rotational frequency of 100 cycles/min. The samples were cured to their optimum cure time. The $t_{90}$ represents the time to obtain 90% of the maximum rheometric torque. It is important to point out here that the rheometric torque and the crosslink density are directly related.

2.2.3. **Moulding of the test samples**

Blank cut from the uncured samples were marked with the direction of the mill grain and DCP samples were vulcanized at 170°C in a hydraulic press under a load of 24.5 x 10^4 N. The benzoyl peroxide (BP) samples were cured to their optimum cure time at 120°C. Nanocomposites were vulcanized at 160°C in a hydraulic press. Uncrosslinked EVA membranes were also prepared.

2.2.4. **Sorption experiments**

The EVA samples for sorption experiments (ASTM D-471) were punched out in circular shape of diameter 19 mm from compression moulded (10cm x 10cm) sheets and were dried in a vacuum desicator over anhydrous CaCl$_2$ at room temperature for about 24 h. The original weight and thickness of the samples were measured before sorption experiments. They were then immersed in solvents (15-20 ml) in closed diffusion bottles, kept at constant temperature in an air oven. The samples were removed from the bottles at periodic intervals, dried for 5-10 s between filter papers to remove the excess solvent on their surfaces and weighed immediately using an
electronic balance (Shimadzu, Libror AEU-210, Japan) that measured reproducibly within \( \pm 0.0001 \) g. They were then placed back into the test bottles. The process was continued until equilibrium swelling was achieved. Since the weighing was done within 40 s, the error associated with the evaporation of solvents is negligible [1]. Similar methodology has been adopted by several researchers [2-11]. The experiments were duplicates or triplicates in most cases and the deviation was within \( \pm 0.08 \) to 0.1 mol %.

The results of the sorption experiments have been expressed as moles of solvent taken by 0.1 kg of the polymer sample, \( Q_t \) mole %, i.e.,

\[
Q_t = \left[ \frac{\text{Mass of solvent sorbed/Molar mass of solvent}}{\text{Mass of polymer}} \right] \times 100 \tag{2.1}
\]

The \( Q_t \) values obtained thereby have been plotted as a function of square root of time, to construct the sorption curves.

**2.2.5. Pervaporation**

A schematic representation of the pervaporation apparatus is represented in Figure 2.2. The permeation cell assembled from two half cells of column couplers made of glass, fastened together by bolted clamps. The capacity of each half cell was about 100 ml and the effective surface area of the membrane is 19.3 cm\(^2\). The membrane was supported on a fine porous stainless steel plate with holes (3 mm) drilled on it. Vacuum at the down
stream side was maintained by using Hindhivac (Ed-6). A pressure of 3.5 to 4 mm of Hg was applied. The membrane was soaked in the mixture for 24 hours and then kept in the pervaporation cell for about 2 hours in each run to reach equilibrium conditions before collecting the permeate. The permeated vapours were completely condensed in a trap placed in a Dewar flask cooled to -40°C using ice-calcium chloride mixture. Complete condensation was effected by placing two traps in series. Different feed compositions were also used. All the experiments were conducted at room temperature.

The performance of a membrane in pervaporation is characterised by permeation rate or flux (kg/m²·h) and selectivity or separation factor $\alpha_i$ [12].

The selectivity is defined as

$$\alpha_{ij} = \frac{Y_i / Y_j}{X_i / X_j} \tag{2.2}$$

where $Y_i$ and $Y_j$ represent the weight fraction of the components in the permeate, $X_i$ and $X_j$ are the weight fraction of the components in the feed, ‘$i$’ is the more permeating component than ‘$j$’.

The permeation rate is the amount of the component permeated in unit time and per unit cross section area of the membrane. The pervaporation separation index (PSI) has been used to evaluate the overall performance of the membranes, which can be determined from the following relation [13].
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\[
\text{PSI} = J(\alpha_{ij} - 1)
\]  

(2.3)

where, \( J \) is permeation rate or flux and \( \alpha_{ij} \) is the selectivity or separation factor.

**Figure 2.2:** Schematic Diagram of pervaporation apparatus: (A) stirrer, (B) permeation cell, (C) membrane, (D) collection traps, (E) Dewar flask, (F) R.B.Flask, (G) pressure gauge, (H) moisture trap, (I) vacuum pump.

### 2.2.6. Vapour permeation

The vapour permeability was determined at room temperature by measuring the weight loss of small vials filled with solvents and tightly closed by a membrane of 100 μm thickness. The weight loss is
proportional to time, area of the membrane, pressure inside the vials and is inversely proportional to the thickness of the membrane.

2.2.7. Gas permeation

The permeability of EVA membrane to pure nitrogen and oxygen was determined at room temperature using the constant pressure/variable volume method. The feed side pressure of the gases was 40 psi. The permeant side was maintained at atmospheric pressure. The test cell was constructed of stainless steel. The effective area inside the cell was 3.14cm². The gas permeated from the active membrane passed through the supporting media of porous stainless steel plates. The two O-rings were used as the sealing agent. Schematic representation of gas permeation apparatus is shown in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3**: Schematic representation of gas permeation apparatus
(A) gas cylinder (B) line regulator (C) test cell
(D) pressure guage (E) micro valve (F) mercury flow meter
2.2.8. Swelling behaviour of the membranes

Initially a piece of dry membrane was weighed and swelled in the solution mixture of known composition for 48 h at room temperature. The swollen membranes were taken out and wiped with tissue paper to remove adherent solvent and then weighed. The difference between the weights gave the amount of solvent absorbed by the polymer. The swelling ratio was calculated using the equation [14].

\[ S = \frac{W_s - W_d}{W_d} \]  

(2.4)

where; \( W_d \) denotes weight of dry membrane, \( W_s \) denotes weight of solvent swollen membrane.

2.2.9. Characterisation of the samples

(a) X-ray diffraction studies

X-ray diffraction (XRD) patterns were taken by using Ni-filtered CuK\(_\alpha\) radiation (\(\lambda=0.154\text{nm}\)) by X’pert diffractometer, Philips at 40 keV and 30 mA. The operating voltage and the current of the tube were kept same throughout the investigation.

(b) Scanning electron microscopic analysis

The polymer samples for scanning electron microscopy (SEM) were prepared by cryogenically fracturing them in liquid nitrogen. These samples were sputter coated with gold and SEM examinations were performed on a Cambridge Instrument (S360) to eliminate the problems
with sample charging. The SEM runs were made by a beam current of \(5 \times 10^{-3}\) A, using a scanning electron microscope (S-2400, Hitachi, Japan). The SEM has been used by several researchers [15-18] for investigating the morphology of polymer systems.

(c) Transmission electron microscopic analysis

Transmission electron micrographs of layered silicate reinforced polymer nano composites were taken in a LEO 912 omega transmission electron microscope with an acceleration voltage of 120 keV. The specimens were prepared using an ultracut E cryomicrotome. Thin section of about 100 nm was cut with a diamond knife at \(-120^\circ\)C

2.2.10. Mechanical properties

The mechanical properties of the polymer were determined to complement the observations from transport studies. For this, the samples were dried at \(60^\circ\)C for 3 h to remove the moisture prior to the tests.

Stress-strain properties

Tensile testing of the samples was done at 25 ± 2°C according to ASTM D-412 test method using dumb-bell shaped test specimens at a cross head speed of 500 mm/min using a series IX automated material testing system 1.38 by Instron Corporation Model 4411 (Canton, MA, USA). The properties were calculated using the equation:

\[
\text{Tensile strength} = \frac{\text{Load at failure}}{\text{Area of cross section}}
\]  
(2.5)
For the measurement of mechanical properties, a minimum of five specimens per sample were tested and an average of these values has been reported.

2.2.11. Gas liquid chromatographic analysis

The permeate and feed compositions were analysed by a Gas Liquid Chromatograph (Shimadzu GC14B, Japan). The column used was BP-1 (Capillary) and the detector was FID (Flame Ionization Detector). Helium was used as the carrier gas and hydrogen and compressed air were used for the flame in FID. The injection port was maintained at a temperature of 240°C, column temperature at 50°C and detector temperature was at 250°C. Toluene was used to dilute the samples (50 µL in 5ml of toluene) and 0.5 µL of the sample was injected. The maximum retention time given was 5 minutes.

2.2.12. Positron annihilation lifetime spectroscopic analysis

Positron annihilation lifetime spectra (PALS) is used to examine the free volume present in unfilled and nanofilled EVA samples. The Positron Lifetime Spectrometer consists of a fast-fast coincidence system with BaF₂ scintillators coupled to photo multiplier tubes type XP2020/Q with quartz window as detectors. The detectors were shaped to conical to achieve better time resolution. A17mCi²²Na positron source, deposited on a pure Kapton foil of 0.0127 mm thickness was placed between two identical pieces of the sample under investigation. This sample-source sandwich
was positioned between the two detectors of PALS to acquire lifetime spectrum. The spectrometer measures 180 ps as the resolution function with $^{60}\text{Co}$ source.

However, for better count rate, the spectrometer was operated at 220 ps time resolution [19]. All lifetime measurements were performed at room temperature and two to three positron lifetime spectra with more than a million counts under each spectrum were recorded. In PALS analysis only two measured parameters namely o-Ps lifetime ($\tau_3$) and o-Ps intensity $I_3$. The o-Ps lifetime $\tau_3$ measures the size of the free volume holes ($V_i$) and $I_3$ is a relative measure of the number of free volume sites in the polymer matrix.

The free volume cavity radius ($R$) is related to the o-Ps pick off lifetime ($\tau_3$) by a simple relation. The underlying assumption in the formulation of this relation is that o-Ps atom in a free volume cell can be approximated to a particle in a potential well of radius $R_0$. The potential is infinite if $r>R_0$ and constant for $r<R_0$. Further, it is assumed that there is an electron layer in the region $R<r<R_0$, with $R_0=R+\delta R$ where $\delta R$ represents the thickness of the electron layer or the probability of overlap of the $P_s$ wave function and electron wave function. The expression connecting the free volume radius $R$ (in nm) and the o-$P_s$ pick-off lifetime $\tau_3$ (in ns) according to Nakanishi et al. [20] is
\[
\frac{1}{\tau_3} = 2 \left( 1 - \frac{R}{R_0} \right) + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right)
\]  \hspace{1cm} (2.6)

Here, the value of $\delta R = 0.1656$ nm was determined by fitting experimental $\tau_3$ values to data from molecular materials with well-known hole size like zeolites [21]. Using this value of $R$, the free volume size ($V_f$) is calculated as $V_f = (4/3) R^3$. Then the relative fractional free volume is evaluated as the product of free volume ($V_f$) and o-P$_s$ intensity, $I_3$ ($\%$).

\textbf{2.2.13. Differential scanning calorimetry}

Thermograms on films were recorded using a Q10 model TA instrument to determine the glass transition temperature. The heating rate used was $10^\circ$C/min. and the purge gas was nitrogen. The samples were analysed from $-50^\circ$C to $200^\circ$C.
References

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