

COMBINING PRODUCT MANUFACTURING WITH PRODUCT APPLICATION FOR HIGH SOLIDS-LOW VISCOSITY LATEXES

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Abstract

Techniques for manufacturing ultra high solids-low viscosity latexes are the subject of industrial research for decades. Unfortunately, few works have proved to provide a truly scientific approach to accomplish this challenge. Furthermore, much of what has been done relies on empirical and tacit knowledge gained with time. Often, the production of high solids-low viscosity latexes has become a goal on itself, with few considerations on the application of the latex. On the other hand, this work is intended to show the possibility of coupling product manufacturing with product application. First the focus is directed to study the effect of the particle size distribution of model pressure sensitive adhesive latexes on adhesive properties. Next, a model assisted methodology for the synthesis of concentrated aqueous polymer dispersions is presented, and it is shown that the model assisted methodology is a powerful tool to enhance the adhesive properties of concentrated water-based acrylic pressure sensitive adhesives.

Introduction

Emulsion polymers are truly product by process. As a consequence, there is a strong interest to develop quantitative relationships between the microstructural properties of the polymer and end-use properties. Such correlations would make possible controlling the final properties of the latex by manipulating the process variables.

The synthesis of high solids low viscosity latexes has long suscitated great interest from both industry and academia ^[1]. Possible advantages of highly concentrated emulsions, understanding by highly concentrated a latex with solids content above 65%, are numerous. The higher unitary usage of industrial installations, faster drying rates and lower transportation cost are some of the advantages that can be mentioned. Due to the potential benefits from highly concentrated latexes bring to producers of polymer dispersions most of the references are found in patents. Scientific literature, which is usually more precise and richer in information, only covers a few of the strategies reported in patents. A general trend is found in all polymerization procedures. They mention either implicitly or explicitly ways of producing a polymer dispersion having a broad PSD, most usually depicted as the sum of a mode of large particles with a mode of small particles ^[1,3].

The shape of the latex particle size distribution is probably the most important variable in designing concentrated aqueous polymer dispersions ^{9,10}. Accordingly, a polydispersed is favored over a narrow

PSD, and the presence of large particle is highly recommended ¹¹. However, few works are dedicated to systematically study the effect of latex PSD on the adhesive properties. Most often, the empirical idea that smaller particle sizes favor adhesive properties prevails ¹². In combining product application with product manufacturing, one of the aims of the work described in this paper is to assess the effect of particle size and PSD on the adhesive properties of films of model PSA. Next, a recently developed synthesis methodology, which is comprised by the combination of a viscosity equation and a polymerization model is used to produce two high solids content latexes. The same formulation is used, however the knowledge based is employed to vary the polymerization strategy in order to generate a different final PSD, capable to enhancing the adhesive properties as well as decreasing the latex viscosity.

Experimental

Materials

Model acrylic PSAs were synthesized by free radical polymerization in dispersed media. All latexes used were based on a standard composition of 2-EHA, MMA and AA, 88.2/9.8/2 wt%, respectively.

Polymerizations were carried out in a 500ml jacketed glass reactor equipped with reflux condenser, thermocouple, stainless-steel stirrer at 250 rpm, nitrogen inlet (nitrogen flow at 10 ml/min), and three inlet tubes. The reactor containing the initial charge was heated to the reaction temperature. Then, for the semi-batch polymerizations the semi-continuous

streams were added into the reactor. After the addition period, the reactor was left for at least 2 hours at the polymerization temperature, then it was cooled to room temperature. No coagulum was found in the reactor walls or in the surface of the stirrer. Table 1 illustrates the formulation and the polymerization procedure used in the synthesis of the two concentrated latexes. Solids contents were measured by gravimetry and particle size distribution by capillary hydrodynamic fractionation (Matec 2000).

REACTIONS	R1 - Bimodal	R2 - Shot addition
Initial Charge	<ul style="list-style-type: none"> · DDI water: 30 g · Large seed latex: 53 g (solids content: 50%, particle size: 590 nm) · Small seed latex: 13 g (solids content: 50%, particle size: 34 nm) 	<ul style="list-style-type: none"> · DDI water: 15 g · Large seed latex: 50 g (solids content: 50%, particle size: 590 nm) · Small seed latex: 6.4 g (solids content: 50%, particle size: 34 nm) · Disponil A3065: 0.23 g
Additional Streams	Feeding time: 240 min.	Feeding time: 240 min.
Initiator	<ul style="list-style-type: none"> · DDI water: 30 g · (NH₄)₂S₂O₈: 2.9 g 	<ul style="list-style-type: none"> · DDI water: 30 g · (NH₄)₂S₂O₈: 2.88 g
Neat Monomer or Pre-emulsion	<ul style="list-style-type: none"> · DDI water: 77 g · Disponil A3065: 1.1 g · Dowfax 2A1: 4.9 g · NaHCO₃: 0.22 g · Monomer *: 292.5 g 	<ul style="list-style-type: none"> · DDI water: 70 g · Disponil A3065: 1.1 g · Dowfax 2A1: 4.8 g · NaHCO₃: 0.22 g · Monomer *: 299.4 g
Small seed latex ⁽¹⁾		<ul style="list-style-type: none"> · Small seed latex: 19.4 g (solids content: 50%, particle size: 34 nm)
Temperature (°C)	70	70
Final total solids content (%)	64.2	67.7

Table 1: Formulations used for the synthesis of the model PSA latexes. Monomer *: The same monomer composition was used in all polymerizations: 2-EHA/MMA/AA – 88.2/9.8/2 wt%. ⁽¹⁾(³)Three shot additions of equal volume at 60 min, 120 min and 180 min.

Two model PSA latexes were used in the assessment of the effect of the PSD on the adhesive properties of films cast therefrom. The large particle size latex had a number average particles size of 580nm, whereas the small particle size latex was characterized by an average of 34nm. Blends of the Large and Small model PSA latexes were all made on wet basis. Latexes' proportions were all calculated on weight basis. The blends are further described in Table 2.

Experiment	Small particles latex, S	Large particles latex, L
S2L8	20% w/w	80% w/w
S4L6	40% w/w	60% w/w
S5L5	50% w/w	50% w/w
S6L4	60% w/w	40% w/w
S8L2	80% w/w	20% w/w

Table 2. Composition of the blends of large and small particle size model PSAs.

Latex Characterization

The glass transition temperature, T_g , of the large and small model PSA latexes were determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min. The DSC 2920 Modulated DSD from TA Instruments was used.

Dynamic shear moduli were measured with a parallel plate rheometer (RDA II, Rheometrics) at frequencies

between 0.02 and 500Hz, and at a temperature varying between –80°C and 150°C. Samples of selected model PSAs films were obtained from dried latexes in the form of discs. The dry polymer samples were deposited between the two 8mm diameter plates of the rheometer, and the oscillatory shear measurements were carried out. The samples were mechanically oscillated at a strain that did not exceed the linear viscoelastic region of the material.

Probe Tack Experiment

The samples were made by depositing the corresponding amount of latex on a polished glass substrate so as to obtain an adhesive film of approximately 100µm thickness. The films were formed from the latexes by water evaporation at 50°C, and further drying until constant weight at room temperature.

The probe tack experiments were done on a custom-designed apparatus adapted on a MTS 810 hydraulic testing machine, schematically shown on Figure 1. The sample is fixed on the upper plate, which is connected to the load cell. Parallelism between the sample and the probe is controlled through micrometer screws. The probe is fixed on the mobile lower shaft and its displacement is controlled with an LVDT transducer. The entire process of contact between the probe and the film, and the subsequent debonding were followed from under the glass slide with a 45° mirror and a video camera placed outside the testing chamber. In order to enhance the definition of the images the sample was illuminated with a fiber optic light source. The displacement resolution of the tack instrument is of the order of 1µm, while the force resolution is approximately 0.2N.

The tack tests procedure consisted of first bringing the probe into contact with the film at a constant speed of 30µm/s. Next, the compressive force of 78.5N (corresponding to 1MPa nominal contact pressure for 100% contact area) was applied. The probe was left in contact with the adhesive for 1s. Finally, the probe was removed at a constant speed, which was varied among the values of 1, 10 and 1000µm/s. All experiments were carried out at room temperature. During each experiment, the force, the displacement of the crosshead, and the test elapsed time were simultaneously acquired. All tests were filmed and tape-recorded with a black and white CCD camera. Selected images were then digitized and analyzed. Digital images were used to assess the real contact area between the probe and the film. Furthermore, digital images were used to compare the debonding stage of different adhesives.

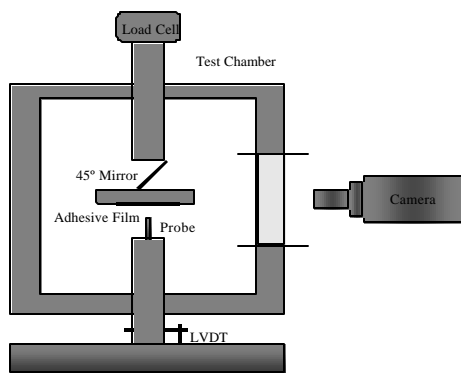


Figure 1. Overall schematics of the probe tack apparatus

Results

The thermographs obtained in the characterization of the Large and Small model PSAs are shown in Figures 2 and 3. A slight difference in the T_g values was observed.

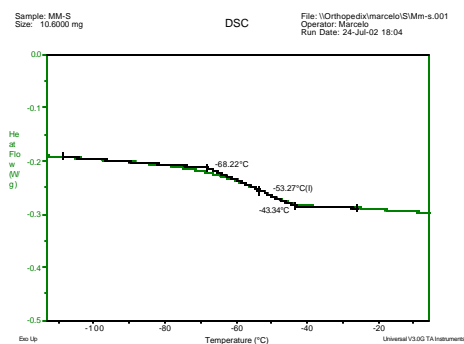


Figure 2. Small particles Latex DSC thermograph.

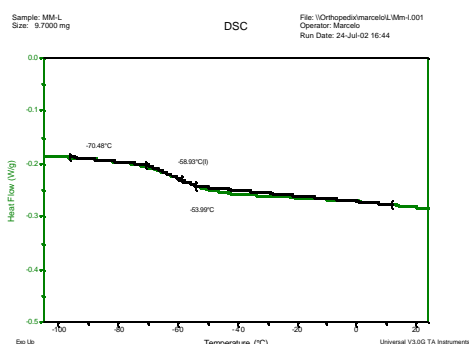


Figure 3. Large particles Latex DSC thermograph.

The PSD characterization of the model PSA latexes used to cast the adhesive films is given in Figures 4. The rheological curves obtained in the characterization of the films made out of the model PSAs small and of the blend S6L4 are given in the Figures 5 and 6 respectively. According the Chang³⁷, the performance of commercial PSAs can be related to the T_g and plateau modulus as well as the frequency dependence of dynamic testing. Good PSA systems should have a depression of modulus at low frequencies (making

bonding favorable) and an elevation in the high frequency modulus (making debonding stronger). All model PSA latexes used in this study showed the characteristics described by Chang³⁷.

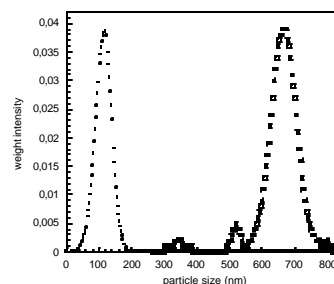


Figure 4. Particle size distribution of the Small (?) and Large (?) model PSA latexes.

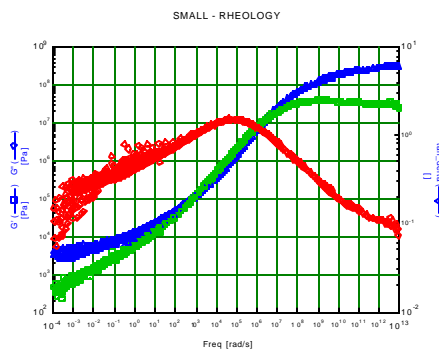


Figure 5. Rheometric curve of the model PSA Small film. $G'(\omega)$, $G''(\omega)$, $\tan \delta(\omega)$

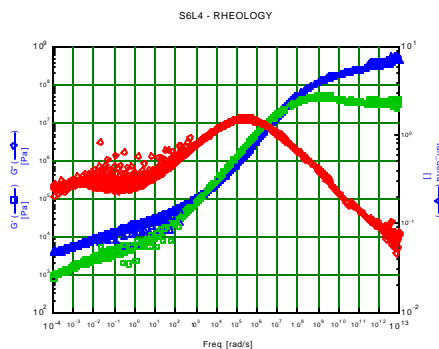


Figure 6. Rheometric curve of the model PSA S6L4 film. $G'(\omega)$, $G''(\omega)$, $\tan \delta(\omega)$

The results given in Figures 5 and 6 showed some slight differences in the value of the model PSA moduli. Rheological measurements were made from dried polymer samples in the form of small disks. Nevertheless, the curves showed a rather similar behavior, with the elastic and viscous moduli increasing with increasing frequency and the same maximum of $\tan \delta$. Accordingly, based on the rheometric results, rather similar adhesive characteristics could be expected from the model PSAs assessed.

Figure 7 shows the $\tan\delta$ at the reference temperature of 30°C for the model PSAs. Some differences can be seen in the master curve of $\tan\delta$. The general physical meaning of $\tan\delta$ is that of a dissipative factor, which can be used as an empirical indicator of PSA performance. Based on the data shown in Figure 7 some differences, which were not clear from Figures 5 and 6, in adhesive properties could be expected between the model PSAs. The Large model PSA would be a more elastic adhesive, the Small, which had a distinctively higher value of $\tan\delta$ in the range of frequencies investigated, would be more viscous, and the blended adhesives would present an intermediary behavior. Nevertheless, the differences should occur only at high debonding rates, where the differences of $\tan\delta$ are more marked. That is, for moderately high and moderately low debonding rate the analysis of the rheological data of the model PSA indicated that they would have an equivalent adhesive performance. Figures 8 to 10 show the probe tack curves of selected experiments with the Small and Large model PSA, as well as the blends made thereof. The debonding rate of the probe tack tests were of 10, 100 and 1000 $\mu\text{m/s}$ for Figures 8, 9 and 10, respectively.

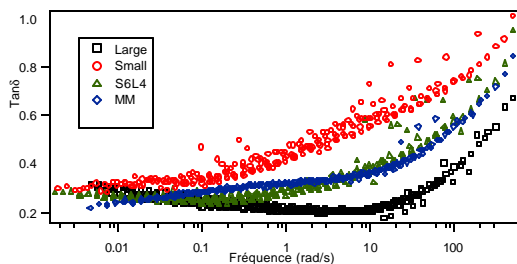


Figure 7. Master curve of the $\tan\delta$ at the reference temperature of 30°C for the model PSAs.

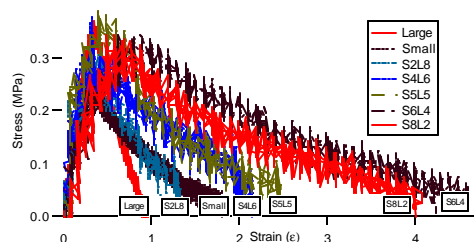


Figure 8. Probe tack curves for debonding rate of 10 $\mu\text{m/s}$.

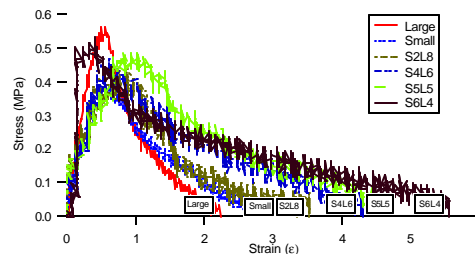


Figure 9. Probe tack curves for debonding rate of 100 $\mu\text{m/s}$

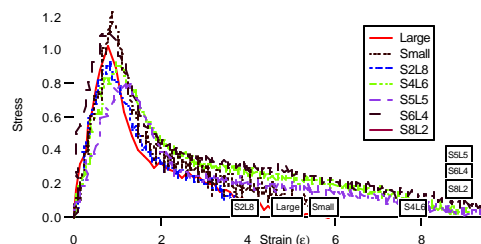


Figure 10. Probe tack curves for debonding rate of 1000 $\mu\text{m/s}$.

It was quite surprising to see remarkably different adhesive properties from the blends made with the Large and Small model PSAs. For blends composed by over 20% of small particle, the probe tack curve showed greater values of ϵ_{max} and W_{adh} than the curves for the pure Large and Small model PSA. At the three different debonding rates, similar values of the curve peak were obtained, irrespective of the model PSA assessed.

A question that immediately arises, given the different probe tack curves, concerns the micromechanism of adhesive failure. As pointed out previously, imaging the probe tack tests helps to elucidate this point. From the video recorded during the tests, key images were digitized. Despite the different probe tack test curves, the pictures were rather similar (results not shown), implying a similar micromechanism of adhesive failure initiated by a cavitation process, and followed by a lateral propagation of the cavities at the interface between the probe and the film. Therefore, the measured values of force and displacement can be directly compared between different films produced from different latexes. The analysis of the pictures from the debonding process of the tests corresponding to the blends of the Large and Small model PSAs also revealed that the adhesive failure occurred by a similar micromechanism.

The average properties of the probe tack tests are illustrated on Figure 11 to 13. The error bars represented in the figures correspond to the deviation obtained in the measurement of the property. Figure 11 shows the maximum stress s_{max} at the three tested debonding rates. Figure 12 shows the maximum strain ϵ_{max} , whereas figure 13 shows the energy of adhesion. These figures show the results for three debonding rates. Regardless of particle size, the values of s_{max} ,

ϵ_{max} and W_{adh} increased with debonding rate. This effect is well documented, and is due to viscoelastic behavior of the adhesive film^{6,17}.

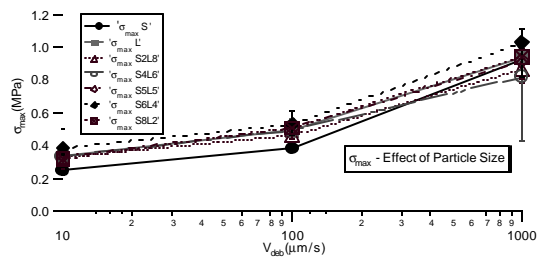


Figure 11. Maximum stress of models PSA at different debonding rates.

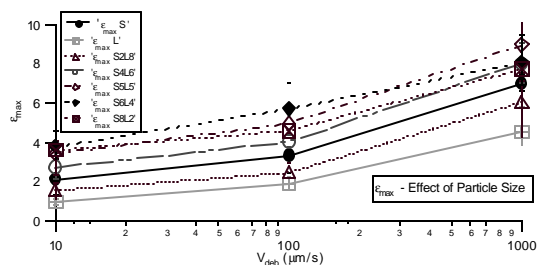


Figure 12. Maximum strain of models PSA at different debonding rates.

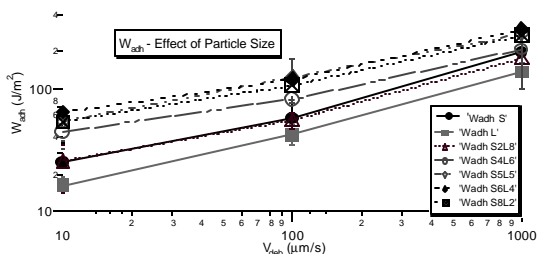


Figure 13. Energy of adhesion of models PSA at different debonding rates.

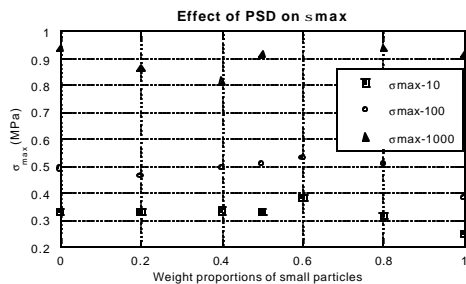


Figure 14. Maximum stress as function of the blend composition of model PSAs.

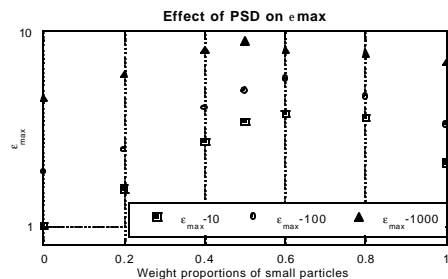


Figure 15. Maximum strain as function of the blend composition of model PSAs.

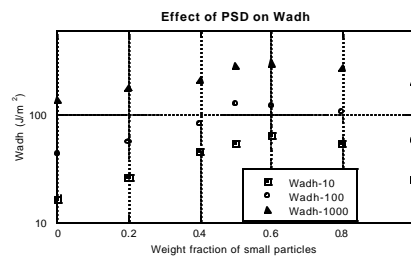


Figure 16. Energy of adhesion as function of the blend composition of model PSAs.

Almost the same value of s_{max} was obtained in all experiments, as shown in Figure 10. The results corroborated with the equivalency already discussed in the rheological experiments, and the similar population of defects in the adhesive layer observed in the images of the probe tack experiment. On the other hand, both e_{max} and W_{adh} showed a marked variation among the model PSAs assessed. Except for the model PSA S2L8, which gave results intermediate from the Large and Small model PSA, synergy was observed for other compositions of the Small and Large model PSA. The probe tack results are further discussed in Figures 13 to 15 as function of the proportion of the Small model PSA latex present in the emulsions used to cast the adhesive films. Figures 13 and 14 give the mean values of the maximum strain and stress, respectively, as function of the particle size composition. The 0% of small particle refers to the Large model PSA. Figure 15 shows the W_{adh} as a function of the PSD of the model PSAs.

Interestingly, a consistent behavior at all tested debonding rates was observed. For blends consisting of equal to or greater than 40 wt% of small particles the adhesive properties were superior to the adhesive properties of the parent compounds. Moreover, the adhesive properties showed a maximum in adhesion energy and maximum strain as a function of the latex PSD used to cast the adhesive film. Blends with 80wt% of small particles also showed synergy, but the results were inferior to the optimum of properties detected at a composition of 60wt% of small particles. The results suggested that for a fixed copolymer composition it would be possible to influence the adhesive properties by changing the PSD of the latex.

The product application characteristic clearly indicated to the product manufacturing step the great potential to play with the latex PSD. In order to study the adhesive properties, model PSA latexes with 50% solids content were used; however, the greatest interest relies on the synthesis of concentrated latex.

Before carrying out the experiments, the polymerizations were simulated using the coupled polymerization-viscosity model developed by do Amaral and Asua⁴. Basically, it consists of a means of computing the particles competitive growth (Equation 1) and then updating the PSD of the polymer dispersion in order to calculate the viscosity of the aqueous polymer dispersion (Equation 2).

$$\frac{dv_i}{dt} = k_p [M]_p \frac{\tilde{n}_i}{N_A} \frac{P_M}{r_p} \quad (1)$$

where k_p is the propagation rate coefficient, $[M]_p$ is the monomer concentration within the polymer particles, P_M is the molecular weight of the monomer, r_p is the polymer density and N_A is the Avogrado number and \tilde{n}_i is the average number of radical per particle.

$$\ln\left(\frac{h}{h_0}\right) = \left(\frac{[h]j_n}{s-1}\right) \left[\left(\frac{j_n-j}{j_n}\right)^{1-s} - 1\right] \quad (2)$$

where h_0 is the continuous media viscosity, $[h]$ is the intrinsic viscosity, f_n is the maximum packing fraction, f the volume fraction and s is the particle interaction coefficient⁴⁶. The great advantage of the proposed viscosity equation is that the magnitude of s is related to physico-chemical characteristics of the system, mainly the surfactant composition and type of initiator. Using this knowledge-based strategy it was possible to predict the final viscosity equation of the polymerization procedure consisting of shot additions of small particles. Accordingly, by such procedure not only the polydispersity of the PSD is broadened, due to the addition of the small particles during the course of the polymerization, but also the viscosity is lowered for a fixed volume fraction. Figure XX compares the predicted evolution of the viscosity during the reaction for the two polymerization procedures. It can be seen that the system obtained by the shot addition methodology is predicted to reach a lower viscosity even at a solids content higher than the final polymer concentration of the reaction using only two polymer seeds.

The PSD obtained for the two latexes is represented in Figure XX, which clearly shows that a bidisperse PSD was obtained for the first polymerization procedure. On the other hand, for the shot addition strategy a very broad a polydisperse PSD was obtained. Table XX shows the final solids content and the value of the viscosity for both latexes. The viscosity results agree with the tendency predicted by the coupled polymerization-viscosity model.

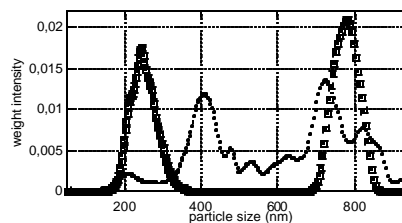
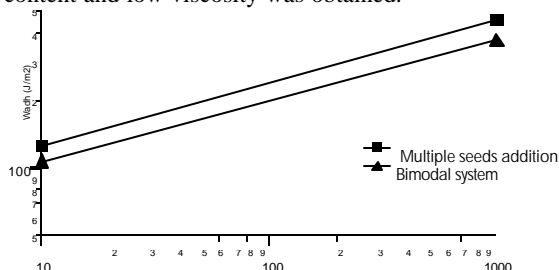


Figure 6. Particle size distribution of the MM2 (—) and MM (---) model PSA latexes.

Now, it is important to turn the attention to the product application. According to the observation for the model systems previously discussed, a broader PSD would enhance the adhesive properties of films obtained from such latexes. Figure XX compares the energy of adhesion of the two concentrated latexes. In spite of the using exactly the same polymerization formulation, only the polymerization procedure was changed, it was possible to enhance the adhesive properties only by playing with the PSD of the latex used to cast the adhesive film. Furthermore, this product application result was obtained in a strategy combined with product manufacture, where a latex with high solids content and low viscosity was obtained.



Conclusions

The probe tack tests showed a marked difference in adhesive properties that could be possibly related to the particle size and PSD of the model emulsion PSA. The characterization of the model PSAs used in the study gave similar results, and the same copolymer composition was used in all polymerizations, remaining the PSD as the main difference among the adhesive latexes.

For the first series of experiments, using a small and a large particle size and blends from both latexes, a marked improvement of the adhesive properties were detected as a function of the PSD. The blends of Small and Large model PSA showed a synergistic effect, overcoming the results of the parent model PSAs. According to the results, the optimum of adhesive properties could be attained for a proportion of small particles close to 60 wt%.

Product manufacturing strategies obtained by the knowledge-based methodology could take advantage of the product application tests. Using a coupled polymerization-viscosity model it was possible to

propose an alternative shot-addition reaction strategy capable of obtaining a model PSA latex with very high solids content, low viscosity. The experimental results were in accordance with the model predictions. Furthermore, it was possible to obtain an adhesive with better properties, just by tuning the product manufacturing conditions.

Acknowledgements

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References

1. A. Guyot, F. Chu, M. Schneider, C. Graillat, T. McKenna *Prog. Polym. Sci.* 2002, 27, 573.
 2. H. Maron, B.P. Madow, I.M. Krieger *J. Colloid Sci.* 1951, 6, 584.
 3. A. Einstein *Ann. Phys.* 1906, 19, 241.
 4. I.M. Krieger, T.J. Dougherty *Trans. Soc. Rheol.* 1959, 3, 137.
 5. M. Mooney *J. Colloid Sci.* 1952, 6, 162.
 6. R.D. Sudduth *J. Appl. Polym. Sci.* 1993, 48, 25.
 7. R.D. Sudduth *J. Appl. Polym. Sci.* 1993, 48, 37.
 8. M. do Amaral, Tese de Doutorado, Universidad del Pais Vasco (Espanha), 2003.
 9. C.S. Chern, C.H. Lin *Polym. J.* 1996, 28, 343.
 10. J. Philip, G. Gnana-Prakash, T. Jaykumar, P. Kalyanasundaram, O. Mondain-Monval, B. Ray *Langmuir* 2002, 18, 4625.
 11. E.J. Schaller, A.E. Humphrey *J. Colloid Sci.* 1966, 22, 573.
 12. F. Chu, C. Graillat, A. Guyot *J. Polym. Adv. Technol.* 1998, 9, 844.
 13. M. do Amaral, J.M. Asua *Macromol. Theory and Simul.* (enviado).
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