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Abstract: Vinyl Acetate was copolymerized with Acrylamide in Four different formulations (95:05%, 90:10%, 85:15% and 80:20 %) (wt%) using redox catalysts by emulsion polymerization at 45 Deg C in water. The emulsions were casted on glass plates to form films. The films were tested for Mechanical properties like tensile strength, elongation at break and tear strength. Water vapour Permeability was determined. Optical property Haze was determined. The films were characterized by FT – IR spectroscopy and by DSC (Differential Scanning Calorimetry) for Tg, Tm and Td. The emulsions were precipitated using non solvent Methanol. The copolymers films were used for testing of MFI to know the flow characteristics.

Key words: Vinyl acetate, Acrylamide, Emulsion copolymerization, Film casting, FT-IR, DSC, Mechanical, Optical, Physical and Thermal properties

I. Introduction

Vinyl Acetate was copolymerized with a number of monomers such as Styrene, MMA, Acrylo Nitrile, Vinyl Chloride, Vinyllidene Chloride (1), Butyl Acrylate, Methyl Acrylate, Acrylic acid (2). The copolymers of Vinyl Acetate with Ethylene (EVA) is a most commercially significant one. EVA polymers have been important for film manufacturing and because of their some what rubbery nature, gloss, permeability and good impact strength, they are of interest as stretch film for meat packaging and cling wrap purposes. EEA is useful for coextruded laminated films (3). EVOH copolymers has excellent barrier properties to gases and moisture vapour. HDPE-EVOH-EVA may be used as barrier film for packaging cereals and the PS-EVOH-PS for coffee and cream food packaging (4). PVAC emulsion are useful as paints and adhesives and are transparent (5).

PVAC on hydrolysis form Poly Vinyl Alcohol (PVOH). Cast films are useful as release film for FRP manufacturing. Incompletely hydrolysed grades have been useful for water soluble packages for bath salts, bleaches, insecticides and disinfectants. Tubular blown films similar to PE has been developed (6).

PVOH and EVOH has advantages and disadvantages regarding their suitability for use in bio-degradable film. The bio-degradability of PVOH is well documented while that of EVOH is under debate. EVA has better processability and more water resistance. EVOH is clearly an attractive to PVOH if it can be proven to be bio degradable (7). The bio- degradation mechanism of PVOH is shown in the literature (8). EVA blends ethyl cellulose was reported (9). The ethyl cellulose imparts bio-degradability to EVA.

Bio degradable water soluble polymers are in their infancy, few examples of commercial value exist, although there is recognition for their need. At this time, there is a developing consensus on some of the requirements (e.g.) the polymer must be biodegrade completely and preferably in their disposal environments such as a waste water treatment facility.

Water soluble polymers are taken to include truly soluble polymers, hydrogels and a few soluble packaging materials such as poly vinyl alcohol and high molecular weight poly ethylene oxide. After use, depending on their characteristics and particular applications, they are discarded as dilute aqueous solutions or into solid waste disposal systems. Those entering aqueous waste water streams may go directly into the environment or more often and preferably, they pass into a waste water treatment facility for remediation generally implies adsorption on sewage sludge. Hydrogels such as superabsorbent polymers in diapers and sanitary products and packaging materials are often landfilled or incinerated. If neither recycling nor any other option for plastics is available, there is really an option for water soluble polymers.

Most acryl amide is used to synthesize poly acrylamides, which find many uses as water-soluble thickeners. These include use in waste water treatment, gel electrophoresis, papermaking, ore processing, and the manufacture of permanent press fabrics. Some acryl amide is used in the manufacture of dyes and the manufacture of other monomers.

Vinyl Acetate – Acrylamide (5-15 wt %) copolymer with emulsions are potentially valuable as adhesives (10), e.g., wood bonding adhesives, as the acryl amide functions in the copolymer both to increase its rigidity and to provide opportunities for cross linking which can further increase the rigidity of adhesive bonds.
However, because of the water solubility of poly acrylic amide, there is significant degree of water solubility in acrylic amide copolymers. Acrylamide was also copolymerized with acrylic acid. The alkaline hydrolysis of Poly acrylic amide is reported (11). Poly acrylic acid is to be hydrolyzed into polyvinyl alcohol for rendering it higher water soluble. It requires higher temperature, energy & higher time. Poly acrylic amide is a water soluble copolymer. So in this present study the vinyl acetate is copolymerized with acrylic amide monomer by emulsion polymerization, to make it more hydrophilic in nature & to study the water solubility & Bio-degradability of the vinyl acetate-acrylamide copolymers. The films will be prepared by casting on an even glass plates. The effect of the copolymer compositions of the vinyl acetate- acrylamide are studied on their mechanical properties & thermal properties. (i.e.) the copolymers are studied for the mechanical properties like tensile strength, elongation at break, tear strength, MFI, Haze and WVTR. Also FT-IR & DSC are used to characterize the copolymers.

Emulsion polymerization technique is used in this study for the synthesis of VA-AA copolymers.

II. Experimental

2.1 Materials

The following materials were used.

1) Vinyl Acetate (98% pure) monomer made of Avre Synthesis Pvt Ltd, Hyderabad, India
2) Acryl Amide (100%) commoner made of Spectro Chem Pvt Ltd., Mumbai, India.
3) Redox Catalysts-Tertiary butyl hydro-per oxide (Spectro Chem) & Sodium bisulphate (Spectro Chem)
4) Surfactant: Dodecyl Benzene sulphonic acid Sodium salt (95%), Loba Chemie, Mumbai
5) Buffer – Disodium hydrogen Phosphate (98%) Fisher Scientific. All these chemicals were supplied by Sri Ramachandra Chemicals suppliers, Chennai.

2.2 Methods: Emulsion Polymerization

Stable aqueous low viscosity emulsions of random copolymers of vinyl acetate and 5-20% acrylic amide by weight of vinyl acetate. The Acrylamide has high reactivity ratio of 9.2 ; Vinyl acetate has 0.09 low reactivity ratio as reported using free radical catalyst Benzoyl peroxide in solution polymerization (12). Also, the reactivity ratios calculated from the Q, e values of Alfrey –Price scheme, the reactivity ratios for Acrylamide is 6.26 and that of VA is 0.031 (13). Hence, the emulsions are prepared by a delayed addition emulsion polymerization technique wherein specific proportions of the total amounts of ingredients are present in the initial charge, the addition of the remaining proportions being at controlled rates. A particular redox catalyst system of a vinyl acetate soluble organic hydro peroxide initiator and a water soluble reducing agent activator, a stable water soluble buffering agent and, optionally, an emulsifying agent are used in carrying out the polymerization, the temperature being maintained below 45°C.

2.3 COPOLYMER COMPOSITIONS:

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>95 : 5 %</th>
<th>90 : 10 %</th>
<th>85 : 15 %</th>
<th>80 : 20 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>80.1 gm.</td>
<td>76.6 gm.</td>
<td>73.0 gm.</td>
<td>69.0 gm.</td>
</tr>
<tr>
<td>Acryl amide</td>
<td>3.5 gm.</td>
<td>7.0 gm.</td>
<td>10.6 gm.</td>
<td>14.6 gm.</td>
</tr>
<tr>
<td>Water</td>
<td>50 gm.</td>
<td>50 gm.</td>
<td>50 gm.</td>
<td>50 gm.</td>
</tr>
<tr>
<td>Tertiary butyl hydro peroxide</td>
<td>1.5 ml</td>
<td>1.5 ml</td>
<td>1.5 ml</td>
<td>1.5 ml</td>
</tr>
<tr>
<td>Sodium bisulphate</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
</tr>
<tr>
<td>Dodecyl Benzene sulphonic acid</td>
<td>0.5 gm.</td>
<td>0.5 gm.</td>
<td>0.5 gm.</td>
<td>0.5 gm.</td>
</tr>
<tr>
<td>Sodium hydrogen phosphate</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
<td>0.4 gm.</td>
</tr>
</tbody>
</table>

2.4 Copolymer Synthesis (95% VA: 5% AA)

In a half liter glass emulsion polymerization kettle, equipped with a large blade stirrer, thermometer, water, condenser, three dropping funnels, and an inlet and outlet for a stream of inert gas, were placed 50 gm. Water, 0.5 gm. Dodecyl Benzene sulphonic acid sodium salt and 0.9gm. Acryl amide to form an aqueous phase into which 7.0 gm. Vinyl acetate containing 0.5 ml tert-butyl were dispersed; the ingredients were dispersed by agitation while a continuous stream of nitrogen was passed through the kettle. The temperature of the mixture was brought to 40 degree Celsius. The low addition of each of the following solutions was initiated, viz: a solution of 0.4 gm. Sodium bisulphite and 0.4 gm. Disodium hydrogen phosphate in 10 ml water, a solution of
2.625 gm. Acryl amide in 14 ml water, and a solution of 1.0 ml tert-butyl hydro peroxide in 73.1 gm. of vinyl acetate. Addition of each of the solutions was continued at rates that completed the additions in substantially the same time of three hours. Copolymerization of the monomers are was noted to commence shortly after addition of the solutions was started, as evidenced by a whitening of the dispersion and a tendency for increasing temperature in the kettle which was precluded by a cooling bath around the kettle. Agitation and 45 degree Celsius temperature was maintained throughout the addition and for an hour subsequent thereto, and then the resulting copolymer emulsion was cooled to room temperature.

Similarly other composition 90 :10% 85 : 15% and 80 :20% of VA: AA are prepared.

The copolymers were precipitated from the Emulsions in a suitable Non-solvent. Methanol is the suitable non solvent for the vinyl acetate- acryl amide copolymer. The copolymers were precipitated by magnetic stirring and the obtained precipitates were filtered and dried.

2.5 Film casting

The copolymer obtained by emulsion polymerization is then casted over a lubricated glass plates. After duration of 36 hours the film is removed with care from the glass plates. Films made from the copolymer emulsion, should not have glass transition value too high.

2.6 Testing and characterization of Copolymer Films

The testings are carried out as per ASTM standards [14]. Tensile properties were determined by using ASTM D882 test method using a UTM Instron M/c (USA). Test specimens for tear resistance are cut as per ASTM1922 standard. This ASTM standard refers the standard test method for propagation tear resistance of plastic film and thin sheeting by pendulum method. The 3.8cm slit is made by a sharp razor blade or equivalent. The MFI test was done as per ASTM D 1238 using a MFI tester (Lloyd UK). MFI is expressed as grams of polymer per 10 minutes of flow time. The films were also characterized by FT –IR (Ferkin Elmer) to know the functional groups and by DSC (Netszch) to know the Tg, m p, and Td. Optical properties such as luminous transmittance and haze were done for the samples on the films. For measuring haze and luminous transmittance, photometer was employed as per ASTM D1003. Water vapor transmission rate was measured using per BS 2782 standard part 8 method 820A. The test specimen is sealed in a Glass beaker holder containing a desiccant (anhydrous CaCl2) in control temperature and humidity conditions. The weight gain was recorded periodically until this become a constant.

III. Results and Discussion

The test results are shown in Tables 1-5 and Figures 1-9.

3.1 Mechanical Properties

Tensile Strength & elongation: The Tensile strength of vinyl acetate-acryl amide copolymers increases & Elongation decreases as the percentage of acryl amide increases (Table 1). This due to the higher Tg, Tm & rigidity of poly acryl amide units which are shown by DSC thermograms (Figures 7-9). The tensile strength of copolymer VA:AA of 95:05 is similar to that of LDPE, VA:AA of 90:10% is similar to that of LLDPE, VA:AA of 85:15% is similar to that of HDPE and VA:AA of 80:20% is similar to that of PP. However, the % elongation at break (Eb) of all formulations are lower than 5% and found to be brittle like photo degraded films. The (Eb) can be improved by blending with flexible polymers like EVA (9) to improve the flexibility and drop impact strength for use as Packaging films.

<table>
<thead>
<tr>
<th>S.NO</th>
<th>SAMPLES</th>
<th>MAXIMUM LOAD (Kgf)</th>
<th>TENSILE STRENGTH (kg/cm2)</th>
<th>ELONGATION AT BREAK (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95 : 5 %</td>
<td>1.76</td>
<td>124.50</td>
<td>4.32</td>
</tr>
<tr>
<td>2</td>
<td>90 : 10 %</td>
<td>2.11</td>
<td>168.87</td>
<td>3.24</td>
</tr>
<tr>
<td>3</td>
<td>85 : 15 %</td>
<td>5.70</td>
<td>285.29</td>
<td>2.32</td>
</tr>
<tr>
<td>4</td>
<td>80 : 20 %</td>
<td>7.16</td>
<td>359.44</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Tear Strength: The specimen used for tear strength is cut in desired shape using the cutter by shape razor blade. Tear propagation strength was determined. The Test results are shown in Table 2. The tear strength of vinyl acetate-acryl amide copolymers decreases with the percentage of acryl amide increases due to more rigidity of VA-AA copolymer since acrylamide units have higher Tg.

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Synthesis, Characterization and Testing of Emulsion Polymerized Vinyl Acetate–Acrylamide

Table 2. Tear Strength of VA-AA copolymers

<table>
<thead>
<tr>
<th>S.NO</th>
<th>SAMPLES</th>
<th>THICKNESS (Micron)</th>
<th>FORCE (gmf)</th>
<th>TEAR STRENGTH (gmf/micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95 : 5 %</td>
<td>54</td>
<td>879</td>
<td>16.28</td>
</tr>
<tr>
<td>2</td>
<td>90 : 10 %</td>
<td>66</td>
<td>879</td>
<td>13.32</td>
</tr>
<tr>
<td>3</td>
<td>85 : 15 %</td>
<td>67</td>
<td>886</td>
<td>13.23</td>
</tr>
<tr>
<td>4</td>
<td>80 : 20 %</td>
<td>69</td>
<td>892</td>
<td>11.97</td>
</tr>
</tbody>
</table>

3.2 Thermal Properties:

MELT FLOW INDEX: MFI decreases as the percentage of acrylamide increases because the molecular weight may increase due to their higher reactivity ratio value of acrylamide monomer (about 7 for Acrylamide and 0.03 for Vinyl Acetate). The test results are given in Table 3.

Table 3 MFI of VA-AA Copolymers

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>MFI gm/10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>95%VA: 5%AA</td>
<td>8.54</td>
</tr>
<tr>
<td>90%VA: 10%AA</td>
<td>5.68</td>
</tr>
<tr>
<td>85%VA: 15%AA</td>
<td>4.32</td>
</tr>
<tr>
<td>80%VA: 20%AA</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Melt flow rate is the rate of extrusion of a thermoplastic material through an orifice of designated dimension under prescribed temperature (250-275 °C and load 2.16, 5, and 10 Kg) depending upon m. p. of copolymers of VA:AA. Melt flow is an assessment of average molecular mass and is an inverse measure of melt viscosity; i.e., high melt flow rate corresponds to low molecular weight and vice versa. Higher MFI polymers are used in injection molding and lower MFI polymers are used with blow molding or extrusion process.

3.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The peak at 1713 cm⁻¹ is for C=O of ester groups of vinyl acetate. The peak of 1602 cm⁻¹ is due to the C=O (ketone) group associated with –NH₂ in acrylamide monomer units. Such these two peaks are present in the copolymer vinyl acetate-acrylamide, it indicates that the two monomers form copolymer during emulsion polymerization. The –CH₃ group of vinyl acetate monomer absorbs at 2954 cm⁻¹. The NH₂ group of acrylamide shows peak at 3400 cm⁻¹ (above 300 degree Celsius). After hydrolysis, the ester groups of vinyl acetate monomer may form –OH groups as PVOH. The –CH₂ methylene group shows peaks in between 2950-2800 cm⁻¹. Also CH group shows peak at 2890 cm⁻¹. From the result of FT-IR we conclude that vinyl acetate-co-acrylamide copolymer has formed. It can determine the amount of component in a mixture or copolymer.

Fig.1 FT-IR spectrum of Poly vinyl Acetate (PVAC)
Synthesis, Characterization and Testing of Emulsion Polymerized Vinyl Acetate – Acrylamide

Fig. 2 FT-IR spectrum of Poly acrylamide (PAA)

Fig. 3 FT-IR spectrum of VA:AA Copolymer (95:05%)

Fig. 4 FT-IR spectrum of VA: AA Copolymer (90:10%)
3.4 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) analyzes thermal transitions occurring in polymer samples when they are cooled down or heated up under inert atmosphere. Melting and glass transition temperatures can be determined as well as the various transition in crystalline mesophases. From the result of DSC (Fig 7-9), as concentration of acrylamide increases the Tg & Tm of vinyl acetate - co-acrylamide copolymer increases.
Fig. 8. DSC of VA: AA Copolymer (90:10%)

Fig. 9. DSC of VA: AA Copolymer (85:15%)

The melting point of VA-AA copolymer of 80:20% is from 247-297 Deg C. Average mp is at 257.7 °C.

3.5 PERMANENCE PROPERTIES (WVTR)

The water vapour transmission rate decreases as the percentage of acrylamide increases (Table 4). This may be due to the increase in intermolecular force of the polyacrylamide units & voids may be less. Hence WVTR decreases.

3.6 OPTICAL PROPERTIES

Haze: The haze decreases as the percentage of acrylamide increases. This shows the amorphous content increases due to irregularities. The crystallinity may reduce and hence luminous transmittance may increase and haze decreases (Table 4).

<table>
<thead>
<tr>
<th>Table: 4 WVTR and HAZE of VA-AA Copolymers</th>
</tr>
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<tbody>
<tr>
<td>S.No</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>1</td>
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<td>2</td>
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<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
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</table>
3.7 WATER SOLUBILITY AND BIO DEGRADATION

The co-polymer undergoes hydrolysis, acetate groups forming (Vinyl alcohol Acrylamide) copolymer. After oxidation the PVOH moieties forms ketone groups. Again after hydrolysis, lowers molecular weight randomly forming ketone groups and carboxylic acid groups similar to PVOH bio-degradation (8) (Fig 10).

Thus the lower molecular weight PVOH-AA & the copolymer will be bio-degradable. The acryl amide makes the VA-AA copolymer more water soluble and helps in faster biodegradation. Poly Vinyl Acetate and Ethylene Co- Vinyl Acetate are slowly Bio-degradable (15, 16) Particularly where there is a high percentage of Vinyl acetate. In the copolymer growth of Fungi on EVA copolymers correlated directly with VA content. The water solubility of Poly vinyl alcohol is a function of crystallinity which in turn is a function of degree of hydrolysis essentially concentration with a maximum solubility occurs at 70-80% hydrolysis (20-30 mol% of Vinyl acetate(17).

Acrylamide concentration increases from 5% to 20% the water solubility time decreases. All the Copolymers of the above four compositions are found to be water soluble in about one-two hours of time. In presence of moisture in the soil it will be swelling and hydrolysable and then bio degradable. Compost can be made in all formulations.

The vinyl acetate- acryl amide copolymer synthesized by emulsion polymerization technique is a water soluble copolymer. During polymerization the poly vinyl acetate is hydrolyzed to poly vinyl alcohol. So, there is no need of post polymerization reaction of converting poly vinyl acetate to poly vinyl alcohol at 90 degree Celsius for 24-48 hours. This involves higher cost of the biodegradable plastics packaging raw materials. Hence, our project is more important since the obtained copolymer is highly water soluble due to their hygroscopic nature. Emulsion polymerization is also very cheaper and consume less time of 2-3 hours under 40-50 degree Celsius. Water is used as medium for emulsion polymerization technique. Since water is used as a solvent for the obtained copolymer emulsion, film casting technique will not give any hazardous solvent atmosphere.

Water-soluble polymers are widely used in many applications such as detergents, paints, chemical intermediates, water treatment, oil fields etc. After their useful life, they are generally discarded into the aqueous environment simply because they are unrecoverable. Most of the synthetic water-soluble polymers are not biodegradable so their fate in the environment is uncertain. There is no evidence that they cause problems, but there is no certainty that they do not. Therefore there is an increasing interest in developing biodegradable
water-soluble polymers to replace those now being used. In this VA-AA copolymer, when acetate groups of VA repeat units hydrolyses, it releases acetic acid (Vinegar) moieties and it is not hazardous.

IV. Conclusion

The tensile strength increases & elongation decreases as the percentage of acrylamide increases in the VA-AA copolymer. Tear strength decreases, Haze decreases, WVTR decreases and MFI decreases as the percentage of acrylamide increases in the VA-AA copolymer. The Melting point increases as the acrylamide content increases. As the vinyl acetate-co-acrylamide is water soluble, they can be used for water soluble packaging such as agricultural chemicals, Laundry detergents, Water treatment chemicals, Toilet blocks, Pigments and dyes, Window washing concentrates and also for conventional disposable packaging.

When we wanted to make bio-degradable VA-AA copolymers, it was found to be water soluble copolymers even with 5% AA in VA-AA copolymer in 1-2 hrs time.

Acknowledgement

Netszch Technologies India Ltd, Chennai, is greatly acknowledged for the testing of DSC and IIT Chennai for FT-IR of our films. We also greatly acknowledge Dr K Palanivelu, Deputy Director & Principal of CIPET Chennai, for providing the Required materials (Monomers & Chemicals)

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