Adhesives for Low-Energy Surfaces

Amaia Agirre,[1] Julia Nase,[2] Costantino Creton,[2] José M. Asua[*1]

Summary: The wetting and adhesive properties of model pressure-sensitive adhesives synthesised by miniemulsion polymerization were investigated. Wetting experiments of aqueous solutions of three different emulsifiers showed that Silwet L-77 (nonionic ethoxylated trisiloxane) was the best wetting agent. Probing adhesive properties, two different structure modifications of the polymer were investigated: a change in the polymer microstructure by the addition of a chain transfer agent and the introduction of a hydrophobic monomer into the polymer backbone. An addition of chain transfer agent was sufficient to obtain a polymer with a significantly different microstructure and, consequently, enhanced adhesion energy but reduced shear resistance. On the other hand, stearyl acrylate (SA) was employed as the hydrophobic monomer and the synthesis was carried out in miniemulsion polymerization which enables the incorporation of hydrophobic compounds without any diffusion limitations. There were almost no differences in the polymer microstructure, whereas, some differences were observed in adhesion properties.

Keywords: adhesives; hardness; microstructure; surfaces; surfactants

Introduction

Polymer films based on polyolefins are widely used in packaging, labeling and food protection. Their increasing presence on the market isn due to a variety of end-use applications and the low production cost.

Polyolefin films coating with a pressure sensitive adhesive is a challenge because of poor adhesion to these substrates. Polyolefin surfaces are indeed characterized by a very low surface energy caused by a lack of polar groups on the surface, which undermines both the wetting of the adhesive over the substrate and the formation of a strong adhesive bonding after solvent evaporation.

Although the adhesion to low-energy surfaces is not yet well understood, attempts have been made to improve the wetting including surface film treatment[1–5], the use of primers and adhesion promoters (coupling agents)[6–8] addition of tackifiers[9–11] and polymers based on silicones[12]. Besides getting relatively poor results, the current technology remains costly or involves solvent-borne polymer adhesives[13].

Concerning the wetting ability, in order to wet a substrate the surface tension of the wetting liquid must not exceed a certain critical value which is characteristic of the particular substrate[14]. The spreading of a partially wetting aqueous drop on a solid hydrophobic surface can be facilitated by adsorption of surfactants on the air/aqueous and aqueous/solid interfaces of the drop. Conventional surfactants are not particularly efficient for this task but superspreaders can achieve a complete wetting of the substrate. Upon water evaporation, a strong bonding between the acrylic polymer of the latex and the polyolefin film would be desirable. The strength of the adhesive bond depends

---

[1] Institute of Polymer Materials (POLYMAT) and Grupo de Ingeniería Química, Edificio Korta I+D+I, The University of the Basque Country, 20018 Donostia-San Sebastián, Spain
E-mail: jm.asua@ehu.es

[2] Laboratoire de Physico-Chimie des Polymères et des Milieux Dispersés ESPCI 10, rue Vauquelin 75231 Paris Cedex 05, France

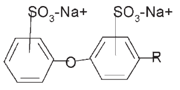
on the level of interfacial interactions between the adhesive and the substrate (hydrogen bonding, entanglements, van der Waals interactions) and on the architecture of the adhesive which controls its viscoelastic properties[15]. Polyolefins are not compatible with the acrylic polymers commonly used as adhesives. Consequently, there is little interpenetration at the interface and weak adhesive bonds are formed. Incorporation of a hydrophobic monomer into the adhesive may improve its affinity to the polyolefin, thereby improving the adhesive strength. Such an incorporation may also change the architecture of the adhesive[16].

This article investigates: i) the use of a superspreader to improve the wetting of low-energy surfaces, ii) the effect of the microstructure of the polymer on the adhesive properties and iii) the effect of introducing stearyl acrylate, a hydrophobic monomer, into the polymer backbone on the adhesion to different low-energy surfaces, Teflon (18 mN/m), untreated polypropylene (32 mN/m) and treated polypropylene (56 mN/m)[17]. Miniemulsion polymerization was employed as it enables the incorporation of hydrophobic compounds without any diffusion limitations[18].

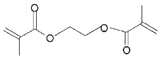
Experimental Part

Materials

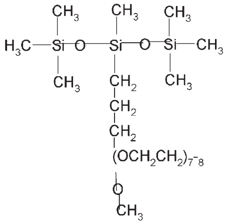
2-Ethylhexyl acrylate (2-EHA) (Quimidroga), methacrylic acid (MAA) (Aldrich), and stearyl acrylate (SA) (Aldrich) were used as received. Dowfax 2A-1 (Dow Chemical Company) was used as emulsifier, SA (Aldrich) as costabilizer and sodium hydrogen carbonate (Panreac) as a buffer. Ammonium persulfate (Fluka Chemika) was used as initiator. Ethylene glycol dimethacrylate (Fluka) was used as crosslinker, whereas n-dodecanethiol (Merck) was used as chain transfer agent (CTA). FC-4430 and Silwet L-77 were used as wetting agents. THF (99.9% GPC, Scharlab) was used as a solvent.



Dowfax 2A-1.



EGDMA.



Silwet L-77.

Preparation of Miniemulsions

Dowfax 2 A-1 was dissolved in water to prepare the aqueous phase, and the monomers, costabilizer, CTA and crosslinker were mixed to prepare the oil phase. The oil phase was added to the aqueous phase and the oil/water mixture was stirred for 20 min with a magnetic stirrer at 700 rpm for pre-emulsification. This coarse emulsion was miniemulsified in a two-valve high-pressure homogenizer (Manton Gaulin, $P1 = 4000$ bar, $P2 = 400$ bar, 7 cycles). The solid content of the miniemulsion was about 50 wt %. To prevent overheating during miniemulsification, the homogenizer had a cooling system.

Miniemulsion Polymerizations

All the semicontinuous polymerizations were seeded. The poly(2EHA-*co*-MAA) seed was prepared batchwise following the formulation shown in Table 1 in a glass-jacketed reactor fitted with a reflux condenser, a sampling device, nitrogen inlet, and a stainless steel impeller at 200 rpm. The reaction was carried out at 70 °C for 2 h; it was kept overnight at 90 °C to decompose the unreacted initiator.

The seeded semicontinuous miniemulsion polymerizations were carried out in a 750 mL glass-jacketed reactor fitted with a

Table 1.
Formulation used to prepare the seed.

Ingredient	Amount (g)
Water	1000.10
2-Ethylhexyl acrylate	979.95
Methacrylic acid	19.94
Stearyl acrylate	40.83
Dowfax 2A-1	22.20
$(NH_4)_2S_2O_8$	3.43

Table 2.
Formulation used in the seeded semicontinuous miniemulsion polymerization for obtaining different polymer microstructure.

Ingredient	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Seed	100	–	–
Water	–	241.06	18.87
2-Ethylhexyl acrylate	–	236.16	–
Methacrylic acid	–	4.82	–
Stearyl acrylate	–	9.68	–
Dodecanethiol	–	–[a)]/0.37[b)]	–
EGDM	–	0.57[a)]/0.56[b)]	
Dowfax 2 A-1	–	5.38	–
$(NH_4)_2S_2O_8$	–	–	1.13

[a)] Latex X3;
[b)] Latex X5.

reflux condenser, sampling device, nitrogen inlet, two feeding inlets and a stainless steel anchor stirrer with two blade impellers rotating at 200 rpm. Table 2 summarizes the formulation used in the semicontinuous experiments for the synthesis of polymers with different microstructure, whereas Table 3 presents the formulations corresponding to the latices synthesised with different SA concentrations.

The experimental procedure was as follows: First, 100 g of the polymer seed (dp = 169 nm, gel content ca. 70%, solids content ca. 50%) was charged into the reactor. When the desired reactor charge temperature was reached, the other ingredients were fed within three hours. Then the reaction was kept for 60 min.

Characterization

Contact angles were measured with the Goniometer OCA 20 by the sessile drop method using the dynamic tracking function (1 frame/s) during one minute over untreated PP.

Monomer conversion was determined by gravimetry. The instantaneous conversion, X_i, was defined as the amount of polymer divided by the amount of monomer and polymer in the reactor. The overall conversion was the amount of polymer divided by the amount of monomer plus the amount of polymer in the formulation. Particle sizes were measured by dynamic light scattering using a Zetasizer Nano Z (Malvern Instruments).

The gel fraction and the swelling degree were determined by 24-h soxhlet extraction with THF. After the extraction, the samples were dried and the gel content was calculated as the ratio of the dry polymer remaining after the extraction to the initial amount of dry polymer. The swelling degree was calculated as the ratio between the swollen polymer after 24-h extraction to the amount of the dried polymer.

The sol molecular weight was determined by the size exclusion chromatography (SEC, Waters). The setting consisted of a pump (Waters 2410) a differential refractometer and three columns in series (Styragel HR2, HR4 and HR6; with a pore

Table 3.
Formulation used in the seeded semicontinuous miniemulsion polymerization with different SA amounts.

Ingredient	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Seed	100	–	–
Water	–	242.16	18.87
2-Ethylhexyl acrylate	–	237.32–17.7	–
Methacrylic acid	–	4.84	–
Stearyl acrylate	–	9.69-29.1	–
$NaHCO_3$	–	1.02	–
Dowfax 2 A-1	–	5.38	–
$(NH_4)_2S_2O_8$	–	–	1.13

size from 10^2–10^6 Å). The analysis was performed at 35 °C with THF as carrier at a flow rate of 1 mL/min. The solution of sol polymer recovered from the Soxhlet extraction was dried in a ventilated oven. After evaporation of THF, the dried polymer was redissolved in THF. Afterwards it was filtered (polyamide filter, $\Phi = 0.45\,\mu m$) and a sample was injected into the SEC.

The adhesive performance of the PSAs produced was evaluated by measuring tack, peel strength and resistance to shear. Tack was assessed by using a custom designed probe tack technique.[19] The samples were made by depositing the corresponding amount of latex on a standard microscope glass slide so as to obtain a dry adhesive film of ca. 100-μm thickness. The films were formed from the latices by water evaporation at room temperature to constant weight. The sample was fixed to the upper plate, whereas the probe (6 mm diameter stainless steel) was fixed on the mobile lower shaft which was connected to the load cell. The entire process of contact between the probe and the film and the subsequent debonding were followed by a video camera placed on a microscope.

The probe test procedure consisted of first bringing the probe into contact with the film at a constant speed of 20 μm/s. Next, the compressive force of 5 N was applied. The probe was left in contact with the adhesive for 1, 10 or 100 s. Finally, the probe was removed at a constant speed. Three speeds were used: 1,10 and 100 μm/s. All experiments were carried out at room temperature.

Peel resistance was assessed by means of the 180° peel test in the cases where Teflon was used as the substrate while the T-peel test[20] was requiered for the cases where treated (TPP) and untreated polypropylene (NTPP) were used. In these tests, a tape was applied to the given substrate and the free end was clamped to the upper jaw of an Instron Tensile Tester, which pulled the tape at a constant speed of 300 mm/min. In this test, the average force required to peel away the tape was recorded. Shear resistance was assessed by the holding power shear test[21,22]. This test consisted in applying a standard area (2.5 × 2.5 cm) of tape on a panel holding 1 kg until failure. The experiments were performed at 30 °C. The adhesive films used in the tests were obtained under standard conditions ($T = 23\,°C$, humidity 55%) by spreading the latex over a flame-treated polypropylene 29 μm thick using a 120 μm multiple gap applicator with reservoir. 1 wt % (relative to the latex) of Silwet L-77 was added to the latex to improve the wetting and, consequently, enable the formation of a good quality film. The films were dried at room temperature for 20 min, afterwards they were introduced into a well ventilated oven at 60 °C for 10 minutes to completely evaporate water. Finally they were allowed to cool to room temperature for 10 min before being cut into the desired dimensions for each test.

Results and Discussion

Figure 1 shows the evolution of the contact angle of the aqueous solution of emulsifiers over untreated polypropylene. It can be observed that Silwet L-77 provided the best wetting results as it yielded the lowest values of the contact angle using the lowest concentration. This might be related to its structure. The oxyethylene chains in water

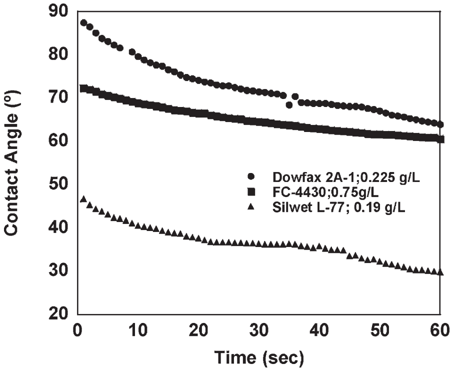


Figure 1.
Evolution of the contact angle over untreated polypropylene for different emulsifiers and concentrations.

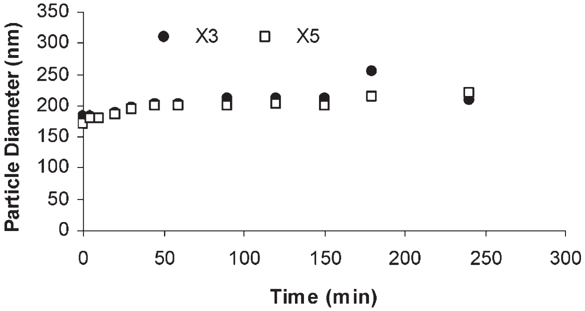


Figure 2.
Evolution of particle size in the seeded semicontinuous miniemulsion polymerization carried out at 70 °C with and without CTA. (Latex X3 (•); latex X5 (□); see Table 2).

adopt a helical conformation whose cross-section increases with the number of oxyethylene groups. The cross-section of the oxyetylene chain is lower or approximately equal to that of the hydrophobic groups. So the trisiloxane chain acts as an umbrella and its cross section determines the distance of closest approach of the molecules on the surface. This stacking structure reduces both solid/aqueous and air/aqueous interfacial energy thus enhancing better wetting.[23] Therefore, Silwet L-77 was added to all the latices after polymerization.

Figure 2 and 3 present the evolution of particle size and instantaneous conversion for the latices synthesised with and without CTA. It can be seen that neither the particle size nor the polymerization kinetics were affected by the presence of the CTA.

Figure 4 and 5 present the gel content and molecular weight distribution of the sol for the final latices, respectively. When the CTA was employed (latex X5), the gel content decreased strongly, whereas the effect of CTA on MWD seems to be negligible. When no CTA was used (latex X3), the low MW_{sol} was obtained because of the transfer from the sol fraction to the gel of long and branched polymer chains, formed by chain transfer to polymer plus termination by combination reactions. On the other hand, in the cases where a higher CTA concentration was used (latex X5), the main termination mechanism was the chain transfer to the CTA. In this way short chains and, as a consequence, low MW_{sol}[24] are obtained. This could explain why differences in the MWD of the sol were not observed.

The effect of the adhesion properties, tack, peel strength and shear resistance are

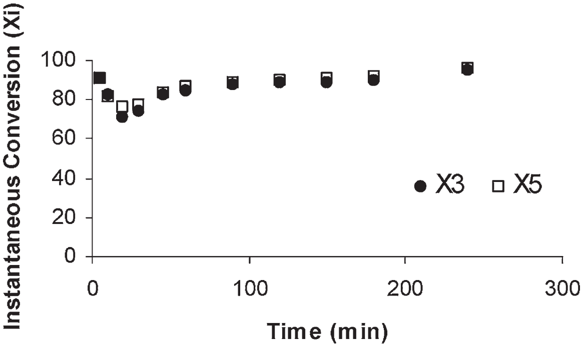


Figure 3.
Evolution of instantaneous conversion in the seeded semibatch miniemulsion polymerization carried out at 70 °C with and without CTA. (Latex X3 (•); latex X5 (□); see Table 2).

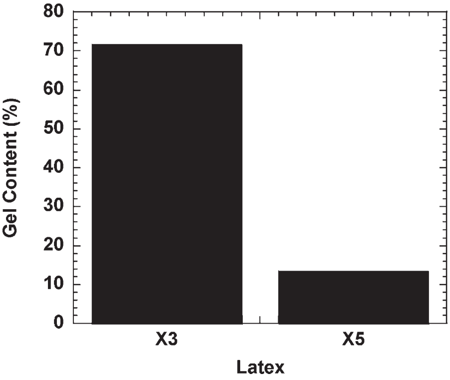


Figure 4.
Gel content for the latices synthesised by seeded semicontinuous miniemulsion polymerization at 70 °C with and without CTA. (Latex X3 and latex, see Table 2).

presented in Figure 6–8, respectively. Probe tack and peel strength present the same behaviour, the best results corresponding to latex X5, which is the latex with the lowest gel content. On the other hand, latex X3, which contained a much higher gel fraction and, consequently, higher cohesion yielded the best shear resistance.

It was observed that the substrate did not present any effect on the peel strength, whereas a significant surface effect on the shear resistance was observed for the X3 latex. However, the effect might not be related to the surface tension but rather to the composition of the substrate, which might promote the interaction of the polymer with the substrate. As it can be seen in Figure 8 better resistance to shear was obtained when polypropylene was employed as the substrate but only slight differences were observed between treated and non treated polypropylene.

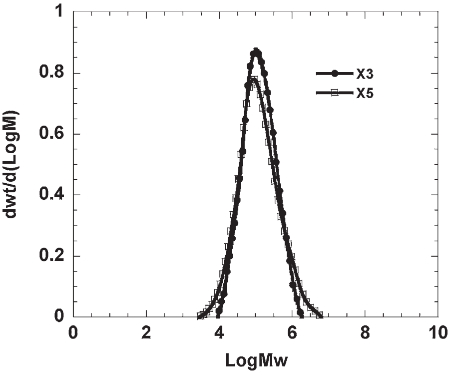


Figure 5.
Molecular weight distributions corresponding to the latices synthesised by seeded semicontinuous miniemulsion polymerization at 70 °C with and without CTA. (Latex X3 (●); latex X5 (□); see Table 2).

Figure 9 and 10 present the effect of the presence of a hydrophobic monomer in the formulations. It can be seen that the same particle size was obtained and that the presence of SA resulted in a slightly slower polymerization rate, but the same final conversion was achieved.

Table 4 displays the effect of the SA concentration on the gel content and swelling degree of the gel fraction for the final latices produced by seeded semicontinuous miniemulsion polymerization, whereas Figure 11 presents, the molecular weight distribution of sol in the final latices. It was observed that the microstructure of the polymer was similar for both of the latices. Therefore, the differences obtained in the adhesion properties, could not be related to neither the polymer microstructure nor the particle size.

Figure 12–14 present the effect of the SA content on the adhesion properties, tack, peel strength and shear resistance, respectively.

Figure 12 shows that the work of adhesion increased with the contact time. This might be related to the hardness of the polymer due to the introduction of SA. SA homopolymer shows the T_g (308 K) which is substantially higher than the T_g of poly(2-EHA) (223 K)[25]. The work of adhesion was higher for the latex containig 12 wt% of SA. A similar behaviour was observed with the peel strength results presented in Figure 13. The possibility of the gel content being responsible for those differences was discarded as both of them present a similar gel content. The results might be explained by the affinity of the polymer to the substrate and the hardness of the polymer. However, Linder et al. have observed that for solution of polySA the work of adhesion and the peel strength improved as the

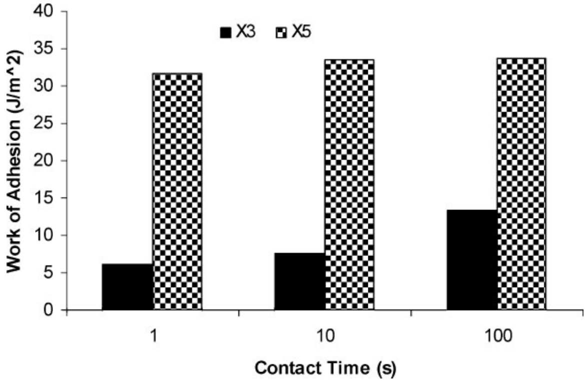


Figure 6.
Effect of the gel content on the work of adhesion obtained by the probe test at different contact times.

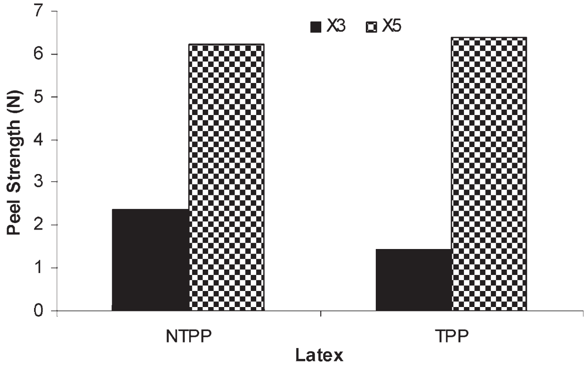


Figure 7.
Effect of the gel content on the peel strength obtained by T-peel experiment with treated and untreated PP and 180°-peel test (Teflon).

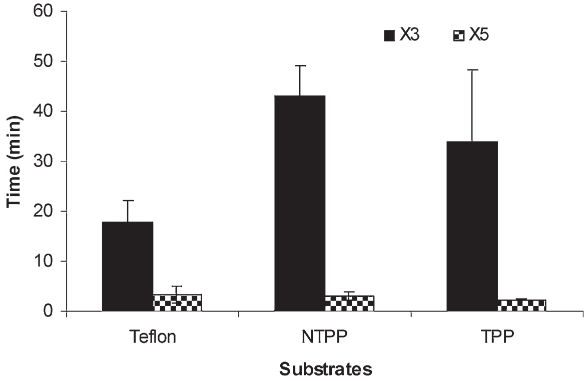


Figure 8.
Effect of the gel content on the shear resistance obtained by the holding power measurement at 30 °C over different substrates.

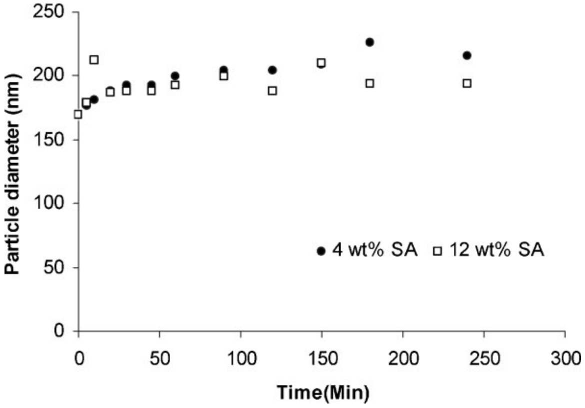


Figure 9.
Evolution of particle size in the seeded semicontinuous miniemulsion polymerization carried out at 70 °C with different SA concentrations.

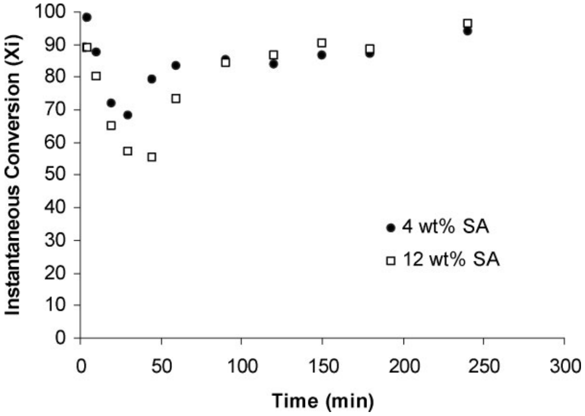


Figure 10.
Evolution of the instantaneous conversion in the seeded semibatch miniemulsion polymerization carried out at 70 °C with different SA concentrations.

concentration of SA increased because the addition of SA makes the adhesive softer in the plateau region. In the absence of mechanical characterization it is difficult to decide whether interfacial interactions or a change in mechanical properties of the polymer are responsible for the change in adhesive properties. A significant contact

Table 4.
Effect of the SA content on the gel content and swelling degree.

SA %	Gel Content (%)	Swelling
4	72.1	15.1
12	69.8	16

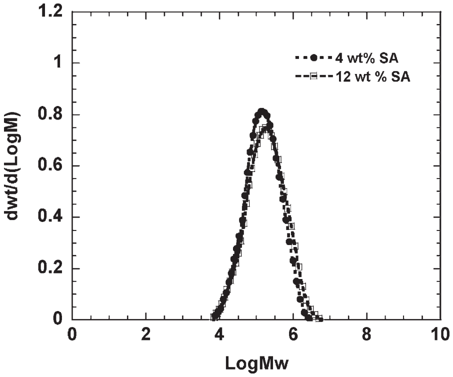


Figure 11.
Effect of the SA content on the molecular weight distributions.

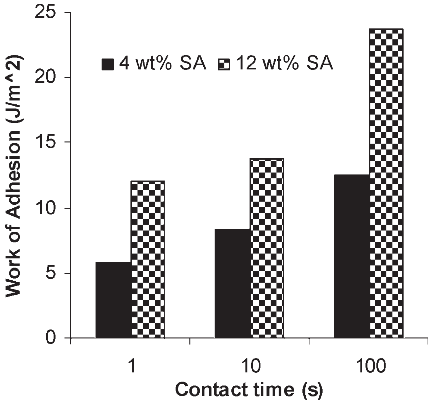


Figure 12.
Effect of the SA content on the work of adhesion obtained by the probe test technique at different contact times.

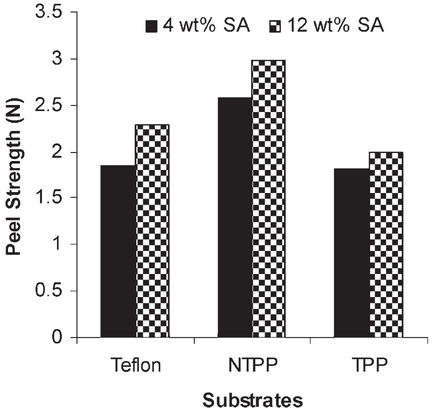


Figure 13.
Effect of the SA content on the peel strength obtained by T-Peel experiment (treated and non-treated PP) and 180°-peel test (Teflon).

time dependence was observed in the tack measurements; this effect became more pronounced with increasing SA concentration.

Figure 14 presents the effect of the SA content on the shear resistance measured on different substrates. It can be seen that no clear effect of the SA content was observed, indicating that shear was mainly controlled by polymer architecture.

Apparently, the effect of the substrate on adhesion properties was only observed for the shear resistance, which might be related to the compatibility of adhesive and substrate.

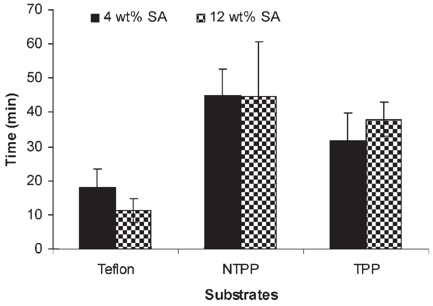


Figure 14.
The effect of the SA content on the shear resistance obtained by the holding power measurement at 30 °C over different substrates.

Conclusion

The effect of emulsifier on the wetting ability and that of polymer microstructure and introduction of a hydrophobic monomer (SA) into the polymer backbone on the adhesion properties on low energy surfaces were investigated.

It was found that Silwet L-77 yielded the best wetting performance; hence it was used as the superspreader to improve film formation.

The substrate effect was observed only in shear resistance where significantly better results were obtained when polypropylene was used as substrate.

It was found that tack and peel strength were higher for the latex with the lowest gel content, while the best shear results were obtained with the most crosslinked polymer.

Polymer microstructure was not affected by the introduction of SA but, rather, the mechanical properties of the polymer through the change in T_g and entanglement structure due to the change in monomer. This was reflected in adhesion properties. At higher SA concentrations, significantly better probe test results were obtained and the peel strength was also slightly improved. No differences in shear resistance were observed but this might be related with to high gel content values.

The introduction of a hydrophobic monomer such as SA improved moderately the adhesion properties over low-energy surfaces.

Acknowledgements: The authors thank the financial support provided by Diputación Foral de Gipuzkoa and the Ministerio de Educación y Ciencia (MEC CTQ 2006-03412).

[1] H. Drnovská, L. Lapcik, Jr., V. Bursiková, J. Zemek, A. M. Barros-Timmons, *Colloid Polym. Sci.* **2003**, *281*, 1025–1033.

[2] M. Lehocký, H. Drnovská, B. Lapcíková, A. M. Barros Timmons, T. Trindade, M. Zembala, L. Lapcík, *Colloids Surfaces A: Physicochem. Eng. Aspects* **2003**, *222*, 125–131.

[3] A. Ricard, *J. Phys. D: Appl. Phys.* **1997**, 2261–2269.

[4] Z. W. Wicks, Jr., N. F. Jones, S. P. Pappas, D. A. Wicks, *Organic Coatings: Science and Technology*, Wiley Interscience, **2007**.

[5] R. A. Ryntz, P. V. Yaneff, *Coatings of Polymer and Plastics*, Routledge, USA **2003**.

[6] E. Tomasetti, S. Vandorpe, D. Daoust, T. Boxus, J. Marchand-Brynaert, C. Poleounis, P. Bertrand, R. Legrasand, P. G. Rouxhet, *J. Adhesion Sci. Technol.* **2000**, *14*, 779–789.

[7] M. F. Sonneschein, S. P. Webb, P. E. Kastl, D. J. Arriola, B. L. Wendt, D. R. Harrington, *Macromolecules*, **2004**, *37*, 7974–7978.

[8] M. F. Sonneschein, B. L. Wendt, WO/2005/082912, (**2005**).

[9] D. J. Kim, H. J. Kim, G. H. Yoon, *Interfacial J. Adhesives* **2005**, *25*, 288–295.

[10] P. B. Foreman, S. M. Shah, R. Chandran, P. S. Eaton, U.S. Patent 6670417, (**2003**).

[11] T. C. Epple, WO 00/11099, (**2000**).

[12] I. S. P. Lee, U.S. Patent 4994538, (**1991**).

[13] D. Caspari, F. Kura, M. Schuette, K. Seeger, U.S. Patent us2003235686 (**2003**).

[14] M. J. Rosen, *Surfactants and Interfacial Phenomena*, 3rd ed., Wiley Interscience, **1989**, *6*, 243–275.

[15] R. Schach, Y. Tran, A. Menelle, C. Creton, *Macromolecules* **2007**, *40*, 6325–6332.

[16] A. Linder, B. Lestriez, S. Mariot, C. Creton, T. Maevis, B. Lühmann, R. Brummer, *J. Adhes.* **2006**, *82*, 267–310.

[17] M. Aouinti, P. Bertrand, F. Poncin-Epaillard, *Plasmas Polym.* **2003**, *8*, 225–236.

[18] J. M. Asua, *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.

[19] G. Josse, P. Sergot, M. Dorget, C. Creton, *J. Adhes.* **2004**, *80*, 87–118.

[20] American Pressure Sensitive Tape Council, PSTC-1M Standard, Resistance to peel for single coated pressure-sensitive tapes 180°angle, **1986**.

[21] American Pressure Sensitive Tape Council, PSTC-7M Standard, Holding power of pressure-sensitive tape, **1986**.

[22] American Society for Testing and Materials, ASTM: D3654/D3654M-02, Standard test methods for shear adhesion of pressure-sensitive tapes, **1999**.

[23] Y. Shen, A. Couzis, J. Koplik, C. Maldarelli, M. S. Tomassone, *Langmuir*, **2005**, *21*, 12160–12170.

[24] C. Plessis, G. Arzamendi, J. M. Alberdi, M. Angley, J. R. Leiza, J. M. Asua, *Macromolecules*, **2001**, *34*, 6138.

[25] J. Brandrup, E. H. Immergut, *Polymer Handbook*, 2nd ed., **1975**.