Synthesis and characterization of a pressure-sensitive adhesive based on an isobutyl acrylate / 2-ethylhexyl acrylate copolymer

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Abstract: A removable pressure-sensitive adhesive was obtained by free-radical emulsion polymerization. The product is a low-viscosity copolymer from different polar and apolar acrylic monomers consisting of microspheres of about 1 μm diameter. 2-Ethylhexyl acrylate and isobutyl acrylate were used as non-polar constituents while acrylic acid and acrylamide provided the more polar constituents to regulate the cohesive force of the adhesive. The amounts of initiator, water and emulsifier (nonylphenol) were varied to obtain the best adhesive properties at the given copolymer composition. The resulting adhesive showed the desired balance of low tack and good adhesive strength in combination with a wide variety of substrates, which made it useful as a removable adhesive for many applications. The product was characterised by viscometry, measurements of tack and peel strength, FTIR, DSC, and microscopy.

1. Introduction

Adhesives based on emulsion polymers are gaining in popularity. Their synthesis is water-based, which implies a significant decrease of the emission of volatile organic compounds and the absence of flammable solvents. High molecular weight compounds can be obtained without decreasing reaction rate and temperature. Acrylic polymers are successfully used in removable as well as in permanent pressure-sensitive adhesives.

In permanent pressure-sensitive applications, acrylics offer good mechanical stability and provide the necessary high tack and peel strength. For removable applications, acrylics offer good mechanical stability and good cohesive strength. Polyacrylate emulsions are used to bind to a variety of substrates including metals, plastics, ceramics, wood, leather and textiles. Global demand for acrylic emulsions in the adhesives market is forecast to exceed 600 000 metric tons by the year 2005.

Monomers used in the production of acrylic pressure-sensitive adhesives (PSAs) can be categorized into three classes. The first class is formed from so-called 'soft monomers' such as n-butyl acrylate, 2-ethylhexyl acrylate or isooctyl acrylate. They show low glass transition temperatures (T_g) and low water solubility. 'Hard monomers' form the second class: short-chain alkyl acrylates, characterized by high T_g values, include methyl methacrylate, ethyl and methyl acrylate. They have higher water solubility. The third class is formed by functional monomers with various functional groups, such as carboxyl or hydroxyl. Examples of functional monomers are acrylic acid and hydroxyethyl acrylate, which have high water solubility.

Depending on the substrate an ideal removable adhesive requires sufficient tack to quickly fix to the desired substrate and adequate peel strength to prevent damage of the surface when the adhesive is removed. An appropriate cohesive strength is also necessary to control the transfer of the adhesive to the substrate. The molecular weight of the acrylic polymer may be raised to improve the cohesive strength but this is limited by the rise of melt viscosity. The content of polar monomers, such as acrylic acid, may also be increased to improve the cohesive strength or the number of covalent cross-links [1,2].

Composition, molecular weight and cross-linking density of the polymers control the adhesion performance of acrylic PSAs. Typically, the relative amounts of soft, hard and functional monomers are adjusted to obtain the desirable adhesion-property balance for a specific application. Those acrylic PSAs with high hydrophobic character yield larger adhesive particles and they have very high peel strength, whereas more hydrophilic adhesives have a smaller particle size and a sufficient cohesive strength [3].

The average molar mass M_c of a polymer chain between two entanglements and the glass transition temperature T_g both influence important properties of an adhesive such as tack, peel strength and shear resistance. The shear resistance and the hardness have high values in polymers with high molar mass and a high glass-transition temperature. Studies of the tack have shown that acrylic PSAs deformed to high extensions show the formation of fibrilar structures. High values of M_c ($\approx 300\,000$ g/mol) are a prerequisite for fibril formation, but these high extensions always come with cohesive failure, which is not acceptable for removable PSAs. Further studies have shown that peel and tack energies show the highest values for polymers with an intermediate molecular mass M_c ($\approx 180\,000$ g/mol) because of the lower glass transition temperature. T_g is one of the crucial parameters for a proper film formation to accomplish a good performance of the final adhesive. The aim is to combine the good properties of high M_c with low T_g. Therefore, most of the acrylic polymers used as PSA should be highly branched or slightly cross-linked with a rather broad molecular weight distribution. A high non-uniformity is essential to have the right balance of adhesive properties over a useful range of temperatures and debonding rates. One possible approach to combine these properties in an effective way could be a phase-separated adhesive with microphase core-shell particles morphology [4-6].

Poly(ethylhexyl acrylate) (PEHA) adhesives have two interesting features: first, the presence of chain branching and a gel fraction that causes hardening of the fibrils and eventual fibril detachment rather than cohesive fracture. Second, the low molecular fractions contribute to the ability of the adhesive to establish contact with a surface during the bonding phase of the adhesive process.

Microspheric PSAs show predictable adhesion behaviour and can be used repeatedly on a variety of substrates over a long period of time without damaging the

substrate when peeled off again. Only a part of the spherical cap of the polymer particles contacts the substrate, thus forming a discontinuous adhesion between the adhesive and the substrate. Since the microspheres are flexible, they can be reversibly deformed and recover their original shape so that they act as a reversible adhesive. Acrylic microspheres in particular are bigger compared with conventional permanent adhesives. A whole range of different morphologies can be obtained depending on the kind of polymerization strategy that is applied: choice of monomers, polymer viscosity and molar mass are important parameters. Emulsion polymerization that uses non-ionic surfactants alone to stabilize the particles yields rather large-sized particles. A bimodal particle size distribution can be obtained, because of partition of the surfactant between aqueous and organic phases. For these reasons, mixtures of anionic and non-ionic surfactants are preferably used in industrial practice to get closer to unimodal or even monodisperse particle size distributions. However, if the composition of such a mixture is not well balanced, higher amounts of non-ionic surfactants result in an increase of the final particle size [7].

The copolymerization of hydrophobic and hydrophilic monomers creates well-defined hydrophobic fragment blocks in the copolymer [8,9]. The use of aqueous surfactant solutions to ensure the solubilization of the hydrophobic monomers has solved the miscibility problems arising from the large differences in polarity of the different monomers. In emulsion polymerization, the hydrophobic monomer is solubilized in micelles, whereas the hydrophilic monomer dissolves in the intermicellar aqueous phase. Polymerization of the monomers in the micelles occurs at a high rate and yields higher degrees of polymerization because of their high local concentration. This one-step copolymerization renders water-soluble copolymers. The microstructure of the copolymer is influenced by the amount of surfactant micelles present during the synthesis. It has been shown that the properties of emulsion-polymerized amphiphilic copolymers can be related directly to the ratio ([H]/[S]) of the concentration of hydrophobic monomer (H) and surfactant (S) [10]. The high local concentration of the hydrophobic monomers in the micelles favours their incorporation in the copolymers as blocks rather than isolated units. In contrast, random copolymer structures are obtained using low ([H]/[S] ratios, typically when surfactant concentration is greater than hydrophobic monomer concentration [11].

In this work we report the properties of pressure-sensitive adhesives based on isobutyl acrylate, 2-ethylhexyl acrylate, acrylic acid, and acrylamide copolymers synthesized at different surfactant/initiator concentrations.

2. Experimental part

Materials

2- Ethylhexyl acrylate (EHA, BASF), isobutyl acrylate (IBA, BASF) and acrylic acid (BASF), were distilled at low pressure in order to remove the inhibitors before use. Potassium persulfate (PPS, Sigma) was chosen as initiator, acrylamide (BASF) as hydrophilic monomer, and nonylphenol (NP20, where 20 designates the average length chain of the ethoxylate, the molar mass of which is 1084 g/mol) as a surfactant. The hydrophobic monomers (EHA and the IBA) were selected because they have boiling points higher than polymerization temperature and they have a certain degree of solubility in water, which is good for the emulsion polymerization [12].

Synthesis of copolymers

The general conditions for the emulsion polymerization were the following: The fixed amounts were 70 g (0.38 mol) of 2-ethylhexyl acrylate, 15 g (0.12 mol) of isobutyl acrylate, 3 g (0.04 mol) of acrylamide, 5 g (0.07 mol) of acrylic acid and 1.0 g (0.0037 mol) of PPS. The amounts of these monomers and the initiator were selected from preliminary experiments where stable emulsions were determined. Then, surfactant and water were added so that the ratios [M]/[S] and [M]/[H$_2$O] were changed to obtain low viscosities, good peel and adequate particle size. Deviations from the monomer/ initiator ratio resulted frequently in an undesired increase of molar mass and solid content.

The pre-emulsifier solution is prepared by mixing (stirring rate 50 rpm) the aqueous and organic phase to a good dispersion. The aqueous phase is a mixture of fixed amounts of hydrophilic monomers (acrylamide, acrylic acid) and a variable amount of water; the organic phase is a mixture of the two hydrophobic monomers (EHA and IBA) and a variable amount of nonylphenol (see Tab. 1).

Tab. 1. Preparation of the adhesives samples

	Sample 1	Sample 2	Sample 3	Sample 4
NP20, mol	0.0046	0.0037	0.0033	0.0028
Water, mol	7.17	7.17	6.61	6.61
I/S (molar) x 100	85.3	107	118	142
I/H (molar) x 100	0.871	0.871	0.871	0.871
[S]/[M] x 100	0.758	0.606	0.550	0.455
[H]/[H$_2$O] x 100	62	66	61	71
[S]/[H] x 100	0.5295	0.4237	0.3813	0.3178

H: Hydrophobic monomer; M: total monomer; I: initiator; S: surfactant.

The copolymerization reactions were carried out in a 500-mL three-neck glass reactor equipped with reflux condenser, mechanical stirrer with stainless steel paddles (250 rpm) (Heidolph model RZR1) and two 3 mL hypodermic syringes. The reactor was charged with the amount of water and thermostated at 80°C. After 10 min, 6 mL 0.0925 M initiator were added with a syringe and 5 min later 30 g of pre-emulsifier solution. Then, every 5 min, 2.5 mL of the pre-emulsion and 0.7 mL of the initiator solutions were dropped from the respective hypodermic syringes during four hours. Finally the system was kept with stirring for two hours (post-polymerization time) and cooled rapidly to 40°C, and then 1.6 mL 50 v/v % H$_2$O$_2$ were added in order to inhibit further polymerization. The pH was less than 5.

The initial amount of monomers is kept constant but its concentration changes since water and surfactant contents are changed. The viscosity, the solid content and the heat transfer depend on the amounts of water present. The amount of surfactant affects the particle size and hence the peel.

Solid content of the emulsions

The initial and final weights after drying at 120°C overnight were used to determine the solid percentage:

% solid = (final weight) / (initial weight) x 100

The samples were cooled at room temperature before re-weighing in order to minimize the error in the measurement.

Infrared spectrometry

Infrared measurements were made in a Perkin Elmer, Spectrun one, with a resolution of 2 cm^{-1} and 16 scans. The samples were washed and centrifuged to separate the solids and then they were dried at 95°C for several hours before to prepare the KBr disks.

Differential scanning calorimetry (DSC)

The glass transition temperatures were determined in a TA Instruments model 2920 equipped with the refrigerated cooling system, using a heating and cooling rate of 10 °C/min, under nitrogen atmosphere at a flow of 40 mL/min. Heating from 25 to 140°C, cooling to -75°C, again, heating from -75°C to 150°C. The last run was analyzed.

Scanning electron microscopy (SEM)

The morphology of the samples was analyzed in a Philips XL30 microscope.

Peel adhesion

The peel was tested using a stress universal instrument, LRX Lloyd Instrument, a 180° peel angle, peel rate of 304.8 mm/min and a dwell time of 20 min. Three samples per adhesive were tested and averaged. The samples were coated (20 g/m^2) onto a biaxially stretched polyethylene film (25 mm wide x 12 cm long, superficial tension of $38 \cdot 10^{-5}$ N/cm) using a hand coating bar. After coating, the samples were dried at 90°C for 10 min. The samples were applied to the standard micro-finish stainless steel panels and left for 20 min before the test. This test was repeated for the adhesives that did not left sticks on the substrate and presented low peel using bond paper as a mechanical support and substrate.

The loop tack

The adhesive samples were coated onto polypropylene film and placed on a stainless steel plate (25 mm x 30 mm x 3 mm). When a complete contact with the steel plate was achieved (25 mm x 25 mm), the plate was fixed to the LRX instrument and pulled away at a rate of 304.8 mm/min. The maxim force needed to separate completely each loop from the plate was measured. Five samples per adhesive were tested and the results averaged.

3. Results and discussion

The monomer composition for an optimal peeling strength with a satisfactory removability from the PE substrate – that is neither damaging the substrate surface on removal nor leaving any trace of adhesive on the substrate – was determined first in a series of experiments. The basic composition of the monomers is described in the experimental section and was subsequently utilized for the following investigations. From commercial PSAs [1], where a mix of short and long chain length monomers was used, as well as a cross-linking agent, an ionic or non-ionic surfactant and inert atmosphere, it is known that a solid content between 50% and 60% is quite effective for PSAs. Our adhesive had the same solid content without using a cross-linking agent but in the presence of acrylic acid, acrylamide and air for cross-linking and better cohesive strength. The presence of air made the synthesis more convenient for practical use.

The range of composition was limited on the side of the initiator concentration to 0.108 M since only at lower concentrations stable emulsions were obtained. Beyond 0.162 M an initiator concentration resulted in higher polymerization rates, exothermic reactions and gelation of the final product.

The surfactant/monomer mole ratio was limited to a range from 0.758 (sample 1) to 0.455 mol-% (sample 4). At the high surfactant concentration end the viscosity of the emulsion was very high and decreased with time, showing tixotropic behaviour. Peel strength as well as the tack were too strong for reversible adhesion. At the low-end surfactant concentration peel strength and tack were too small for an effective removable adhesive. In general, it can be stated that viscosity, peel strength and tack strongly depend on the surfactant concentration and both go through an optimum around 0.455 mol-% surfactant (with respect to the monomer content).

Solid content and viscosity of the emulsion increase with decreasing surfactant concentration. At the same time the number of particles N_p increases [13,14] according to

$$N_p \sim [I]^{0.4}\,[S]^{0.6}$$

with [I] and [S] being the initiator and surfactant concentrations, respectively.

The solid material is mainly the polymer but it also contains surfactant and residual monomers because these do not evaporate at 120°C. The degree of polymerization x_n decreases with the surfactant concentration according to the following equation:

$$x_n = k_p N[M]/\rho$$

where ρ = rate of generation of radicals in 1/(mol·s), [M] total molar monomer concentration, N = number of particles of polymer/cm^3, k_p = propagation rate constant in litres/(mol·s). According to the Smith-Ewart theory, the number of polymer particles is determined by the number of micelles. In order to have more particles, the number of micelles has to be increased. A higher surfactant concentration (at constant initiator concentration) causes a larger number of micelles. This means more polymer particles and a higher viscosity of the emulsion and results in an adhesive with higher peel strength. The results are shown in Fig. 1.

The different solid contents are due to the different degrees of polymerization. The rate of polymerization is the same as the rate of consumption of monomer. Monomer disappears faster when there are more particles. In order to have more particles there must be more micelles. If the surfactant concentration is increased, this causes more micelles. If the concentration of initiator remains constant this results in more

particles and less radicals. This means that the number of radicals per micelle drops below one. In other words, the rate of termination will be low since there are fewer radicals and, therefore, different degrees of polymerization are obtained.
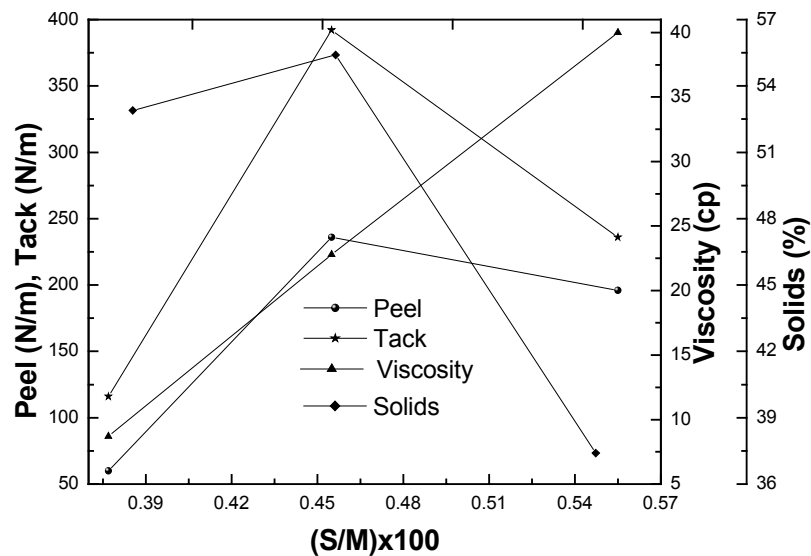

Fig. 1. Molar ratio of surfactant to total monomer vs. tack, peel and viscosity of the adhesive samples

Sample 4 showed optimal reversible adhesive properties, and on a paper support it could be removed from a steel substrate. At least over a period of three days the peel strength was constant at about 236 N/m.

Morphology of the samples

The morphology of the samples was studied by SEM and optical microscopy (Fig. 2). The particle size was from 1 to 2 µm and presented a monodisperse particle size distribution.
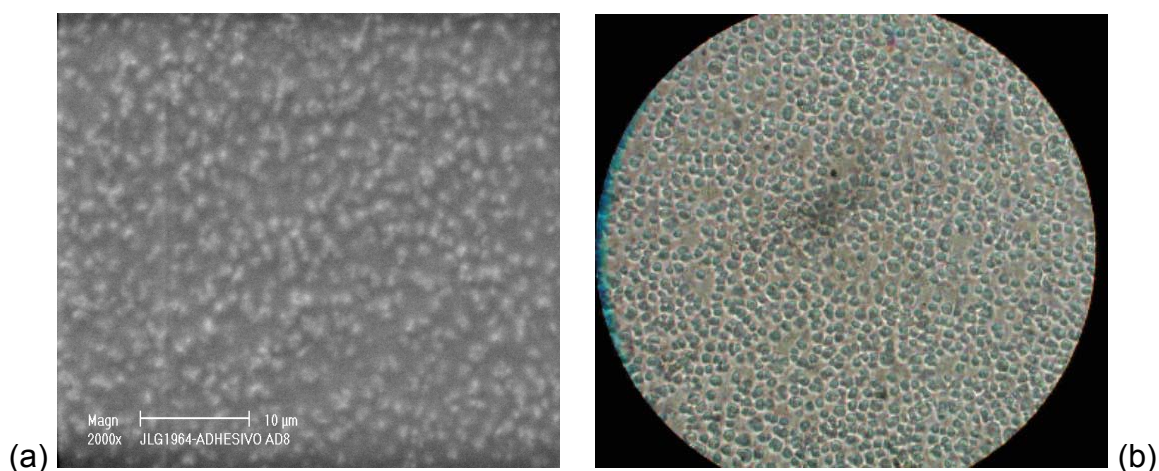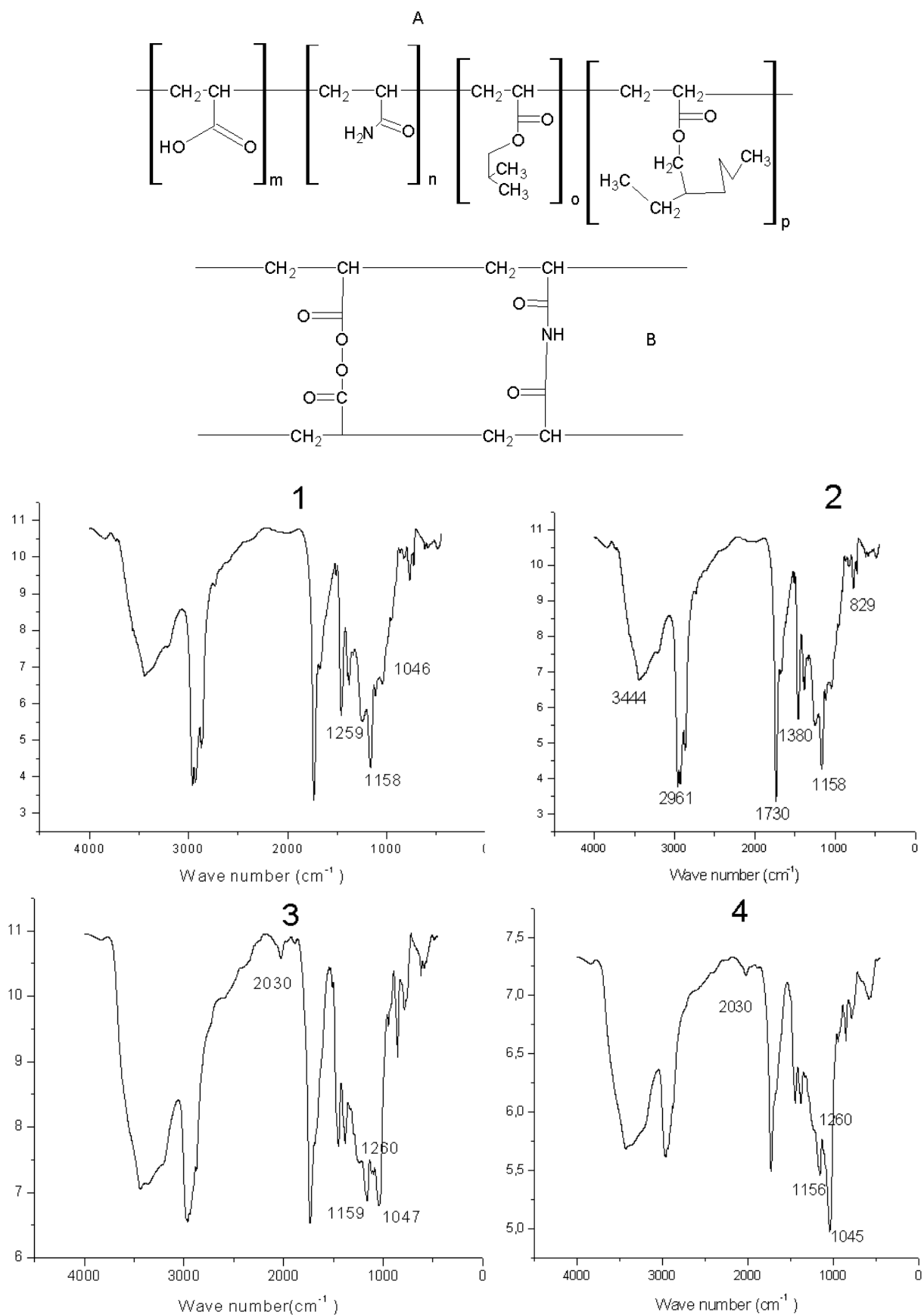

(a)

(b)

Fig. 2. (a) SEM micrograph of adhesive sample 4; (b) optical micrograph of adhesive sample 4

Fig. 3. Infrared spectra (transmittance in % vs. wave number) of adhesive samples 1, 2, 3 and 4

IR and DSC

The infrared spectra of samples are shown in Fig. 3. Tab. 2 presents the analysis of the absorption bands of samples 3 and 4. These samples show absorptions at 2030 and 1045 or 1047 cm^{-1} corresponding to the imide and diester peroxide vibration, respectively, that are making the cross-linking between chains (see Fig. 3, diagram B). Samples 1 and 2 do not show these cross-linked bonds, their structure could be sketched as shown in part A of the diagram.

Tab. 2. Infrared frequencies of samples 3 and 4

Frequency ν/cm^{-1}	Functional group
3444	OH of acrylic acid and NH of the acrylamide
2961	CH stretch
2030	-(CO-NH-CO)- imide group
1730	CO stretch
1391	C-O stretch of IBA
1380	C-O stretch of EHA
1158	CO flexion
1095	-(CO-O-)
1045 or 1047	-(CO-O-O-CO)- diester peroxide
853	NH flexion out of plane of amide

The cross-linking density is higher for samples 3 and 4, as can be deduced from the glass transition temperatures, -13°C and -14°C, respectively, compared with -53°C for samples 1 and 2 (see Fig. 4).
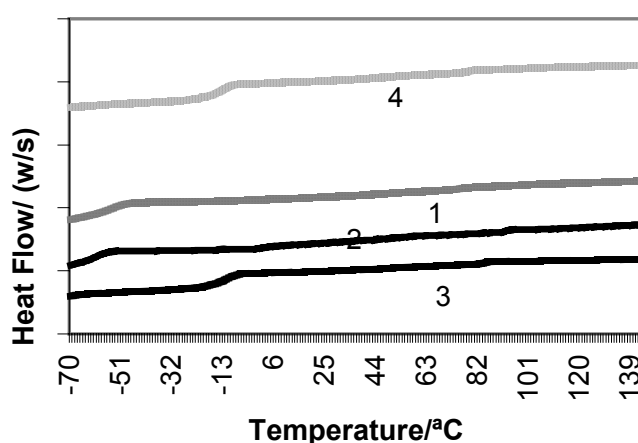

Fig. 4. DSC thermograms for adhesive samples 1 - 4

4. Conclusions

This preparation did not include a cross-linking agent as it had been used in a commercial preparation [1,2] but the samples and particularly samples 3 and 4

showed certain degree of cross-linking. The possible cross-linking could be due to the fact that the tertiary CH groups of the hexyl chains and CH neighbours to the C=O double bonds can form free radicals that are stabilized by an induction effect or per resonance and that can cure in air. In the preparation of the pre-emulsion the alkyl acrylate resin is mixed with the acrylic acid and acrylamide monomers before the polymerization; the free radical of the acrylic acid reacts with the more reactive monomer forming blocks of these monomers but the appearance of graft free radicals allows curing (cross-linking) in air [15,16]. Also the acrylamide can be distributed in the organic and aqueous phases. Part of the acrylamide can form part of the main chain of the polymer and can form imide bonds.

An increase of the initiator concentration increases the polymerization rate and the polymerization degree but there is no time for the curing process since the free radicals on the main chain are more reactive than free radicals on the graft sites. The slow addition of the initiator during six hours leads to a higher monomer conversion.

Sample 4 results in a stable emulsion without coagulation, with a low volatile organic content, high cohesive force and low peel. The level of grafting and cross-linking is high but did not inhibit the film formation. This sample could not be characterized by GPC and NMR since it was not completely soluble in tetrahydrofuran or dimethyl sulfoxide.

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