

“SYNTHESIS & CHARACTERIZATION OF WATER SOLUBLE VINYL ACETATE – ACRYLAMIDE – STYRENE TERPOLYMER”

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ABSTRACT

Acryl Amide is often, copolymerized with Acetate to induce high water solubility for Re-Moisturable Adhesive and Easy Disposable Packaging Applications. Though, highly water soluble, it has comparatively poor strength, poor clarity and high cost. In some cases, the high water solubility itself prevents any possible practical applications. So in this present study, the vinyl Acetate was terpolymerized with Acryl Amide and Styrene monomers, in 3 different comparisons, viz. (95%VA-5%AA)-5%, (95%VA-5%AA)-10% STY, (95%VA-5%AA)-15% STY by weight of Vinyl Acetate, through Delayed Emulsion polymerization technique, to impart a comparatively high strength, clarity at a low cost and a controlled water resistance, thus improving applicability. The casted terpolymer films were initially characterized using Fourier Transformed Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA). Later, Tensile properties-strength, Elongation at break; Optical properties-Haze, Luminous transmittance, Opacity; Thermal Property-melting point were determined through ASTM standards. Finally, to assess the applicability of the terpolymer, Water Solubility and Peel strength was determined through standard testing methods. The results indicated that the copolymer composition containing 10% styrene had the most optimum properties with regard to Re-moisturable Adhesive Applications. Easy Disposable packaging could be another potential avenue for the above synthesized terpolymer.

1. EXPERIMENTAL WORK

The following materials were used.

- Vinyl Acetate (98% pure) monomer made of Avre Synthesis Pvt Ltd, Hyderabad, India
- Styrene, 98% made of Avre Synthesis Pvt Ltd, Hyderabad, India
- Acryl Amide (100%) comonomer made of Spectro Chem. Pvt Ltd., Mumbai, India.
- Redox Catalysts-Tertiary butyl hydro-per oxide (Spectro Chem) & Sodium bisulphate (Spectro Chem)
- Surfactant: Dodecyl Benzene sulphonic acid Sodium salt (95%), Loba Chemie, Mumbai
- Buffer – Disodium hydrogen Phosphate (98%) Fisher Scientific.

Methods: Emulsion Polymerization

Stable aqueous low viscosity emulsions of random copolymers of vinyl acetate and 5-20% acryl 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 (8). 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 (9). 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.

COPOLYMER COMPOSITIONS:

INGREDIENTS	(95°/o VA- 5°/o AA)-5°/o STY	(95°/o VA- 5°/o AA)-10°/o STY	(95°/o VA- 5°/o AA)-15°/o STY
Vinyl acetate	80.1 gm.	80.1 gm.	80.1 gm.
Acryl amide	3.5 gm.	3.5 gm.	3.5 gm.
Styrene	3.5 gm.	7.0gm.	10.5 gm.
Water	50 gm.	50 gm.	50 gm.
Tertiary butyl hydro peroxide	1.5ml	1.5ml	1.5ml
Sodium bisulphite	0.4 gm.	0.4 gm.	0.4 gm.
Dodecyl Benzene sulphonic Acid sodium salt	0.5 gm.	0.5 gm.	0.5 gm.
Disodium hydrogen phosphate	0.4 gm.	0.4 gm.	0.4 gm.

In a 1 liter round bottom flask emulsion polymerization, equipped with a magnetic stirrer, thermometer, water, condenser, dropping funnels, and an inlet and outlet for a stream of inert gas, were placed 50ml Water, 0.5 gm. Dodecyl Benzene sulphonic acid sodium salt and 0.9gm. Acryl amide to form an aqueous phase into to which 7.0 gm. Vinyl acetate containing 0.5 ml. tert-butyl, 0.9ml styrene were dispersed; the ingredients were dispersed by agitation while a continuous stream of nitrogen was passed through the RBF. 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 and 2.6ml styrene. 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 RBF 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 (95%VA-5%AA)-5%STY, (95%VA-5%AA)-10%STY, (95%VA-5%AA)-15%STY 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 – styrene copolymer. The copolymers were precipitated by magnetic stirring and the obtained precipitates were filtered and dried.

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.

1. RESULTS AND DISCUSSION

FTIR SPECTRA

The following were the spectra obtained through FTIR spectroscopy:

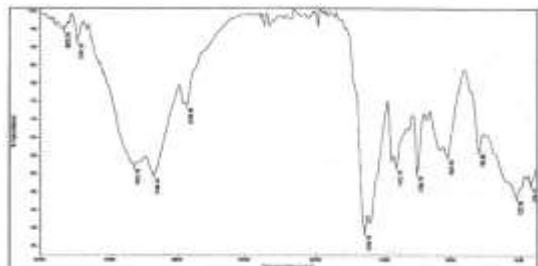


Figure a.) FTIR Spectra for (95% VA-5% AA)-5% STY

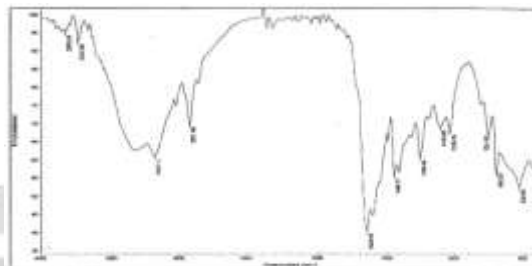


Figure b.) FTIR Spectra for (95% VA-5% AA)-10% STY

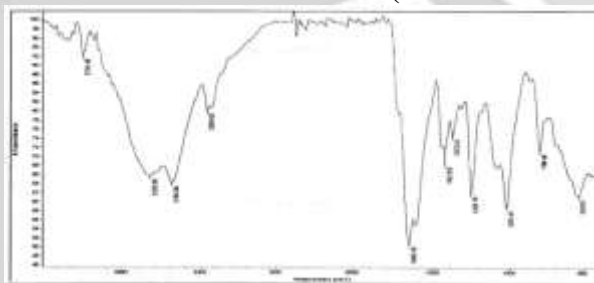


Figure c.) FTIR Spectra for (95% VA-5% AA)-15% STY

In the FTIR Spectra of all the samples; peaks corresponding to Vinyl Acetate, Acryl Amide and Styrene are clearly visible.

Vinyl Acetate may be characterized by the following peaks:

- The peak at 1713 cm^{-1} , corresponding to $\text{C}=\text{O}$ of the ester groups of Vinyl Acetate.
- The peak at 2954 cm^{-1} , corresponding to $-\text{CH}^3$ of Vinyl Acetate.
- The peak at 3331 cm^{-1} , corresponding to $-\text{OH}$, produced after hydrolysis of acetate group in Vinyl Acetate.
- The peak in between $2950\text{--}2800\text{ cm}^{-1}$, corresponding to $-\text{CH}^2$ methylene group.

Acryl Amide may be characterized by the following peaks:

- The peak at 1602 cm^{-1} , corresponding to $\text{C}=\text{O}$ (ketone) group associated with $-\text{NH}_2$ in acryl amide monomer units.
- The peak at 3400 cm^{-1} , corresponding to $-\text{NH}^2$ group of Acryl Amide.
- The peak in between $2950\text{--}2800\text{ cm}^{-1}$, corresponding to $-\text{CH}^2$ methylene group.
- The peak at 2890 cm^{-1} , corresponding to $-\text{CH}$ group.

Styrene may be characterized by the following peaks:

- The peak at 1625 cm^{-1} , corresponding to the pendant benzene ring of the Styrene units.
- The region 532 cm^{-1} , corresponding to Styrene.

Thus, the terpolymer can be said to have formed successfully.

TGA Thermograms

The following were the thermograms obtained through TGA

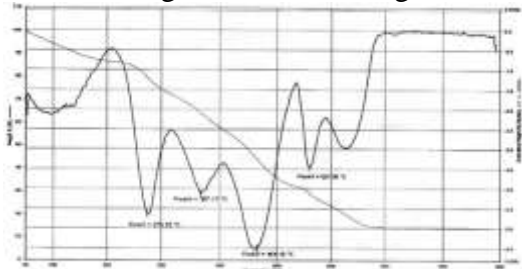


Figure d.) TGA Curves for (95% VA-5% AA)-5% STY

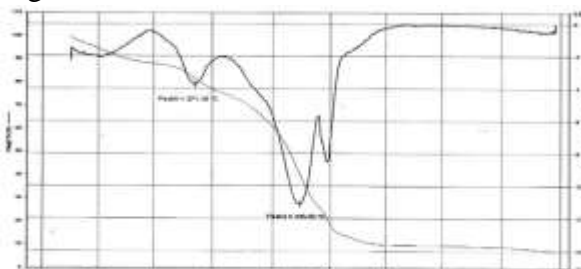


Figure e.) TGA Curves for (95% VA-5% AA)-10% STY

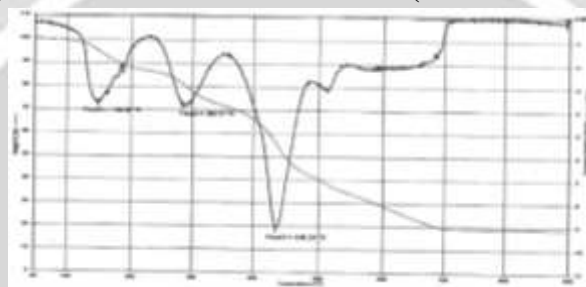


Figure f.) TGA Curves for (95% VA-5%, AA)-15% STY

The following details could be inferred from the above thermograms:

The thermograms for all the compositions showed many stages of degradation. The stages were in the following order: Moisture Vaporization < Vinyl Acetate Decomposition < Acryl Amide Decomposition < Styrene Decomposition < Other Moieties Decomposition.

Residue of varying amounts is clearly evident from the Thermograms. These may be nitrides, nonvolatile oxides (Such as that of Sodium) or simple impurities. However, the residue was not analyzed.

Mechanical Properties:

Table 1. Tensile Strength

Legend	Maximum Elongation at Legend Load (Kgf)	Ultimate Tensile Strength (Kgf/cm ²)	Elongation at Break (%)
(95% VA- 5% AA)-5% STY	3.123	66.973	50.871
(95% VA- 5% AA)-10% STY	3.907	83.781	11.382
(95% VA- 5% AA)-15% STY	Test Sample could not be extracted due to high brittleness of the casting.		

From the above observations, it is evident that:

- The Maximum Load (Kgf) and the Ultimate Tensile Strength Break (%) (Kgf/cm²) values increased with the increase in the styrene content in the terpolymer.

Also, the Elongation at Break (%) value decreased with the increase in the styrene content in the terpolymer.

The reason for the increase in Maximum Load, Ultimate Tensile Strength and the decrease in Elongation at Break with the styrene content can be attributed to the increase in the rigidity of the polymer chains due to the incorporation of the bulky pendant group- Benzene Ring from Styrene units.

Optical Properties

The following were the observations from the Optical test:

Table 2. Optical Properties

Legend	Transparency %	Haze %	Opacity %
(95% VA- 5% AA)- 5% STY	71.5	86.16	28.5
(95% VA- 10% AA)- 10% STY	87.3	70.17	12.7
(95% VA- 5% AA)- 15% STY	Test Sample could not be extracted due to high brittleness of the casting.		

From the above observations, it is evident that:

- The Transparency (%) value increased with the increase in the styrene content in the terpolymer.
- Hence, the Opacity (%) and Haze (%) decreased with the increase in the styrene content in the terpolymer.

The above-said behavior could be reasoned by the increase in the steric hindrance with addition of styrene, due to its bulky pendant benzene ring, that increases the amorphous nature and thereby, improves the optical properties.

Thermal Properties - T_m

Rate of Temperature Rise: 20°C/min.

Table 3. Melting T_m

Legend	Melting Point (°C)
(95% V A-5% AA)-5% STY	243.5
(95% V A-10% AA)-10% STY	223.0
(95% VA-15% AA)-15% STY	213.7

From the above observations, it is evident that:

- The Melting Point ($^{\circ}\text{C}$) decreased with the increase in the styrene content in the terpolymer.

This behavior could be explained by the fact that Styrene units melt at low temperature compared to Acryl Amide units.

Water Solubility

The following were the observations from the Water Solubility test:

Concentration : 0.01%

At Room Temperature;

Table 4. Water solubility at Room Temp.

Legend	Dissolution Time, t_D (Sec)
(95% V A-5% AA)-5% STY	> 1 Hour
(95% V A-10% AA)-10% STY	> 1 Hour
(95% VA-15% AA)-15% STY	> 1 Hour

Table 5. Water solubility at 60 $^{\circ}\text{C}$

Legend	Dissolution Time, t_D (Sec)
(95% V A-5% AA)-5% STY	12.67 min
(95% V A-10% AA)-10% STY	29.08 min
(95% VA-15% AA)-15% STY	40.22 min

2. CONCLUSION

- The terpolymer was successfully synthesized using Delayed Emulsion Polymerization technique also, Characterization and Testing of the prepared terpolymer was successfully done.

The properties of the terpolymer varied with the styrene content:

- The Tensile Strength had increased with the Styrene content, however, Elongation at Break reduced.
- The Transparency had increased, but the Haze and Opacity reduced with the Styrene content.
- The Melting Point had decreased with the increase in the Styrene content.
- All the compositions were Water Soluble. The Dissolution Time increased with the increase in Styrene content.

Thus, the 10% STY composition can be used as a Re-Moisturable Adhesive due to its optimum properties

Also, the 5% STY composition can be used for Water Soluble Packaging applications due to its suitability for the same.

3. REFERENCES

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