NOVEL HYBRID EMULSION PRESSURE SENSITIVE ADHESIVES

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Abstract

It is well-known that hybrid polymer materials that combine different polymers often exhibit superior properties to their each individual constituent polymer, such as rubber toughened epoxies and certain engineering plastics such as the acrylonitrile-butadiene-styrene copolymer (ABS). Moreover, in recent years the development of polymer emulsions for coating and adhesive applications has progressed significantly because they are more environmentally friendly than their solvent counterparts. To take the advantage of both technologies, we have successfully developed a novel hybrid polymer emulsion by incorporating a vinyl acetate-ethylene copolymer dispersion as the seed with subsequent emulsion polymerization of acrylic and/or methacrylic monomers. The application of such hybrid polymer emulsions as pressure sensitive adhesives is demonstrated. The performance advantages of such hybrid polymer emulsions over their physical blend counterparts are discussed.

Introduction

Pressure sensitive adhesives (PSAs) are simply soft polymers characterized by instantaneous adhesion on most surfaces upon application of a light pressure. However, the design of a PSA suitable for a certain application is rather complex and depends heavily on polymer chemistry (e.g., acrylic vs. silicone) and/or formulation to achieve a properly cross-linked polymer network with optimized adhesion properties. Due to the increasingly stringent environmental regulations, acrylic polymer emulsions have been extensively used in the PSA industry for a variety of applications such as labels, graphics and tapes because they are more environmentally friendly than their solvent counterparts.

Meanwhile, there is also an increasing interest in developing hybrid polymeric materials based upon combinations of different polymer backbone chemistries because the resulting materials may exhibit superior properties as compared to the properties of their individual component polymers. Rubber toughened epoxies and certain engineering plastics such as ABS are examples of such classical hybrid materials.

Thus, a rational and perhaps feasible approach to improve and/or adjust the performance of a PSA is to incorporate another polymer to generate hybrid materials. These hybrid materials could potentially lead to a combination of favorable properties from each individual polymer component into one PSA. For example, a polyether-polyacrylate type PSA system has been successfully developed for foil tape applications in the HVAC industry with high holding power in addition to its superior adhesion on low surface energy substrates. [1] Another such example is to graft a rubber component to an acrylic backbone to increase its compatibility with non-polar tackifiers to enable good bonding to low surface energy substrates.[2]

Over the years, several hybrid latexes such as alkyd/acrylic, polyurethane/acrylic and inorganic/organic polymer latexes have been developed and reported in the literature. Udagama et al. reported the synthesis of acrylic-polyurethane (PU) hybrid latexes by miniemulsion polymerization and their applications as PSAs[3]. Degrandi-Contraires et al. studied the mechanical properties of the corresponding adhesive films obtained from such acrylic-PU hybrid particles.[4] Due to its inherent heterogeneous structure, the acrylic-PU hybrid adhesive has shown a clear improvement in its shear resistance while being able to maintain acceptable adhesion for standard PSA applications.

Although acrylic emulsion polymers are well established for PSA applications, the building blocks for these adhesives make use of acrylic monomers, which are mainly produced from propylene and have experienced significant cost and supply fluctuations over the years. In comparison, the supply of ethylene is more abundant and stable. And, it is well believed that ethylene is more sustainable than propylene from an economic stability perspective.

Comment [ADU1]:

Among ethylene based polymers, vinyl acetate-ethylene (VAE) dispersions are copolymers produced by emulsion polymerization of the hard/polar vinyl acetate monomer and the soft/hydrophobic ethylene monomer. It should be noted that VAE copolymers differ from their counterpart ethylene-vinyl acetate (EVA) copolymers with the difference in their monomer composition. While vinyl acetate is the major component in a VAE copolymer, ethylene is the major component in an EVA copolymer. VAE copolymer dispersions are commercially available in large quantities and are routinely utilized in numerous large volume industrial applications such as paints and coatings, carpet-backing, paper and paperboard coatings, nonwovens, adhesives, redispersible powders and building and construction products.

For PSA applications, VAE copolymers are generally characterized by moderate peel adhesion, low tack, high shear and very limited compatibility with tackifiers. Therefore, it is our goal in this study to incorporate ethylene based polymers, specifically VAE copolymers, into acrylic emulsion PSAs for advantages in performance and/or economics.

In this report, preliminary results are presented from the latest development in the acrylic emulsion PSA technology by leveraging hybrid emulsion technology for desirable PSA performances.

Experimental

Hybrid Emulsion Synthesis

To make a 20/80 (wt/wt) VAE/acrylic hybrid emulsion, into a glass reactor equipped with a reflux condenser, a thermocouple, a pre-emulsion inlet tube, an initiator inlet tube and a pitched turbine agitator, there was charged a pre-determined amount (i.e., 20% of the total polymer weight) of a vinyl acetate-ethylene copolymer dispersion and deionized water. Separately, a monomer mixture (80% of the total polymer weight) consisting of acrylic/methacrylic monomers such as butyl acrylate, 2-ethyl hexyl acrylate, methacrylic acid and acrylic acid was added to deionized water containing suitable surfactants to make a pre-emulsion. The reactor charge was heated to 80 °C, to which was added ammonium persulfate to initiate the polymerization.

After 10 minutes the pre-emulsion was added to the reactor over a period of 230 minutes. Twenty-five (25) minutes after the start of the pre-emulsion, an initiator solution consisting of ammonium persulfate in deionized water was introduced into the reactor for a period of 230 minutes. Fifteen (15) minutes after the initiator solution ended, 19% ammonia was added to the reactor over 10 minutes. After that, the reactor was maintained at 80 °C for 90 minutes. Then, the contents were cooled to ambient temperature and discharged for further testing and evaluation.

Preparation of VAE/Acrylic Physical Blend

To make a 20/80 (wt/wt) VAE/acrylic physical blend, a pre-determined amount (i.e., 20% of the total polymer weight) of a VAE dispersion was slowly added to the corresponding amount of an acrylic emulsion PSA under good agitation. The mixture was blended for at least 30 minutes before subsequent testing and characterization.

PSA Tests

For each PSA sample, the emulsion adhesive was directly coated onto 50 micron thick MYLAR® at a dry coat weight of 22 g/m^2 (grams per square meter), then dried at 120 °C for 5 minutes. Peel values were measured in lb/inch at 12 inch/minute crosshead speed after the specified dwell (i.e., 15 minutes or 24 hours) on stainless steel panels. Loop tack was measured in lb/inch on stainless steel panels according to PSTC-5. Shear values, i.e., time durations in minute until failure, were measured using ½″ × ½″ inch samples with 500 gram weight on stainless steel panels. All tests were performed in a controlled environment room of 21 °C and 50% relative humidity.

Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of hybrid emulsion polymers were measured by DSC, Model Q2000 scanning calorimeter made by TA Instruments, New Castle, DE. The adhesive samples were prepared by direct coating onto a silicone release liner at a dry coat weight of about 25 g/m^2, and then dried at 120 °C for 5 minutes.

Capillary Hydrodynamic Fractionation (CHDF)

The particle size and particle size distribution of VAE/acrylic hybrid emulsions were characterized by CHDF, Model 2000, manufactured by Matec Applied Science, Northborough, MA. All samples were prepared by diluting the original emulsion sample to approximately 1% solids and filtered through a 2.7 micron filter before injection into the CHDF column.

Optical Microscopy

Optical microscopy was performed on Olympus SZX7. The adhesive samples were prepared by direct coating onto 50 micron MYLAR® at a dry coat weight of about 25 g/m^2, and then dried at 120 °C for 5 minutes.

Results and Discussion

Figure 1 below shows the optical micrograph of an adhesive film made from a physical blend of a VAE dispersion and a commercial acrylic emulsion PSA. Due to the incompatibility between the VAE dispersion and the acrylic emulsion, coating defects can be clearly seen in the adhesive film. Those defects will certainly have a detrimental effect on its adhesion performance and visual appearance.

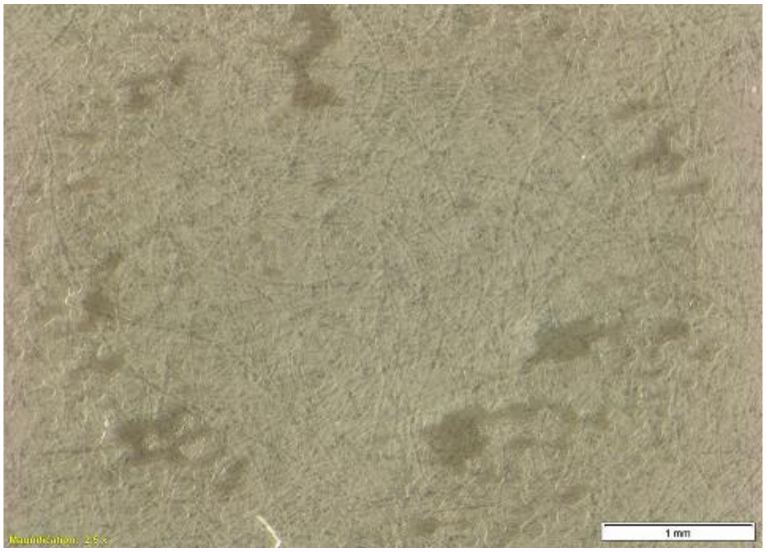

Figure 1. Optical micrograph of an adhesive film prepared with a VAE/acrylic physical blend

In comparison, a defect-free adhesive film can be obtained with the developed VAE/acrylic hybrid emulsion technology as demonstrated in Figure 2. In the hybrid emulsion, the acrylic monomers are polymerized with the VAE dispersion as the seed instead. Therefore, the mismatch between a VAE dispersion and an acrylic emulsion can be overcome. That will allow the incorporation of VAE dispersions into acrylic emulsions for PSA applications.

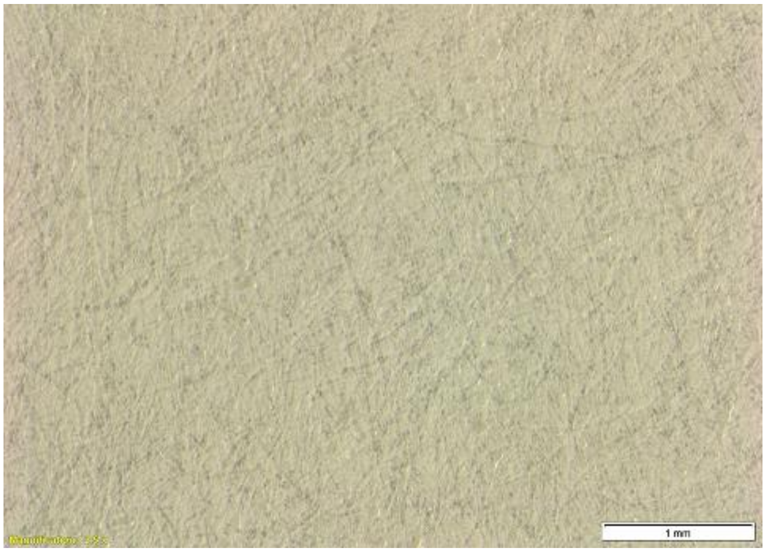

Figure 2. Optical micrograph of a VAE/acrylic hybrid emulsion

Figure 3 below describes the particle size profile of a VAE/acrylic hybrid emulsion, Sample A, as a function of pre-emulsion feeding time measured by CHDF. As can be seen in the chromatograph, the hybrid emulsion particles were growing over time but with only one population of emulsion particles throughout the polymerization without noticeable occurrence of secondary nucleation of new particles. Presumably, a core-shell type of particle morphology might be achieved in hybrid emulsion A.

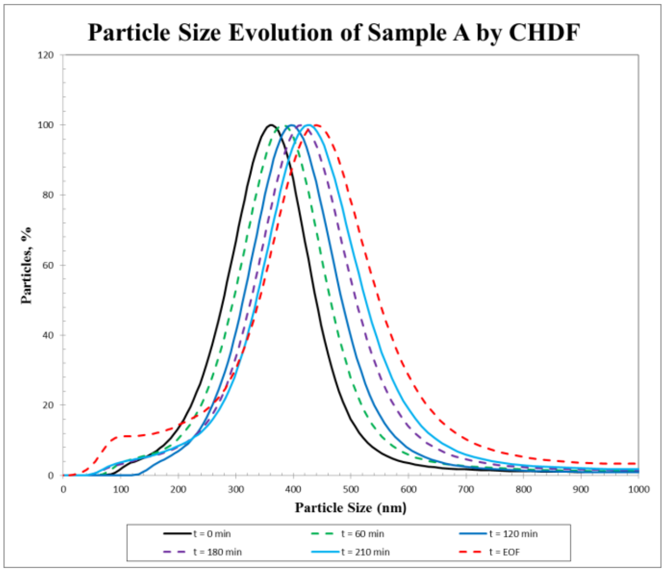

Figure 3. CHDF chromatography of VAE/acrylic hybrid emulsion A

However, as pointed out by Stubbs et al.[3], latex particles made from sequential emulsion polymerization may exhibit a wide range of particle morphologies. The morphology and/or structure of such latex particles results from a number of complex interactions between the thermodynamic and kinetic aspects of an emulsion polymerization process.

Meanwhile, as in conventional emulsion polymerization, the particle size and/or particle size distribution of VAE/acrylic hybrid emulsions can be affected by composition and process parameters. As exhibited in Figure 4, a secondary nucleation of new particles can be clearly seen in hybrid emulsion Sample B 60 minutes after the start of the pre-emulsion feed resulting in two distinct particle populations. As a result, a bimodal particle size distribution has been observed in the final hybrid emulsion product.

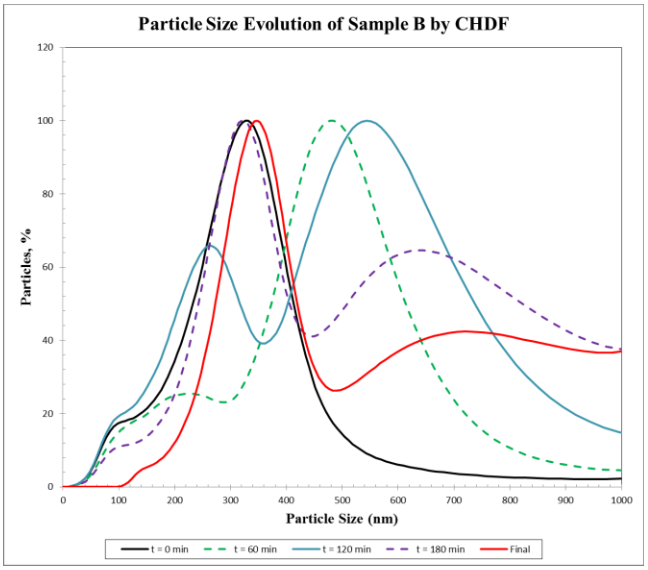

Figure 4. Particle size evolution of VAE/acrylic hybrid emulsion B by CHDF

Due to their chemical nature, VAE copolymers are usually not compatible with acrylic polymers. As a result, phase separation can be expected in such hybrid emulsions. And, it is well-known that such phase separated systems are usually characterized by distinct T_gs with each T_g corresponding to each individual phase.

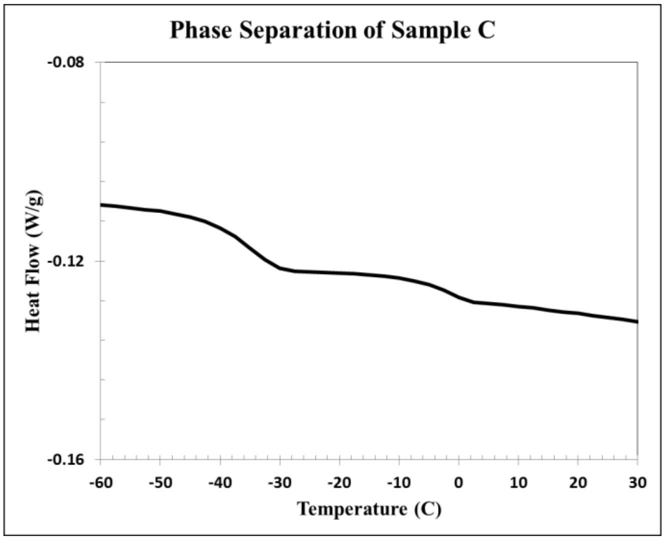

Figure 5. DSC scan of the hybrid emulsion C

Figure 5 represents the DSC scan of a hybrid emulsion PSA, Sample C. Obviously, two T_gs can be observed. The T_g at about 0 °C corresponds to the VAE copolymer dispersion used as the seed to make this hybrid emulsion while the T_g at about -35 °C correlates well to the polymerized acrylic polymer.

The developed VAE/acrylic hybrid emulsions can be found useful in PSA applications. Table 1 below compares the PSA performance of two hybrid emulsions, Sample D and Sample E, side by side with a control emulsion PSA (i.e., the acrylic control) and their physical blend counterpart. The acrylic emulsion control is a commercially available PSA. Twenty percent (20%) of a VAE copolymer dispersion was incorporated in the physical blend and the hybrid emulsions were prepared according to the methods as described in the Experimental section.

Table 1. PSA performance of hybrid emulsion D and E

Sample ID	General Purpose Acrylic PSA	Acrylic Control	Physical Blend	Hybrid D	Hybrid E
VAE/Acrylic (wt/wt)	n/a	0/100	20/80	20/80	20/80
180° Peel, 15 min	3.0	5.3	2.8	2.4	2.6
180° Peel, 24 hour	4.0	5.6	3.9	4.5	5.0
Loop tack	3.8	4.6	3.3	3.5	3.6
Shear, min	360	350	220	370	260

The acrylic emulsion control is a permanent PSA characterized by its high peel adhesion with cohesive failure mode. The 20/80 VAE/acrylic physical blend exhibits both lower peel adhesion and lower cohesive strength than the acrylic emulsion control. This result is not surprising since the incorporated VAE is not a PSA at room temperature with a T_g at about 0 °C by itself. In comparison, the hybrid emulsions, Sample D and Sample E, which have the same monomer composition as the acrylic emulsion control used to prepare the physical blend, exhibit some interesting PSA performance.

Although both hybrid emulsion D and E exhibit lower initial peel adhesion (i.e., at 15 minute dwell) with adhesive failure mode, their peel adhesion performance increased dramatically within a period of 24 hours with a failure mode change from adhesive at 15 minute dwell time to cohesive at 24 hour dwell. Therefore, both hybrid emulsion D and E seem to be useful for applications where temporary repositionability or removability of a PSA from a substrate is required. In addition, the hybrid materials also compare very favorably with a commercial general purpose acrylic emulsion PSA.

Furthermore, the developed VAE/acrylic hybrid emulsion technology can also be used to control the peel adhesion of acrylic PSAs. Table 2 shows the PSA properties of hybrid emulsion F and G, in comparison with the same acrylic emulsion control and their physical blend counterpart above.

Table 2. PSA performance of hybrid emulsion F and G

Sample ID	Removable PSA Control	Acrylic	Physical Blend	Hybrid F	Hybrid G
VAE/Acrylic (wt/wt)	n/a	0/100	20/80	28/72	20/80
180° Peel, 15 min	0.4	5.3	2.8	1.5	2.3
180° Peel, 24 hour	0.8	5.6	3.9	1.5	2.5
Loop tack	1.0	4.6	3.3	1.9	2.6
Shear, min	500	350	220	1100	400

As can be seen, for the 20/80 (wt/wt) physical blend, its peel adhesion increased by about 40% within 24 hours together with a failure mode change from adhesive to adhesive/cohesive. However, the hybrid emulsion F and G show little peel adhesion build-up within the same period of dwell time, even better than the commercial removable PSA control. Therefore, hybrid emulsion F and G are promising for removable PSA applications where no or little adhesion increase over time is desired. It is interesting to see that a non-PSA type of VAE copolymer dispersion can be used to control/minimize the adhesion build-up over time in an acrylic emulsion PSA.

Conclusion

A novel VAE/acrylic hybrid emulsion technology has been successfully developed via VAE seeded emulsion polymerization of acrylic and/or methacrylic monomers. Phase separation has been observed in such hybrid emulsions. Its applications in PSAs have been demonstrated with the potential to expand the performance window and/or application spaces of conventional all acrylic based PSAs.

Reference

1. Zajaczkowski Michael J., "Acrylate-Polyether Based Pressure Sensitive Adhesives", *PSTC TECH 30*, 2007.
2. Forman Paul et al., "Rubber-Acrylic Hybrid Pressure Sensitive Adhesives", *PSTC TECH XXIV*, May 2001.
3. Udagama Ravindra et al., *Macromolecules*, 44, pp. 2632-2642, 2011.
4. Degrandi-Contraires Elise et al., *Macromolecules,* 44, pp. 2643-2652, 2011.
5. Stubbs Jeffrey M. et al., *Journal of Coatings Technology and Research*, 5, pp. 169-180, 2008.

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