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Synthesis and Evaluation of Adhesion Properties of Homogeneous and Core-Shell Pressure-Sensitive Adhesives

R. Mascorro,[1] *Ma. Elena-Navarro,*[1] *H. Dorantes,*[2] *M. Corea**[2]

Summary: Pressure-Sensitive Adhesives (PSAs) are used for many applications (e.g. tapes and labels), and the market is still growing as new applications are regularly discovered. Emulsion polymerization is widely used to produce water-based PSAs. In this work, the influence of morphology, diameter and acrylic acid concentration in the particles on adhesion properties (peel, tack and shear) was studied. To do so, two series of homogeneous and core-shell latex particles of poly(butyl acrylate-2-ethylhexyl acrylate) with different concentrations of acrylic acid (0, 1, 3 and 5 wt%) and three different average diameters, were synthesized by means of emulsion polymerization techniques. The materials were characterized by dynamic light scattering, zeta potential and transmission electronic microscopy. The contents of acrylic acid in the polymer and dispersed medium were determined and the higher quantity of it was found within the particles. The best equilibrium between adhesion properties was found in the core-shell particles with 3 wt% of AA.

Keywords: acrylic latex; loop tack; peel adhesion; pressure-sensitive adhesives; shear strength

Introduction

Adhesion is an area of widespread interest from both scientific and technical standpoints.[1] Pressure-Sensitive Adhesives (PSAs) are very important for their commercial use in applications such as labels, tapes,[2,3] protective films and medical[4] and cosmetic products,[5,6] as well as in sophisticated technologies such as nanotechnology, microelectronics and biotechnology.[7] PSAs are viscoelastic-elastomeric materials that can adhere strongly to solid surfaces upon application of light contact pressure and short contact time.[8,9] They develop significant adhesion forces upon contact with a substrate without requiring a chemical reaction,[10] due to (a) the mechanical bonding between the adhesive and adherent, and (b) chemical forces, either primary covalent bonds or polar secondary forces, between the two.[11] The PSA adhesion properties are the result of three processes. First, when PSA-coated tape or label is bonded onto a substrate, the adhesive flows instantly to form intimate contact with the substrate even under a gram of contact force. Second, adsorption must take place by intermolecular interaction. Third, when the PSA tape is peeled off from a substrate, large viscoelastic energy dissipation must occur to get high-peel energy.[8] The strength of bonded systems is normally determined by mechanical tests characterizing primary properties[12] (peel, tack and shear), which give macroscopic information of the bond strength.[13] A balanced combination of tack, peel force and shear strength is of primary concern for PSA production. Peel strength

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[1] Instituto Politécnico Nacional, ESIQIE, Departamento de Ingeniería Química SEPI, UPALM, Edificio Z-6, Del. Gustavo A. Madero, C.P. 07738, Col. San Pedro Zacatenco, México D.F.

[2] Instituto Politécnico Nacional, ESIQIE, Departamento de Ingeniería Metalúrgica y Materiales SEPI, UPALM, Del. Gustavo A. Madero, C.P. 07738, Col. San Pedro Zacatenco, México D.F
E-mail: mcorea@ipn.mx; mcoreat@yahoo.com.mx

represents the force required to remove a standard PSA strip from a specific test surface under a standard test angle (90 or 180°) under standard conditions.[14] It is the resistance to bond separation of two flexible materials or of a flexible and a rigid material when the flexible material is pulled from the joined surface.[15] This property is very complex because due to it is affected by many factors, which include wetting of the substrate surfaces, interactions with the substrate and mechanical properties of the adhesive. Loop tack is the adhesive property related to bond formation. It has been defined as the property that enables an adhesive to form a bond with the surface of another material upon brief contact under light or no pressure.[1,16] Shear is the increase in strain with time after stress is suddenly applied and maintained constant, or as a resistance to flow under stress. Usually, it represents the length of time it takes for a standard strip of PSAs to fall from test panel after application of a load.[14]

Growing environmental pressures and the advent of increasingly strong legislation concerning solvent emissions have forced the coating industry to seek to replace solvent-borne adhesives with all-solids coatings and/or water-borne coatings.[17,18] One method of obtaining these type of materials is by means of emulsion polymerization, which is a free-radical-initiated chain polymerization, where a monomer or mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant.[19,20] It is estimated that 40% of PSAs are produced using emulsion polymerization.[12]

In most latex applications, several monomers are incorporated into the polymer by copolymerization in order to impart the desired properties. Acrylic-based PSAs are commonly used due to their inherent tack, optical clarity, good resistance toward oxidation, UV radiation, and relatively low cost.[21,22] Other advantages of acrylic dispersions are their high solids content, their ease of application, and the fact that they may be formulated, in many instances, without the need for addition of tackifiers.[23] In addition, their properties can be easily modified by incorporating different monomers during polymerization.[24] The monomers typically used to produce the commercial PSA latexes are n-butyl acrylate (BuA) and 2-ethylhexyl acrylate (EHA), which produce high molar mass, permanently tacky polymers (i.e., with a very low glass transition temperature, Tg).[25]Carboxylic acid containing monomers, such as methacrylic acid (MAA) or acrylic acid (AA), are included at low levels because, after neutralization, the acid groups enhance latex colloidal stability, facilitate stronger bonds to polar substrates and provide physical crosslinking via ion clustering.[26,27] In addition, latex systems with controlled particle morphology, specifically, core-shell particles have been studied to improve their properties and performance.[28-31] This type of structures are prepared by two-stage emulsion polymerization.[28,32,33]

In this work, the influence of morphology, diameter and acrylic acid concentration in the particles on adhesion properties (peel, tack and shear) was studied. To do so, two series of homogeneous and core-shell latex particles of poly(butyl acrylate-2-ethyl-hexyl acrylate) with different concentrations of acrylic acid (0, 1, 3 and 5 wt%) and three different average diameters, were synthesized by means of emulsion polymerization techniques. The materials were characterized by dynamic light scattering, zeta potential infrared spectroscopy and transmission electronic microscopy. The content of acrylic acid into polymer and dispersed medium was determined and higher quantity of it was found within the particle. The best equilibrium between adhesion properties was found in the core-shell particles with 3 wt% of AA.

Experimental Part

Materials

The monomers n-butyl acrylate (BuA), 2-ethyl hexyl acrylate (EHA), and acrylic acid (AA) (National Starch & Chemical) were commercial grade and were used as received. Sodium dodecylbenzene sulfonate (SDBS) and potassium persulfate (from Aldrich) were reactive grade and were employed as surfactant and initiator, respectively; both were used without purification. The dispersion medium was distilled water.

Latex Preparation

The PSAs were prepared via emulsion polymerization. All reactions were carried out in a semi-continuous reactor consisting of a jacketed rector and a feeding tank. A continuous flow of pre-emulsion material was ensured by a dosing pump. The reactor consisted of a 1-L stirred glass reactor under a dynamic flow of N_2 and at a temperature of 70 °C, controlled by a thermal bath. The stirring rate was adjusted to 250 rpm. In all cases, 0, 3 or 10 g of poly(BuA) seed were synthesized as the first stage in order to modify the final average diameter of the particle. The acrylic acid concentration inside the particles was varied between 0, 1, 3 and 5 wt%. The total solids content was near 40 wt% in all cases.

The homogenous particles were synthesized in two steps, including the seed, while the core-shell latex particles were prepared by three consecutive polymerization sequences. The core-shell particles were prepared at a core/shell ratio of 70/30 w/w. The acrylic acid concentration was only varied in the shell of the particle. In both cases, the number of particles in the system was maintained constant. The formulations for latex with 1wt% of acrylic acid for homogeneous and core-shell particles are shown in Tables 1 and 2 respectively.

Table 1.
Formulation of the recipe for homogeneous latex particles with 1 wt% of AA.

Component	Content (g)	
	Reactor	Feeding Tank
n-butyl acrylate	2.5	126.7
2-Ethyl-hexyl-acrylate	2.5	126.7
Acrylic acid		2.6
Initiator solution 2 wt%	7.0	35.0
Surfactant solution 0.5 wt%	3.5	
Surfactant solution 3.73 wt%		113.0
Water distilled	190.0	

Gravimetry

The total solid content, T_s, in latexes is defined as $T_s = t_F \times 100$ where $t_F = m_P / m_L$, being m_P the mass of the polymer, and $m_L = m_S + m_P$, the total mass of latex where m_S is the mass of the solvent. A series of latex samples were weighed and placed in a previously weighed aluminum trays, obtaining m_L. The samples were dried and they were weighted again. The weights of the trays were subtracted obtaining m_P. Because:

$$m_P = t_F m_L, \tag{1}$$

the final solid content can be calculated from the slope of a plot fittings plots of m_P versus m_L.

Particle Diameter, Zeta Potential and Molecular Weight

The hydrodynamic diameter, zeta potential and determination of molecular weight of the series of homogeneous and core-shell particles were measured using a Malvern Zetasizer Nano Zs instrument at 25 °C. The samples were diluted at 10 ppm. The measurements were made in triplicate.

Table 2.
Formulation of the recipe for core-shell latex particles with 1 wt% of AA.

Component	Content (g)		
	Reactor	Feeding tank 1	Feeding tank 2
n-butyl acrylate	5.0	89.5	37.2
2-Ethyl-hexyl-acrylate		89.5	37.2
Acrylic acid			2.6
Initiator solution 2 wt%	7.0	25.0	10.0
Surfactant solution 0.5 wt%	3.5		34.0
Surfactant solution 3.73 wt%		79.0	
Water distilled	190.0		

The average diameters of particles were calculated using equations (2) and (3) and the polydispersity index (PDI) with equation (4).[34,35]

$$D_n = \frac{\sum n_i D_i}{\sum n_i} \tag{2}$$

$$D_W = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \tag{3}$$

$$PDI = \frac{D_W}{D_n} \tag{4}$$

where n_i is the number of nanocomposite particles with diameter D_i.

The static light scattering was used to determine the molecular weight of PSAs. The pure solvent (zero concentration) and samples of diluted latex at three different concentrations (5, 10 and 15 ppm) were measured. From this measurement a Debye plot can be generated. The intercept of the extrapolation to zero concentration was calculated for determine the molecular weight.

Infrared Spectroscopy

The homogeneous and core-shell acrylic latex particles were characterized by IR spectroscopy. A sample of solid polymer with KBr were prepared and pressed into a disk. The spectrum was measured in the range of 400 to 4000 cm^{-1} at ambient temperature. The IR analysis was carried out in a NICOLET Model Impact 400-D IR spectrophotometer.

Transmission Electron Microscopy (TEM)

The morphology of particles was confirmed by TEM. The latex samples were greatly diluted. A drop was placed onto the carbon cooper grid and set to dry for 2 h at ambient temperature. The samples were observed in a JEOL electron microscope at an accelerating voltage of 80 kV.

Mechanical Properties

Pressure_sensitive tapes with DuPont Mylar® 200-A, 2 mm thick backing were prepared by applying these acrylic emulsions with a K-22 bar, at an average consumption of 20-22 g of dry adhesive per square meter of surface. The film was dried in a furnace for 2 minutes at 130 °C. These films were used to measure of adhesion properties: peel, tack and shear. All measurements were made in triplicate.

Peel

The performances of the pressure-sensitive homogeneous and core-shell acrylic emulsion adhesives were measured by means of the 180° peel test as per ASTM D 903 specification. It involved the stripping of a PSA tape from an assembly, which was bonded with another flexible or rigid surface. The tests were performed on a standard tensile testing machine (Sintech testing instrument model M181730/092297). The gauge stripping length of 150 mm, at 50 mm/min was employed in all cases.

Tack

The tests were performed according to the 90° ASTM D2979-01 specification on Sintech testing instrument model M181730/092297. The PSA tape was brought into contact with a glass supported under low contact pressures for a short time and then pulled away at 30.48 cm/min. The maximum peak force of separation was registered.

Shear

The cohesive strength was measured by means of a shear adhesion test ASTM D3983-98(2004) specification. The tests were performed in a PSA tester Shear Council H-8 instrument. Over 15 minutes, a load of 0.5 kg in the vertical direction was applied on the PSA tape.

Results and Discussion

Figure 1 shows the dry polymer mass (m_P) as a function of latex mass (m_L) for core-shell particles with 1 wt% of acrylic acid. The slope is the mass fraction of solids in the latex samples.

Total solids contents of homogeneous and core-shell latex particles are shown in Tables 3 and 4, respectively.

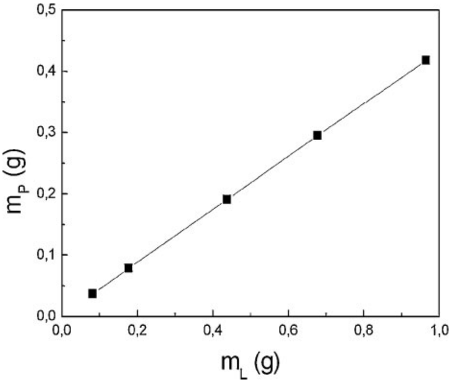

Figure 1.
Dry polymer mass as a function of latex mass.

From the gravimetry results, it can be observed that the PSAs were synthesized with high solids content, up to 40 wt%.

Varying the quantity of seed in the reactor between 0, 3, and 10g, PSAs of three different final average diameters were synthesized. Thus, the acrylic acid concentration was varied for each system, between 0, 1, 3, and 5 wt%. The average diameters of the particles as a function of acrylic acid concentration for PSAs with homogeneous and core-shell morphologies are presented in Figure 2a and 2b, respectively.

The results show that an increase in the quantity of monomer in the seed has its consequence an increase in the final average diameter of particles in both systems. However, the increase in the acrylic acid concentration does not have an effect on the final size of the particles.

Using equation (4) and the results of average particle diameters, the polydispersity index was calculated, finding that the homogeneous and core-shell acrylic PSA are monodispersed, because all had values near 1. This was confirmed by transmission electron microscopy.

The zeta potential was measured as a function of final average diameter and acrylic acid concentration inside the particle. The results are presented in Figure 3a and 3b for homogeneous and core-shell PSAs respectively.

In both morphologies, the zeta potential is increased if the average particle diameter is increased. This behavior is due to the hydrophilic nature of the carboxylic groups of acrylic; for this reason, they are located mainly on the surface of particle. If the diameter is greater, then there are more groups on the surface of the particle. Thus, if there is an increased content of carboxylic groups, the zeta potential is also increased, causing a decrease in the stability of the colloidal system. That means that the system approaches the instability zone of ± 30 mV. This behavior is more evident in the core-shell PSAs because the acrylic acid is added to the shell of the particle.

Table 3.
Total solid content in the homogeneous latex particles.

Seed (g)	Solid Content (wt%)			
	0 wt% AA	1 wt% AA	3 wt% AA	5 wt% AA
0	42.00 ± 8.51E-04	42.01 ± 6.45E-04	41.43 ± 2.32E-03	42.78 ± 5.92E-04
3.0	40.89 ± 7.23E-04	41.35 ± 1.25E-03	40.64 ± 7.25E-04	42.61 ± 9.67E-04
10.0	41.67 ± 5.02E-04	42.37 ± 1.37E-03	42.45 ± 2.05E-04	41.76 ± 6.93E-04

Table 4.
Total solid content in the core-shell latex particles.

Seed (g)	Solid Content (wt%)			
	0 wt% AA	1 wt% AA	3 wt% AA	5 wt% AA
0	43.6 ± 9.22E-04	43.36 ± 1.04E-03	43.613 ± 3.6E-04	43.39 ± 2.44E-03
3.0	43.66 ± 1.7E-02	43.42 ± 3.45E-03	43.63 ± 1.01E-03	43.28 ± 1.04E-03
10.0	42.67 ± 2.73E-04	42.89 ± 7.12E-04	43.126 ± 7.63E-04	42.55 ± 2.48E-03

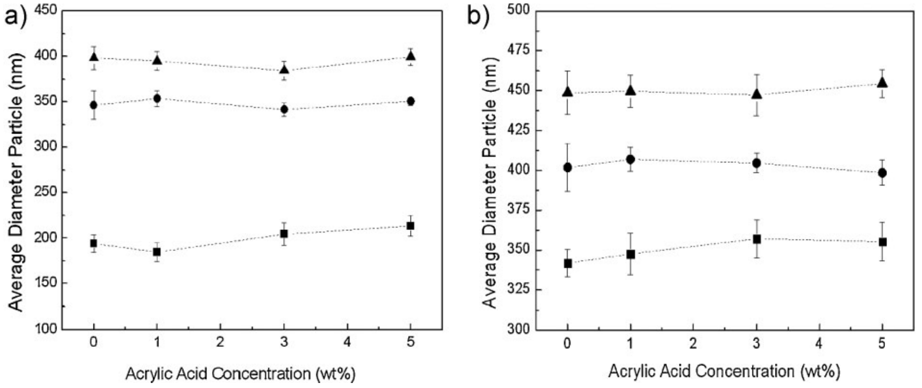

Figure 2.
Average particle diameter for a) homogeneous particles and b) core-shell particles, as a function of acrylic acid concentration (■ 0 g of seed, ● 3g of seed and ▲ 10g of seed).

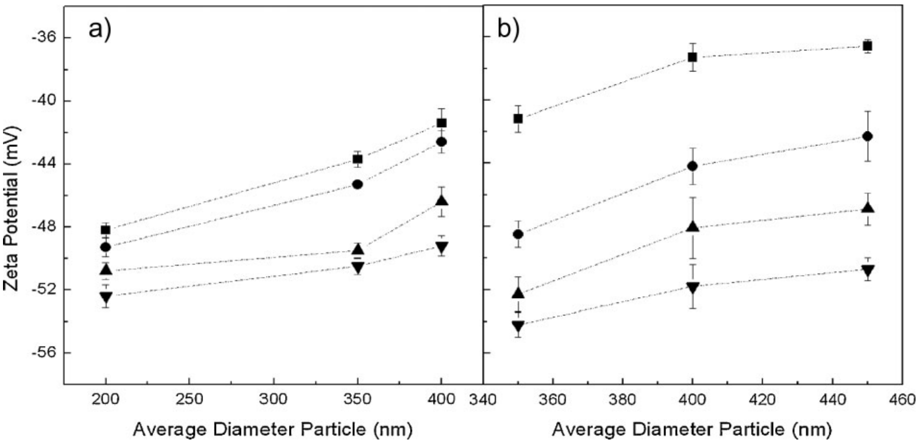

Figure 3.
Average zeta potential for a) homogeneous particles b) core-shell particles, as a function of average particle diameter (▼0 wt%AA, ▲ 1wt% AA, ●3 wt% AA, ■ 5wt% AA).

Static light scattering was used for determined the molecular weight. The results are shown in Figure 4a and 4b for homogeneous and core-shell PSAs, respectively. In the case of homogeneous particles, it can be observed that increased acrylic acid concentration results in decreased molecular weight. This is due to the acrylic acid having a high solubility in water and competing with the capture of radicals generated in the dispersed phase. This behavior is not the same for the core-shell particles, where the acrylic acid is added in the third stage. Thus their molecular weight is one order of magnitude greater that of homogeneous particles.

The quantity of acrylic acid within the particle and in the dispersed media was determined. The results are shows in Tables 5 and 6 for homogeneous and core-shell particles. It was found that most of the acid was within the particles.

The polydispersity and morphology of acrylic PSAs were confirmed by means of transmission electron microscopy. Figure 5a and 5b, shows the images of homogeneous and core-shell particles of acrylic PSAs, respectively.

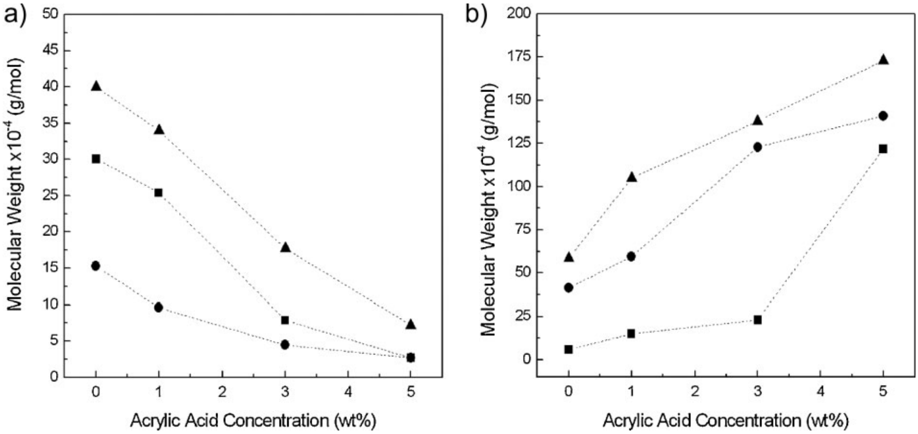

Figure 4.
Molecular weight for a) homogeneous particles b) core-shell particles, as a function of acrylic acid concentration (● 0g of seed ■ 3g of seed, ▲10g of seed).

Table 5.
Acrylic acid in the particles and in dispersed media in homogeneous PSAs.

Seed (g)	Acrylic acid concentration (wt%)	Percent of acrylic acid in the particle (wt%)	Percent of acrylic acid in dispersed media (wt%)
0	1	99,8364	0,1636
	3	99,9653	0,0347
	5	99,9416	0,0584
3	1	99,7793	0,2207
	3	99,9526	0,0474
	5	99,9379	0,0621
5	1	99,8852	0,1148
	3	99,9684	0,0316
	5	99,9662	0,0338

Table 6.
Acrylic acid in the particlea and in dispersed media in core-shell PSAs.

Seed (g)	Acrylic acid concentration (wt%)	Percent of acrylic acid in the particle (wt%)	Percent of acrylic acid in dispersed media (wt%)
0	1	99,66	0,34
	3	99,83	0,17
	5	99,88	0,12
3	1	99,67	0,33
	3	99,84	0,16
	5	99,90	0,10
5	1	99,62	0,38
	3	99,81	0,19
	5	99,87	0,13

The mechanical properties of peel adhesion, loop tack and shear strength were determined by means of ASTM specifications. The results are shown in Figure 6a and 6b for homogeneous and core-shell morphologies, respectively.

Peel adhesion is the strength required to remove the adhesive from a surface at specific angle (90°-180°). In both acrylic PSAs, the peel adhesion is increased with the increasing of acrylic acid concentration up to a concentration of 3wt%, this the

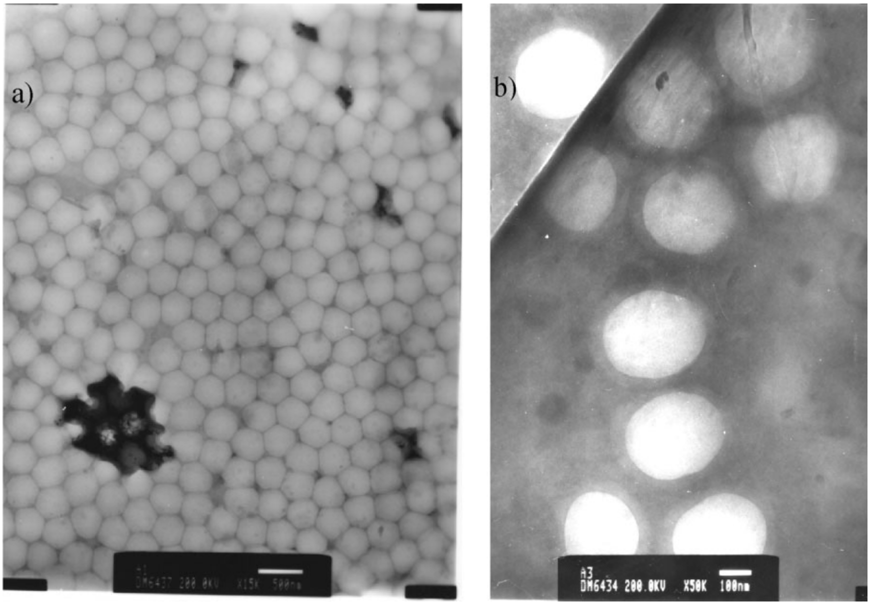

Figure 5.
Transmission electron micrographs of a) homogeneous particles and b) core-shell particles.

property decreases. Thus, the adhesive with 3wt% of AA is the most difficult to separate the adhesive from the substrate. This behavior is cause by AA sites for hydrogen bonding; these increase the cohesive strength of the material and the interaction with the probe surface,[26] which and is more drastically seen for the core-shell structure because the polar groups are only located in 30% of each particles. With increasing average diameter there is a decrease in the peel adhesion because the contact area decreases.

Loop tack is related to the Tg of the material and is the material capacity to make physical bonds with other materials with brief contact under light or no pressure. The results for both morphologies show an increase in the thing property with increasing of acrylic acid concentration, because there is a high concentration of charges on the particle surface which allows for improved intimate contact with the substrate during the bonding step. With respect to the average particle diameter, the loop tack decreases when the diameter increases, because the packing density during the film formation process is higher with small particles than with bigger particles.

Shear strength results in flow of the adhesive after the initial contact. It is related to the resistance of the internal structure of the material size of particle and the molecular weight of the polymer. In this case, the mechanical property is increased when the acrylic acid amount is increased. That means that the concentration of COOH groups is higher on the particle surface, which increases the interaction between the substrate and the PSA due to the formation of hydrogen bonds between the polymer chains, with the effect being stronger cohesion. This property is increased with increased average particle diameter. This behaviour is better in the core-shell particles than in homogeneous particles because the core-shell acrylic PSAs have a higher molecular weight than do the homogenous PSAs.

Conclusion

Two series of monodispersed acrylic PSAs with homogeneous and core-shell morphol-

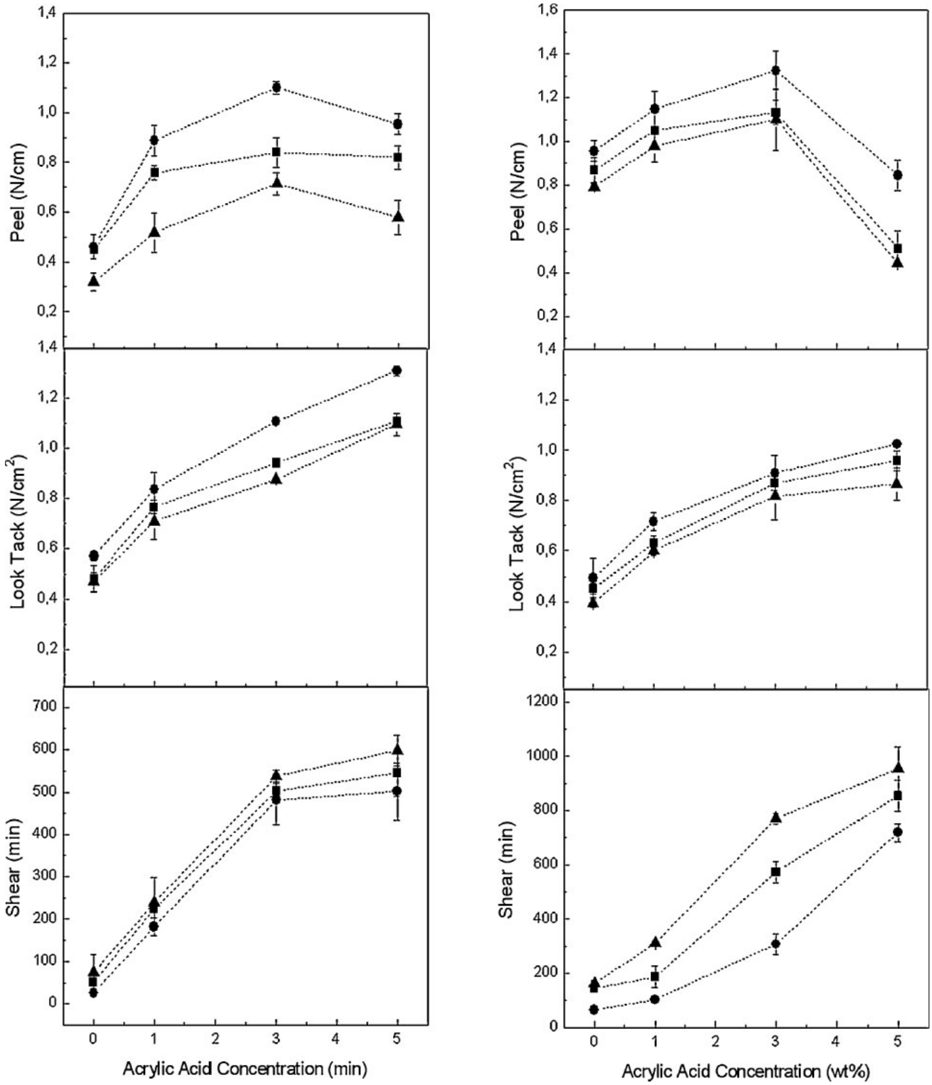

Figure 6.
Mechanical properties of a) homogeneous particles and b) core-shell particles as a function of acrylic acid concentration (● 0g of seed ■ 3g of seed, ▲10g of seed).

ogies were synthesized by means of emulsion polymerization in stages. The latexes were obtained with solid content higher than 40 wt%. Three average particle diameters were obtained, varying the content of monomer in the seed (0 g, 3 g and 10 g of BuA)

The measurements of zeta potential determined that there was high concentration of acrylic acid in the PSAs, decreasing in colloidal stability.

The molecular weight of homogeneous particles was lower than the molecular weight of core-shell particles by one order of magnitude due to carboxylic groups being added in the last stage. With both morphologies the 99 w% of acrylic acid was found inside the particle.

Regarding mechanical properties, the peel adhesion is increased with the increasing acrylic acid concentration; the best value was reached at 3wt% of AA. This behaviour is more drastic for core-shell PSAs.

The loop tack and shear strength for two morphologies were directly proportional to the acrylic acid concentration, as higher values were reached when the acrylic acid was 5wt%. However, the loop tack decreases while the shear strength decreases with increasing average diameter of the particles. The values of shear strength for core-shell acrylic PSAs are higher than those of homogeneous PSAs due to core-shell structures having a higher molecular weight.

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