Role of Operating Conditions in Determining Droplet Size and Viscosity of Tackifier Emulsions Formed Via Phase Inversion

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Water-based pressure-sensitive adhesives are formulated by combining a polymer latex with a tackifier emulsion. The latter is an oil-in-water emulsion made by the process of phase inversion. The phase inversion itself is carried out in a stirred tank fitted with a heating jacket by progressively adding water to a water-in-oil emulsion. The point of onset of phase inversion and the characteristics of the emulsion that is formed depend on process conditions; these include temperature, rate of water addition, and agitation speed. The role of these operating conditions is elucidated here. Increasing temperature delayed the onset of phase inversion slightly, but it did not affect emulsion particle size, provided it remained below a critical value. Agitation speed had to be increased upon increasing the water flow rate to prevent increasing the particle size. Finally, the point of onset of phase inversion could be predicted reasonably well using a model available in the literature. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 96–106, 2011

Keywords: tackifier dispersions, phase inversion emulsification, operating conditions, dual coaxial multi-staged impellers, pressure sensitive adhesives

Introduction

Water-based pressure sensitive adhesives (PSAs) are widely utilized in labels, tapes, self-adhesive postage stamps, removable note pads, and medical bandages.[1] They are formulated by combining a tackifier emulsion with a natural or synthetic rubber latex. Tackifiers are resinous emulsions that help to impart tack or stickiness to the adhesives and to balance the cohesive/adhesive performance. When pinewood is distilled, the product is rosin acid, a three-member ring compound containing one carboxylic acid group.[2] Upon reacting rosin acid with potassium hydroxide (KOH), one gets potassium rosinate, a soap which can act as an emulsifier. The rosin acid can also be reacted with ethylene glycol, and the result is a low molecular weight, low softening-point rosin ester which is the primary constituent of a tackifier emulsion. To synthesize the tackifier emulsion, an aqueous KOH solution is added to a molten mixture of rosin ester and some rosin acid under incessant agitation. Water is then continuously fed to the system. At some point, the water-in-oil (W/O) emulsion that is initially formed inverts to give an oil-in-water (O/W) emulsion, and this is the tackifier emulsion. Ideally, the diameter of the dispersed oil droplets in the tackifier emulsion is in the sub-micrometer range, and it is of interest to know how the droplet size, size distribution, and emulsion viscosity depend on the process operating conditions. Note that the role of the relative amounts of the

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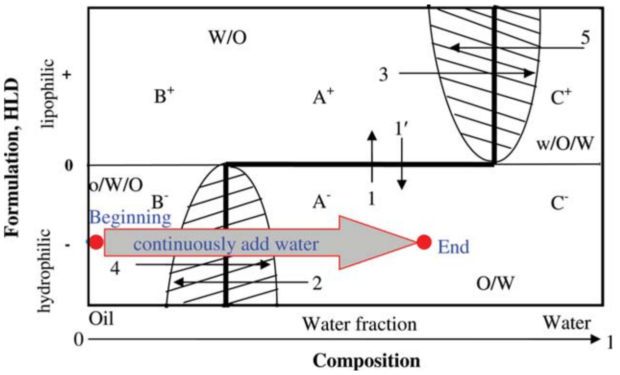


Figure 1. Formulation-composition two-dimensional map showing standard inversion and dynamic inversion loci.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

starting materials has already been addressed in our earlier work.[2]

It is worth mentioning that direct emulsification, that employs shear flow, cannot be used to make tackifier emulsions. This is because the viscosity of the molten resin exceeds that of water by at least two orders of magnitude, and, under these conditions, the viscous oil drops cannot be reduced in size.[3] A logical alternative is the use of the process of "catastrophic inversion" wherein phase inversion is induced by increasing the dispersed phase volume fraction. This technique also has other advantages over direct emulsification.[4,5] One is to yield smaller and more uniform particle sizes, whereas another is to require much less mechanical energy. In addition, one avoids the significant temperature rise that is usually witnessed during direct emulsification.

Emulsion Phase Behavior

The phase behavior of an oil–water-surfactant system is found to be governed by the following four factors[2,6,7]: (1) qualitative composition variables such as the nature of the surfactant and the two phases; (2) quantitative composition variables such as the relative amounts of oil, water, and the surfactant; (3) physical properties of the fluids such as viscosity and density; and (4) formation variables which include the manner of addition of materials (whether periodically or continuously), the feed rate of the initially dispersed phase, the agitation speed plus geometrical parameters like the impeller shape, size, and arrangement within the vessel.

The effects of the first and second categories of factors can be shown by means of the generalized formulation-composition two-dimensional phase map given in Figure 1.[2,8] Here, the water–oil composition is represented on the abscissa, whereas the hydrophilic–lipophilic deviation (HLD) is represented on the ordinate. The positive HLD in the upper part of this figure favors the formation of a W/O emulsion, whereas the negative HLD in the lower part favors an O/W emulsion. However, when the water volume fraction is close to either zero or unity, multiple or "abnormal" emulsions are formed due to a conflict between the effects of formulation and composition. The different regions can be separated by the bold stair-shaped line shown in Figure 1, and this is called the standard emulsion inversion locus. If one crosses the vertical portion of this line along any of the paths numbered 2–5, one observes catastrophic inversion.[5,9] A characteristic feature of catastrophic inversion is the presence of hysteresis zones, shown as shaded areas in Figure 1. This means that if the water volume fraction is increased and the system goes from region B^- to A^-, phase inversion will be delayed, and it will not take place at the moment the solid vertical line is crossed. Furthermore, although Paths 4 and 5 both result in catastrophic phase inversion (from abnormal to normal), systems that follow Path 5 have been more extensively studied. This is because the external phase here is initially water, and electrical conductivity data can indicate changes in the dispersed phase content before phase inversion. When the system follows Path 4, however, the continuous phase is oil, and electrical conductivity data are not very informative. They can only identify the onset of phase inversion. Nonetheless, from the viewpoint of industrial applications such as manufacturing paints, cosmetics and adhesives, $B^- \rightarrow A^-$ (Path 4) is the more important case.[7,8]

For the sake of completeness, we mention that crossing the horizontal portion of the inversion locus, as indicated by arrows 1–1′, leads to "transitional" phase inversion. This can be brought about either by changing the temperature or by changing the formulation, and it is frequently used to make nanoemulsions.[10,11] It should be noted, though, that Figure 1 provides qualitative understanding only. Experiments are still needed to quantitatively determine the actual point of phase inversion and the properties of the emulsions formed as a result of catastrophic inversion.

Role of Operating Conditions

Operating conditions are part of the fourth category of factors governing the behavior of emulsions. These usually consist of the feed rate of the initially dispersed phase, the agitation speed, and temperature. The effect of agitation speed is the most frequently investigated, and it represents the influence of the rate of energy input to the system. Quinn and Sigloh[12] and Selker and Sleicher[13] found that increasing the agitation intensity influenced the onset of phase inversion at low stirring speeds. Phase inversion occurred earlier when the system went from O/W to W/O, but it was delayed when the system went from W/O to O/W. This was confirmed by the work of Guilinger et al.[14] and Kumar.[15] However, these effects were not observed at high stirring speeds, and this was true regardless of other parameters such as the mixer volume, impeller size, and impeller type.[16] Other studies, though, have reported that increasing stirring energy caused a delay of phase inversion from abnormal to normal.[7] Also, Mira et al.[17] found that the maximum delay occurred at some intermediate agitation intensity rather than at very high or very low stirring intensities. Note that, in all these studies, the flow was either in the transitional or the fully turbulent regime at all the agitation speeds examined.

As far as the effect of the feed rate is concerned, Brooks and Richmond[18] and Tyrode et al.[8] found that a low feed rate of the dispersed phase led to a decrease in the volume fraction of the dispersed phase at the point of phase inversion. The limiting case of a low feed rate is the null feeding rate, resulting in a static process.[8,19] Here, the original

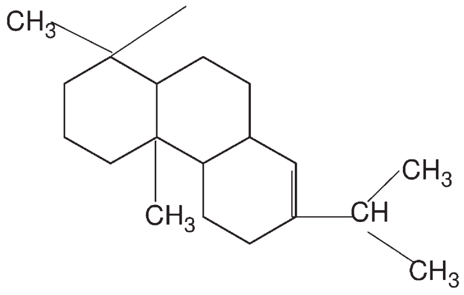


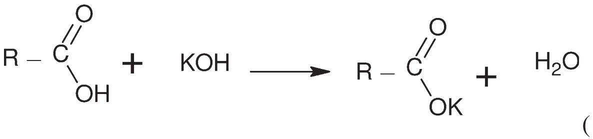
Figure 2. The molecular structure of the group R in rosin acid.

water/oil ratio determines whether phase inversion occurs or not. According to Sajjadi,[19] only when the water/oil ratio is above a critical value does phase inversion take place (W/O→O/W). The static process is, however, only of academic interest, because it has not found practical applications since the time to induce phase inversion is very large.

In the present work, we have systematically changed the operating conditions, and examined the influence of these changes on the point of onset of phase inversion and on the morphology and viscosity of the resulting emulsions. This work was done using an instrumented mixer which has been described in detail in the past.[9] The recipe used to make the tackifier emulsions was not changed during this phase of the investigation, since the effect of changing the recipe has already been examined.[2]

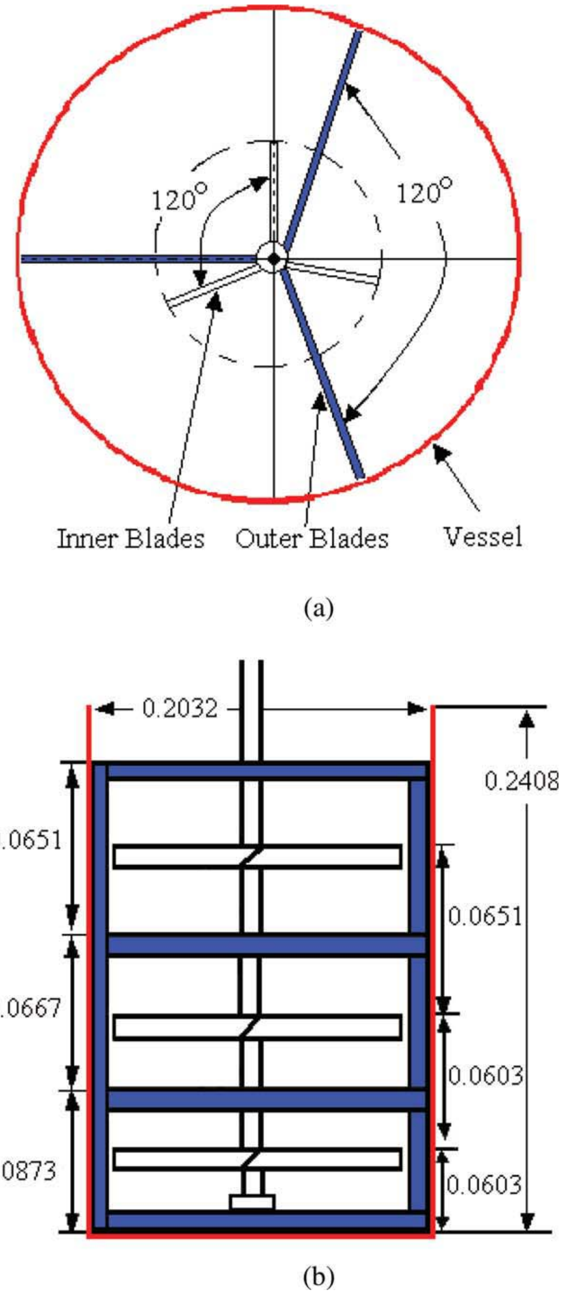
Materials, Equipment, and Experimental Procedure

A rosin ester with a softening point of 25°C from Arizona Chemical (Panama City, FL), a partially hydrogenated wood rosin acid from Hercules (Wilmington, DE) and 45 wt % aqueous KOH solution from Charkit Chemical Corporation (Darien, CT) as well as distilled water were used to make the tackifier emulsions. The specific molecular structures of the rosin ester and the rosin acid are available in the literature.[20,21] When the rosin acid reacts with potassium hydroxide to form a surfactant, the reaction may be represented as:


$$\mathrm{R{-}C(=O)OH} + \mathrm{KOH} \longrightarrow \mathrm{R{-}C(=O)OK} + \mathrm{H_2O} \qquad (1)$$

where the molecular structure of R is shown in Figure 2.

All the emulsification experiments were conducted in the instrumented mixer shown in Figure 3.[9] On the basis of industry practice, for 10 kg of the final emulsion, the initial material fed to the mixer was composed of 5.4 kg rosin ester and 0.162 kg rosin acid. The contents were kept in the molten state at a constant temperature by recirculating hot water through the jacket surrounding the 4 *l* capacity cylindrical mixing tank, and 0.086 kg KOH solution was then added. Agitation was provided by coaxial dual multi-staged impellers. Each of the two impellers can be independently rotated in both directions at different speeds. There are three blades in each stage of both impellers and these are equally spaced around a circle (see Figure 3a). The inner member is a 0.154 m diameter pitched-blade three-staged turbine. The outer member is a 0.2032 m diameter four-staged anchor impeller that functions not only as a stirrer but also as a scraper to remove any accumulation from the vessel wall. The scraping action is needed because the system studied here is very viscous. In the present case, the impellers were counter rotated. The mixer is instrumented, and the variables that can be monitored continuously include the electrical resistance of the emulsion, torque exerted on the inner impeller, agitation speeds of both impellers, power consumption of both



(a)

(b)

Figure 3. (a) Top view of the instrumented mixer and (b) front view of the mixer.

All dimensions are in meters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

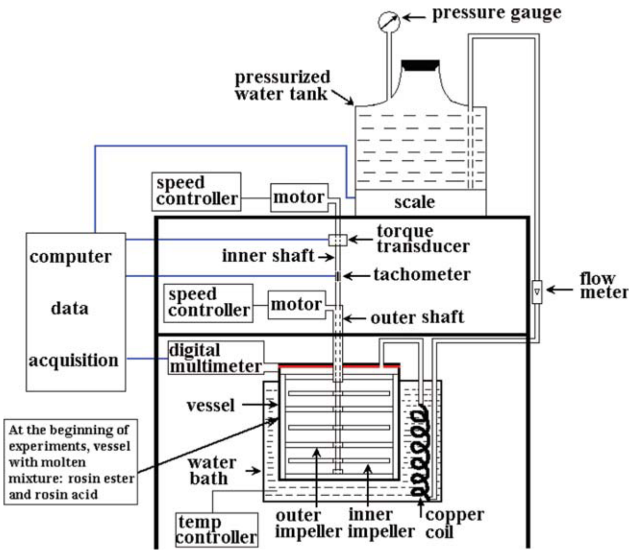


Figure 4. Schematic diagram of the experimental set up.

(Reproduced from Ref 9, with permission from Measurement Science and Technology) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].[9]

impellers, and the flow rate of the feed water. A torque transducer (model: A90-222505-B, Magna-Lastic Devices) was installed on the shaft of the inner impeller to monitor torque, and all variables were recorded by a customized LabVIEW® program. The entire experimental setup is shown in schematic form in Figure 4; additional details are available in Song's dissertation.[20]

The typical sequence of events during the process of emulsification is shown in Figure 5. Once the KOH solution was added to the molten mixture of rosin ester and rosin acid, distilled water was continuously introduced into the tank. At some point, the W/O emulsion that was initially formed inverted to an O/W one. The occurrence of phase inversion was judged by in situ measurements of torque and electrical resistance. After phase inversion, more water was continuously added to dilute and stabilize the newly formed emulsion system.

Once each experiment was complete, samples were collected and analyzed. Key measurements included the particle size and size distribution and the emulsion viscosity. The particle size and size distribution were determined with a laser diffraction particle analyzer (LS230, Beckman Coulter, Fullerton, CA), whereas the sample viscosity was measured using a Brookfield RVT viscometer at room temperature. From the industrial standpoint of quality control, the final emulsion, usually exhibiting shear-thinning behavior, was considered to be good if the mean particle size was less than one micrometer and if the emulsion viscosity ranged between 200 and 2000 mPa s at 20 rpm on a Brookfield viscometer at room temperature. These specifications ensure emulsion stability and proper operation of the subsequent adhesive coating process.

The viscosity of the emulsion changes with time during the experiment, and this becomes obvious simply by observing the consistency of the liquid in the tank. At any given time, the fluid is also shear thinning, so that there is likely to be a variation in viscosity with position in the tank. In this situation, one can define a spatially-averaged viscosity based on torque measurements, and this is a commonly-accepted procedure that is based on the work of Metzner and Otto.[22] If two identical sets of mixing equipment are filled to the same height, one with a Newtonian liquid and the other with a non-Newtonian liquid, and are agitated at the same speed, then the effective viscosity of the non-Newtonian fluid can be calculated as[20,23]:

$$\eta_{\text{non-Newtonian}} = \eta_{\text{Newtonian}} \frac{\text{Power or Torque}|_{\text{non-Newtonian}}}{\text{Power or Torque}|_{\text{Newtonian}}} \qquad (2)$$

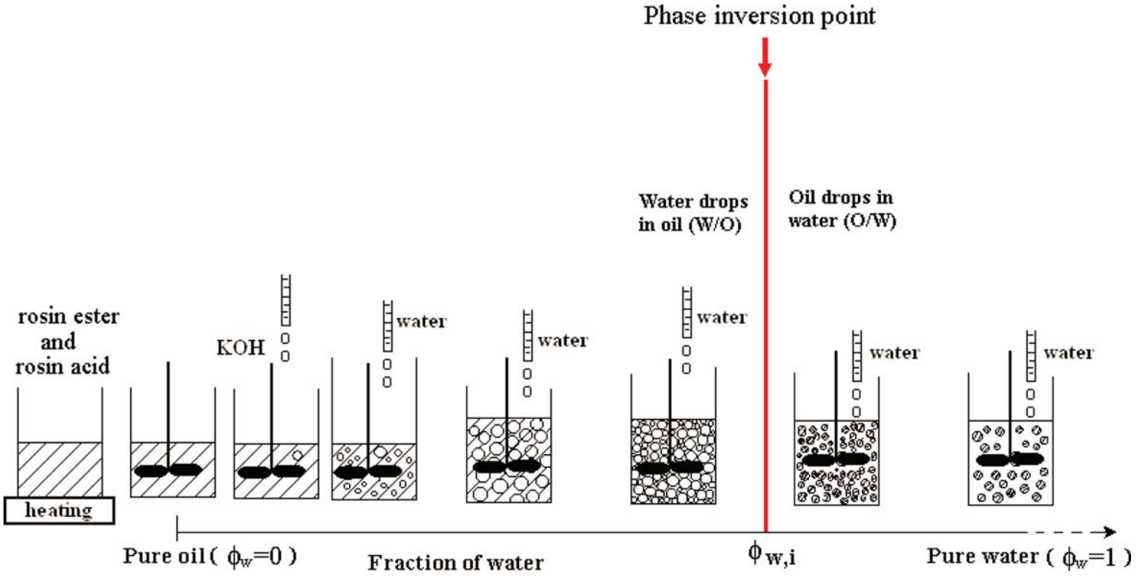


Figure 5. Schematic representation of the emulsification process.

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provided that the flow is laminar. In the present case, the Newtonian liquid used was corn syrup of known viscosity, and the torque needed to stir it was measured as a function of height of liquid in the tank. Concerning the emulsion, torque values were measured in situ during the process of making the tackifier emulsion, and, since the water feed rate is known, the liquid level in the vessel is also known at each time instant. Consequently, the effective viscosity of the emulsion can be computed through the use of Eq. 2. The computed result is just one kind of average viscosity, and other averages can be defined. In the present case, the flow inside the tank should be well mixed and there should be no dead zones due to the mixer configuration used (see Figure 3b). As a consequence, we believe that the conclusions that we have drawn with the use of the average viscosity as defined by Eq. 2 are unlikely to change even if another measure of the average viscosity were to be used.

In closing this section, we mention that the above procedure of computing the effective viscosity was used at only one agitation speed when the inner and outer impellers were rotated at speeds of 30/31 rpm, respectively. Under these conditions, the flow is expected to be in the laminar regime, and this conclusion was reached by using the lowest values of the measured viscosity to calculate the Reynolds number for a coaxial mixer.[24] Also, as pointed out by Carreau et al.,[25] the laminar flow region actually persists to larger Reynolds numbers for shear-thinning fluids as compared to Newtonian liquids.

Results and Discussion

The operating conditions whose influence was examined in this article included the system temperature, the water feed rate, and the impeller rotation speed, whereas the recipe was kept unchanged; the acid number, expressed as mg KOH needed to neutralize 1 g of resin, was 25, and the KOH number, defined as mg KOH/gram of resin, was 7.[2] The system temperature was changed by controlling the jacket temperature, and this was varied from 43.3 to 54.4°C. The water feed rate before phase inversion was systematically varied from 10 to 50 ml/min, whereas the post-phase-inversion water flow rate was set to 50 ml/min, since this had no noticeable influence on the final emulsion properties.[9] Consequently, all flow rates mentioned here are flow rates before phase inversion. The agitation speed of the counter-rotating inner/outer impellers was set at one of three levels of 30/20 rpm, 30/31 rpm, or 70/50 rpm, respectively. The values of these process conditions were chosen based on industrial experience as well as a vast number of preliminary experiments.[20]

The base case

The different process conditions were changed around a set of reference conditions. These were a jacket temperature of 51.7°C, water feed rate of 20 ml/min, and agitation speed of 30/31 rpm. It was found that phase inversion occurred at 22.76 water vol %, and the resulting mean particle size was 0.646 μm. The measured viscosity at room temperature when using a Brookfield viscometer was 240 mPa s at 20 rpm.

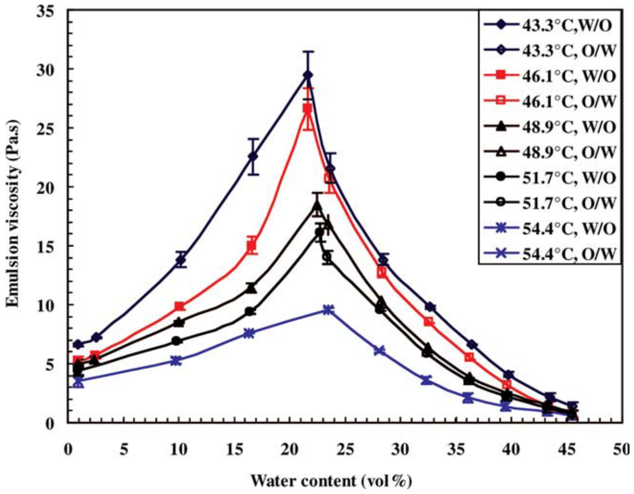

Figure 6. Emulsion viscosity vs. water content at different jacket temperatures.

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Effects of jacket temperature on phase inversion and on final emulsion size and viscosity

The temperature in the mixing vessel could not be measured directly because the impeller scraped the vessel walls, and this precluded the use of thermocouples. Instead, the liquid temperature in the heating jacket was controlled, and it was assumed that this temperature was representative of the system temperature. Results for the effective viscosity at a constant water feed rate of 20 ml/min and a fixed impeller agitation speed of 30/31 rpm are shown in Figure 6. At each temperature, the viscosity (or torque) increases monotonically with time before phase inversion, but it decreases progressively after phase inversion. The increase in viscosity before phase inversion is due to an increase of the dispersed phase concentration. The torque increases for the same reason, although the increase in the total system volume also plays a minor role. The decrease in viscosity after phase inversion can be attributed to the drastically lower viscosity of the continuous (aqueous) phase and also to the decreasing dispersed phase concentration.[9,23]

Figure 6 also shows that the emulsion viscosity during the process of tackifier synthesis increases, as expected, with the decrease of jacket temperature. In addition, it reveals that phase inversion occurs at a very slightly lower water content as temperature decreases. This effect on phase inversion is related to the change in the continuous phase viscosity. As observed by Selker and Sleicher,[13] the tendency of the continuous phase to become the dispersed phase increases as its viscosity increases.

At room temperature, the tackifier emulsion is actually a solid-in-liquid suspension, and the measured average particle size is shown in Figure 7. It is seen that the temperature of synthesis does not influence the average particle size (measured at great dilution) significantly, except at the highest jacket temperature of 54.4°C. The large mean particle size at the highest temperature is probably the result of the decreased shear stress that is needed to overcome the

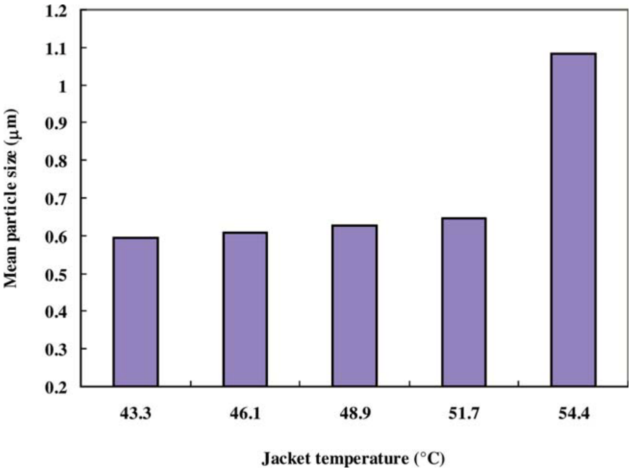

Figure 7. Effect of the jacket temperature on the mean particle size of final emulsions.

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interfacial stress during the process of drop break up. The particle size distributions were also found to be similar except at the highest temperature. As the average particle size and size distribution are the same in each case and since the total dispersed phase concentration is the same, one would expect the suspension viscosity to be the same. However, it was found that the suspension viscosity increased with a decrease in the temperature at which the emulsion was formed. This is shown in Figure 8, where a linear scale has been used on the ordinate to magnify any differences. The exact reason for this behavior is not clear. It may be due to the fact that the dispersed phase is not composed of non-interacting solids. Indeed, solid–solid agglomeration was observed during the process of viscosity measurement.

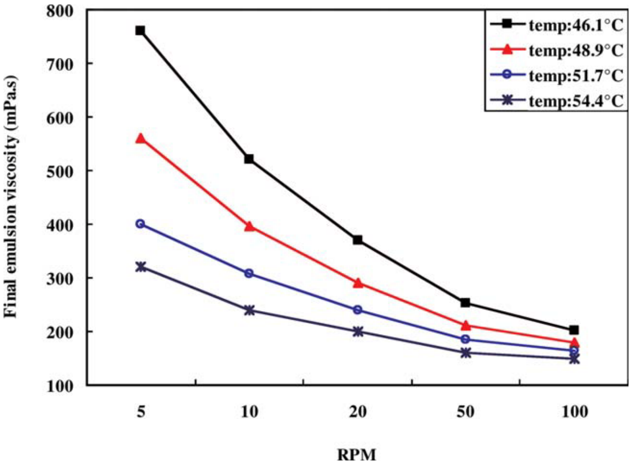

Figure 8. Final emulsion viscosity as a function of shear rate at different jacket temperatures.

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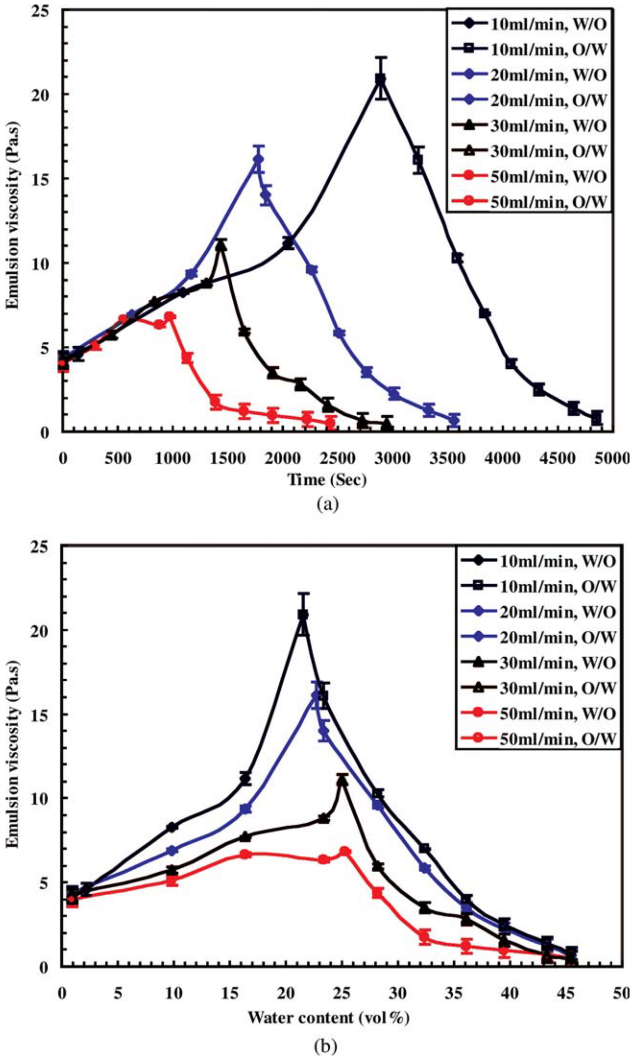

Figure 9. (a) Emulsion viscosity vs. time at different water flow rates and (b) emulsion viscosity vs. water content at different water flow rates.

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Effects of water feed rate on phase inversion and on final emulsion size and viscosity

Figures 9a, b exhibit the time dependence of the emulsion viscosity during the tackifier synthesis process upon changing the water flow rate from 10 to 50 ml/min; the jacket temperature is constant at 51.7°C and so is the inner/outer impeller speed at 30/31 rpm. Figure 9a reveals that, as the water flow rate decreases, not only does the emulsion viscosity increase significantly during the process, the time required for the occurrence of phase inversion also increases considerably. As a result, the total process time goes up as well. However, when the data of Figure 9a are replotted in Figure 9b to show the added water content on the abscissa, it is found that phase inversion takes place at gradually lower water volume fractions as the water flow rate decreases. This is due to the presence of a hysteresis zone in

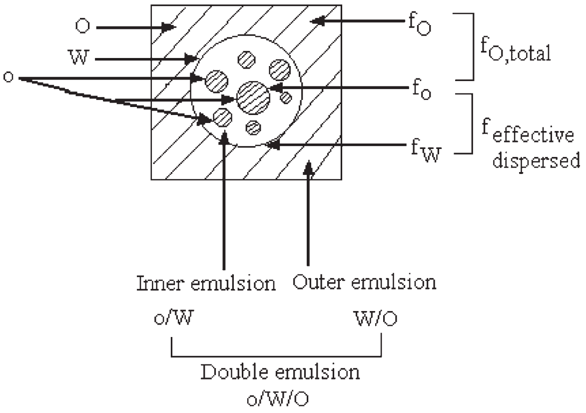

Figure 10. Schematic representation of o/W/O double emulsion.

a dynamic phase inversion system as compared to a pre-equilibrated one. This statement also implies that the further the system deviates from the equilibrium state, the later the phase inversion takes place. Also, notice that a lowered water feed rate leads to agitation for a longer time period which results in more thorough mixing. This aspect very likely promotes the formation of a double emulsion, as shown diagrammatically in Figure 10 according to the mechanism proposed by Tyrode et al.[8] As can be seen from Figure 10, the dispersed phase is water, and water drops are dispersed in the continuous phase (the most external phase) oil, which forms the outer emulsion, W/O. Also, some oil (the most internal phase) is entrained in the dispersed phase water drops, which forms the inner emulsion, o/W, giving an o/W/O double emulsion. Notice that the overall dispersed phase volume fraction is the summation of the volume fraction, f_W, of the water drops and the volume fraction, f_o, of the trapped oil droplets; this sum is often called the effective dispersed volume fraction. As a consequence, the formation of a double emulsion increases the effective concentration of the dispersed phase, and this leads to a high viscosity. This also means that it requires a smaller amount of water to trigger phase inversion. In other words, the formation of a double emulsion contributes to the onset of phase inversion at a lower water content.[8,18,23] As the water flow rate is increased, the tendency to form double emulsions will decrease, and the emulsion viscosity will reduce as observed in Figures 9a, b. Another consequence of the formation of a double emulsion is the reduction of the mean particle size in the final emulsion. This is because small oil droplets already exist (in the water drops) before phase inversion. Furthermore, the increased emulsion viscosity contributes to the breakup of large drops, again giving finer emulsions. This is verified in Figures 11 and 12 which show that, as the water feed rate is decreased, the average particle size decreases and the size distribution narrows. As a consequence, the room-temperature viscosity of the final emulsion increases with a decrease in the water feed rate. This is shown in Figure 13.

Figures 11 and 12 do not show data at the highest flow rate of 50 ml/min, because the dispersed phase aggregated to such an extent that it was impossible to measure the particle size. Note that Figure 12c exhibits a bimodal distribution with one peak being larger than 1 μm. This implies that the energy input during mixing was insufficient to compensate for the increasing water flow rate. The mixing was no longer as thorough as before, and this is why the particle size increased.

From the viewpoint of reducing both power consumption and process time, the results presented here would favor a higher water feed rate. However, as the water flow rate is

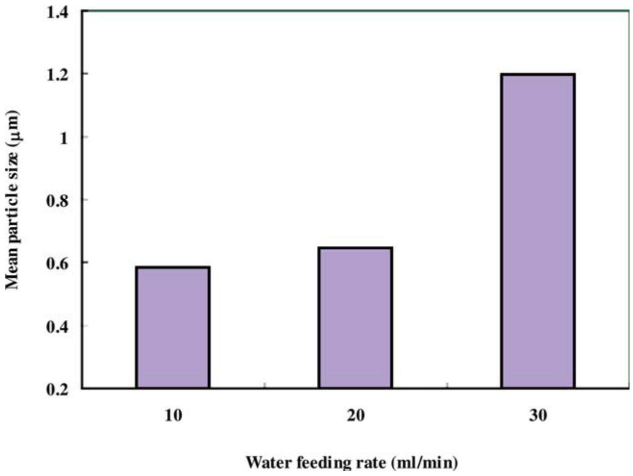

Figure 11. Effect of the water flow rate on the mean particle size in the final emulsion.

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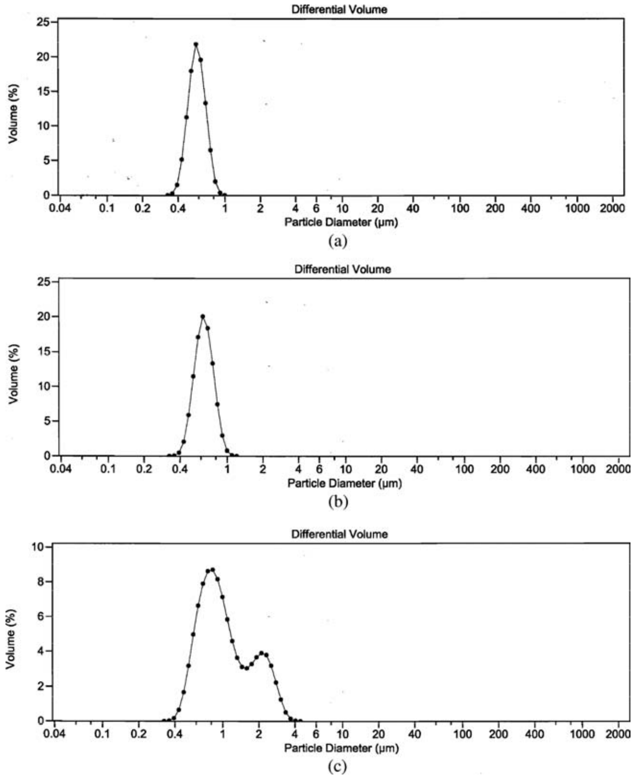

Figure 12. Particle size distributions of final emulsions.

(a) Water flow rate is 10 ml/min; (b) water flow rate is 20 ml/min; and (c) water flow rate is 30 ml/min.

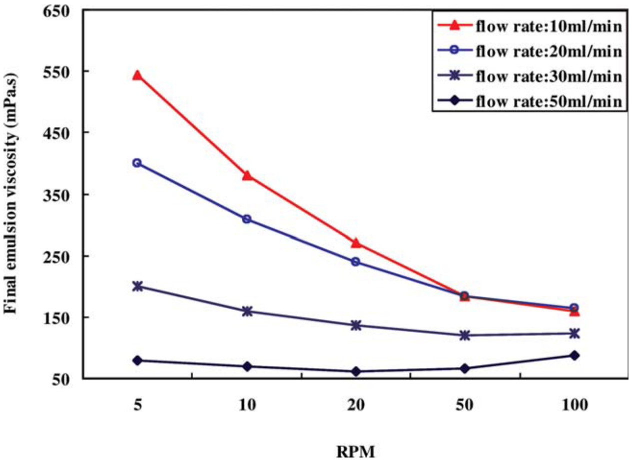

Figure 13. Final emulsion viscosity as a function of shear rate at different water flow rates.

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increased, larger particle sizes can result, and this can also lead to emulsion instability. Consequently, the process conditions used in practice are a compromise between process time and product quality.

Effects of agitation speed on phase inversion and on final emulsion size and viscosity

Because an increase in water flow rate requires a matching increase in the mixing power to ensure the maintenance of the quality of the final emulsions, agitation speed and water flow rate have to be changed in tandem. Thus, three levels of agitation speed of the inner/outer impellers, 30/20 rpm (low), 30/31 rpm (medium), and 70/50 rpm (high) were examined at two levels of water feed rate, 10 ml/min (low) and 50 ml/min (high), at a constant jacket temperature of 51.7°C.

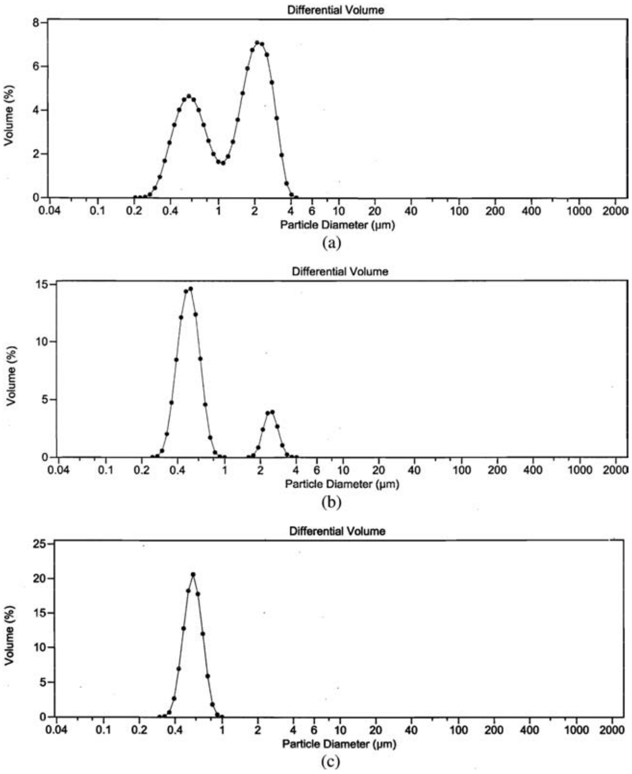

Figure 15. Particle size distributions of final emulsions.

(a) Speed of inner/outer impellers is 30/20 rpm; (b) the speed of inner/outer impellers is 30/31 rpm; and (c) the speed of inner/outer impellers is 70/50 rpm.

Results for the average particle size obtained in experiments conducted at the high flow rate of 50 ml/min are shown in Figure 14. It is seen that the mean particle size decreases as the agitation strength increases. However, the

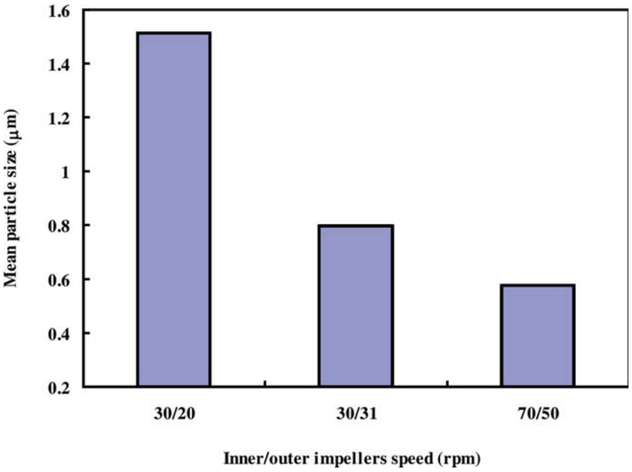

Figure 14. Effect of speed of inner/outer impellers on the mean particle size of final emulsions at a water flow rate of 50 ml/min.

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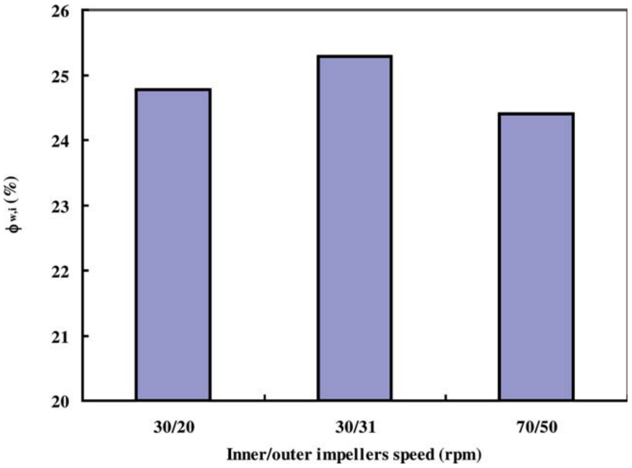

Figure 16. Effect of speed of inner/outer impellers on the phase inversion point, $\phi_{w,i}$, at a water flow rate of 50 ml/min.

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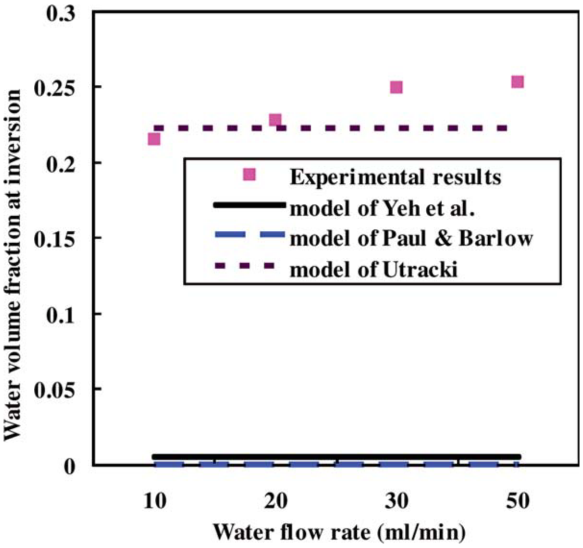

Figure 17. Comparison of predicted onset of phase inversion with data at different water flow rates.

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change in the average particle size is more pronounced when the agitation speed is increased from 30/20 rpm to 30/31 rpm than when the agitation speed is increased further to 70/50 rpm. This suggests that the intermediate agitation strength provides almost sufficient mixing at the chosen water feed rate. The resulting particle size distributions are shown in Figures 15a–c, and these are bimodal at the two lower agitation speeds. At the agitation speed of 30/20 rpm, there is a large peak above 1 μm and a smaller peak below 1 μm. When the agitation speed is increased to 30/31 rpm, the relative heights of the two peaks are reversed and the size distribution becomes narrower. Finally, Figure 15c exhibits the desired particle size distribution at the highest agitation speed of 70/50 rpm. These trends are not surprising. Increasing energy input leads to enhanced shear stresses that result in drop break up, all else being equal. But, there exists a limitation of this action. In other words, once the stress (or the agitation speed) exceeds a certain value, it has no further appreciable impact on particle size. The use of very high agitation speeds is also not favorable from the industrial point of view. This is because the high energy input induces foaming which tends to degrade adhesive performance since the adhesion strength is reduced.

The effects of agitation speed on emulsion size, viscosity, and phase inversion behavior at the low flow rate of 10 ml/min have been discussed in detail previously.[9] It was found that when the agitation speed was increased from 30/20 rpm to 30/31 rpm, the mean particle size decreased somewhat. However, once the speed was further increased to 70/50 rpm, there was no additional change in the average droplet size. This is consistent with the findings at the higher flow rate.

Finally, it appears that agitation speed does not affect the onset of phase inversion significantly at the high flow rate as shown in Figure 16. This is in contrast to the finding that at the low flow rate of 10 ml/min, phase inversion took place earliest at the intermediate agitation speed of 30/31 rpm.[9] The exact reason for this observation is not clear. As reported in the literature,[17] agitation speed affects phase inversion in a complicated manner. On the one hand, high agitation speeds are helpful in providing good mixing which favors the formation of double emulsion and subsequent phase inversion. On the other hand, high agitation speeds can also cause drop break up and the release of entrained drops from within the double emulsion.

Phase inversion prediction using the models available in the literature

Theoretical models which seek to predict the onset of phase inversion have been sought for decades.[26] On the basis of experiments conducted by vigorous manual shaking of the contents of a flask, Yeh et al.[27] concluded that phase inversion was controlled by viscous forces and proposed a direct relationship between the phase inversion point and the viscosity ratio,

$$\phi_{\mathrm{d,i}} = 1\Big/\left(1 + \sqrt{1/\lambda}\right) \tag{3}$$

in which $\phi_{\mathrm{d,i}}$ is the dispersed phase volume fraction at the point of phase inversion and λ is the ratio of the dispersed phase viscosity to the continuous phase viscosity. Paul and Barlow[28] proposed a slightly different criterion based on the behavior of polymer blends. According to these authors, if the viscosity ratio is close to unity

$$\phi_{\mathrm{d,i}} = 1/(1 + 1/\lambda) \tag{4}$$

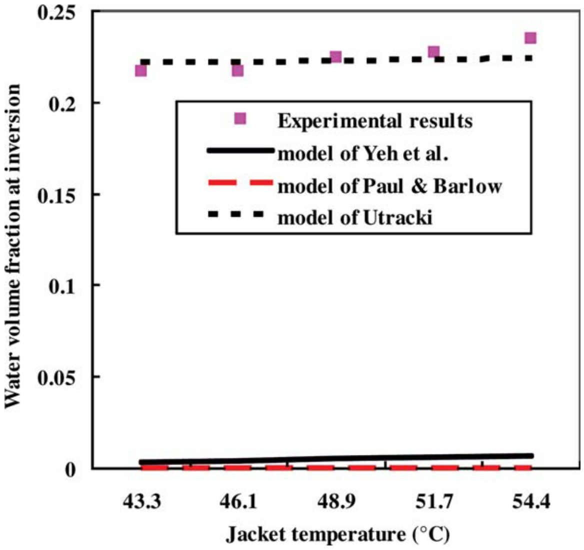

Figure 18. Comparison of predicted onset of phase inversion with data at different jacket temperatures.

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One would expect that Eqs. 3 and 4 would be inadequate for describing the data obtained in the present study since the viscosity ratio is not close to unity, and the onset of phase inversion is found to depend on factors besides the viscosity ratio alone.

By assuming that a mixture of two immiscible polymers A and B phase inverts when the viscosity of A in B equals the viscosity of B in A, Utracki[29] proposed that

$$\phi_{\mathrm{d,i}} = \left(1+\phi_{\mathrm{m}}\left(\lambda^{1/([\eta]\phi_{\mathrm{m}})}-1\right)\right)\Big/\left(1+\lambda^{1/([\eta]\phi_{\mathrm{m}})}\right) \qquad (5)$$

where $[\eta]$ is the emulsion intrinsic viscosity, and ϕ_{m} is the maximum packing volume fraction. Note that Eq. 5 is valid even for viscosity ratios that differ from unity,[30] and, in its derivation, the Krieger-Dougherty equation[31] is used for relating the dispersed phase viscosity to the volume fraction. Given their origins, it is not surprising that Eqs. 4 and 5 have been used for explaining the behavior of molten polymer blends. However, it is surprising that they have not been used for emulsions made from mobile liquids.

When one examines the value of the water volume fraction at the point of onset of phase inversion for the system at hand, one finds that this quantity varies only slightly with changes in temperature and water feed rate. However, as shown in Figures 17 and 18, Eqs. 3 and 4 which involve the viscosity ratio alone, cannot represent the experimental results. Indeed, due to the very large viscosity ratio of the tackifier emulsions, the lack of agreement is such as to make these equations completely inapplicable. The predictions of the model proposed by Utracki, however, are in reasonable accord with experimental data, even though the model does not take into account the effect of water flow rate. Note that in preparing Figures 17 and 18, the values of the intrinsic viscosity $[\eta]$ and the maximum packing volume fraction ϕ_{m} were taken to be 2.5 and 0.78, respectively. The viscosity ratio, λ, was 1.28×10^{-5}, 1.89×10^{-5}, 2.74×10^{-5}, 3.87×10^{-5}, and 5.27×10^{-5} at the temperatures of 43.3, 46.1, 48.9, 51.7, and 54.4°C, respectively.

Conclusions

The influence of operating conditions including jacket temperature, water feed rate, and agitation speed on final emulsion properties and phase inversion behavior has been investigated systematically in the synthesis of tackifier emulsions. Jacket temperature was not found to affect emulsion particle size as long as it was below a critical value. On the other hand, an increase in temperature resulted in slightly delayed phase inversion. The effects of water flow rate and agitation speed on phase inversion behavior were coupled. To obtain ‘‘good emulsions,’’ a higher water flow rate necessitates a correspondingly higher agitation strength. In practice, there is a tradeoff between the water flow rate and the agitation speed. Finally, of the three popular models available for predicting the onset of phase inversion, only one model gave reasonable agreement with experimental data.

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