



Synthesis and Optimization of a Four-component Acrylic-based Copolymer as Pressure Sensitive Adhesive

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Received 22 July 2009; accepted 7 March 2010

A B S T R A C T

A pressure sensitive adhesive (PSA) based on acrylic monomers was synthesized. For this purpose a solution copolymerization process was conducted for preparation of an acrylic copolymer containing 2-ethylhexylacrylate (2-EHA), 2-hydroxyethyl acrylate (2-HEA), glycidyl methacrylate (GMA) and vinyl acetate (VAc), using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The initial amounts of feed monomers were constant in all formulations (2-EHA/VAc/ HEA/GMA; 67%, 28%, 4.9%, 0.1% by weights). With variation of different parametric conditions such as reaction times (3.5, 6.5 and 9.5 h), temperatures (70, 80 and 90°C) and initiator concentrations (0.25, 0.5 and 1 wt%) the copolymerization reactions were optimized. The adhesive properties have been evaluated in terms of intrinsic viscosity, glass transition temperature (T_g), peel strength and tack value for all samples. It was observed that the trends in peel strength and intrinsic viscosity variations are approximately correlated with the above changing parameters. The synthesized PSAs show good adhesive properties and could be easily peeled off from the surface without leaving any residue on the surface. These samples with satisfactory adhesion properties were characterized by Fourier transform infrared, proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry and gel permeation chromatography. Based on the optimum time (3.5 h), temperature (70°C) and initiator concentration (0.5 wt%), a formulation with the best adhesion properties and high conversion (86%) was selected as the optimized PSA and it was compared with a commercialized PSA namely Duro-Tak 2287.

Key Words:

acrylic;
pressure sensitive adhesive;
solvent based polymerization;
optimization;
glass transition temperature.

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

poly(*n*-butyl acrylate), poly(2-ethylhexyl acrylate), and poly(isooctyl acrylate), have enjoyed the fastest growth in commercial applications [2]. Acrylic PSAs are homopolymers of acrylic esters and their copolymers with other various acrylic or vinylic monomers that are well-known as self-adhesive compounds with remarkable tack, adhesion and

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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 [2]. 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 pressure sensitive adhesives 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]. Tack is affected by wettability. Low T_g and low molecular weight (M_w) also increase the mobility of polymer chains leading to high tackiness due to high wettability [7,8]. 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(*n*-butyl acrylate) (BA) and poly(2-ethylhexyl acrylate) (2-EHA), as soft homopolymers or together as a copolymer provide 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 methyl methacrylate (MMA), vinyl acetate (VAc), styrene (S) and acrylic acid (AA) may be added to provide sites for cross-linking reactions or, as in the case of acrylic acid, to improve latex 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 [10]. Addition of a small amount of functional monomers such as hydroxyethyl acrylate (HEA) and glycidyl methacrylate (GMA) increases hydrophilicity and creates cross-linking sites which promote adhesion of the PSA with its increased moisture permeability [11].

Czech [12] studied the preparation of solvent-based PSAs including 2-ethylhexyl acrylate and acrylic acid in an organic solvent in presence of cross-linkers. It was observed that the peel adhesion decreased with increased amount of cross-linker. Bhabhe et al. [13] studied the solvent-based synthesis of copolymers of methyl methacrylate and acrylate comonomers and investigated the concentration effect of soft and hard monomers on adhesion properties. Tipre et al. [14], investigated the preparation of acrylate-based PSAs including 2-ethylhexyl acrylate, methyl methacrylate, acrylic acid and vinyl acetate by solution polymerization and studied the optimization of polymerization by different reaction parameters such as reaction time, temperature and initiator concentration. These adhesives are used for design of a drug-in-adhesive type transdermal therapeutic system for many drug types.

According to the best of our knowledge there is no published report regarding the synthesis of copolymer containing 2-ethylhexyl acrylate (2-EHA), hydroxyethyl acrylate (HEA), glycidyl methacrylate (GMA) and vinyl acetate (VAc). In this study, acrylate pressure sensitive adhesives were prepared by free radical solution polymerization in presence of 2,2'-azobisisobutyronitrile (AIBN). The polymerization reaction was optimized with several parameters including reaction temperature, reaction time and initiator concentration. To attain optimized conditions, the effect of these variables on overall conversion in each step was evaluated. The copolymers have been characterized by FTIR, ^1H NMR, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). The adhesive properties of these copolymers such as peel strength and tack values were also studied. Finally, the optimized sample was compared with a commercialized PSA.

EXPERIMENTAL

Materials and Methods

2-Ethylhexyl acrylate (2-EHA, 99%), vinyl acetate (VAc, > 99%) and ethyl acetate were purchased from Merck (Germany); 2-hydroxyethyl acrylate (2-HEA, > 97%), glycidyl methacrylate (GMA, > 97%) and 2,2'-azobisisobutyronitrile (AIBN) as an initiator were purchased from Fluka (Swiss). Duro-Tak (2287) was purchased from National Starch and Chemical Company (USA). Duro-Tak (2287) is an acrylic-based adhesive copolymer containing acrylate comonomers. Polyester/ethyl vinyl acetate (Scotch Pak9732) as a backing layer of 85 μm (3 M, USA) thickness was used. All chemicals of reagent grades were employed without further purification.

A solution polymerization technique was carried out in ethyl acetate by using AIBN as a free radical initiator. The monomers selected including 2-ethylhexyl acrylate (2-EHA) as tackifying monomer, vinyl acetate (VAc) as hardening monomer, hydroxyethyl acrylate (HEA) and glycidyl methacrylate (GMA) as functional monomers. Percentage of monomers employed were according to monomer content of commercialized PSA namely Duro-Tak 2287 [15]. Accordingly, the initial percentages of monomers were constant in all formulations (2-EHA: VAc: HEA: GMA; 67%, 28%, 4.9%, 0.1% by weights). The polymerization was carried out in a 500-mL four-necked jacketed glass reactor, equipped with a reflux condenser, an efficient stirrer, one dropping funnel and a nitrogen inlet.

Initially the reactor was charged with a half portion of each reacting monomer, solvent and initiator solution; then the mixture was heated in one selected temperature of 70, 80, or 90°C. When the refluxing process started, the remaining monomers, the solvent and the initiator solution were added dropwise for about 1 h while stirring at the same temperature, followed by polymerization reactions carried out at specified time (3.5, 6.5 and 9.5 h). At the end of reaction, the solvent was added to cool the reaction mixture. On completion, the reaction was quenched with sodium metabisulphite aqueous solution. The polymer was further purified by reprecipitation from ethyl acetate into methanol to remove the unreacted monomers. The purified

polymer was then dried under vacuum at 40°C until constant weight was achieved [14,16]. The conversion calculation method was according to the following equation:

$$\text{Overall conversion} = W_t / \Sigma M_0 \times 100 \quad (1)$$

where, W_t is the mass of copolymer after drying in vacuo at 40°C for 24 h and ΣM_0 is the mass of initial monomer fraction [17].

Characterization

The average molecular weight of the optimized copolymer was determined using gel permeation chromatography (GPC) technique (Agilent 1100 series) at ambient temperature. A sample in tetrahydrofuran was placed in Agilent 1100 series, consisting of a refractive index detector RI. The column used was Agilent PL gel 10 μm .

The intrinsic viscosity measurement for copolymer was carried out with a Brookfield NV(RVT) viscometer in ethyl acetate (50% solid), using a speed of 3 rpm, spindle TR8 and at ambient temperature.

The FTIR spectra were taken using an Equinox 55 (Bruker, Germany). The adhesive sample was placed as a thin film on a KBr disk and dried in an oven at 50°C for 1 h.

^1H NMR spectra were recorded on a 400 MHz Bruker spectrophotometer using CDCl_3 as a solvent.

Glass transition temperature (T_g) of all adhesive samples was determined by differential scanning calorimeter (DSC) (PL, UK) at a heating rate of 10°C/min from -100°C to +300°C. The sample was cooled in liquid nitrogen and the recording was carried out by a programmed heating rate of 10°C/min. The T_g of all samples is taken as the midpoint of the heat flow curve.

Peel Strength Measurement at 180°

A general method employed for sample (PSA tape) preparation was as follows:

An appropriate amount of acrylic PSA was coated onto a backing layer by a film applicator (Elcometer 3580) at a controlled specified thickness. The coated product at first was placed at room temperature for 20 min and then placed in an oven at 50°C for 45 min to drive off the remaining volatile processing solvent.

Dried PSA tapes with 45 μm thickness were pressed in stainless steel plates by 5 kg rubber roller passing twice over the samples. Peel tests were carried out according to the ASTM D3330 on adhesive-coated tapes with 25 mm width. After preparation of PSA tape/stainless steel joints, they were stored at room temperature for 20 min. Peel force in 180° direction was measured for at least three samples at a peel rate of 30.5 cm/min at room temperature using Chemie Instruments adhesive/release tester AR-1000 (Fair Field, Ohio, USA) [18].

Probe-tack Test

Tack tests were carried out for adhesive tapes each with 45 μm thickness. According to ASTM D3121 by using Chemie Instruments Probe-Tack PT-500 (fair field, Ohio, USA) for at least four samples [18].

RESULTS AND DISCUSSION

Optimization of Reaction Conditions

Various reaction parameters like reaction time,

initiator concentration and reaction temperature were tested in relation to adhesive properties of the polymer.

Optimization of polymerization reaction was investigated in three steps. The reaction condition for maximum conversion was considered as optimum condition. Initially the polymerization reactions were carried out at three different temperatures such as 70°C, 80°C and 90°C to evaluate their effects on polymer yield. In the next step the effect of varying reaction time such as 3.5, 6.5 and 9.5 h on reaction conversion was assessed. At the last stage, the initiator concentrations of 0.25, 0.5 and 1 wt% were used to examine conversion efficiency. The results are given in Tables 1 to 3. The percentage of overall conversion was obtained as 86% under optimized condition. The optimum conditions were attained by reaction time (3.5 h), reaction temperature (70°C) and initiator concentration (0.5 wt%). It was also observed that, the performance of samples prepared at optimized conditions was almost the same as commercialized PSA namely Duro-Tak 2287.

Table 1. Effect of reaction temperature.

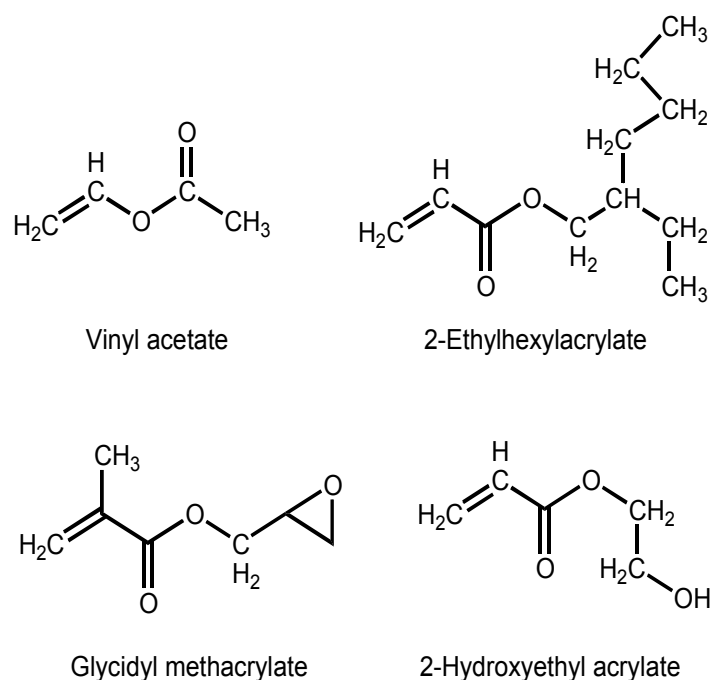
Code	Temperature (°C)	Time (h)	AIBN (%)	Overall conversion (%)	T _g by DSC (°C)	Intrinsic viscosity (cP)	Peel (N/25 mm)	Tack (N/mm ²)
PSA1	70	3.5	1	77±2	-41	7255±0.1	14.5±0.1	4.6±0.3
PSA2	80	3.5	1	77±2	-50	2330±0.2	8.8±0.2	4.6±0.1
PSA3	90	3.5	1	77±2	-47	3676±0.1	2.4±0.1	3.6±0.1

Table 2. Effect of reaction time.

Code	Temperature (°C)	Time (h)	AIBN (%)	Overall conversion (%)	T _g by DSC (°C)	Intrinsic viscosity (cP)	Peel (N/25 mm)	Tack (N/mm ²)
PSA1	70	3.5	1	77±2	-41	7255±0.1	14.5±0.1	4.6±0.3
PSA4	70	6.5	1	71±2	-49	7545±0.1	16.3±0.2	4.4±0.1
PSA5	70	9.5	1	69±2	-52		17.5±0.3	4.3±0.2

Table 3. Effect of initiator concentration.

Code	Temperature (°C)	Time (h)	AIBN (%)	Overall conversion (%)	T _g by DSC (°C)	Intrinsic viscosity (cP)	Peel (N/25 mm)	Tack (N/mm ²)
PSA6	70	3.5	0.25	76±2	-43	5450±0.2	13.6±0.7	4.2±0.3
PSA7	70	3.5	0.5	86±2	-43	11223±0.1	15.3±0.5	4.4±0.1
PSA1	70	3.5	1.0	77±2	-41	7255±0.1	14.5±0.1	4.6±0.3



Scheme I. Chemical structures of the monomers.

Effect of Temperature on Copolymerization

Initially the effect of temperature (70°C, 80°C and 90°C) on copolymerization conversion at constant reaction time (3.5 h) and initiator (AIBN) concentration (1 wt%) was studied. High temperature would result in faster initiator decomposition, thereby increasing the reaction rate followed by rapid pressure built up of the system [11,17]. Also the polymerization rate was strongly influenced by the size of the monomer side groups (steric effect), which had significant effect on the T_g of copolymers [13,19,20]. The structures of monomers are depicted in Scheme I. The results due to varying temperatures are shown in Table 1. Glass transition temperature was decreased from 70°C to 80°C, while it was increased from 80°C to 90°C. According to Kajtna studies [19], it seems that due to chain transfer process the T_g is decreased by increasing reaction temperature from 70°C to 80°C and consequently by greater intermolecular interactions at reaction temperature beyond 80°C the T_g of the polymer is increased. Therefore, it was concluded that a reaction temperature of 70°C was an optimum condition to obtain good conversion and adhesion properties with high intrinsic viscosity.

Effect of Reaction Time on Copolymerization

In the second stage, the copolymerization was carried out at optimum temperature (70°C) and at various reaction times (3.5, 6.5 and 9.5 h). Table 2 shows the effect of reaction time on polymer yield and other properties. The results indicated that by increasing the reaction time, the T_g of final copolymer is decreased while the intrinsic viscosity is increased. According to the Bhabhe's studies [13], increase in the chain length results in the reduction of T_g value of the polymer. However, some specific chains have stiffening effect or the hydrogen bonding between the comonomer residues. It is highly probable that higher molecular weight species which form cross-linking via hydrogen abstraction of the tertiary carbon atoms are due to the presence of higher number of these sites per chain [2]. Therefore, by producing high molecular weight and highly branched macromolecules, there is a possibility of chain transfer and hence increased viscosity [2,20]. Generally, T_g of comonomers is calculated from the Fox's equation.

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} + W_3/T_{g3} + W_4/T_{g4} \quad (2)$$

where, W_1 , W_2 , W_3 and W_4 are weight percentages of

Table 4. Homopolymer glass transition temperature.

Homopolymer	T _g (°C)
2-Ethylhexyl acrylate	-70
Glycidyl methacrylate	46
Hydroxyethyl acrylate	-15
Vinyl acetate	30

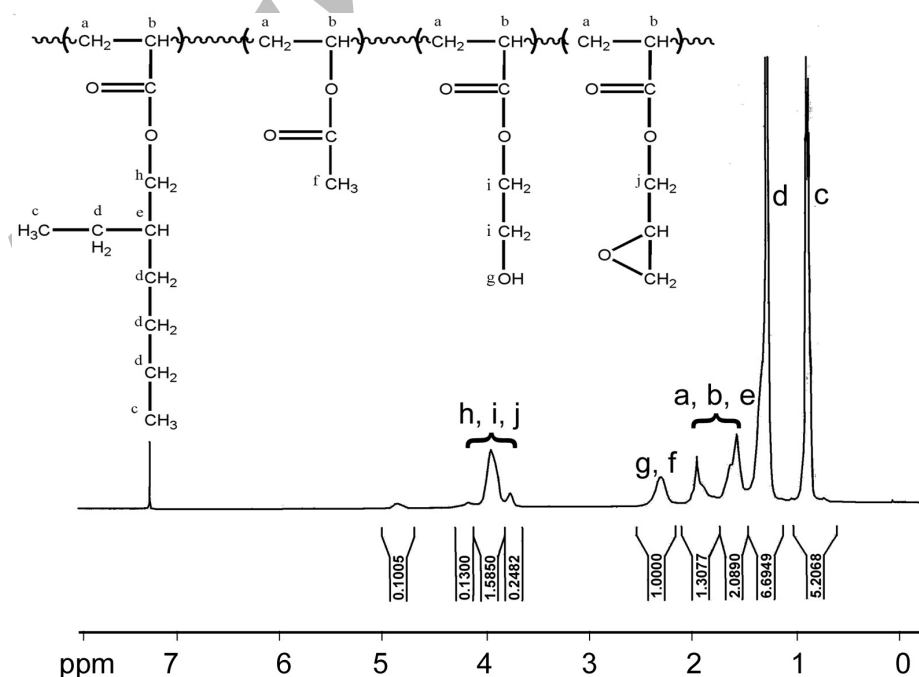
the system reaction components [21]. On the basis of Fox's equation and T_g of homopolymers (Table 4), the theoretical T_g of the final copolymers was obtained at about -47°C. In spite of the fact that the initial amount of monomers is constant in all formulations but the T_g of the final polymers is changed by varying reaction time and temperature; most likely due to differences in reactivity ratios of the monomers, leading to different conversion rates and final copolymer compositions in which the changes in the arrangement of the monomers in the final copolymer occurred under imposed various conditions.

Effect of Initiator Concentration on Copolymerization Process

At the final stage, the copolymerization was carried out at optimum temperature (70°C), reaction time

(3.5 h) and various initiator concentrations. According to literature [17,19], an increase in the initiator concentration leads to higher polymerization rate and lower degree of polymerization, e.g. increase in AIBN content changes the copolymerization conversion and other ultimate properties. As shown in Table 3, the overall conversion and the intrinsic viscosity of copolymer are dependent on the initiator concentration, a similar phenomenon which is reported in literature [22]. According to Table 3, the T_g values are more or less unaffected by initiator concentration. The intrinsic viscosity is increased from 0.25 wt% to 0.5 wt% of AIBN, but from 0.5 wt% to 1 wt%, the viscosity is lowered. Probably, lowered viscosity is due to shorter kinetic chain lengths and shorter links between the cross-linking sites, which are characteristics in reaction medium with higher initiator concentration [19].

Based on the favourable overall conversion and viscosity, the 0.5 wt% of AIBN is found to be an optimum concentration for the initiator. Therefore the optimum conditions were observed at: specific reaction time (3.5 h), reaction temperature (70°C) and initiator concentration (0.5 wt%), and the adhesive prepared at this conditions (PSA7) was selected as optimized sample, because of superior adhesion

**Figure 1.** ¹H NMR spectrum of optimized PSA.

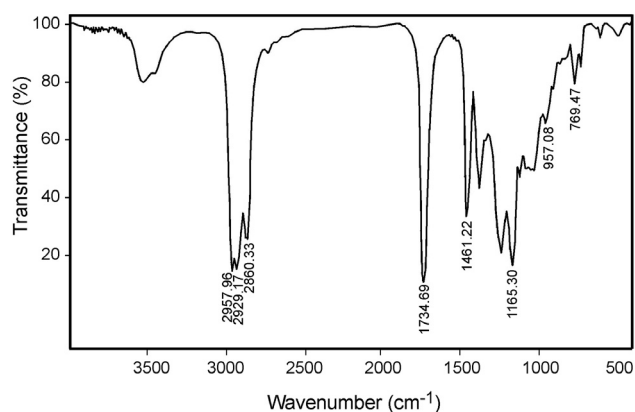


Figure 2. FTIR spectrum of optimized PSA.

properties.

Characterization of Acrylic Copolymer

The synthesized PSA has good transparency and good adhesion properties. The optimum formulation for highest conversion was obtained and characterized. For this purpose the ^1H NMR, FTIR, DSC and GPC of optimum sample were studied.

The ^1H NMR for the optimized PSA sample is shown in Figure 1. ^1H NMR (d, ppm, reference to TMS, in CDCl_3): 0.8-1 (CH_3 on the ethylhexyl group), 1.2-1.4 (CH_2 on the ethylhexyl group), 1.4-2.0 (CH on the ethylhexyl group and CH , CH_2 on the vinyl linkage), 2.2-2.4 (CH_3 group attached to the COO side group of vinyl acetate and OH group of hydroxyethyl acrylate), 3.8-4 (CH_2 groups attached to the COO side groups). The disappearance of peaks due to unsaturated protons (vinyl groups of monomers) between 5 and 6 ppm, indicates the absence of monomer impurities and the synthesized

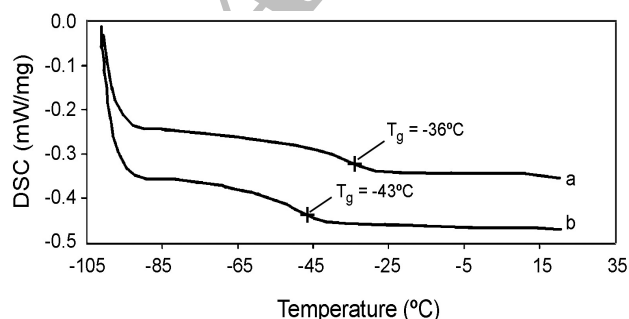
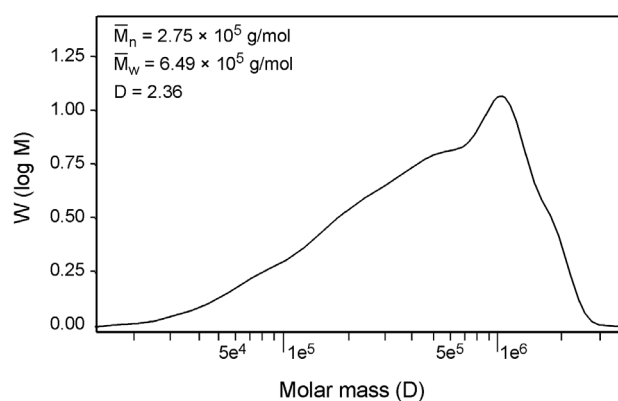
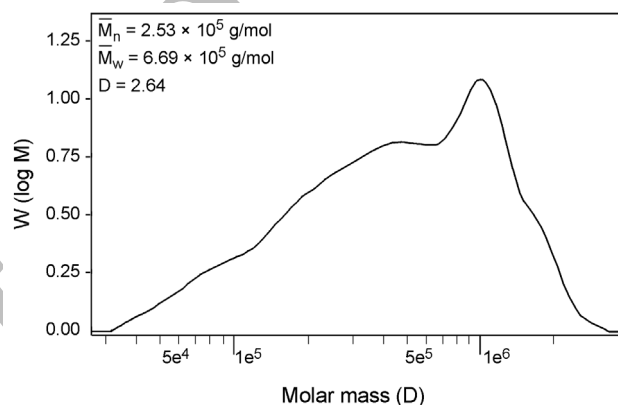


Figure 3. DSC curves of Duro-Tak 2287 (a) and optimized PSA (b).



(a)



(b)

Figure 4. GPC curves of Duro-Tak (2287) (a) and optimized PSA (b).

copolymer included all initial monomers [14]. In FTIR spectrum (Figure 2), the characteristic absorption bands of $-\text{COC}$, $\text{C}=\text{O}$, and $-\text{CH}_2$ and $-\text{CH}_3$ are shown at 1165, 1733, and 2850-3000 cm^{-1} , respectively. The disappearance of a band at 1600 cm^{-1} is an indication of the absence of monomer impurities [13]. In DSC thermogram (Figure 3), the T_g value of optimized copolymer (PSA7) was found to be -43°C . Also the average molecular weight of the optimized copolymer obtained by GPC was found to be 6.7×10^5 g/mol (Figure 4).

Adhesion Properties

The peel strength of the copolymer is dependent on copolymerization reaction conditions and also it is a function of molecular contacts which depends on the diffusion and molecular weight [14,16]. On the other hand, the molecular weight of the copolymers is significantly influenced by the polymerization

Table 5. Influence of reaction parameters on the properties of pressure sensitive adhesive (PSA).

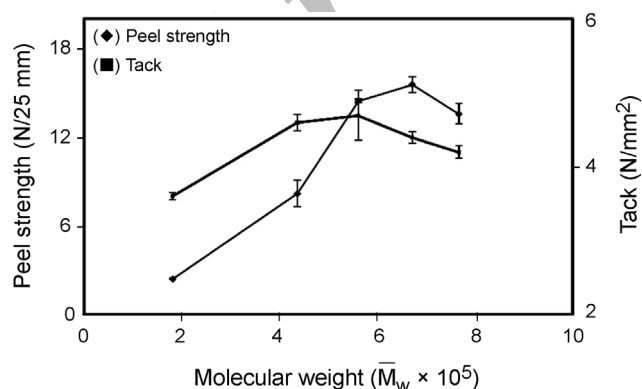
Code	Intrinsic viscosity (cP)	$\bar{M}_n \times 10^5$ (g/mol)	$\bar{M}_w \times 10^5$ (g/mol)	Peel (N/25 mm)	Tack (N/mm ²)
PSA1	7255±0.1	1.59	5.60	14.5±0.1	4.6±0.3
PSA2	2330±0.2	1.45	4.36	8.8±0.2	4.6±0.1
PSA3	3676±0.1	2.83	1.82	2.4±0.1	3.6±0.1
PSA6	5450±0.2	2.62	7.65	13.6±0.7	4.2±0.3
PSA7	11223±0.1	2.53	6.70	15.3±0.5	4.4±0.1

Table 6. Comparison of a commercial pressure sensitive adhesive with an optimized sample.

Code	T _g by DSC (°C)	Intrinsic viscosity (cP)	Peel (N/25 mm)	Tack (N/mm ²)	Molecular weight (g/mol)
Duro-Tak (2287)	-36	11562±28.5	14.9±0.5	4.6±0.1	6.5 × 10 ⁵
PSA7	-43	11223±20.5	15.3±0.5	4.4±0.08	6.7 × 10 ⁵

conditions. Both peel strength and tack values are measures of adhesive performance which depend significantly on viscous flows during bonding and viscoelastic energy dissipation during debonding process. Because both tack and peel are the outcomes of viscoelastic processes, they bear direct relationship to the molecular weight of the polymer and its entanglement [2,22]. It is observed from Table 5 that the trends in peel strength and molecular weight (\bar{M}_w) with increased reaction temperature and AIBN content are approximately similar. It is also observed that molecular weight is decreased with increased reaction temperature and AIBN content, due to

increases in free radical generation. It is found that very low \bar{M}_w compositions, although give a high viscous flow because of plasticization effect, but do not give high viscoelastic energy dissipation during debonding because the filament fractures very quickly due to lack of entanglement [23]. Therefore, the peel and tack of very low \bar{M}_w compositions are lower (Figure 5). As \bar{M}_w is increased, peel and tack values are increased up to optimum points and then, further increase in \bar{M}_w causes a decrease in peel and tack (Figure 5). This is expected because very high \bar{M}_w , especially when \bar{M}_n is also high, gives less viscous flow during bonding and more elastic response during debonding [2].

**Figure 5.** Effect of molecular weight on adhesive performance.

In order to verify this assumption, we investigated the properties consisting of intrinsic viscosity, glass transition temperature, peel strength, tack value and molecular weight of optimized sample and compared them with commercial PSA of the same monomers namely Duro-Tak (2287). The results obtained in Table 6 confirm that the synthesized copolymer at optimum conditions is comparable with Duro-Tak (2287).

CONCLUSION

The synthesized PSAs have demonstrated good

adhesive properties and could be easily peeled off from the surface without leaving any residue on the surface. It is also concluded that different polymerization reaction temperatures and times have significant influence on the rate of polymerization and other properties of the products. Due to the maximum overall conversion, the optimum conditions were selected at: reaction time (3.5 h), reaction temperature (70°C) and initiator concentration (0.5 wt%). Consequently it was observed that the peel and tack have the maximum values at this condition and all properties are comparable with the commercial PSA with the same initial monomer composition namely Duro-Tak (2287).

ACKNOWLEDGEMENT

The authors like to express their gratitude to Ms H Mivehchi for the linguistic corrections and critical comments of the manuscript.

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