The Role of Components in Waterbased Microsphere Acrylic Psa Adhesive Properties

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Summary: In this paper the batch suspension copolymerization of ethyl acrylate/2 ethyl hexylacrylate (EA/2-EHA) for production of suspension-based microsphere acrylic pressure sensitive adhesives (PSA) is presented. The effects on the adhesion properties of PSA different process (reaction temperature and stirrer speed) as well as chemical parameters (amount of EA, initiator concentration) are discussed. The conversion was monitored in-line using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and the results were compared with the standard gravimetrical method. The glass transition temperatures (T_g) of the PSAs were measured using differential scanning calorimetry (DSC) technique, while molecular weight distribution (MWD) was determined by gel permeation chromatography (GPC). The adhesion properties of PSAs were characterized via the measurements of tack, peel adhesion and peel strength. The results of the experiments have shown that the kinetics of the suspension polymerization for production of PSAs is significantly affected by temperature of polymerization and the initiator concentration, but are shown to be relatively independent of the EA amount and the stirrer speed. The tack, peel and shear strength depend on the mean particle size and particle size (PS) distribution (PSD) and T_g. The mean particle size and PSD depend primarily on the stirrer speed during the PSA synthesis process, while the T_g is most affected by amount of EA used for the synthesis. The results have also shown a rather unexpected relationship between MWD of the PSAs and the applicative properties: tack, peel and shear are seen to be increasing to the decreasing values of weight average MWD, which is the exact opposite of the previously published research. The most likely explanation for this relationship is the formation of a gel during the synthesis of PSA.

Keywords: acrylic adhesive; ATR-FTIR; microsphere; PSA adhesive

Introduction

Pressure sensitive adhesives (PSA) have become a part of everyday life. They are characterized by instantaneous adhesion upon application of light pressure.[1] One of the most widely used PSA adhesives are acrylic polymers. They have a dominant position in the marketplace due to the polymer's saturated nature and its resulting resistance to oxidation (beside acrylic polymer only the silicone adhesives have this property). Polyacrylate films are opaque and do not yellow upon exposure to sunlight.[2] Acrylic polymers are available as solutions, aqueous emulsions and suspensions, hot melts and 100% reactive solids. Commercially the solution polymerization was first, while interest in the emulsion polymers increased (and still does) with the need to solve the solvent emission problems, and produce more environmentally friendly products.[2] Hence the solution polymerization was replaced with the emulsion and suspension poly-

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merization processes, which are relatively simple methods for production of PSAs. They do not require high temperature and pressure, otherwise in results of manufactured material are quite different: the most distinct difference is the resultant particle size (PS) and particle size distribution (PSD). The products of suspension polymerization are commonly referred as microspheres (or microbeads) and consist of spherical polymer particles in the 10–250 μm range. Particles sizes of less than 2 μm are characterized as emulsion or dispersion elements. The main difference in the performance of microsphere suspension–based and emulsion-based PSA is the consequently the different PSD of material produced by the respective synthesis process. The PSD drastically affects the characteristic of the film formed by the PSA upon its application. In emulsion systems, the fine adhesive particles, when dried, coalesce to form a continuous film. This smooth adhesive film in prolonged contact with a surface will increase in contact and peel strength with time. On the other hand in the case of the microsphere adhesive, the adhesion arises from the physical structure. The formed film is discontinuous and spheres are in contact with surface only at their tops, which causes lower peel strength, but also improves their removability.

The advantages of the suspension polymerization lie in good heat transfer, simple temperature control, low viscosity and easy removal of polymer particles.[3] The particle size depends on the geometric (reactor type, size of the vessel, ...), process (rate of polymerization, temperature, stirrer speed, suspending agent...) and physical parameters (interfacial tension, viscosity, density). In practice, the geometric factors are determined by the productivity requirements, while the operating parameters are dictated by the polymerization kinetics. The particle size distribution (among other parameters) has great influence on the rheological characteristics of PSA dispersions. These are very important for the coating machinery, while the rheological characteristics of dried PSA dispersions are important for the performance of the adhesive systems.[4] Suspension-based type of PSA have some unique properties such as controlled tack and removability over time.

The properties of the suspension-based microsphere PSA will depend upon balance of three basic applicative properties: tack (the ability to adhere quickly), peel strength (the ability to resist removal by peeling), and shear resistance (the ability to resist flow when shear forces are applied). The balance between these three properties is changed according to the specific end use of the PSA.[5] Tack, peel and shear are influenced by the properties of the base polymer. Inherent properties, such as copolymer composition and microstructure, molecular weight and distribution are among the most influential parameters affecting the PSA properties directly, as well indirectly through their influence on the physical properties (e.g., glass transition temperature, T_g) and thus also the rheological properties of polymer (e.g., viscoelastic regions, moduli).[6]

The basic monomers used for PSA polymerization, whether suspension or emulsion, are acrylic esters that yield soft and tacky polymers. The T_g values for the PSA are in the range of $-15\,^{\circ}$C to $-5\,^{\circ}$C, many commercial PSAs have much lower T_g (i.e. $-60\,^{\circ}$C).[1] The selection of monomers is dictated by the intended application of the PSA and the desired end-product properties.[6] For microsphere suspension-based PSA synthesis two basic monomers are used: 2-ethylhexyl acrylate (2-EHA) and iso-octyl acrylate (isomer of 2-ethylhexyl acrylate), which provide tack and flexibility of the adhesive.[2] They are characterized as "soft monomers" and they assure low T_g of the polymer since the adhesion of the PSA microsphere particles arises from its physical structure. Other monomers (e.g., butyl acrylate, BA) are not suitable for production of suspension-based PSA because the T_g of homopolymer is too high for this type of adhesive. Monomers with higher T_g values (e.g. methyl acrylate

(MA) and ethyl acrylate (EA)) or so-called ''hard monomers'' are added to enhance cohesion of the adhesive, concomitantly also the shear strength. The polymerization of emulsion-based PSA was already studied extensively. The effect of addition of a high T_g monomer with intent to increase the shear strength with little effect on the tack and peel values was studied by Tobing et. al.[7] The different composition profiles of copolymer latex particles derived from 2-ethyl hexylacrylate/methyl acrylate with similar molecular weight distributions on the adhesive properties were investigated by Laureau et al.[8] The possibility of tuning the adhesion properties through different holding tank temperatures, different types of chain transfer agents and the post-polymerization process was studied by Alarcia et al. [9] The effect of methyl methacrylate (MMA) on the tack in MMA/2-EHA copolymers for emulsion-based PSA was reported by Aymonier et.al.[10] The amount of high T_g monomer should be kept as low as possible in order achieve a good balance in the basic PSA properties.[1] This raw materials may provide different chain flexibility and intermolecular forces, especially in low T_g pressure sensitive adhesives. Generally, low T_g values ensure very high tack, medium T_g polymers have optimum peel and acceptable cohesive strength. It is possible, to some extent at least, to correlate the peel adhesion with the T_g. A polymer, which is too soft and fails cohesively when peeled, can be improved by copolymerization with a monomer that raises its T_g. In the case of suspension-based PSA this can be achieved by copolymerization of 2-EHA with one of the monomers with higher T_g (EA or MA). The T_g values of these two monomers are: $-24\,^{\circ}$C for ethyl acrylate and $+10\,^{\circ}$C for methyl acrylate. The product of copolymerization is a polymer, which has a higher T_g (depends on the amount of comonomer) and concomitantly higher cohesion and shear strength. Among the most important parameters in the multicomponent polymerizations are the reactivity ratios of monomers. The greater the difference in the reactivity ratios the greater the possibility of composition drift, which is defined as the change in the chemical composition of the polymer formed throughout the reaction. Our review of the literature revealed no published data for the reactivity ratios of EA and 2-EHA. The microstructural properties of the polymer also influence the applicative properties of the PSA. An important problem regarding the use of the acrylic monomer system is the possible formation a gel phase during the polymerization process.[11] The relative amounts of the sol and gel polymer phase as well as molar mass distribution of the sol fraction, and the cross-linking density of the gel fraction are among the most important factors that influence the adhesive properties. [12]

Among the important factors, which are important for the successful synthesis of an appropriate adhesive is also monitoring of the polymerization reaction. There is a substantial interest in suspension and emulsion polymerization process for the continuous monitoring of the conversion, polymer composition, molecular weight and particle size. The increased quality of the end product can be achieved with utilization of modern in-line monitoring techniques. The main difference between the on-line and in-line measurement principles is that the in-line technique does not require sampling devices (e.g., sampling loop) and is performed in-situ, usually using an immersion probe.[13] The monitoring of the polymerization process is often difficult due to physico-chemical nature of the polymerization process.[14] The emulsion and suspension polymerization processes can be monitored using different techniques. The calorimetry technique is based on the heat generated during the polymerization process and enables on-line monitoring of the conversion and polymer composition.[15–17] Densiometry is also another possible on-line measuring technique, which is based on measuring the density of the reaction mixture.[18] The determination of the residual monomer content is also possible with a combination of ultrasound reaction monitoring, mass balance and gas chromatography as an off-line, on-line or in-line technique. [19,20] A lot of attention has been devoted to the spectroscopic techniques for the conversion and copolymer composition monitoring. Among them are the fluorescence, ultraviolet, Raman, near infrared (NIR) and mid infrared (MIR) spectroscopy, which can all be employed in-situ to give real-time structural and kinetic data. The most promising spectroscopic techniques for the monitoring of heterogeneous polymerizations are NIR, MIR and Raman spectroscopy.[21] For bulk, solution and emulsion polymerization NIR spectroscopy has been applied, which offers chemical and structural information. Application of MIR spectroscopy offers more information compared to NIR spectroscopy. In some recent studies the application of ReactIR analysis system (ASI Applied Systems, Inc., Mettler Toledo) has also been reported for the in-line monitoring of polymerization reactions. The system is based on ATR-FTIR (Attenuated Total Reflectance – Fourier Transform Infrared) spectroscopy and has been adopted for studies in the field of solution and emulsion polymerization of butyl acrylate, vinyl acetate, methyl methacrylate and styrene monomers.[14,22–24]

In this paper the suspension copolymerization of pressure sensitive adhesives (PSA) derived from 2-EHA and EA is presented. The effect of EA comonomer on PSA properties was determined by measuring the adhesion properties (tack, peel and shear). Additionally T_g, molecular weight and its distribution (MWD), particle size (PS) and particle size distribution (PSD) as well as the kinetics of polymerization were also characterized.

Experimental Methods

Monomers 2-EHA and EA were purified by conventional methods, and then subjected to vacuum distillation under nitrogen atmosphere. Initiator (dibenzoyl peroxide (DBP)) and the surface-active agents were applied in the commercially available form without further purification. The applied surface-active agents were: the modified ester of sulfocarboxylic acid (BEH), and ethoxylated oleil alcohol (BES). As the continuous aqueous phase, the distilled and deionised (DDI) water with the addition of thickening agent (crosslinked acrylic acid (BRA)) was used. Different types of homopolymer, derived from 2-EHA and copolymers EA/2-EHA, were synthesized under different process conditions.

The suspension adhesives were synthesized in a 500 ml glass reactor equipped with a reflux condenser, a Rushton turbine, N_2 purge, thermometer and ReactIR IC10 diamond composite probe (positioned approximately 5 mm above the agitator blades). Predetermined amounts of the continuous phase (DDI water and BRA), and the suspending agents were filled to the reactor, and pH value was regulated to 7,0 to 7,2. After 10 minutes of mixing and nitrogen purging both monomers (2-EHA and EA) with dissolved initiator DBP were added in the reactor and the reaction mixture was then heated to the temperature of 64 °C (heating time about 17 minutes). At this temperature the polymerization process starts, and the reaction mixture is heated to the specified set-point temperature (70, 80, 85 or 90 °C). The collection of IR spectra was started at 60 °C. After the polymerization process the reaction mixture was heated at 75 °C for 60 minutes and then cooled down to 20 °C.

Different process and operating parameters were investigated. Experimental conditions are summarized in Table 1. First the amount of comonomer EA was changed from 0% to 15 wt. % (Run 1 to 5). The wt. % of EA refers to amount of EA in the reaction mixture. Phase ratio between monomers and continuous phase was constant for all experiments. Reaction temperature was regulated to 70 °C, but it was not possible to achieve completely isothermal conditions in the reaction mixture, because of the highly exothermic nature of the polymerization reaction. At the second stage only 3 wt. % of EA was used, and the

Table 1.
Experimental conditions (the amounts of DDI (242,3g), BRA(8,4g), BEH (4g) and BES (3,2g) are the same for all experiments).

Run		monomer		initiator	stirrer speed	set-point reaction temperature
		EA (g)	2-EHA (g)	DPB (g)	(min^{-1})	(°C)
1	0 wt.% EA	0	141,6	0,56	500	70
2	3 wt.% EA	12	129,6	0,56	500	70
3	5 wt.% EA	20	121,6	0,56	500	70
4	10 wt.% EA	40	101,6	0,56	500	70
5	15 wt.% EA	60	81,6	0,56	500	70
6	3 wt.% EA, 80 °C	12	129,6	0,56	500	80
7	3 wt.% EA, 85 °C	12	129,6	0,56	500	85
8	3 wt.% EA, 95 °C	12	129,6	0,56	500	95
9	3 wt.% EA, [init] = 1.6 mmol/l	12	129,6	0,14	500	70
10	3 wt.% EA, [init] = 25.2 mmol/l	12	129,6	2,24	500	70
11	3 wt.% EA,stirrer speed 400 min^{-1}	12	129,6	0,56	400	70
12	3 wt.% EA,stirrer speed 600 min^{-1}	12	129,6	0,56	600	70

set-point reaction temperatures were changed from 80, 85 and 95 °C respectively (Runs 6 to 8). In Run 9 and 10 the concentration of DBP initiator (1,6 and 25,2 mmol/l) was changed, and copolymers with 3% EA were synthesized. The stirrer type was Rushton turbine operating at 500 min^{-1} and the set temperature was 70 °C for both experiments. Finally the influence of the stirrer speed on the PSD was determined in the range of 400 to 600 min^{-1} (Runs 11 and 12).

Samples of microsphere PSA synthesized with different amounts of ethyl acrylate from 0% (neat 2-EHA) 3, 5, 10 and 15 weight % were coated on glass plates and dried in a vacuum dryer at 60 °C for 4 hours. DSC analyzing technique with Mettler Toledo DSC821 was employed to determine the T_g of the adhesive. Standard 40 μl alumina pans with perforated lids were used.

The number average molecular weight (M_n) and the weight average molecular weight (M_w) were determined by gel permeation chromatography (GPC) using polystyrene standards. The samples were dissolved in (1% w/v solutions) tetrahydrofuran, which was also used as carrier solvent at a rate of 1 ml min^{-1}. The PLgel mixed-bed 5 μm (300 × 7,5 mm) column and Perkin Elmer series 200 pump in combination with Waters Associated Differential Refractometer were used. The samples for GPC analysis were homopolymer synthesized only from 2-EHA (Run 1), copolymer with 3 wt. % of EA at 70 °C (Run 2), copolymer with 3 wt. % of EA at 95 °C (Run 8), copolymer with 15 wt. % of EA at 70 °C (Run 5) and finally copolymer with 3 wt. % of EA at 70 °C synthesized with higher initiator concentration (Run 10).

Particle size and PSD was determined by the static laser scattering technique on the Microtrac S3500 PS analyzer.

Adhesion properties were measured on the adhesive coatings coated on a pilot coating machine. The addition of extra thickening agent was necessary in order to obtain the desired viscosity of the adhesive (approximately 300 mPas). Total solids content in adhesives was 33,5%. Adhesive was coated on substrate by a Mayer bar (a stainless steel bar, around which a wire has been wound) on the pilot coating machine. The substrate was siliconized transfer belt. Coating weight of the dry adhesive was approximately 10 g/m^2, and was regulated by the pressure of Mayer bar on the silicone belt and the speed of silicone belt. After the coating, the adhesive was dried employing the infrared (IR) drying technique. The drying oven was equipped with two medium wave IR heating sources (3 kW power output each). The speed of the belt was also controlled in order to achieve the desired moisture ratio in the adhesive coating. After drying the adhesive was transferred from the transfer belt to the paper substrate.

Three different test methods were used: the peel adhesion at 180° (Finat test method (FTM 1)), the probe test (Polyken test) and the shear resistance (FTM 8). FTM 1 test is designed to quantify the permanence of adhesion or peelability of PSA adhesives. Peel adhesion is defined as the force required to remove pressure sensitive coated material, which has been applied to a standard test plate under the angle of 180° and speed of 300 mm/min.[25] The sample strips were 25 mm wide and at least 175 mm long. The adhesion was measured 20 minutes after application. The peel adhesion is expressed as the average result for three strips per sample, in units Newtons per 25mm width.

FTM 8 test method is used to determine the ability of an adhesive to withstand static forces applied in the same plane as the coated adhesive. It gives an indication of the likely mode of bond failure (adhesive failure or cohesion failure). Resistance to shear surface is defined as the time required for a standard area of pressure sensitive coated material to slide from a standard flat surface in a direction parallel to the surface.[25] Because shear forces for microsphere adhesives are relatively low, 0.250 kg weights were used instead of the more common 1 kg. Shear resistance is expressed as the average time taken for three strips (per sample) to shear from the test plate. The test strips were 25 mm wide and had a minimum length of 175 mm.

For determination of the initial adhesion or tack, the probe test (Polyken test) was used. The device measures the force requried to separate stainless steel probe from the adhesive under low pressure and short contcact times. The tack is expressed as the average of six measurments in units of gram. Standard deviation for the measurements of tack was calculated.

Results and Discussion

The FTIR-ATR spectra of raw 2-EHA and EA are shown in Figure 1. The main characteristic bands attributed to C=C are at 1619, 1637 and 1408 cm^{-1}.[26]

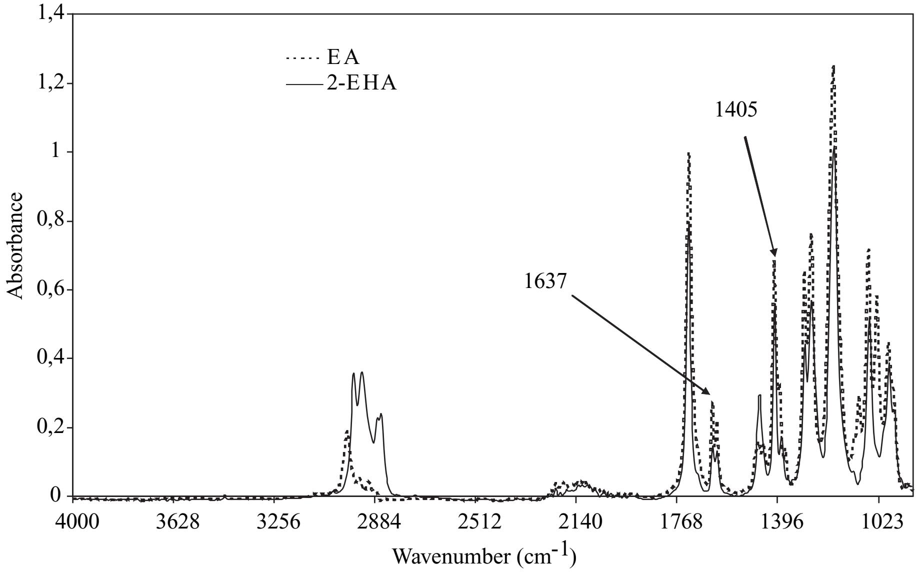

Figure 1.
FTIR-ATR spectra of monomers (2-EHA and EA).

The characteristic bands for both monomers are at the same wavelength as seen in Figure 1. For that reason we cannot calculate the conversion of individual monomers and copolymer composition, but only the overall conversion. Reaction spectra of the suspension copolymerization of EA/2-EHA are shown in Figure 2.

The strong absorbtion band of water in the 1640 cm^{-1} wavenumber region does not allow the calculation of monomer conversion from the absorbtion bands at 1637 and 1619 cm^{-1}. Although we may subtract the continuous phase spectra from the reaction spectra after the polymerization process, this procedure yields only higher noise in the absorbance intensities. Because of these limitations, the overall conversion can only be calculated from the absorption bands that are characteristic for the polymer build-up during the course of polymerization. The appearance of an absorption band at the wavenumber 1161 cm^{-1} is noticeable. This absorbtion band can be assigned to the C–C stretching vibration and may be employed for the calculation of the overall conversion.

Because the on-line measurement of absorbance was used and the temperature in the reaction mixture was not constant, the normalization function could not be used. The recording of FTIR spectra was started at 60 °C in all experiments, since the exothermic polymerization reaction begins at approximately 64 °C. As the polymerization process proceeds, the temperature increases to the set value, and this temperature elevation influences the monomer absorbance bands. In fact, multivariate calibration methods, such as Partial Least Square (PLS) or Principal Component Analysis (PCA), must be used to minimize the effect of the temperature on absorbance. However, the absorbtion band at 1161 cm^{-1} may still be used for the comparative purposes. The suitability of the selected absorbtion band was estimated by comparing the results obtained by this method with those from the conventional gravimetrical analyse. (Figure 3).

The experimental error in the determination of conversion with the gravimetrical method is estimated to be in a range of approximately 10% (the error bars on the points), as the phase ratio between the monomer and the continuous phase changes during the polymerization process due to the constant removal of the reaction mixture samples for the analysis. The final conversion of monomer was 100% in all reported experiments and was calculated from the amount of dry residue in the suspension sample.

The first set of the time-conversion curves corresponds to different amounts of EA comonomer in the monomer mixture. The results are presented in Figure 4.

As can easily be seen from the Figure 4., the conversion curves are practically identical for all experiments, and thus the

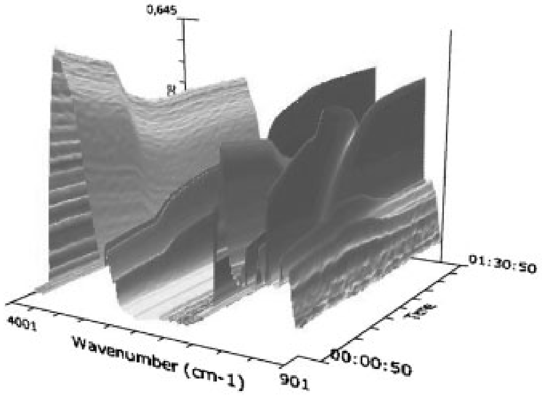

Figure 2.
Time dependence of FTIR spectra for suspension polymerization process in the range 4000 to 900 cm^{-1}.

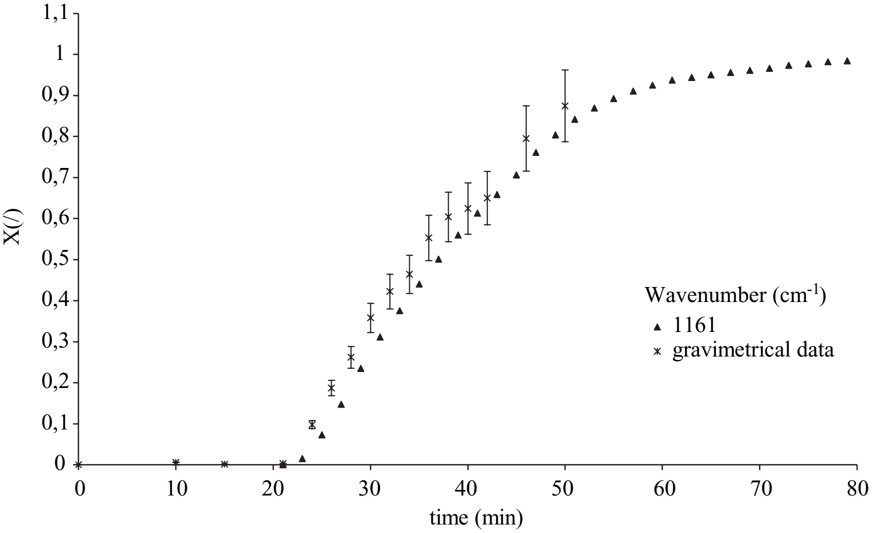

Figure 3.
The conversion versus time curves as determined by ReactIR system and the gravimetrical analysis (error bars).

conversion of monomer seems practically independent of the amount of EA in the monomer blend. The small differences in conversion between 0 wt. % and 15 wt. % of EA may be attributed to the different temperature in the reactor. It was not possible to obtain exactly equal temperatures in the reactor, since the heats of polymerization are quite different for both of the monomers. The heat of polymerization of EA (655 kJ/kg) is almost twice the heat of polymerization of 2-EHA (332 kJ/kg). Additionally the reactivity ratios for the monomer mixture also vary as the weight ratio in the monomer mixture is changed.

The time – conversion curves for different temperatures of the polymeriza-

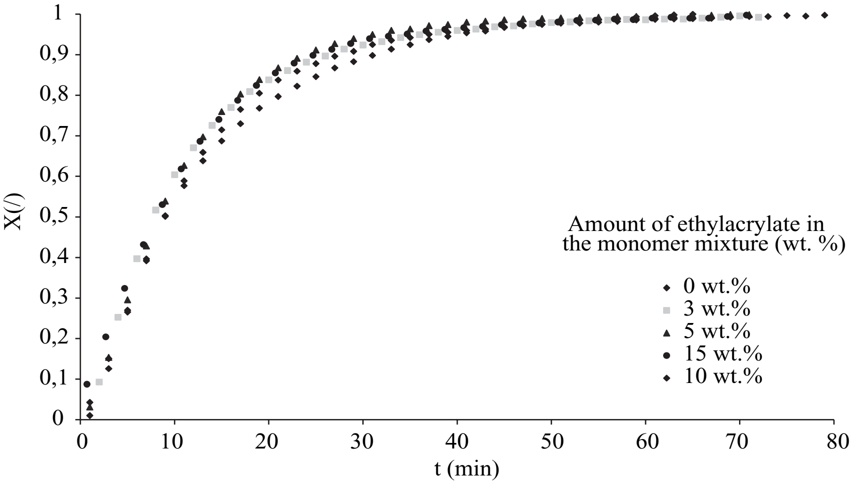

Figure 4.
Time-conversion curves for different amounts of ethyl acrylate in the monomer mixture.

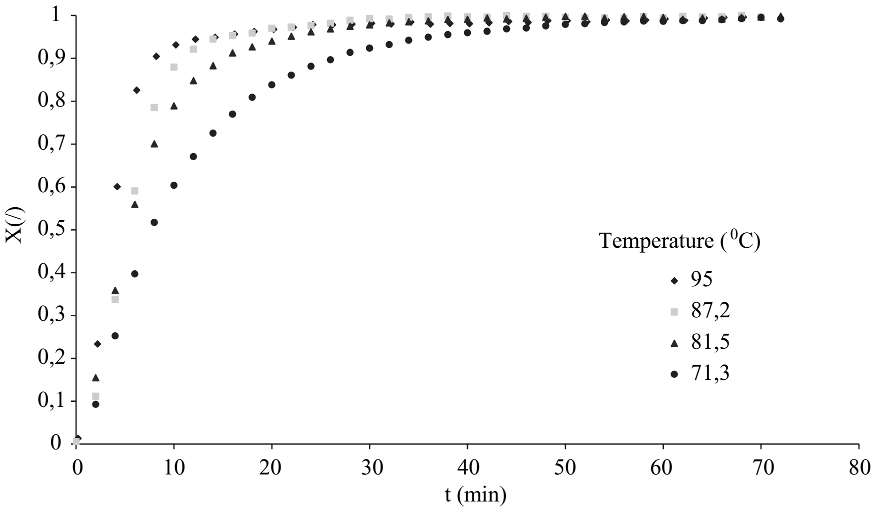

Figure 5.
Time-conversion curves for different temperatures of polymerization.

tion process (Runs 2 and 6 to 8) are presented in Figure 5. Four different temperatures of polymerization were investigated for the monomer mixture with 3 wt. % of EA, at the stirrer speed of 500 min^{-1}.

As could be expected from the theory of radical polymerization process, the rate of polymerization is higher at the higher reaction temperatures since the rate constant for the initiator decomposition is temperature dependant. In the case of acrylic monomers it is also monomer concentration dependant. Recent studies show that the acrylate chain-growth kinetics are complicated by the intramolecular transfer (backbiting) events to form a mid-chain radical structure of lower reactivity.[27,28] These mechanisms have a significant effect on the acrylate polymerization rate, even at low temperatures. The temperature evolution of the polymerization reaction for Runs 2 and 6 to 8 is presented in Figure 6.

The influence of the stirrer speed on the time-conversion curves is demonstrated in Figure 7. The stirrer speed was 400, 500 and 600 min^{-1} (Runs 2, 11 and 12, respectively).

These results are similar to those obtained from the experiments studying the influence of different amounts of EA comonomer (Figure 5). As with the amount of EA content, we can conclude that the stirrer speed exerts little if any influence on the course of polymerization. The small deviations in the monomer conversion can be attributed to the temperature variation among different experiments. Hence the main influence the stirrer speed does exert is not on the polymerization process, but rather on the characteristic of the manufactured material. Specifically the PS and PDS are significantly affected by this process parameter as demonstrated by Figure 8. As can be seen from this figure, the mean PS values were 78 μm at 400 min^{-1}, 62 μm at 500 min^{-1} and 40 μm at 600 min^{-1}.

The influence of different initiator concentration on the time evolution of conversion is presented in Figure 9 (Runs 2, 9 and 10). As can be seen these results are comparable to those obtained at different temperatures of polymerization reaction (Figure 5), i.e., the higher the initiator concentration, the higher the rate of polymerization.

DSC technique was used to determine glass transition temperature for five differ-

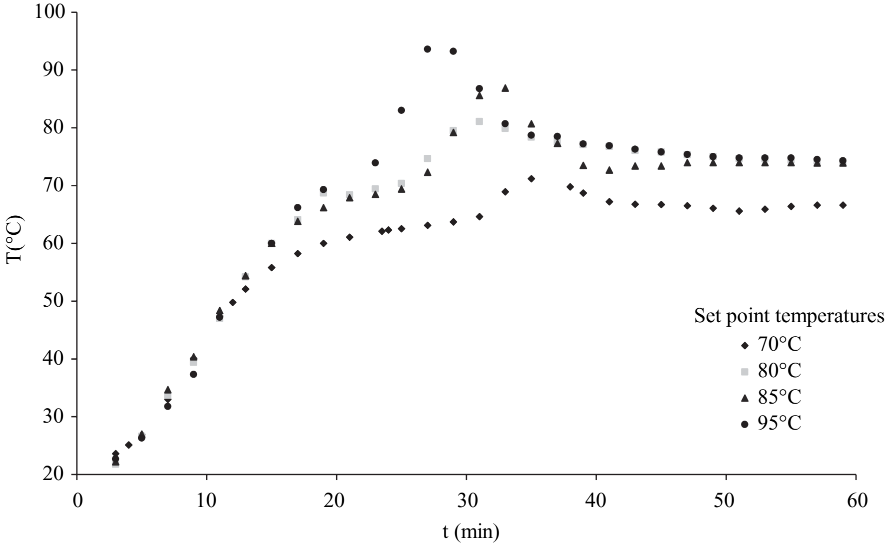

Figure 6.
The temperature evolution for Runs 2 and 6 to 8.

ent adhesives. The influence of EA content on the T_g was determined varying its weight ratio from 0% (neat 2-EHA) 3, 5, 10 and 15%. Phase ratio between monomer and continuous phase was constant at 35,5 %. The values of other process parameters (stirrer type and speed, temperature) were also constant. The T_g increased with the increasing amount of ethyl acrylate (EA), as expected. The T_g of homopolymer derived from neat 2-EHA equals −65,1 °C and is increased to −45,6 °C, for 15 % of EA comonomer. Results are presented in Table 2.

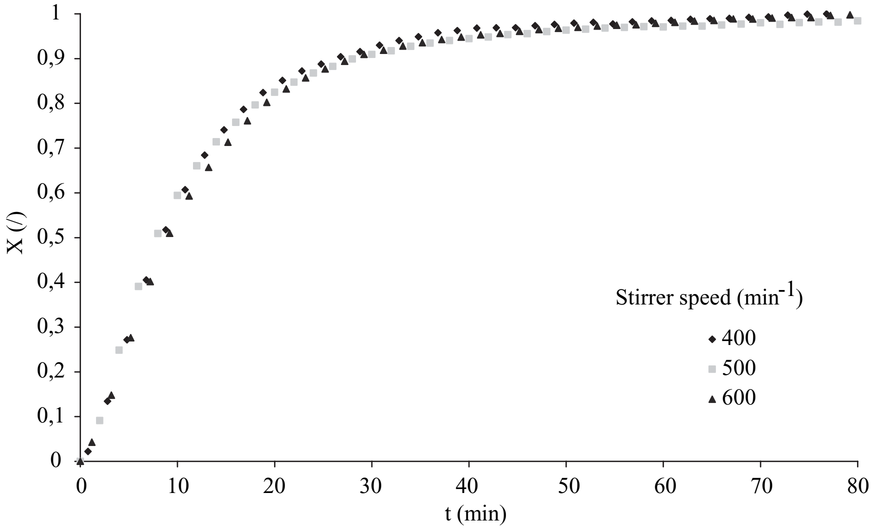

Figure 7.
Time – conversion curves for different stirrer speed.

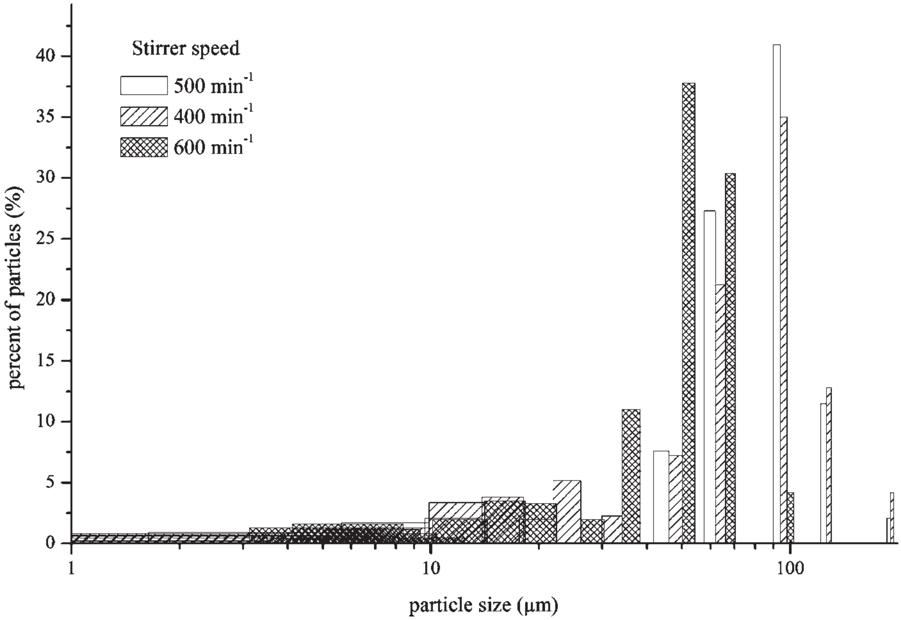

Figure 8.
Particle size distributions for adhesives synthesized at different stirrer speed.

Molecular weight and molecular weight distribution of adhesives are presented in Figure 10.

Weight average molecular weight, number average molecular weight and polydispersity index are gathered in Table 3.

The lower measured values of molecular weight obtained with copolymerization of EA/2-EHA (as compared to neat 2-EHA) may imply that in the former case a certain amount of gel was formed. During the synthesis gel is formed in acrylate polymers

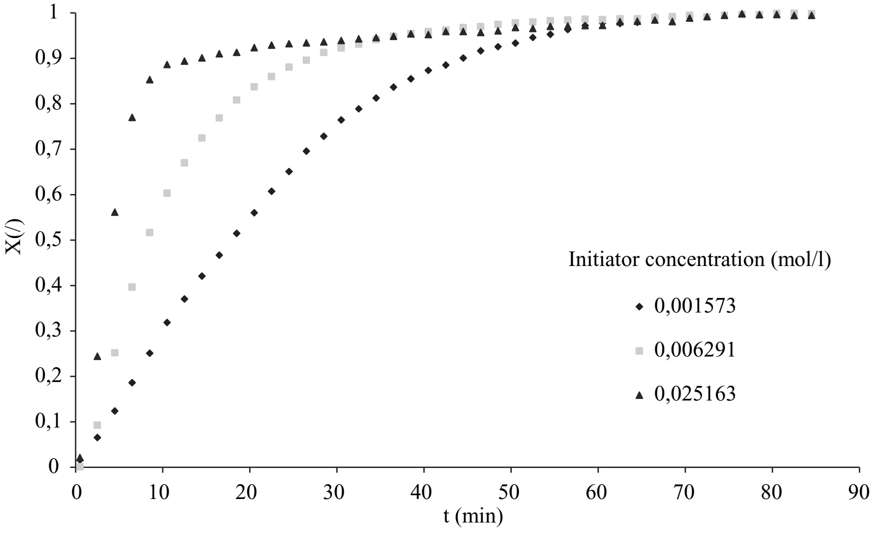

Figure 9.
Time – conversion curves for variable initiator concentration.

Table 2.
Measured values of glass transition temperature.

wt. % of EA /	T_g °C
0%	−65.1
3%	−60.7
5%	−57.7
10%	−48.3
15%	−45.6

by the combination of chain transfer to polymer, which leads to long chain branches in the polymer, and termination by combination of branched growing radicals, which leads to network formation and eventually gel. The measured values of molecular weight of the selected samples (copolymers of EA/2-EHA) pertain to the soluble fraction and that soluble fraction has got a lower molecular weight. The gel content could not be determined in the experimental work reported in this study, leaving this important issue a matter of future research.

The measured adhesive properties of different PSAs are gathered in Table 4.

The main goal of this study is to determine the influence physico-chemical and process parameters of the suspension copolymerization on the applicative properties of the PSAs (the most important are adhesion properties). The tack values for experiments with different amounts of EA are in the range of 40 to 50 g. This implies that the amount of EA comonomer, which lowers the T_g of the copolymer and hence the stiffness of microspheres, does not

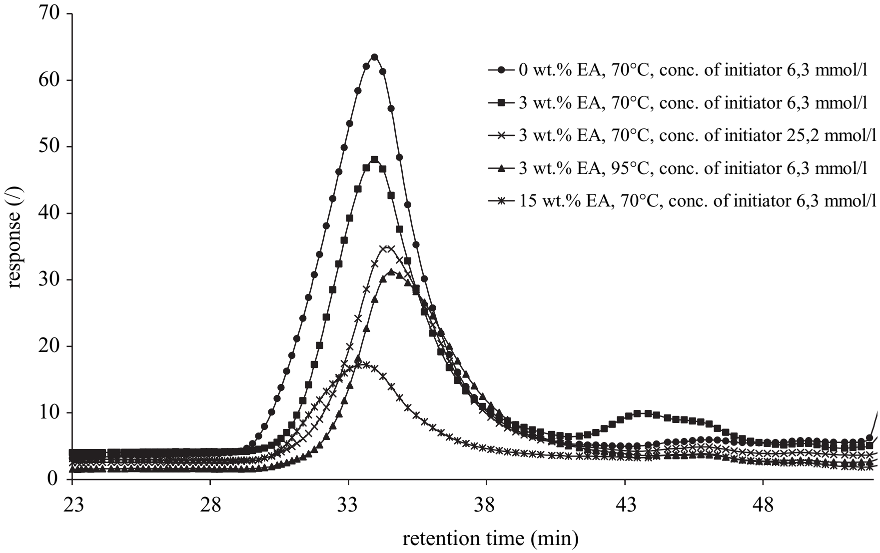

Figure 10.
Molecular weight distributions for PSAs prepared under different conditions.

Table 3.
Weight and number average molecular weight for Runs 1, 2, 5, 8 and 10.

Sample	Run	M_w	M_n	Polydispersityindex
0 wt.% EA, 70 °C, [init.] = 6,3 mmol/l	1	2044017	379121	5,39
15 wt.% EA, 70 °C[init.] = 6,3 mmol/l	5	1580987	10407	151,92
3 wt.% EA, 70 °C[init.] = 6,3 mmol/l	2	1181309	14309	82,56
3 wt.% EA, 70 °C, [init.] = 25,2 mmol/l	10	943284	23998	39,31
3 wt.% EA, 95 °C, [init.] = 6,3 mmol/l	8	659619	23668	27,87

Table 4.
Measured tack, peel and shear values for different types of adhesive.

Run	1	2	3	4	5	6
	0 wt.% EA	3 wt.% EA	5 wt.% EA	10 wt.% EA	15 wt.% EA	3 wt.% EA, 80 °C
Tack (g)	49,5 ± 5,5	41,2 ± 1,5	49,5 ± 2,7	40,7 ± 1,8	37,5 ± 4,9	59,3 ± 4,2
Peel (cN/25 mm)	6,7	11,3	8,3	3,9	2,6	16,1
Shear (min)	4:00:37	4:30:09	3:04:19	2:14:20	0:24:00	4:02:30
Run	7	8	9	10	11	12
	3 wt.% EA, 85 °C	3 wt.% EA, 95 °C	3 wt.% EA, [init] = 1,6 mmol/l	3 wt.% EA, [init] = 25,2 mmol/l	3 wt.% EA, stirrer speed 400 1/min	3 wt.% EA, stirrer speed 600 1/min
Tack (g)	74,3 ± 5,1	71,5 ± 8,2	44,8 ± 2,8	62 ± 3,7	40,5 ± 2,0	64,2 ± 3,3
Peel (cN/25mm)	20,2	34,1	6,7	15,3	3,7	7,1
Shear (min)	4:14:44	13:28:00	1:44:00	7:38:00	1:00:00	4:52:00

affect initial adhesion. The presented measurements of the molecular weight are very inconclusive since gel content in the adhesives could not be measured. The variation of the results of the tack measurements obtained at a specific set of process parameters (never exceeding ±5g) can be attributed to a slight variation of the coating weight of the adhesives. The peel values do not follow the same trend as the tack measurements. There is a slight increase from 0 to 3 wt. % of EA, but the peel values decrease as the amount of EA is further increased. The stiffness (as the consequence of lower T_g values) of microspheres with 15 wt. % EA is much higher then the stiffness of microspheres with 3 wt. % of EA. The coated microspheres on the substrate cannot deform under applied pressure, and the result is a lower force required to remove the coated adhesive from the glass substrate. The MWD analyses, as already noted, are inconclusive. The previously published studies indicate, that polymers with lower molecular weights have poor adhesion properties although, they might exhibit good tack values.[2] It is generally considered that the peel and tack values increase with the increasing molecular weight, until a certain maximum is reached, commonly at a fairly low molecular weight. A further increase in the molecular weight then causes a decrease or levelling of these properties. A good PSA will show only minor variations of tack with the increasing molecular weight in the region past the transition area.[2] Also the resistance to shear increases with the increasing molecular weight and it starts to decreases at a fairly high molecular weight. The results in our study contradict this expected behavior, since the peel and shear values increase with lower molecular weight. The most probable explanation for such a relationship is, that the gel formation influences the measured molecular weights since they pertain only to the soluble sol fraction. The shear values may also be explained the same way. From the obtained results in this study the maximum amount of EA in the monomer mixture should not exceed 10 wt. % in order to obtain PSA with acceptable adhesion properties.

The reaction temperature has a very strong influence on tack values: they increase from 40 g (for 70 °C) to over 70 g (for 87 °C and 95 °C). This increase may be attributed to higher rate of polymerization process at the higher temperatures and therefore to higher contents of formed gel. Similar conclusions are also drawn from the peel and shear analysis. The increase in the measured values is noticeable, as the polymerization temperature is increased especially at 95 °C (Table 4). The tack likewise increases with increasing initiator concentration. Also the peel and shear values show the same trend with the increasing initiator concentration.

Finally the tack values are also significantly affected by the stirrer speed during the polymerization, via the resultant PSD of PSA. The influence of the PSD is even more clearly manifested in the measured sheer strength values, which exhibit the same relationship as the tack. This is most likely due to the fact that the density of particles in coating is higher in case of smaller particles, and consequently more surface area is available for the adhesion process.

Conclusions

The main trends from this study can be summarized as follows. Different temperatures of the polymerization reaction and initiator concentration have an influence on the rate of suspension polymerization. On the other hand, different amounts of the EA and stirrer speed do not have any major influence on the kinetics. Higher amounts of EA increase the T_g of the polymer and thereby changes the applicative adhesion properties. With higher stirrer speed lower mean particle sizes are achieved, which are important for adhesive properties as seen from measured values. Tack, peel and shear values are dependant on mean particle size and PSD. The higher is the glass transition temperature of the base polymer, the lower are measured peel and shear values but initial adhesion (tack) values are in the same range. The most important process parameters in the suspension polymerization are initiator concentration and temperature of polymerization. With higher initiator concentration and reaction temperature, higher values of tack, peel and shear values are measured. From the measured values of tack, peel and shear optimum process parameters for the synthesis of acrylic microsphere adhesive may be determined. Since no gel content in the PSA was measured, we cannot adopt any conclusions about the influence of molecular weight on adhesive properties. The amount of formed gel and the influence on adhesion properties content in the suspension will be the main goal of our future study.

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