



Synthesis and Characteristics of 2-Ethylhexylacrylate Acrylonitrile Methacrylic Acid and Vinyl Acetate Emulsions for Water Born Pressure Sensitive Adhesives

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ABSTRACT

Pressure sensitive adhesives (PSAs) based on acrylic monomers was synthesized. For this purpose emulsion, polymerization process was conducted for the preparation of an acrylic copolymer containing 2-ethylhexylacrylate, vinyl acetate, methacrylic acid (MAc), and acrylonitrile using potassium persulfate as an initiator. The monomers were feeding different ratios with increasing 2% and 4% MAc and acrylonitrile. The adhesive properties have been evaluated in terms of viscosity, solid content, glass transition temperature (T_g), peel strength, and shear strength value for all samples. It was observed that trends peel strength and shear strength variations are correlated with the changing parameters. The synthesized PSAs show good adhesive properties and could be easily peeled off from the surface BOPP and stainless steel. These samples with satisfactory adhesion were characterized by Universal Testing Machine. Fourier transforms infrared, differential scanning calorimeter.

Key words: Acrylonitrile, Methacrylic acid, 2-ethylhexylacrylate, Bopp and pressure sensitive adhesives.

1. INTRODUCTION

Pressure sensitive adhesives (PSAs) are viscoelastic materials that can adhere strongly to solid surfaces upon application of light contact pressure for a short contact time [1]. They do not undergo any physical transformation or chemical reaction during the bonding process. Among different base polymers used in making PSAs, high alkyl acrylates, such as 2-ethylhexylacrylate (2-EHA), vinyl acetate (VAc) monomer, methacrylic acid (MAc), and acrylonitrile, have enjoyed the fastest growth in commercial applications [2]. Acrylic PSAs are homopolymers of acrylic esters and their copolymers with other various acrylic or vinyl monomers that are well-known as self-adhesive compounds with remarkable tack, adhesion, and cohesion properties [3]. Their popularity is mainly attributed to high optical clarity, oxidative and ultraviolet resistance, migration resistance, low toxicity and low cost. Acrylic PSA polymers are coated onto tape or label in one of the forms of hot melt, solvent borne, or water borne. Thus, they are central to the present generation of efficient double-sided self-adhesive tapes, splicing tapes, protective foils, films for the graphics market, and various medical products [4]. Although PSA can be obtained by different polymerization processes such as solution,

emulsion and radiation curing, most acrylic PSAs are solvent-based due to the desirable adhesion properties, resistance to water, solvents, and plasticizers, and ageing performance [4,5]. The adhesion properties are characterized by three basic applicative properties: Tack (measuring the adhesive's ability to adhere quickly), peel strength (measure of resistance to removal by peeling), and shear resistance (measure of resistance to flow under shear forces) [6-8]. Peel strength data can give more information about the adhesive characteristics and its expected performance. Peel adhesion is dependent on viscoelastic properties of adhesives and the surface properties of both adhesive and substrate [9]. Poly 2-EHA, as soft homopolymers or together as a copolymer provides dry films with low glass transition temperatures (T_g) with sufficient tack and immediate adhesion property. To improve the room temperature performance of such polymers, it is necessary to raise their T_g . Raising the polymer's T_g is achieved by copolymerization with hard monomers (which form polymers of higher (T_g)). Any of a number of "stiffening" or secondary monomers are suitable to raise the polymer's T_g . Secondary monomers - such as methacrylate (MA), VAc, and acrylic acid (AA) - may be added to provide sites for cross-linking reactions or, as in the case of AA, to improve latex

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colloidal stability and enhance adhesion. A copolymer molecular weight distribution and gel content are also important parametric functions which greatly assist in the adhesion performance of PSAs that are strongly influenced by secondary monomers. Addition of a small amount of functional monomers such as MAcid and acrylonitrile increases hydrophilicity and creates cross-linking sites which promote adhesion of the PSA with its increased moisture permeability [10].

According to the best of my knowledge, there is no published report regarding the synthesis of copolymer containing 2-EHA, methacrylic acid and acrylonitrile, VAc. In this study, acrylate PSAs were prepared by free radical emulsion polymerization in the presence of potassium persulfate. The copolymers have been characterized by Fourier transform infrared (FTIR), differential scanning calorimeter (DSC), and the adhesive properties of these copolymers such as peel strength and shear strength values were also studied.

2. EXPERIMENTAL

2.1. Materials

The EHA monomer (industrial grade), VAc monomer, MAcid, acrylonitrile purchased from Visen Industries (India) sodium bicarbonate and potassium persulfate (Merck). Emulsifier Diachi Karkaria Ltd. (India). De-ionized water was used throughout the polymer preparations.

2.2. Synthesis of 2-EHA and VAc Acrylonitrile and MAcid by Emulsion Polymerization Method

These emulsions were prepared by free radical polymerization. The polymerization was carried out in a 1000 ml four necked round bottom flask immersed in a constant temperature water bath at 80°C, equipped with a reflux condenser, stirrer, dropping funnel and a nitrogen inlet. De-ionized water, 3.24 g surfactant was dissolved in de-ionized water and buffers (0.5%) were initially charge and maintained 100 rpm. Separately 304.17 g 2-EHA and meth AA 6.48 g, and VAc monomer 12.96 g (Sample 8) as per recipe Table 1 were mixed. Then, initiator was prepared by adding 0.75 g of potassium persulfate into 35 g of de-ionized water and stirred using a magnetic bar. Approximately 25% the initiators were added and followed by the delayed addition of 5% of the total monomer mixture. The initiation occurred after 10 min with the

appearance of a light blue color. Then, 75% of the monomer was added dropwise over 4 h. At the end remaining mixture was added dropwise over 1 h. The balance 75% initiator was added equal parts during the reaction at regular intervals continuously. Then, bath temperature was increased to 90°C and stirring was continued for another 1 h. The residual trace mixture, if any was removed by blowing nitrogen gas over the emulsion. The emulsions mass ratios of monomers and surfactant were varied as summarized in Table 1. The reaction mixture was then cooled to below 40°C and filtered into a suitable container.

2.3. Total Solids Content

The total solids content of latex is the percentage by mass of the whole, which is nonvolatile at 105°C for 2 h in an open atmosphere oven. A quantity of latex is weighed in a flat-bottomed glass dish (m°) and dried in an oven at 105±5°C to the constant weight in 2 h, and the remaining polymer film is weighed again to find the quantity of the weight of the residue (m). The ratio of the remaining solids over the total initial weight (100 m/m°) gives the total solids content.

2.4. Viscosity

Viscosity measurement is an indication of the flow properties and latex rheology and is of great practical relevance for their industrial applications. Brookfield viscometers have limited accuracy to follow continuously the viscosity changes caused by temperature changes or associated with non-Newtonian flow behavior. In addition, Brookfield viscometer readings are affected by turbulence and to some extent, by angle of immersion of the spindle.

2.5. Peel Strength Test (ASTM D330)

The peel strength is the measure of the average force to part two bonded materials such as tape, labels, textile, or plastic films. The strength is calculated during a peel test at a constant speed rate by divided the average force required during the test by the unit width of the bonded samples. Depending on materials, norms, products, the tests can be done with different angles: 90° and 180° are commonly used [11]. The peel tests can be performed on containers such as jars, cans, trays, or pockets and pouches. In this case, tests are available at different angles which can be close to the product use. Peel test at 45°C. In the case of adhesive materials, we

Table 1: Batch recipes (All values based on total monomer % weight).

Sample	2-EHAM	VAM	MAcid	Acrylonitrile	Surfactant
8	94	4	2	0	1
9	92	4	4	0	1
10	94	4	0	2	1
11	92	4	0	4	1

MAcid=Methacrylic acid, 2-EHA=2-ethylhexylacrylate

do not use the first peak, we measure the average force during the test divided by the width of the sample, and we obtain a resistance value in lb/in.

All PSAs latex obtained was coated on BOPP using a micron rod. The adhesive coated tape was dried at 100°C for 10 min. To measure the adhesive coating weight, first take a Bopp sheet 200 mm × 75 mm weighted without adhesive. The coating weight was calculated from the difference between BOPP tape with adhesive and without adhesive and expressed as 25± 5 g adhesive per square meter film. The adhesive-coated samples were left for 24 h in a controlled environment at room temperature.

A specimen of 24 mm × 175 mm was cut in the machine direction and laminated onto the clean stainless steel test plate using finger pressure. A standard pressure roller was rolled across the testing sample to obtain a line pressure equal for 24 mm. The average force to peel 180° the specimen from test plate was recorded. The testing speed for Universal Material Testing Machine was 300 mm/min.

2.6. Shear Strength Test

The manufacture of sticker and label laminate producers as an indicator of adhesive cut ability and die cut ability. Shear strength was the resistance of an adhesive coated label stock on a standardized surface to shear at a constant rate. For shear strength also used 25 g per dry adhesive weighed per square meter film. To measure the adhesive dynamic shear resistance first a 150 mm × 12.7 mm strip of adhesive laminate was prepared. One end of the adhesive laminate was adhered to a clean stainless steel test plate with a 12.7 mm × 12.7 mm contact area. A standard pressure roller was rolled across the bonded area which formed an adhesive bond. Dwell time between roll down and testing was 20 min. Grip separation speed at 5 mm/min was applied to the free end of the test piece in the length direction. The adhesive layer resists the deformation. The maximum force shears [12].

2.7. Glass Transition Temperature

T_g of the PSAs was determined by a DSC with T_A instrument Q-1000 with a scan rate of 10°C over a temperature range of -60-100°C. The glass transition temperature was taken as the midpoint of the heat

capacity transition between the upper and lower points of deviation from the extrapolated liquid gas lines.

2.8. FTIR Spectroscopy

The FTIR spectra were recorded on a Nicolet 940 FTIR spectrometer about 0.5 g sample is dissolved in chloroform of HPLC grade and made into a thin film transparent film and subjected to IR measurements at 400-4000 cm^{-1} . The attenuated total reflection infrared spectroscopy was employed.

3. RESULTS AND DISCUSSION

3.1. Viscosity and Solid Content

Viscosity of the PSAs at room temperature (30°C) using a Brookfield DV-E Viscometer using appropriate spindles. The viscosities of copolymer are given in Table 2.

The results obtained in Table 2 shows the viscosity of the PSAs increased with hard monomer content increased. Sample 8 and 9 met AA increased with based on total monomer content and sample 10 and sample 11 acrylonitrile was increased.

The solid content results obtained shows in Table 2. All the feed monomer conversion to the polymer by the evaluation of nonvolatile content and conformed that all the monomer formed copolymer of emulsions.

3.2. Peel strength and Shear Strength of PSAs

3.2.1. Monomer composition on adhesive performance

The effect of monomer composition on peel strength is shown in Figure 1. It is interesting to note that for the PSA series investigated, the PSA with increasing MAcid and acrylonitrile content exhibited the higher peel strength. The peel stress was sensitive to monomer content. Low 2-EHA and high MAcid content provided the highest peel stress. A work was performed to study the effect of incorporating 2-EHA in PSAs. The results showed an increase in gel content as the weight fraction of EHA increased. The shear strength in figure increased proportionally MAcid and acrylonitrile concentration. The flow of adhesive, or wetting of the substrate, must be dominated high T_g monomer content (Figure 2).

The effect of monomer composition on peel strength and shear strength is shown in Figures 3 and 4. The PSAs

Table 2: Viscosity and solid content of the pressure sensitive adhesives.

Sample	2-EHAM	VAM	MAcid	Acrylonitrile	Emulsifier	Viscosity in cps	Solid%
8	94	4	2	0	1	300	55
9	92	4	4	0	1	340	55
10	94	4	0	2	1	320	55
11	92	4	0	4	1	360	55

MAcid=Methacrylic acid, 2-EHA=2-ethylhexylacrylate

Table 3: Differential scanning calorimetry.

Sample	T _g values (theoretically)	T _g values (visually observed)
Sample 8	-62°C	-55°C
Sample 9	-60°C	-51°C
Sample 10	-61°C	-52°C
Sample 11	-58°C	-48°C

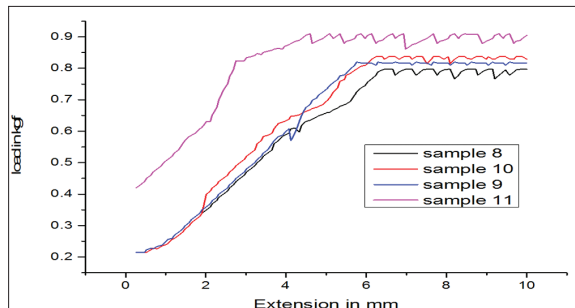


Figure 1: Peel strength of pressure sensitive adhesives evaluated by Universal Testing Machine.

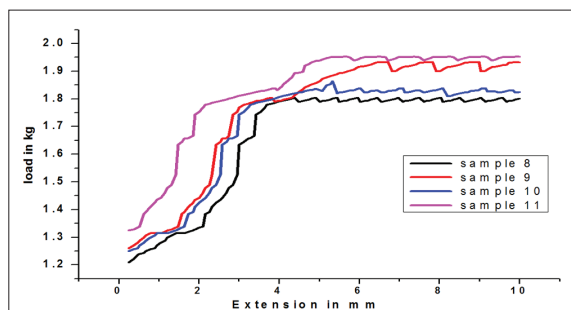


Figure 2: Shear strength of pressure sensitive adhesives evaluated by Universal Testing Machine.

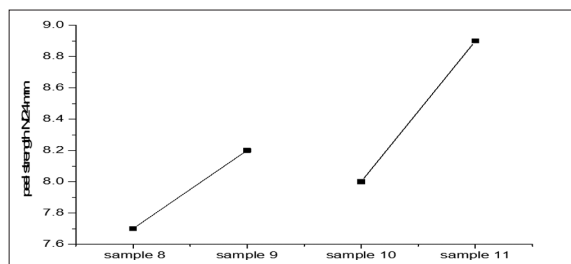


Figure 3: Methacrylic acid and acrylonitrile content effect on peel strength of pressure sensitive adhesives.

with increasing of MAcid and acrylonitrile content exhibited the higher peel and shear strength of PSAs.

3.3. DSC

Table 3 shows the glass transition temperature increased with hard monomer content MAcid and acrylonitrile increased. The T_g increased similar with peel and shear strength was increased in PSAs (Figure 5).

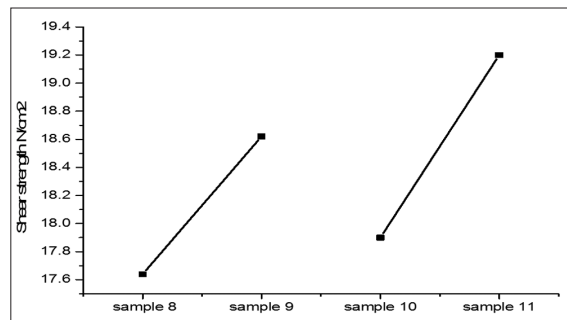


Figure 4: Methacrylic acid and acrylonitrile content effect on shear strength of pressure sensitive adhesives.

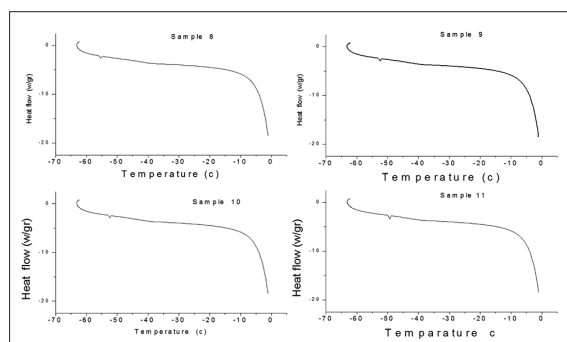


Figure 5: Differential scanning calorimeter thermograms of acrylic pressure sensitive adhesives Sample 8 to Sample 11.

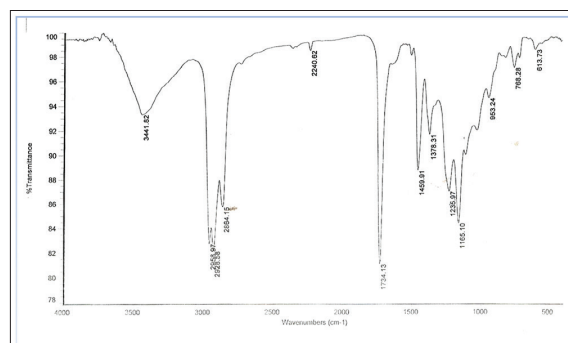


Figure 6: Fourier transform infrared spectrum was obtained from Sample 8.

3.4. FTIR

The FTIR spectrum of PSAs obtained is shown IR spectra in Figures 6 and 7. The bands at 2958, 2928, and 2865 cm⁻¹ were due to C-H strong bonding 2-EHA and VAc copolymer were characterized. Moreover, the absorption peak 953 cm⁻¹ showed wave number of vinyl group. The appearance of peak wave number at 1235 cm⁻¹ was resulted decomposition of initiators of potassium persulfate free radicals to commence the polymerization. The peak at 1165 cm⁻¹ showed primary alcohol bonding vinyl in it backbone structure. Moreover, the peak at 1734 cm⁻¹ was acetate and ester functional groups are present.

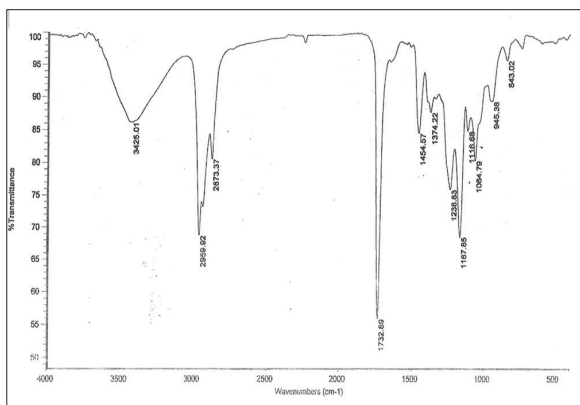


Figure 7: Fourier transform infrared spectrum was obtained from Sample 10.

4. CONCLUSION

The experimental design was used to investigate the influence of acrylonitrile and MAcid, on the adhesive properties of 2-EHAM/VAM emulsion-based PSAs. Indications from design experiments were that these might be the most influential variables when all other factors were kept constant. The PSAs has shown that the most influential variable affecting T_g was the amount of acrylonitrile and MAcid. Adhesive performance of peel and shear strengths was investigated on two different substrates using stainless steel and BOPP. And the results were found the properties of peel strength and shear strength of the PSAs. In addition to the polymer composition, which was previously found to be a dominant factor, this is probably variable affecting the properties of the final performance characteristics of 2-EHAM/VAM/MAcid, 2-EHAM/VAM/ACN emulsion-based adhesives. The copolymers of PSAs gave good PSA tapes of BOPP. The PSAs will belong to health and environment friendly high performance adhesives that are multifunctional.

5. REFERENCES

1. I. Benedek, L. J. Heymans, (1996) *Pressure-Adhesives Technology*, New York: Marcel Dekker Inc.
2. R. Jovanovic, F. T. Mckenna, (2004) Empirical modeling of butyl acrylate/vinylacetate/acrylic acid emulsion-based pressure-sensitive adhesives, *Macromolecular Materials and Engineering*, **289**: 467-474.
3. I. Benedek, (1999) *Development and Manufacture of Pressure Sensitive Products*, New York: Marcel Dekker Inc.
4. L. A. Cannon, R. A. Pethrick, (1999) Effect of the glass-transition temperature on film formation in 2-ethylhexyl acrylate/methyl methacrylate emulsion copolymers, *Macromolecules*, **32(22)**: 7617-7629.
5. R. S. Tigh, V. Evren, (2005) Synthesis and characterization of pure poly(acrylates) latexes, *Progress in Organic Coatings*, **52**: 144-150.
6. I. Satas, (1989) Acrylic adhesives. In: D. Satas, (Ed.), *Handbook of Pressure Sensitive Adhesive Technology*, New York: Van Nostrand Reinhold Co., p396-456.
7. H. Ismail, Z. Ahmad, F. W. Yew, (2011) Effect of monomer composition on adhesive performance for water borne acrylic pressure-sensitive adhesives, *Journal of Physical Sciences*, **22(2)**: 51-63.
8. M. D. Gower, R. A. Shanks, (2004). The effect of varied monomer composition on adhesive performance and feeling master curves for acrylic pressure-sensitive adhesives, *The Journal of Applied Polymer Science*, **93**: 2909-2917.
9. S. D. Tobling, A. Klein, (2001) Molecular parameters adhesive performance and their relation to the adhesive performance of acrylic pressure-sensitive adhesives, *The Journal of Applied Polymer Science*, **79**: 2230-2244.
10. R. Jovanovic, K. Quzineb, (2004) Butyl acrylate/methyl methacrylate latexes: Adhesive properties, *Macromolecular Symposia*, **206**: 43-56.
11. ASTM D330/D3330M - 04 Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape, (2007) *Annual Book of ASTM Standards*, Vol. 15.06. Philadelphia, PA: American Society for Testing and Material.
12. PSTC-10, Peel Adhesion of Pressure Sensitive Tape, (2007) *Test Method for Pressure-sensitive Adhesive Tapes*, 15th ed. Northbrook, IL: Pressure Sensitive Tape Council.

*Bibliographical Sketch



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