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Effect of Monomer Composition on Adhesive Performance for Waterborne Acrylic Pressure-Sensitive Adhesives

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Abstract: *A series of pressure-sensitive adhesives (PSAs) with different monomer composition was prepared using emulsion polymerisation. The monomers were butyl-acrylate (BA), 2-hydroxyethyl acrylate (2-HEA), acrylic acid (AA) and 2-ethylhexyl acrylate (2-EHA). The adhesive performance was studied at 4%, 8% and 12% 2-EHA content based on total monomer (BOTM) composition. The adhesives obtained with constant thickness were coated onto a Kraft paper and evaluated for adhesive performance by measuring their tackiness, peel strength and shear strength. As the 2-EHA content increased, shear strength and peel strength were found to increase. The results also show that the loop tack decreased when the 2-EHA content increased. Peel strength and shear strength showed an increase with smaller particle size of latexes obtained. Positive effect of smaller particles on shear strength and peel strength relate to the tighter packing provided by smaller particles during the drying process, thus increasing the area of contact.*

Keywords: pressure-sensitive adhesives, acrylic, emulsion polymerisation, particle size

Abstrak : *Sekumpulan pelekat sensitif tekanan telah disediakan dengan komposisi monomer yang berlainan dengan menggunakan kaedah pempolimeran emulsi. Monomer yang digunakan dalam sintesis ini terdiri daripada butil akrilik (BA), 2-hidrosilethil akrilik (2-HEA), asid akrilik (AA) dan 2-ethilheksil akrilik (2-EHA). Sifat-sifat pelekat dikaji pada nisbah monomer 2-EHA pada 4%, 8% dan 12% berdasarkan jumlah komposisi monomer. Emulsi akrilik seterusnya ditampal dengan ketebalan gam yang sama pada kertas Kraft untuk menyediakan spesimen untuk mengkaji sifat-sifat pelekat termasuk jelujur, kekuatan pengupasan dan kekuatan ricih. Kekuatan ricih dan kekuatan pengupasan bertambah apabila komposisi 2-EHA meningkat. Keputusan kajian membuktikan jelujur berkurang apabila komposisi 2-EHA meningkat. Kekuatan pengupasan dan kekuatan ricih bertambah apabila saiz partikel emulsi akrilik berkurang. Saiz partikel emulsi akrilik yang kecil menunjukkan pengaruh terhadap kekuatan ricih dan kekuatan pengupasan disebabkan susunan partikel yang kecil lebih rapat semasa proses pengeringan, dan seterusnya meningkatkan kawasan sentuhan.*

Katakunci: pelekat sensitif tekanan, akrilik, pempolimeran emulsi, saiz partikel

1. INTRODUCTION

The aim of the study is to investigate the effect of 2-ethylhexyl acrylate content on the adhesive performance of the resultant polymers through measurement of shear strength, loop tack and peel strength. Adhesives are defined as substances capable of holding at least two surfaces together. Acrylic pressure-sensitive adhesives (PSAs) obtained by emulsion polymerisation are characterised as adhesive which can adhere strongly to solid surfaces upon application of light contact pressure and short contact time. It is used in pressure sensitive tapes, labels, note pads, automobile trim and a wide variety of other products. There are three different types of PSAs used commercially today. They are solvent borne, water borne (emulsion) and hot melt (100% solid).[1]

In recent years, increasing social and political awareness, coupled with the tightening of worldwide environmental legislation such as strict volatile organic compound (VOC) level reduction as required by the EPA Clean Air Act (Title 5), has forced coating industries to decrease the levels of pollutant substances released to the atmosphere. Solvents from the coating industry are considered to be volatile organic substances. For this reason, there is an increasing tendency to move away from conventional solvent-borne coating to those that use water as fluid vehicle.[2]

Several researches[3–5] have reported the work on PSAs using different type of monomer in various recipe formulations. A PSA must be soft and tacky, hence, its glass transition temperature (Tg) should be low, ranging from –20°C to–60°C. Polymers with low Tg typically from a class of alkyl acrylates such as poly(butyl acrylate) and poly(2-ethylhexyl acrylate) are inherently soft and tacky but do not posses adequate shear strength.[3] As the 2-EHA content increased, the latex gel fractions were found to increase.[5]

During the drying process, the largest particle sizes imparted some inherent weakness to the peel strength property.[6] However, the shear strength increased with decreasing particle size.[6,7]

The materials used for this research were monomers butyl-acrylate (BA), 2-hydroxyethyl acrylate (2-HEA), acrylic acid (AA), 2-ethylhexyl acrylate (2-EHA), emulsifiers, initiators ammonium persulfate, $NaHCO_3$ and doubly deionised water. The proportion of 2-ethylhexyl acrylate content was studied at 0%, 4%, 8% and 12% based on total monomer composition. The influence of particle size on PSAs was investigated.

2. EXPERIMENTAL

2.1 Materials

All the reagents were used as supplied. The BA, AA and 2-EHA monomers were all commercial grades available from BASF (Malaysia) Sdn. Bhd. 2-HEA was obtained from Acros Organics Belgium. The initiator used was ammonium persulfate obtained from Merck & Co., Inc. Tert-butyl hydroperoxide and sodium formaldehyde sulfoxylate were obtained from Megachem Limited. Sodium hydrogen carbonate was obtained from R&M Chemicals. Deionised water was used throughout the polymer preparations. The polymerisation surfactant used was an anionic surfactant from Rhodia Malaysia Sdn. Bhd. Its active solid was 33 wt%. The surfactant system employed was referred to as surfactant A and its composition cannot be revealed for proprietary reasons.

2.2 Preparation of Acrylic PSA Using Semicontinuous Emulsion Polymerisation

2.2.1 Preparation of monomer pre-emulsion charge

5.4 g surfactant A was dissolved in deionised water and placed in a vessel equipped with stirrer. Separately, 314.45 g butyl acrylate, 6.48 g 2-hydroxyethyl acrylate and 3.24 g acrylic acid were mixed. The water-surfactant mixture was placed under high shear agitator at 300 rpm. The monomer mixture was slowly added into the water-surfactant mixture under sufficient stirring to make a monomer pre-emulsion. The mixing time required was 10 min. The resulting monomer emulsion was homogenous, viscous and milky in appearance. The mass ratios of monomers and surfactant were varied as summarised in Table 1.

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

Run	BA	2-HEA	AA	2-EHA	Surfactant A
1	97	2	1	0	1.67
2	93	2	1	4	1.67
3	89	2	1	8	1.67
4	85	2	1	12	1.67
5	97	2	1	0	2.0
6	97	2	1	0	2.5
7	97	2	1	0	3.0

2.2.2 Preparation of initiator delayed feed

The initiator delayed feed was prepared by adding 0.78 g of ammonium persulfate into 34.58 g of deionised water and stirred in using a magnetic bar.

2.2.3 Polymerisation procedure

The reactions were performed in a 1 liter, glass made, round-bottomed reactor flask with an IKA mechanical agitator and stirred at 200 rpm. The reactor flask was equipped with reflux condenser, thermocouple and polytetrafluoroethene stirrer. 1.14 g sodium hydrogen carbonate and 150 g of deionised water were charged to a 1 liter glass made, round-bottomed reaction flask and heated to 84°C with stirring. Initial initiator was made by adding 0.78 g ammonium persulfate into 3.6 g deionised water in a separate vessel and stirred in using magnetic bar. At 84°C, initial initiators was added, and after 2 min, monomer and pre-emulsion and delayed initiator was fed for 4 hours using a peristaltic pump via silicone tubing, and the feed rate monitored volumetrically. Polymerisation temperature was maintained at 82–85°C, and agitation rate was increased if necessary. After feed, the monomer mix beaker was flushed with water, and was post-heated for 30 min. The reaction mixture was then cooled to below 40°C and filtered into a suitable container.

2.3 Particle Size Characterisation

The particle size distribution (PSD) of the final latexes were determined using CILAS 1180 Laser Particle Size Analyzer. Samples for particle size analysis were prepared by diluting PSA obtained in deionised water. After dilution, the latex samples were then injected into the instrument.

2.4 Dynamic Shear Test

Shear strength is also an important industry test, often used by label laminate producers as an indicator of adhesive cuttability and die cuttability. Shear strength was the resistance of an adhesive coated label stock on a standardised surface to shear at a constant rate.[7]

To measure the adhesive dynamic shear resistance, first a 150 × 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 × 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 measured was the dynamic shear.

2.5 Loop Tack, PSTC-16

Loop tack is an adhesive performance indicator often used within industry to gain a measure of the capability of a PSA to adhere immediately to a substrate under light pressure. The loop tack was measured as the force required to separate the adhesive from the adherend at the interface shortly after they have been brought into contact under a load equal only to the weight of the pressure sensitive article on a 24 × 24 mm surface contact area.[8]

Tack was measured using the PSTC-16 standard. A specimen of 24 × 125 mm was cut and formed into a loop using staples. A loop with the adhesive facing outside was formed and placed in the upper grip of a Universal Material Testing Machine. The loop was then brought into contact with the substrate mounted onto a loop tack fixture inserted into the bottom grip. When the loop was covered with a 24 × 24 mm surface of acrylic sheet, the upper grip was brought up at a crosshead speed of 300 mm/min. The maximum force required to remove the specimen was recorded as the loop tack.

2.6 Peel Adhesion of Pressure-Sensitive Tape (ASTM D330)

Peel adhesion is defined as the force required to remove pressure sensitive coated material which has been applied to a standard test plate. According to ASTM D330, Test Method A was chosen which gives a measure of the adherence when peeled at 180^o angle, to a standard test panel for a single coated tape.[9,10]

Each PSA latex obtained was coated onto Kraft paper by using a laboratory coater (Chem Instruments) equipped with a wire-wound drawdown bar. The adhesive coated paper were dried at 105°C for 4 min. To measure the adhesive coating weight, a 200 × 50 mm sample of adhesive laminate and Kraft paper without coating was obtained by cutting around the edges of a 200 × 50 mm template. The coating weight was calculated from the difference between Kraft paper with adhesive and without adhesive and expressed as gram adhesive per square metre film. The adhesive-coated samples were left for 24 hours in a controlled environment (23 ± 2°C, 50 ± 5 relative humidity) chamber prior to testing the adhesive properties.

A specimen of 24 × 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 to 2040 g for 24 mm ± 35%. The average force to peel the specimen from test plate was recorded. The testing speed for Universal Material Testing Machine was 300 mm/min.

2.7 Fourier-transform Infrared Spectroscopy (FTIR)

The FTIR spectra were recorded on a Perkin-Elmer FTIR at 4 scans from 4000 to 400 cm^{-1}. The attenuated total reflection infrared (ATR-IR) spectroscopy was employed.

2.8 Stereo Zoom Microscope

Stereo zoom microscope is an optical microscope equipped with computerised system to capture the images of sample. A stereo zoom microscope was used to feature large and high-resolution images of adhesives left on Kraft paper and stainless steel testing panel after shear strength testing.

3. RESULTS AND DISCUSSION

3.1 Effect of Varied Surfactant Content on Particle Size of Latexes

Table 2: Result of testing of PSAs for Run 1 to Run 7.

Run	Surfactant A (% BOTM)	Particle Size, dp (nm)	Total Solid Content (%)
1	1.67	0.48	56.22
2	1.67	0.40	56.32
3	1.67	0.45	55.46
4	1.67	0.42	56.12
5	2.0	0.43	55.91
6	2.5	0.39	55.80
7	3.0	0.24	55.42

Table 2 shows the total solid content results varied from 55.42% to 56.12% for runs 1 to 7. The results indicated that all the runs were completed successfully with conversions exceeding 99% in most cases when compared to targeted total solid content. Surface active agent was added for a stable monomer emulsion in water. The table also shows the decrease in particle as the surfactant content increased from 1.67% to 3.0% based on total monomer content for runs 1, 5, 6 and 7. In conventional emulsion polymerisation, when the concentration of surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate to form small colloidal clusters referred to as micelles. In principle, polymer particles can be formed by the entry of radicals into the micelles, precipitation of growing oligomers in the aqueous phase and radical entry in monomer droplets. As the amount of monomers was kept constant, the number of micelles increased with the increasing surfactant content, therefore more sites for polymerisation occurred and smaller particle size of latexes formed. The surfactant was useful to control the particle size of latexes.

3.2 Effect of Particle Size on Adhesive Performance

Figure 1 shows the effect of latexes particle size on loop tack of PSA obtained. Loop tack is determined by the Tg or softness of the copolymers. Druschke et al.[11] reported that tack increased for acrylic homopolymers as Tg decreased; this is consistent with the work of Aubrey.[12] Constant monomer composition was used for runs 1, 5, 6 and 7, and therefore, the results obtained did not display any dependence of loop tack on particle size of latexes. Figure 2 and Figure 3 show the effect of latexes particle size on peel strength and shear strength of PSA obtained. It can be observed that peel strength and shear strength increased with smaller particle size of latexes. As reported by Dube et al.,[6] during the drying process, the largest particle sizes imparted some inherent weakness to the peel strength property. Shear strength increased with decreasing particle size.[6,7] A possible explanation for the positive effect of smaller particles on shear strength relates to the ability of these smaller particles to pack more tightly together during the drying process, thus increasing the area of contact between the adhesive and the substrate.

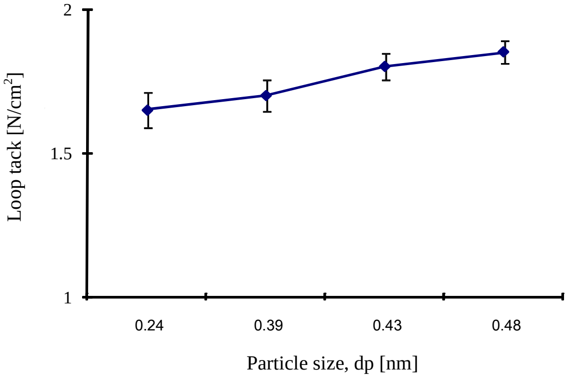

Figure 1: The effect of latexes particle size on loop tack of PSA.

3.3 Effect of Monomer Composition on Adhesive Performan e

Figure 4 shows that loop tack decreased with increasing 2- HA content. Higher sol fractions allowed intimate contact with the substrat during the bonding step.[13] The effect of monomer composition on peel strengt is shown in Figure 5. It is interesting to note that for the PSA series investiga ed, the PSA with increasing of 2-EHA content exhibited the higher peel strengt compare to formulation without 2-EHA composition. According to Shanks et al.,[5] the peel stress was sensitive to monomer content. Low BA or high EHA content provided the highest peel stress. A work was performed to study the effect of incorporating 2-ethylhexyl acrylate in PSAs by Gower and Shanks.[5] The results showed an increase in gel content as the weight fraction of EHA increased. Tobing and Klein[13] found that as gel content increased, peel strength also increased. The shear strength in Figure 6 increased proportionally to 2-EHA concentration. The flow of adhesive, or wetting of the substrate, must be dominated by the 2-EHA content. The higher shear strength with increasing of 2-EHA content was due to entanglements of the ethylhexyl side groups.[5]

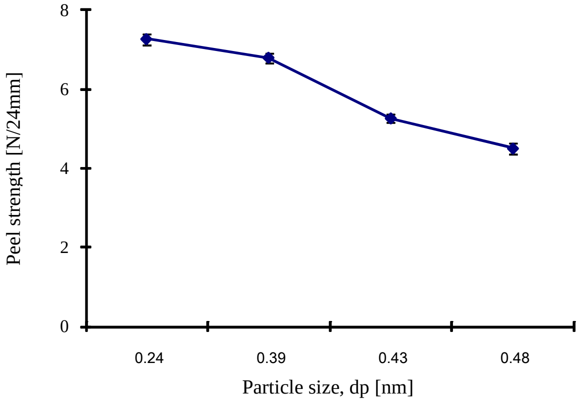

Figure 2: The effect of latexes particle on peel strength of PSA.

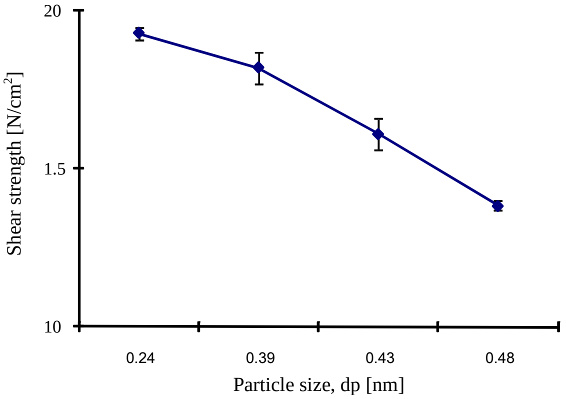

Figure 3: The effect of latexes particle size on shear strength of PSA.

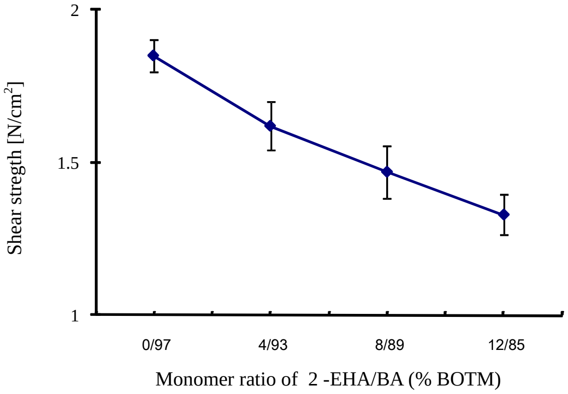

Figure 4: The effect of 2-EHA/BA monomer ratio on loop tack of PSA (AA was fixed at 3% BOTM).

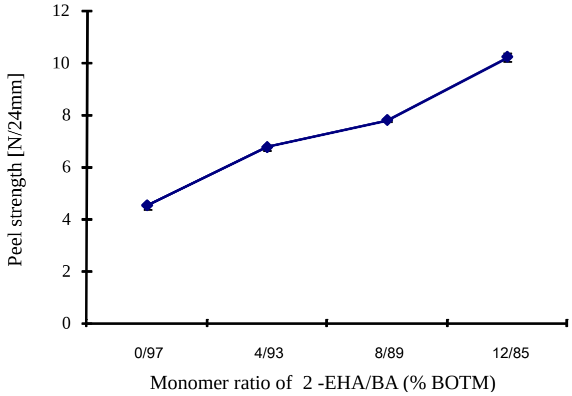

Figure 5: The effect of 2-EHA/BA monomer ratio on peel strength of PSA (AA was fixed at 3% BOTM).

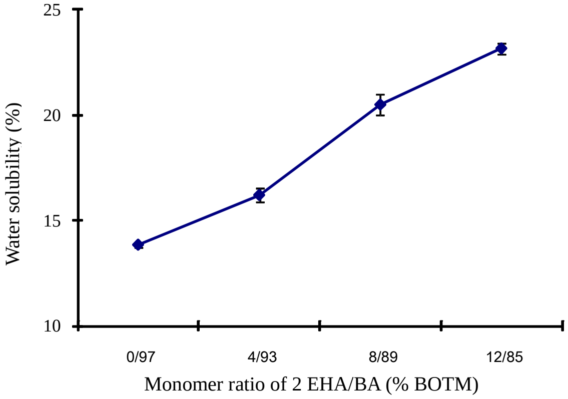

Figure 6: The effect of 2-EHA/BA monomer ratio on shear strength of PSA (AA was fixed at 3% BOTM).

3.4 Stereo Zoom Microscope

The stereo zoom microscope photos of the adhesive left on Kraft paper and testing sheets after shear strength testing at 0%, 4%, 8% and 12% 2-EHA content based on total monomer composition are shown from Figure 7 to Figure 10 respectively. The microscope photos showed little adhesives left on 0% 2-EHA content testing sheet and the most adhesives left on 12% 2-EHA content testing sheet. The microscope photos also indicated that the 12% 2-EHA content coated Kraft paper showed hairy condition. This observation was due to the increasing shear strength when 2-EHA content increased. The results indicated that adhesives resist the deformation until maximum shear strength was applied. Therefore, more adhesives were left on both Kraft paper and testing sheet when shear strength increased.


(a) (b)

Figure 7: Stereo Zoom Microscope photos of the adhesive left on (a) testing sheets after shear strength testing and (b) Kraft paper at 0% 2-EHA content at magnification 45X.

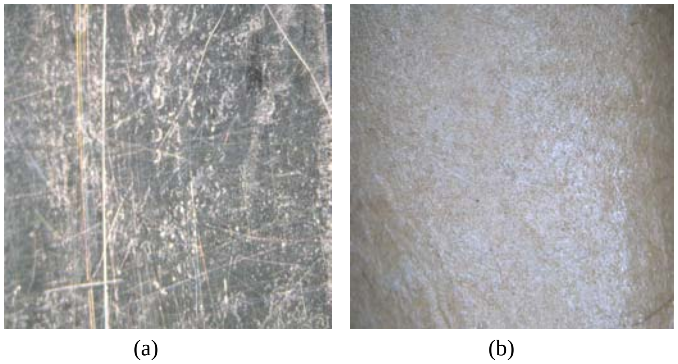
(a) (b)

Figure 8: Stereo Zoom Microscope photos of the adhesive left on (a) testing sheets after shear strength testing and (b) Kraft paper at 4% 2-EHA content at magnification 45X.

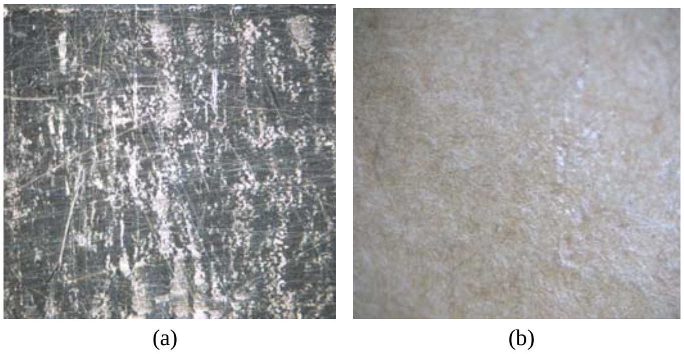
(a) (b)

Figure 9: Stereo Zoom Microscope photos of the adhesive left on (a) testing sheets after shear strength testing and (b) Kraft paper at 8% 2-EHA content at magnification 45X.

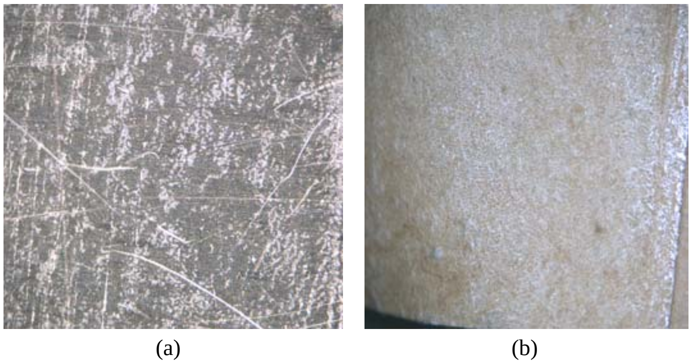
(a) (b)

Figure 10: Stereo Zoom Microscope photos of the adhesive left on (a) testing sheets after shear strength testing and (b) Kraft paper at 12% 2-EHA content at magnification 45X.

3.5 FTIR Spectroscopy

The FTIR spectrum of PSA obtained is shown in Figure 11. The band at 2958 cm^{-1}, 2934 cm^{-1} and 2873 cm^{-1} was due to C-H strong alkyl bonding. 2-ethylhexyl acrylate and butyl acrylate added as co monomer were characterised by absorption peak of strong alkyl bonding from 2970 cm^{-1} to 2850 cm^{-1}. 2-hydroxyethyl acrylate also showed a tendency to have primary alcohol bonding in its backbone structure by absorption peak at 1064 cm^{-1}. The FTIR spectra of acrylate emulsion exhibited that all monomers added participated in the polymerisation process.

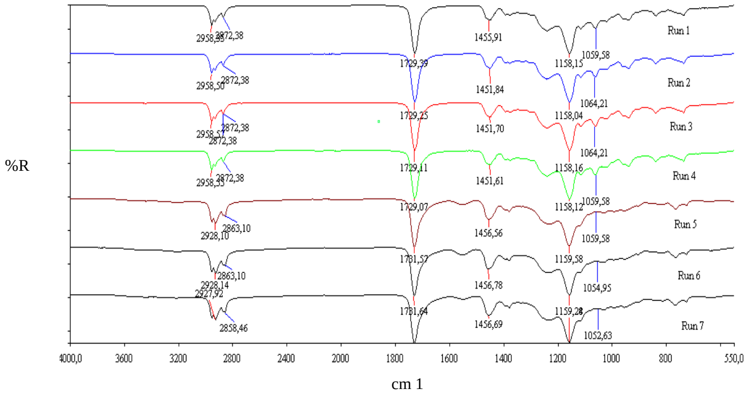

Figure 11: FTIR spectrum for PSA obtained.

All polymer produced also showed weak wave number of vinyl group which was characterised by 970 cm^{-1} to 1000 cm^{-1}. Monomers were converted to polymer through emulsion polymerisation process. The appearance of peak wave's number at 1242 cm^{-1} was resulted from decomposition of initiator ammonium persulfate. The initiator decomposed which yielded sulphate anion free radicals to commence the polymerisation.

4. CONCLUSION

Pressure-sensitive adhesives (PSAs) were prepared from acrylate monomers (BA, 2-HEA, AA, 2-EHA) by using emulsion polymerisation. PSA with increasing of 2-EHA content showed higher peel strength and shear strength compare to formulation without 2-EHA composition. As the 2-ethylhexyl acrylate content increased, the loop tack was found to decrease. Peel strength and shear strength showed an increase with smaller particle size. Positive effect of smaller particles on shear strength relates to the tighter packing provided by smaller particles during the drying process, thus increasing the area of contact.

5. ACKNOWLEDGEMENTS

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