INTERACTIONS AMONG INDIVIDUAL COMPONENTS OF AN ADHESIVE FORMULATION AND THEIR AFFECTS ON COATABILITY

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Introduction

One challenge of product development is simultaneously optimizing conflicting attributes. Many formulators have experienced the frustration caused when closing in on one particular target decreases performance for another. Unfortunately, many attributes depend on the same fundamental parameter. In such cases, if this parameter is used to optimize one attribute, often detrimental effects can be seen in others. The present study will address strategies in formulating the wet properties of aqueous adhesives for optimum performance on coaters. What appears to be a rather simple task can have subtleties which if well understood, can lead to more robust operations.

Formulators of aqueous adhesives have many raw materials at their disposal such as polymer emulsions, tackifiers, surfactants, crosslinkers, fillers, thickeners, and defoamers which they must design around targeted adhesive performance and coater operation. Many of these are added at low levels, that is, on the order of a percent or less. However, some formulations require the mixture of polymer emulsions and tackifiers, which are generally used at levels well over a percent. It is the interaction of these major components that typically sets what types as well as the levels of the minor components that will need to be added. On the other hand, there is some flexibility with the selection of the major components where different ones may be chosen that give similar adhesive performance yet have different properties in the wet stage. In fact, suppliers of these components can often intentionally vary the characteristics of their dispersion.

Raw Material Specifications

Most raw materials have a set of specifications which include solids, viscosity, and pH. Perhaps the first consideration of how things will behave on a coater is if the viscosity is in the appropriate range. Even if it is, there is no guarantee that material will coat well. Part of this is because most emulsions are shear thinning, that is, viscosity decreases as shear is applied. The measurement of viscosity as a function of shear rate is considered to be part of its rheology (the study of flow and deformation). Since different parts of a coating process apply different shear rates, it is best to try to correlate viscosity at the shear rate that is being applied by coating at the point under consideration.

Usually specifications are given based on measurements at lower shear rates such as a Brookfield viscometer. Data that are supplied below are based on Brookfield measurements and are used as an illustration what effects can be observed. A more thorough analysis would include data over a range of shear rates that is relevant to the coating process being considered.

In addition, differences in the pH of two materials can result in unanticipated results, especially when one of the emulsions is self thickening. The base or acid in one system can activate and depress the self thickening mechanism in the other. In this case, substantial changes in viscosity can occur when the systems are mixed. Also stability issues can arise if the different components are stabilized by different mechanisms.

Rheology and Coating

One characteristic of a dispersion that impacts how well it coats is its rheology and this must be well optimized for any individual coater. The challenge here is that in the pressure sensitive adhesive industry, there are still a wide variety of coaters that are used. No one formulation fits all. For example, most gravure coaters require lower viscosities so that gravure cells can be readily filled and emptied.

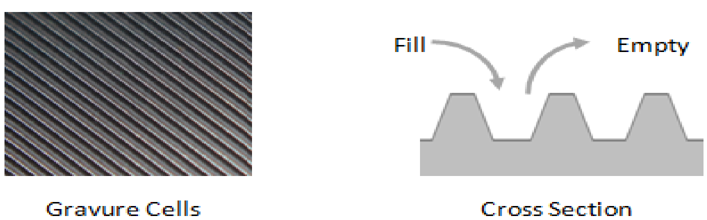

Figure 1. Gravure Cylinder

Wire wound rod coaters also generally prefer lower viscosities, mainly because higher viscosity can result in poorer coat weight control at higher line speeds. Other coaters, such as slot die and curtain coaters prefer higher viscosities. For example, if the viscosity is too low, the region between a die and backing roll can have poor stability in slot die operations. Also, too low of a viscosity can destabilize the free falling emulsion, also known as the curtain, in curtain coaters and cause the emulsion to break up.

Table 1. Rheology for Common Coaters

Coating Method	Common Brookfield Viscosity Range	Common Rheology Profile
Reverse Gravure	150 – 400 cps	Shear Thinning
Slot Die	500 – 2000 cps	Optimum Window
Wire Wound Rod	50 – 300 cps	Shear Thinning
Curtain	500 – 1500 cps	Optimum Window

Design of Emulsion

It is well known that the viscosity of an emulsion depends on its solids content as well as its particle size. If the emulsion is comprised of a single, unimodal particle size distirbution, then either higher solids or smaller particles lead to higher viscosity.

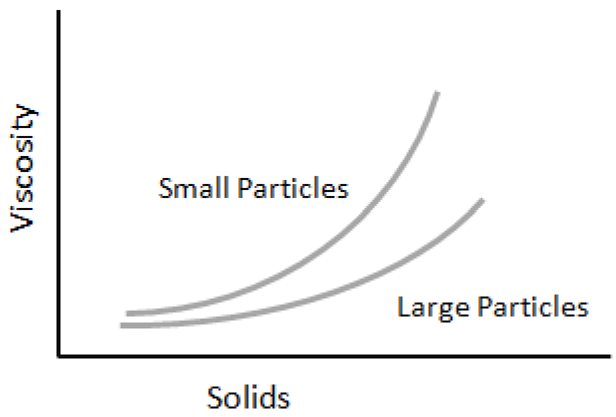

Figure 2. Impact of Particle Size on Viscosity

One advantage of emulsion polymerization is that it is relatively easy to set particle size. Nevertheless, the smaller the particle size, the more difficult it is to make a higher solids emulsion owing to viscosity constraints. To illustrate this, a range of acrylic pressure sensitive adhesives were prepared where all the attributes of the polymerization were maintained except particle size. In this particular case, the only reactant that was varied was the amount of preform seed used to set the particle size. The more seed that is used, the more particles formed and the smaller each particle is. Moreover, water was added to keep roughly the same in-process viscosity throughout the runs. Applying these restrictions led to following series:

Table 2. Unimodal Acrylic Emulsions

Sample	% Solids	Viscosity (cps)	Particle Size (nm)
A	56.1	98	550
B	55.4	132	335
C	55.6	108	406
D	55.7	142	318
E	53.3	173	219
F	52.7	165	213

Unimodal systems can have solids limitations. As an example, consider the case where unimodal particles are packed as closely as possible. As can be seen in Figure 3, there is clearly space between the particles where smaller particles could be placed.

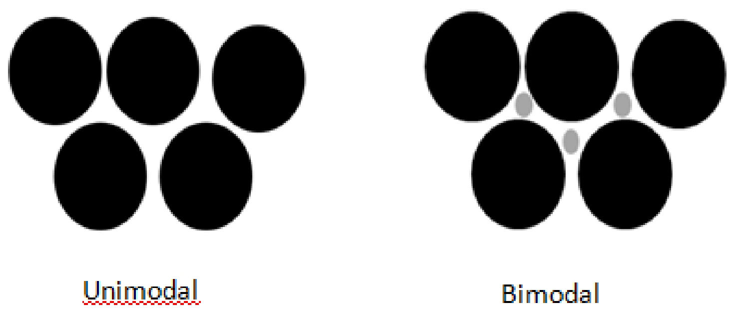

Figure 3. Packing Efficiencies

In a bimodal distribution, it is relatively a straight-forward exercise to vary the diameter of one mode to establish optimum packing. In reality, many commercial products are comprised of several modes and hence the response surface for optimum packing is much more complex.

The same theory can be applied to what happens when emulsions are blended. As an example, mixtures of the various emulsions (Acrylics A, C, and F) were prepared as blends along with a small amount of thickener and viscosities were measured. All samples were adjusted to 52% solids. When an experimental design is used to characterize the response, it can be clearly seen that certain combinations lead to minimum viscosities.

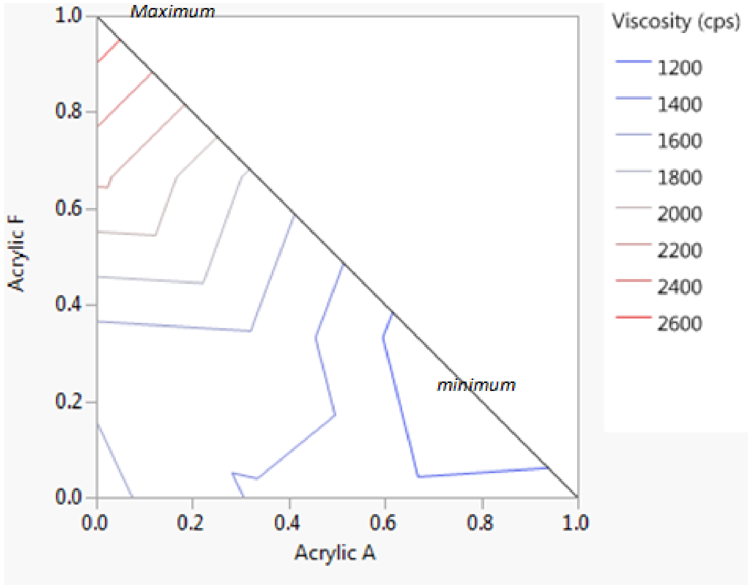

Figure 4 Viscosity of Acrylic Emulsion Mixtures

Although Acrylic C is not explicitly listed, its level can be inferred since the sum of all components must equal 1. These data behave as expected, the maximum viscosity is observed at 100% small particle size (Acrylic F). Also, an absolute minimum is observed when a combination of the largest particle size and smallest is used. Note there is a much weaker minimum in combinations that just consist of Acrylic F and Acrylic C.

Other Blends

Formulators have numerous commercial products from which to choose for optimizing the adhesive performance characteristics of their formulation. Perhaps one of the most common formulating components that can comprise a significant portion of a mixture (>10%) is tackifier. Tackifiers are usually produced by a much different process than emulsions. Most commonly, mechanical means are used to disperse the molten tackifier along with a phase inversion process. Although it is a very effective method, particle size distributions are broader, tend to be unimodal, and multimodal distributions with well targeted sizes are not produced. However, the mean of the particle size itself can be controlled. Typically, tackifiers are added to improve tack and peel. When formulating with tackifiers, there are limited ranges that produce an advantaged result in adhesive properties. As an illustration, a tackifier ladder in acrylic emulsion was prepared and loop tack on stainless steel was measured according to PSTC test method #16.

Table 3. Loop Tack and Tackifier Level

Tackifier level (%)	0	10	20	30	40	50
Loop Tack (lb/in)	1.4	2.4	2.7	2.9	3.4	1.8

At lower levels of tackifier, there is too little material in the formulation to have significant impact in properties. At levels over 50%, tack decreases which can be caused by either increasing the glass transition temperature too much or incompatibility. In any event, these data demonstrate why 10% to 40% tackifier level is a suitable starting point for so many mixture designs.

When mixing components with different breadth of the particle size distribution, the viscosity response becomes even more complex, and a tackifier – acrylic emulsion blend is a prime example. Samples prepared by emulsion polymerization can have much narrower particle size distribution than those prepared by mechanical means.

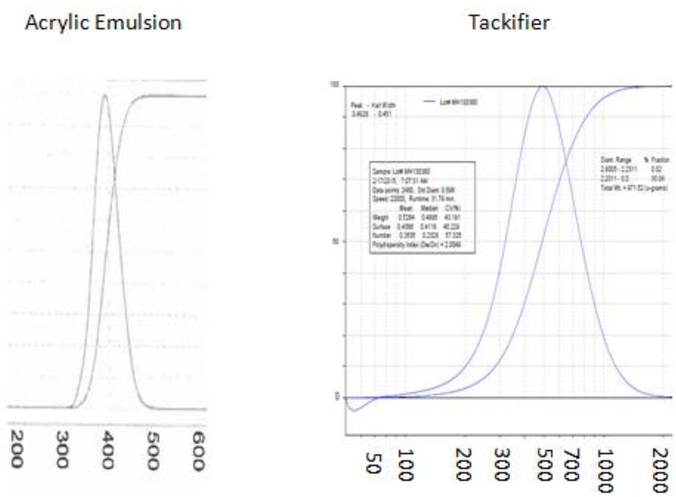

Figure 5. Particle Size Distributions of Selected Emulsions

To illustrate this point, two tackifiers were selected with a mean particle size of 270 nm and 360 nm and were each blended with unimodal acrylic emulsions. In particular, each mixture design consisted of three components, a tackifier, Acrylic A and Acrylic F emulsions.

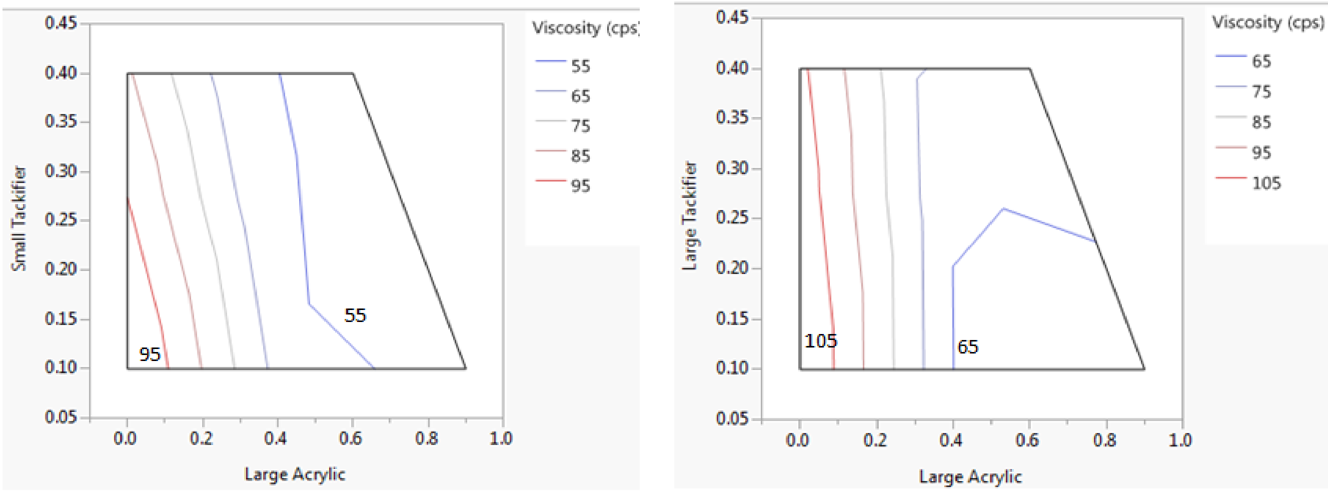

Figure 6. Tackifier in a Bimodal Acrylic Emulsion

Since it is highly desirable to restrict the over tackifier level to commonly used levels, the boundary condition of the overall level of tackifier was set between 10% and 40% of the formulation. That is, switching from a large mode tackifier to a small one represents at most a 20% change in viscosity.

Adjusting Rheology

As mentioned above, various coaters used to make pressure sensitive articles have different rheological requirements. One approach to adjusting rheology is through the addition of thickeners or addition of water. Even when the adjustments are straight forward, they do have some potential downsides. If thickeners are to be added, they do require adequate mixing time and some effort in "titrating" in the required level to reach the targeted viscosity. Although water is easy to add, dilution of emulsion requires additional heat and energy to dry.

Drying

Previous studies have shown that both solids and chemistry are critical for optimum drying. If just the effect of solids is considered, its impact on drying can be determined from pilot line studies. For example, if a given composition is prepared at two different solids levels, relative drying rates can be established by studying exit web temperatures from various oven zones and visual appearances as a function of line speed. For example, Table 4 illustrates that 8% lower solids material dries at about 15% to 20% slower rate and hence even solids differences at these levels can have a measurable impact.

Table 4. Impact of Solids on Drying Rates

Solids	Speed (ft/min)	Oven Temps(°C)	Zone 1 Appearance	Zone 2 Appearance
53%	7	38/37/74	Clear	Clear
	8	39/37/67	Clear	Clear
	9	37/34/65	Slight Haze	Clear
	10	36/35/62	Milky	Slight Haze
61%	7	58/56/77	Clear	Clear
	8	45/46/76	Clear	Clear
	9	46/47/69	Clear	Clear
	10	44/47/68	Slight Haze	Clear

Conclusion

Aqueous adhesives with a better coating quality and improved drying characteristics can be formulated through judicious selection of raw materials. At equal solids, blending one emulsion into another can potentially increase or decrease viscosity. With the range of materials a formulator has at hand, there is some flexibility in tailoring the viscosity simply by carefully selecting their wet attributes. This can diminish the need to dilute to achieve lower viscosity or adding thickener for higher viscosity.

Acknowledgements

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