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Mechanical Characterization of Vinyl Acetate Based Emulsion Polymer Blends

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SUMMARY: Emulsion blends comprise an important commercial area of polymer blend utility. Surprisingly, the fundamental study of emulsion blends is rarely noted in the literature. This study investigates emulsion blends of poly(vinyl acetate) (PVAc) and vinyl acetate-ethylene copolymers (VAE), where both components employ poly(vinyl alcohol) (PVOH) as the protective colloid. PVOH comprises the continuous phase in the emulsion cast films for both the individual components and the blends. This provides an example whereby excellent adhesion can be expected between the particles comprising the blend. The combination of low T_g/high T_g emulsion blends has been noted to be of interest, and the PVAc/VAE emulsion blends noted here offer an excellent model to study.

The PVAc/VAE blends protected with PVOH exhibit poor mechanical compatibility even though there is good adhesion. Conventional theory based on polymer/filler combinations predicts a rapid loss in elongation as filler content increases if excellent adhesion is observed. The PVAc/VAE blends (where PVAc is the filler) also exhibit similar behavior. This result implies excellent adhesion may not be desired where a compliance mismatch occurs for emulsion blends. The polymer/filler theories do not properly predict PVAc/VAE blend tensile strength results. A newer approach termed the equivalent box model (EBM) employing percolation theory agrees well with experimental results.

Melt mixing of the low/high compliance PVAc/VAE emulsion blends yields a significant improvement in mechanical compatibility. This indicates that a heterogeneous mixture of the same components yields better mechanical results than an array of particles with excellent adhesion between the particles.

Introduction

The investigation of polymer blends over the past three decades has covered virtually every area involving commercial polymer blends (e.g. rubber blends, engineering polymer blends, polyolefin blends). One area where only limited fundamental/experimental studies have been reported involves simple emulsion blends. Commercially, emulsion

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blends are utilized in various adhesion and coating applications to achieve specific end-use properties to optimize performance. In spite of the significant commercial activity, no comprehensive reviews or detailed studies have been reported. The reference texts detailing polymer blends (1-3) have only minor references to emulsion blends. Core-shell technology, as a subset of emulsion blends combining diverse polymers, is discussed in many reviews (4-6) and countless individual references. This specific subset of emulsion blends is referenced many more times than the simple emulsion blends. There appears to be recent interest in the fundamentals of emulsion blends as will be discussed. A particular area of interest in emulsion blends involves the combination of low T_g and high T_g emulsion particles to achieve unique property combinations.

The emulsion blends of interest here are those mixed only in the liquid state and cast as a film, coating or adhesive layer with no shear applied after water removal. Consolidation of the particles comprising the blends occurs via water evaporation and interpenetration of the particles via molecular diffusion. Molecular diffusion will occur between the particles if thermodynamically favorable. With immiscible emulsion blends the unfavorable thermodynamics will result in limited interpenetration across the particle interfaces. The consolidation of particles with water evaporation from an emulsion has been described by several references and theories over the years and was recently reviewed by Dobler and Holl (7). The general description of latex particle consolidation involves four specific stages as noted by Boczar et al. (8). These stages are: 1.) homogeneous dispersion of latex particles in water prior to evaporation. 2.) evaporation of water leading to close packed particles 3.) disappearance of the water phase leaving a compacted (hexagonal) particle array and 4.) polymer self-diffusion leading to a homogeneous, isotropic film. In the last stage, an immiscible emulsion blend will not diffuse across the interface and mix with particles of different composition. The resultant properties of the immiscible emulsion blend might be expected to be less than for a miscible blend or an array of homogeneous particles.

The emulsion polymers employed in this study include poly(vinyl acetate) (PVAc) and vinyl acetate-ethylene copolymers (VAE) with poly(vinyl alcohol) (PVOH) as the protective colloid. The emulsions chosen are commercially available and thus represent typical PVOH-protected vinyl acetate based emulsions. The preparation of these emulsions is discussed in various reviews including references 9-11. The phase structure of a PVOH-stabilized PVAc has been reported by Richard (12) noting that PVOH retains continuous phase structure after water removal. Thermal annealing resulted in further consolidation of the PVOH to yield a higher level of continuity as judged by the modulus plateau between the T_gs of PVAc and PVOH. The utilization of PVOH protected VAE emulsions for many of the applications is due to the excellent adhesion of PVOH with cellulosic-based substrates. It has been shown that PVOH and cellulose are miscible (13) thus demonstrating the reason for the observed adhesion.

Fundamental and experimental investigation of the characteristics of simple emulsion blends is rarely noted in the literature, however, there are a number of recent papers worthy of discussion. Many of these papers discuss the combination of a high T_g emulsion polymer blend with a low T_g emulsion polymer (low compliance/high compliance combination). Often the high T_g polymer is not film forming at room temperature whereas the blend is film forming. Chevalier et al. (14) studied the structure of polystyrene/poly(n-butyl acrylate) films cast from an emulsion blend employing small-angle neutron scattering. It was noted that dense clusters of polystyrene particles exist in the cast film which can coalescence into large particles above the T_g of polystyrene. This cluster/coalescence behavior can be prevented by employing a two stage core-shell preparation of the same blend. Feng et al.(15) investigated the film formation of high (poly(methyl methacrylate)(PMMA))/low(n-butyl methacrylate-n-butyl acrylate)(nBMA-nBA copolymer)) T_g emulsion polymer blends. It was observed that the PMMA particles retained their original spherical shape in the blends. Conditions were found where transparent films were observed with uniform dispersion of PMMA particles. Turbid films were also observed where PMMA clusters were found. In another study by Feng and Winnik (16), the drying rate of the PMMA/nBMA-nBA copolymer blend was compared to the unblended constituents. It was found that intermediate compositions dried slower than unblended components. Lepizzera et al. (17) studied the film forming characteristics and mechanical properties of low/high T_g emulsion blends. The maximum weight fraction of the high T_g emulsion polymer for transparent and void-free films was found to be 0.55. The elongation at break was found to be higher than predicted from a perfect adhesion model. Debonding (at strains much lower than sample failure) was observed for these blends indicating less than perfect adhesion. It was found that the real tensile strength (assuming constant volume—no void formation) reached a maximum at 0.3 weight fraction addition of the high T_g emulsion polymer. Eckersley and Helmer (18) also studied the film formation and mechanical properties of low/high T_g emulsion blends. Blocking resistance was improved with high T_g polymer addition. The particle size ratio was found to be an important variable with the best performance with high values for low T_g/high T_g particle size ratio. Several patents have also noted interest in low T_g/high T_g emulsion blends primarily for coating applications (19,20).

Experimental

This study investigates polymer blends comprised of poly(vinyl alcohol) protected poly(vinyl acetate) (PVAc) and vinyl acetate-ethylene (VAE) copolymer emulsions. These emulsion polymers are commercially important for a large number of adhesive applications including wood glue, paper and cloth binder, caulk compositions, film lamination and adhesive bonding for diverse substrates. The preparation and properties of these polymers have been previously discussed in many references, including 10 and 11. The choice of PVOH-protected vinyl acetate based emulsions for emulsion blend studies is based on the expectation that PVOH at the interface between the particles will provide translation of mechanical properties across the interface thus allowing for mechanical compatibility even if the individual blend components are not miscible. Stress-strain data will be employed to assess the level of mechanical compatibility. A generalized behavior of mechanical incompatibility, mechanical compatibility, and synergistic mechanical behavior is illustrated in Figure 1.

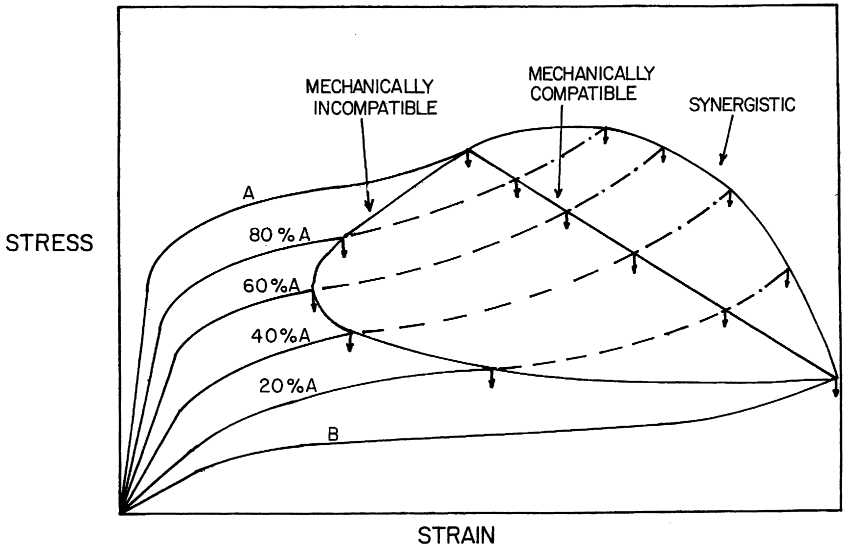

Figure 1 - Generalized Stress-Strain Behavior of Emulsion Blends

The emulsion polymers utilized for this study are listed in Table 1 along with relevant data. The blends were prepared by simple shear mixing for several minutes followed by casting onto glass plates. After drying at 23 °C and 50% RH for 24 hours, the cast films (~20-30 mils thick) were removed from the glass plates and placed on silicone release paper and dried for a further 24 hours at 23 °C and 50% RH. The samples were placed in a desiccator for further drying (at least five days). Tensile specimens (ASTM D-1708 type) were cut from the dry films for stress-strain measurements on an Instron testing machine. A Rheometrics Solids Analyzer (RSA II) was used to obtain the tensile dynamic properties of the emulsion cast films. Data were obtained every 6 °C over the -100 to 150 °C range using a deformation frequency of 6.28 rad/sec. A one minute soak time was used to ensure isothermal conditions.

Table 1. Description Of Emulsions Utilized In This Study

	T_g °C	Volume Fraction		
	(DMA)	Vinyl Acetate	Ethylene	PVOH
PVAc	43	0.94	0	0.06
VAE-1	25	0.83	0.13	0.04
VAE-2	9	0.71	0.24	0.05
VAE-3	1	0.59	0.36	0.05

Experimental Results

The characterization of the unblended emulsions using dynamic mechanical analysis was conducted first. The key question to be resolved with these data is the level of PVOH continuity existing in the emulsion cast specimens. This is important relative to the experiments discussed later involving the blends. The variation of the dynamic mechanical properties as the ethylene content of VAE is increased is illustrated in Figures 2 and 3, for E' and tan δ, respectively. Several conclusions can be drawn from the data. First a modulus plateau between the T_g of the VAE and the PVOH protective colloid is observed. At the T_g of PVOH (~85 °C), a drop in modulus is observed and a peak in tan δ is also quite apparent indicating possible continuous phase structure for the PVOH. As the ethylene content is increased in the VAE copolymer, a broadening of the VAE glass transition is observed along with a decrease in peak height of tan δ. This is hypothesized to be due to an increase in microheterogenity with increased ethylene content. This is presumably due more to process variations (i.e. ethylene pressure) than the modest reactivity ratio difference. The prominent transition for PVOH and modulus plateau between the T_g's for VAE and PVOH indicates that PVOH maintains continuous phase structure in the cast films.

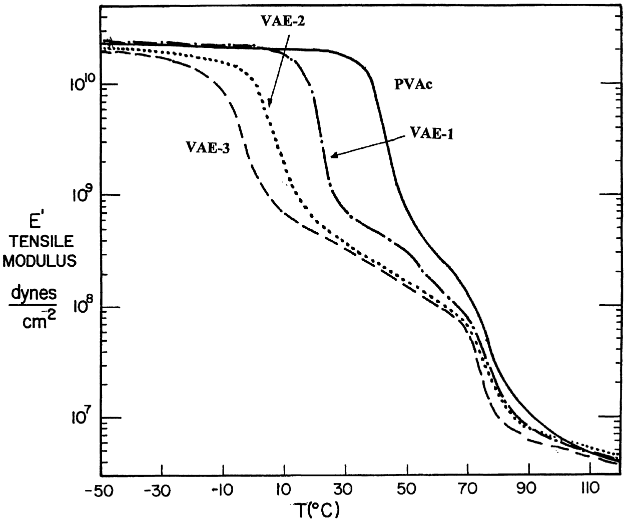

Figure 2 - Tensile Modulus, E', for Vinyl Acetate-Ethylene Copolymers with Varying Ethylene Content

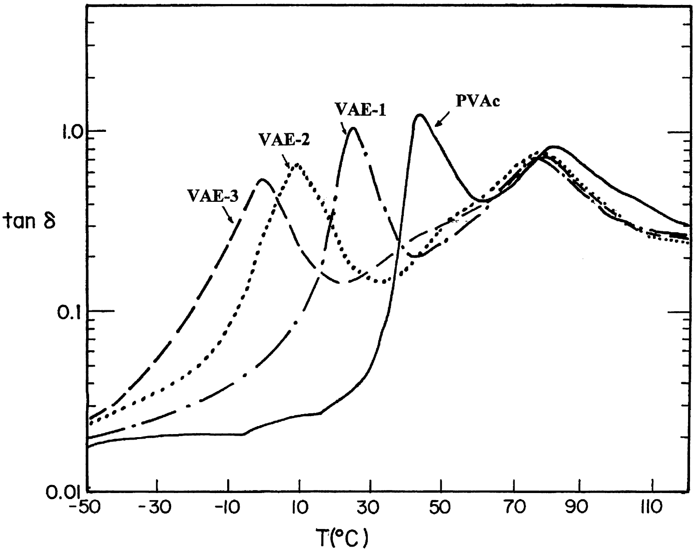

Figure 3 - Tan δ for Vinyl Acetate-Ethylene Copolymers with Varying Ethylene Content

The phase behavior of PVOH protected VAE was compared as a room temperature emulsion cast film, compression molded film at 130 °C, and melt mixed at 130 °C followed by compression molding at 130 °C. The dynamic mechanical results for VAE-2 are illustrated in Figures 4 and 5 for E' and tan δ, respectively. The PVOH transition is prominent for the room temperature emulsion cast film but progressively disappears with further temperature and shear exposure. This well indicates a change in morphology from a PVOH-continuous phase to a dispersed phase structure. In order to assess the level of continuous structure of PVOH in VAE, Kerner's analysis(21) will be employed to predict the modulus of a PVOH-continuous phase structure and a VAE-continuous phase structure. Kerner's equation is:

$$E = E_c \frac{\{\phi_d E_d / [(7-5\upsilon_c)E_c + (8-10\upsilon_c)E_d]\} + [\phi_c / 15(1-\upsilon_c)]}{\{\phi_d E_c / [(7-5\upsilon_c)E_c + (8-10\upsilon_c)E_d]\} + [\phi_c / 15(1-\upsilon_c)]} \qquad (1)$$

where E, E_c, and E_d are the respective modulus values of the blend (emulsion system), the continuous phase and the discontinuous phase components, ϕ_c and ϕ_d are the volume fractions of the continuous and dispersed phases and ν_c is the Poisson's ratio for the continuous phase. If PVOH is the continuous phase, $E_c \sim 1.5 \times 10^{10}$ dynes/cm^2 ; $E_d \sim 10^7$ dynes/cm^2, $\nu_c \sim 0.35$, $\phi_c = 0.05$, and $\phi_d = 0.95$ (estimates at 50 °C from extrapolation of experimental data). Substitution into Kerner's equation yields $E = 5.1 \times 10^8$ dynes/cm^2. The experimental value (at 50°C) for the emulsion is 3.1×10^8 dynes/cm^2. If VAE is the continuous phase, Kerner's equation predicts a modulus of 1.13×10^7 dynes/cm^2. Thus while PVOH is not entirely continuous in the emulsion cast structure, it does have a major contribution (e.g. 60%) and this structure leads to a modulus of 30 times (comparison at 50 °C) that of the VAE continuous structure exhibited by the melt mixed emulsion.

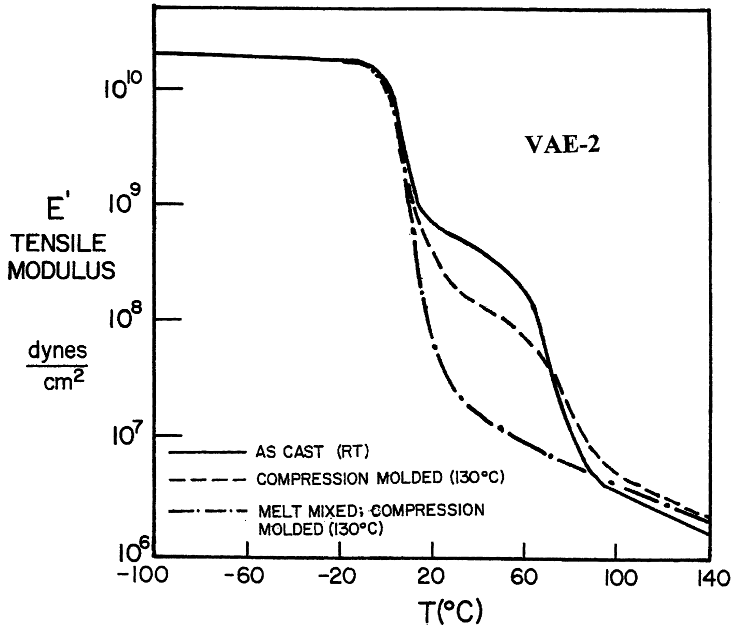

Figure 4 - Tensile Modulus, E', Results for VAE-2 as a Function of Sample Preparation

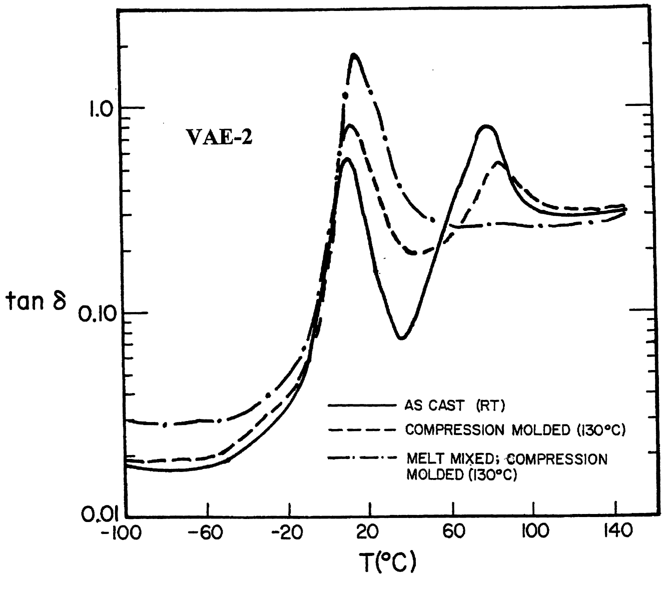

Figure 5 - Mechanical Loss, tan δ, Results for VAE-2 as a Function of Sample Preparation

As noted in the discussion earlier, there has been considerable interest in emulsion blends comprising a low T_g component with a high T_g emulsion component to achieve intermediate properties. The resultant blend is an array of particles which, unless miscible, will have limited interpenetration of polymer chains across the interface. With the PVOH-protected emulsions described here, the PVOH protective shell around the emulsion particles may allow for improved transfer of stress across the interface thus allowing for compatibilization of immiscible blends. Emulsion blends of VAE-1 and VAE-2 were prepared under three conditions: 1) emulsion cast 2) emulsion cast and compression molded at 130 °C and 3) emulsion cast, melt mixed (brabendered) at 130 °C and compression molded at 130 °C. The dynamic mechanical results are illustrated in Figure 6. These results parallel the results for VAE-2 shown in Figures 4 and 5. It is clear that PVOH maintains a level of continuous behavior in the emulsion cast film. The tan δ data in Figure 6 indicates phase separation for the as cast blend. As increased temperature and/or shear exposure occurs, the transitions show decreased two phase behavior indicating partial miscibility occurring between the blend constituents.

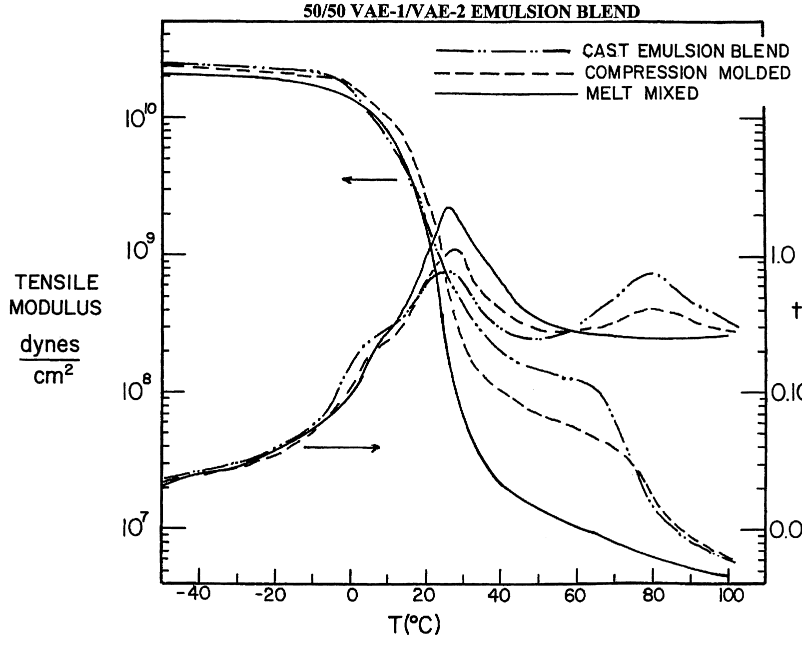

Figure 6 - Dynamic Mechanical Results for 50/50 (by wt) Blend of VAE-1/VAE-2

With this scenario in mind, blends of PVAc and a low T_g VAE (VAE-3) were prepared by simple mixing followed by casting into thick films for drying and mechanical characterization. The stress-strain data on these blends are illustrated in Figures 7 and 8 for samples tested dry and after 85% relative humidity aging. It is apparent from the data that mechanical compatibility is not achieved with this blend under either dry or humid conditions compared to the unblended constituent values. This appears to be an expected result for emulsion blends comprised of low T_g and high T_g emulsions. This apparent mechanical incompatibility is referred to as **"compliance mismatch"**.

The phase behavior of PVAc and VAE-3 emulsion blends can be assessed from the modulus versus composition data. The prediction of the modulus of polymer blends (and phase separated block copolymers) has been recognized to follow relationships developed earlier for other property predictions. Kerner (21) noted that the conductive properties of composites such as dielectric constant, magnetic permeability, electrical and thermal conductivity can be modeled by similar equations which could also be utilized for modulus predictions. Nielsen (22) noted that the equations for prediction of the elastic modulus of composites are of a general form:

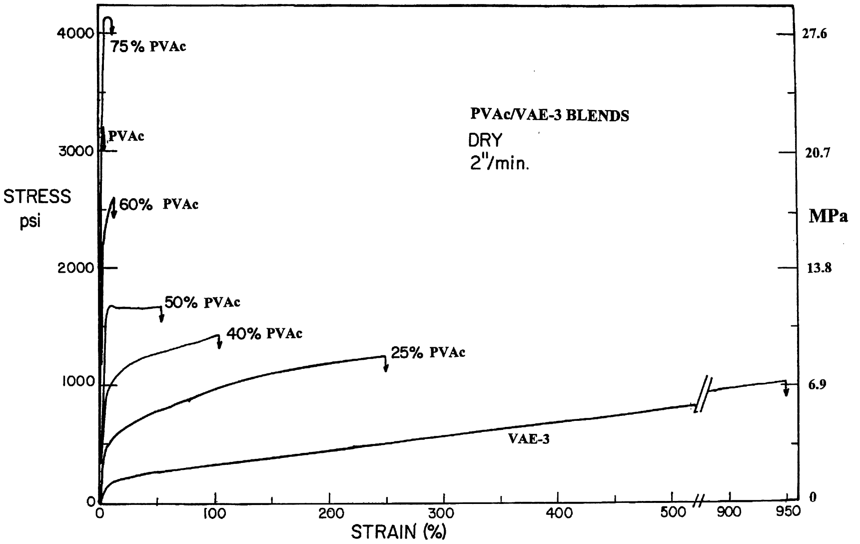

Figure 7 - Stress-Strain Data on PVAc/VAE-3 Blends (dry; 2"/min strain rate; 23 °C)

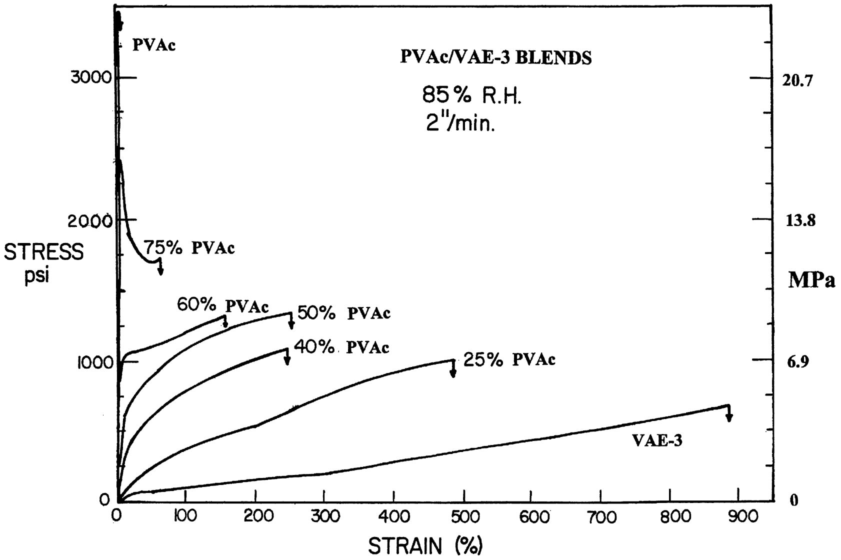

Figure 8 - Stress-Strain Data on PVAc/VAE-3 Blends (85% RH equilibrated; 2"/min strain rate; 23 °C)

$$E/E_m = (1 + AB\phi_d)/(1 - B\phi_d) \qquad (2)$$

where E and E_m are the elastic moduli (shear, tensile or bulk) of the composite and the matrix respectively, ϕ_d is the volume fraction of the dispersed phase. The constant B is equal to

$$B = ((E_d/E_m) - 1/((E_d/E_m + A) \qquad (3)$$

where E_d is the elastic modulus of the dispersed phase, and A is a constant accounting for dispersed phase geometry and Poisson's ratio of the matrix. A = k -1 where k = 2.5 for a suspension of rigid spheres in a matrix where Poisson's ratio = 0.50. Other theories have been proposed by Bruggeman (23), Takayanagi (24), Hashin and Shtrikman (25) and Hashin (26). In the analysis of polymer blends, the lower and upper bounds of elastic modulus behavior can be determined from the series and parallel models:

$$\text{Parallel Model:} \quad E = E_1\phi_1 + E_2\phi_2 \qquad (4)$$

$$\text{Series Model:} \quad (1/E) = (\phi_1/E_1) + (\phi_2/E_2) \qquad (5)$$

In the case where $E_1 > E_2$, the parallel model approximates the blend where polymer 1 is the continuous phase and the series model approximates the blend where polymer 2 is the continuous phase. This simple approach works well at both ends of the composition range but fails to adequately predict the results at intermediate composition. Kerner's equation noted earlier has been shown to work well for two phase polymer systems (27) and will be employed in this analysis. A simple modification of Kerner's equation can be employed to determine where the phase inversion point occurs. If we assume that $E = x_1E_1 + x_2E_2$ where E_1 and E_2 are the moduli from Kerner's equation where E_1 is calculated for polymer 1 as the continuous phase and E_2 is calculated for polymer 2 as the continuous phase with the proviso that $x_1 + x_2 = 1$; then the contribution of polymers 1 and 2 to the continuous (or dispersed) phase is equal to 1. This requirement basically assumes no anisotropic behavior in the blend. In order to predict the values of x_1 and x_2, the only theory available is based on percolation theory. As a cast emulsion blend will be comprised of an array of spheres (in reality hexagonally packed), the film should be isotropic and thus the use of Kerner's equation should be a realistic assessment of the continuity of the phase structure. Kerner's equation was employed in the analysis of the phase behavior of PVAc/VAE-3 blends shown in Figures 7 and 8. The experimental results are shown in Figures 9 and 10 for the PVAc/VAE-3 blends under dry and 85% RH conditioning respectively. The results at low VAE-3 content show that PVAc is clearly the continuous phase. Significant differences are observed between the dry and 85% RH results. The point of phase inversion for the dry samples is at almost 60% volume fraction of the lower modulus VAE-3 whereas at 85% RH the phase inversion point is at only 36% volume fraction VAE-3. The modulus of the PVOH interface is a significant factor in the modulus results. Obviously this is not a two phase system but is indeed a three phase system where the major continuous phase is PVOH. Modeling the blend by a two component system (PVAc/VAE-3) does not in reality work. However, the results do give some interesting conclusions in spite of the assumptions made. The modulus versus composition data behaves more like the higher modulus PVAc over the composition range for the dry specimens. This is not surprising because PVOH (when dry) is the primary continuous phase and possesses a modulus similar to PVAc; the continuous phase mechanically would then be PVOH + PVAc thus yielding the observed result. When the samples are tested at 85% RH, the PVOH is considerably lower in modulus and closer to the VAE-3 modulus, thus the blend appears to have more VAE-3 continuity.

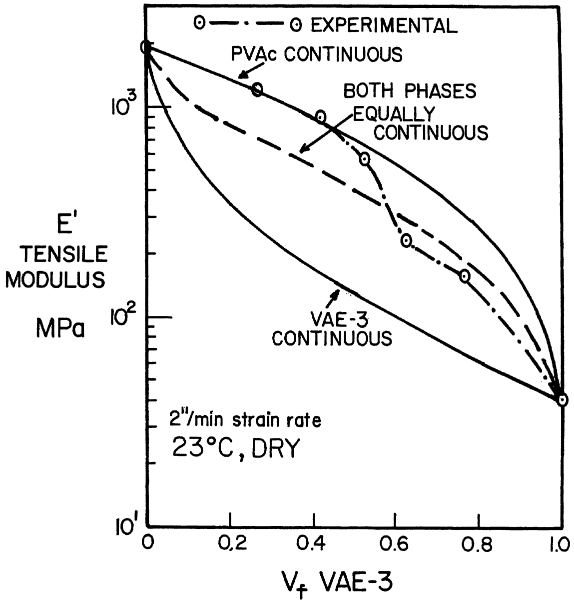

Figure 9 - PVAc/VAE-3 Modulus Behavior as a Function of Composition Compared to the Prediction of Kerner's Equation (dry; 23 °C; 2"/min strain rate)

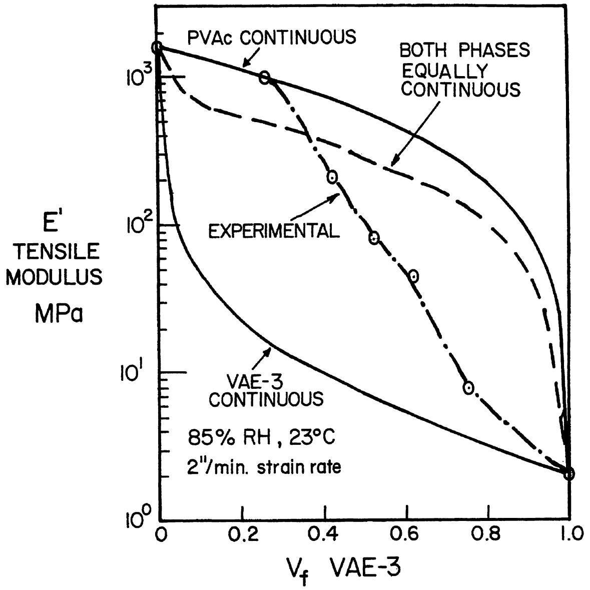

Figure 10 - PVAc/VAE-3 Modulus Behavior as a Function of Composition Compared to the Prediction of Kerner's Equation (85% RH; 23 °C/min strain rate)

While the prediction of the modulus of phase separated blends can be modeled by existing theories, the modeling of ultimate properties (e.g. tensile strength, ultimate elongation) is less reliable as ultimate properties are much harder to model than transport properties (heat, electrical, permeability) or modulus properties. There are references in the literature predicting the ultimate properties of filled polymers which can be extended to include phase separated emulsion blends comprised of hard and soft emulsion particles. One of the earlier papers by Nielsen (28) noted that the elongation of a soft (low modulus) polymer containing rigid (high modulus) particles will exhibit an elongation equal to:

$$\varepsilon_b = \varepsilon_{bo}(1 - \phi_f^{1/3}) \qquad (6)$$

where ε_b = elongation at failure of the filled polymer, ε_{bo} = elongation at failure for the soft polymer (unfilled) and ϕ_f = volume fraction of the filler. This analysis assumes perfect adhesion. In the case where no adhesion is observed, higher elongation at failure is expected, as noted by Nielsen employing the theory of Sato and Furukawa (29). In composites comprised of hard particles (spheres) in a soft matrix, the average local strain, ε_L, of the soft (continuous) matrix is higher than the macroscopic strain, ε_M, of the composite film. The strain-amplification can be determined from the following equation as noted by Lepizzera et al. (17):

$$\varepsilon_L = \varepsilon_M(1 + 2.5\phi + 14.1\phi^2) \qquad (7)$$

where ϕ is the volume fraction of hard spheres. This assumes (although not specifically noted) perfect adhesion. The difference between this prediction and the Nielsen model is due to the difference between a square and a circle (two dimension) and a cube and a sphere (three dimension).

Comparison of the experimental elongation data with theory is noted in Figure 11. The results on PVAc/VAE-3 blends tested under dry conditions show elongation at failure to be lower than the perfect adhesion model and the results on these blends at 85% RH show data between the perfect and no adhesion models (closer to perfect adhesion). Since PVOH is connected to both phases and forms the interfacial region between the individual particles (as demonstrated from dynamic mechanical analysis), the observation of "perfect adhesion" is expected. The lower adhesion with 85% RH (as noted by the models compared with experimental data) may be more related to an interface offering an intermediate modulus between the particles. This would allow for a higher observed elongation, as cavitation at the interface would occur at higher elongations. At any rate, theory predicts a counter-intuitive results; namely, lower adhesion yields a blend exhibiting a higher elongation and thus a higher observed mechanical compatibility. Thus theory does better at predicting results than the expectation that "perfect" adhesion would yield the best properties for emulsion blends comprised of low and high compliance materials.

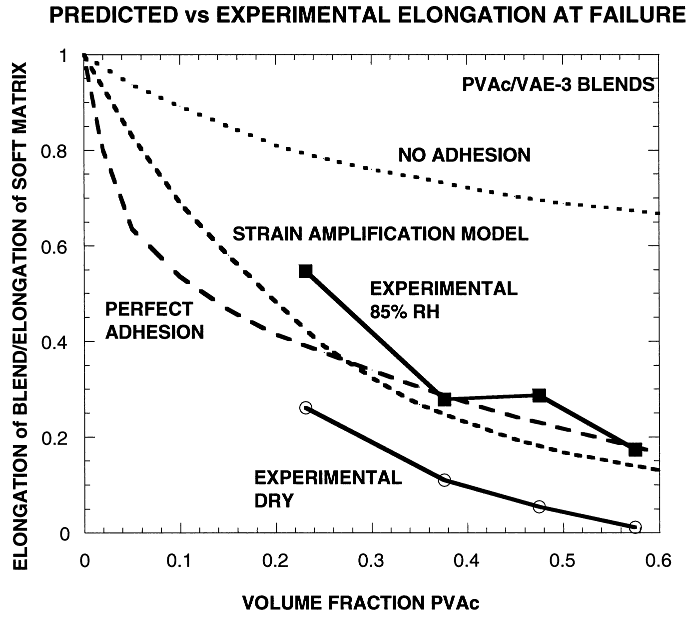

Figure 11 - Elongation at Failure (23 °C; 2"/min strain rate) of PVAc/VAE-3 Blends Compared to Various Predictions

The results for tensile strength have been modeled by Nielsen (28) where no adhesion is observed and where adhesion is observed predicted by models of Kerner (21) and Eiler-van Dijck (30).Our experimental results are compared with these theories for PVAc/VAE-3 emulsion blends in Figure 12. The theories show a reduction in tensile strength with filler addition at low levels of filler. Eilers-van Dijck theory shows an increase in tensile strength above 40% volume fraction filler. The experimental data for PVAc/VAE-3 blends exhibit a significant deviation (positive) versus theory when PVAc is considered the "filler" phase for VAE-3. This is partly due to the ability of the PVAc "filler" phase to exhibit continuous phase behavior. PVAc is film forming at room temperature thus has the ability to form continuous phase structure during film casting. Although PVAc has a T_g above room temperature, water sorption reduces the T_g to a level whereby film formation is possible at room temperature (23 °C). The theories assume the filler will be totally the dispersed phase at all levels of addition. With the PVAc/VAE-3 emulsion blends, PVAc can exhibit a continuous phase contribution at modest levels of addition which increases to complete continuous phase contribution at high levels of PVAc. For dry samples, the continuous phase behavior is enhanced due to combination of the blend PVOH continuous phase structure with PVAc as noted in Figure 9.

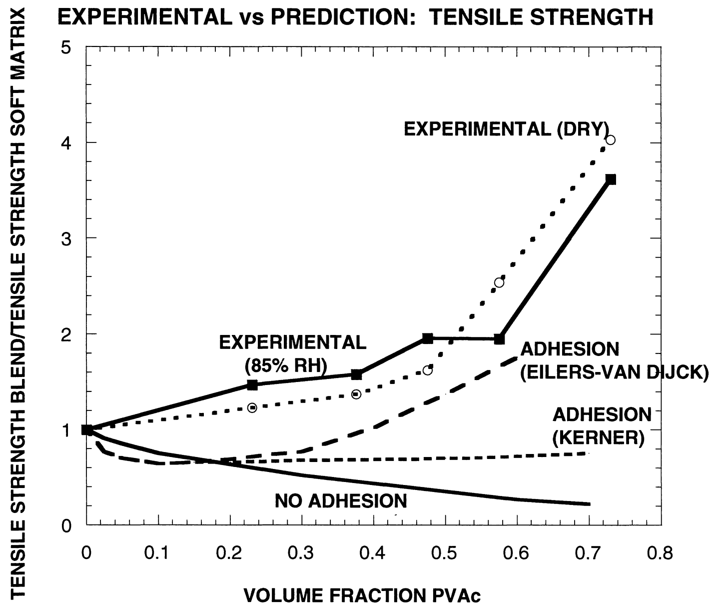

Figure 12 - Tensile Strength (23 °C; 2”/min strain rate versus Various Predictions

Another more recent model proposed to predict the ultimate properties of heterogeneous polymer blends is termed the equivalent box model (EBM) and is a combination of the parallel and series models as noted by Kolarik [(31)]. At high volume fraction of the soft polymer, the series model dominates; and at high volume fraction of the hard polymer, the parallel model dominates. At intermediate values, both series and parallel models contribute to the overall predictions. The model is shown in Figure 13. The tensile strength, σ_b, predicted by the model is:

$$\sigma_b = \sigma_1\phi_{p1} + \sigma_2\phi_{p2} + \sigma_1\phi_s \qquad (8)$$

where σ_1, σ_2, and σ_s are the tensile strength's of component 1 and component 2 and $\sigma_1<\sigma_2$. ϕ_{p1} and ϕ_{p2} are the parallel contribution of polymers 1 and 2 to the volume fraction. ϕ_s is the series volume fraction contribution and is equal to $\phi_{s1} + \phi_{s2}$. A is the interfacial adhesion where A = 0 (no adhesion) and A = 1 (perfect adhesion). The volume fraction contributions are calculated based on percolation theory (32) for the modulus of a two component blend:

$$E = E_o(\phi - \phi_{cr})^T \qquad (9)$$

where E = modulus of the blend, E_o is a constant, ϕ is the volume fraction, ϕ_{cr} is the percolation threshold volume fraction and T is the critical universal exponent. For discrete spherical domains (as would be expected for a cast emulsion blend),ϕ_{cr} = 0.156 and T = 1.833 for a three dimensional lattice. The expressions to predict ϕ_{p1} and ϕ_{p2} are:

$$\phi_{p1} = [(\phi_1 - \phi_{1cr})/(1 - \phi_{1cr})]^{T1} \quad \text{and} \quad \phi_{s1} = \phi_1 - \phi_{p1} \qquad (10)$$

$$\phi_{p2} = [(\phi_2 - \phi_{2cr})/(1 - \phi_{2cr})]^{T2} \quad \text{and} \quad \phi_{s2} = \phi_2 - \phi_{p2} \qquad (11)$$

ϕ_{1cr}, ϕ_{2cr}, T_1 and T_2 can be considered adjustable parameters. As a first approximation, ϕ_{1cr} and ϕ_{2cr} = 0.156; and T_1 and T_2 = 1.833 will be assumed based on the expected discrete domains exhibited by emulsion blends (i.e., not shear mixed; basically hexagonal arrays approximated by spheres). The calculations for PVAc/VAE-3 blends will be done based on a two phase model assuming the unblended properties of PVAc/PVOH and VAE-3/PVOH cast films. In essence, the blend is a three phase system of PVAc/VAE-3/PVOH as PVOH resides at the interface of the blend as well as the unblended constituents. The calculated properties are noted in Table 2. The predicted versus experimental results show reasonably good agreement when the yield strength of PVAc is utilized in the calculations. Very poor agreement is observed when the tensile strength of the cast PVAc is employed. The tensile strength of the cast (unblended) PVAc is quite low due to brittle failure significantly below the yield strength. In the blends, PVAc is "impact modified" by the presence of VAE-3, as evidenced by the stress-strain data on the 75/25 (by wt.) blend of PVAc/VAE-3. The yield strength of PVAc is 7100 psi (49MPa) based on results extrapolated from testing at a lower strain rate to 2"/min and this is a more realistic value for use in this model. Using this value yields much better agreement of prediction versus experimental and gives credence to the equivalent box model in predicting the tensile strength of emulsion blends.

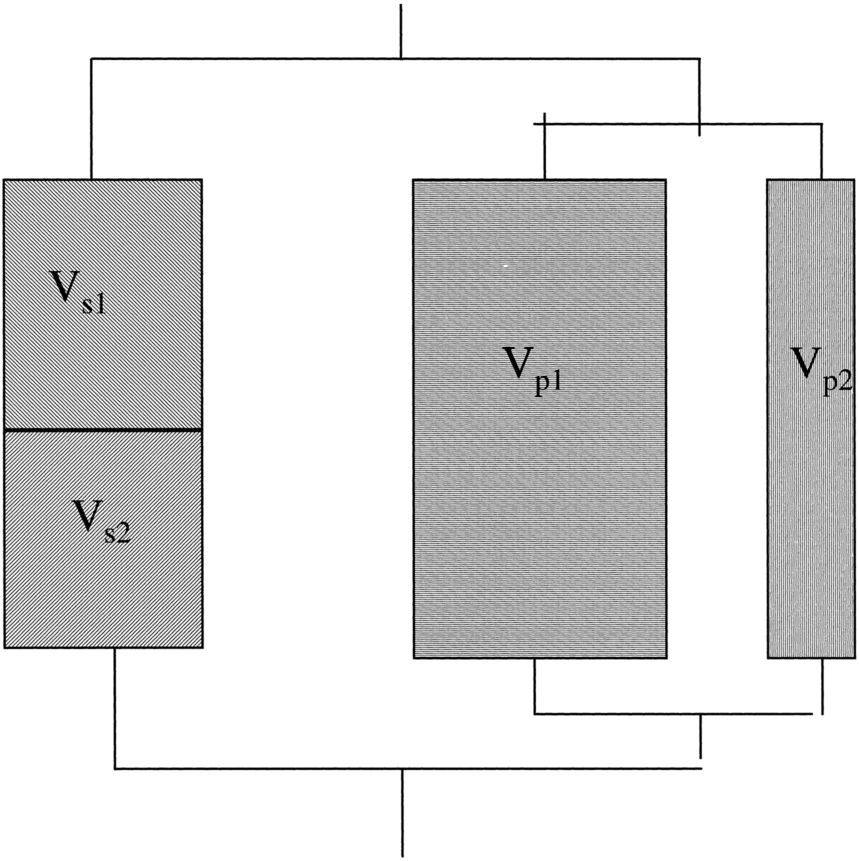

Figure 13 - Equivalent Box Model Representation of Series and Parallel Contributions

Table 2. Results From The Equivalent Box Model

	Volume Fraction PVAc				
	0.231	0.376	0.475	0.575	0.730
ϕ_{p1}	0.558	0.339	0.219	0.122	0.0255
ϕ_{p2}	0.0118	0.0851	0.168	0.277	0.493
ϕ_{s1}	0.211	0.285	0.306	0.303	0.245
ϕ_{s2}	0.219	0.291	0.307	0.298	0.237
Predicted TS MPa	7.43	8.52	9.76	11.4	14.6
Experimental TS MPa	8.62	10.0	11.7	17.9	28.6
Predicted TS (based on PVAc YS) MPa	7.74	10.8	14.3	18.8	27.8

In order to compare the emulsion blends (in which the particles retain their initial dimensions) to a melt mixed blend where more intimate mixing of the particles is achieved, samples were melt mixed at 120-130 °C and then compression molded at 130 °C. An intermediate case was tested where the emulsion cast blend was compression molded at 130 °C. The stress-strain data employing these conditions are illustrated in Figure 14. Melt mixing yields a significant improvement in mechanical compatibility as evidenced by the much larger area under the stress-strain curve.

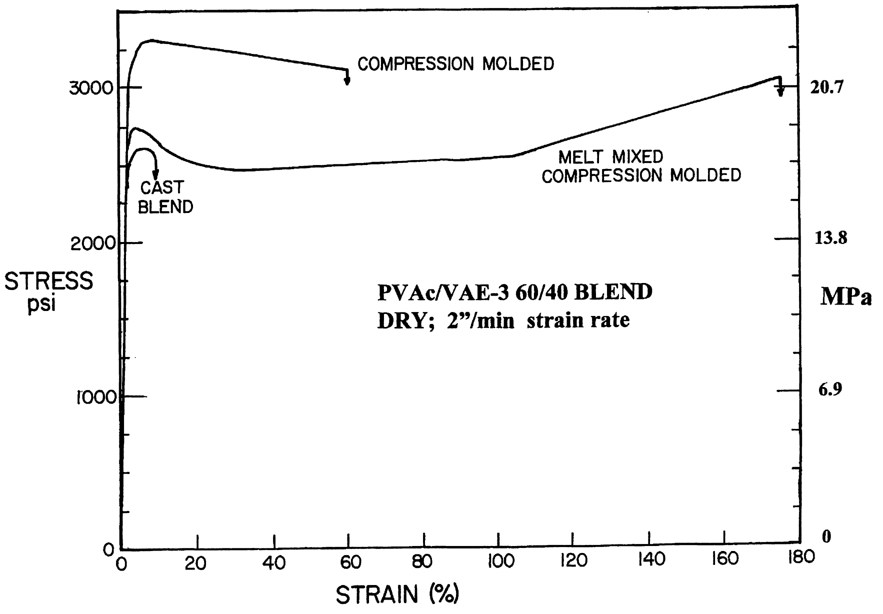

Figure 14 - Stress-Strain Data on 60/40 (by wt) PVAc/VAE-3 Blend (dry; 23 °C; 2" min strain rate) as a Function of Sample Preparation

It has been demonstrated that compliance mismatch in emulsion blends can yield a mechanically incompatible system even though adhesion between the phases is excellent. A number of examples have been observed that where the compliance is reasonably matched good mechanical compatibility can be achieved even when the components are not miscible and interpenetration across the interface is not thermodynamically favorable. One such example is a blend of VAE-3 with a carboxylated styrene-butadiene emulsion (Dow 620). The components are transparent to translucent in cast films whereas the blend is opaque and glossy implying a two phase system. The stress-strain data shown in

Figure 15 show that the blend offers mechanical compatibility with properties between the constituents.

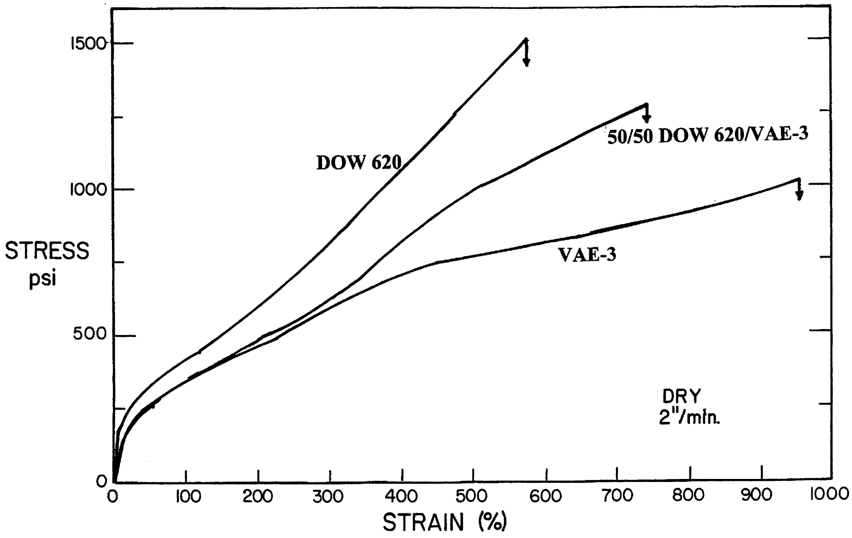

Figure 15 - Stress-Strain Data on 50/50 (by wt) Blend of SBR (Dow 620)/VAE-3 (dry; 23 °C; 2"/min/strain rate

Conclusions

VAE and PVAc emulsions utilizing PVOH as the protective colloid have been shown to exhibit PVOH continuous phase behavior in cast emulsion films. The PVOH protected emulsions thus provide a model system for investigating the mechanical characteristics of a low T_g/high T_g emulsion blend as adhesion between the particles is expected to be high as the PVOH retains continuous phase behavior in the blends.

The stress-strain behavior of PVAc/VAE blends exhibit poor mechanical compatibility in spite of the expected excellent adhesion between the particles comprising the blend. Theory predicts a large decrease in elongation at failure for rigid (PVAc) particle addition to a soft matrix (VAE). The experimental results agree and indicate that a compliance mismatch leads to mechanical incompatibility if excellent adhesion between the particles comprising the blend is achieved. This result provides the hypothesis that lower adhesion may be preferred where a compliance mismatch results in emulsion blends. This is counter-intuitive to expected behavior but does agree with theory.

The prediction of tensile strength for the blends using models based on polymer/filler composites shows poor agreement. A recent approach termed the equivalent box model (EBM) employing percolation theory yields good agreement with experimental results if the yield strength of PVAc is employed in the calculation instead of the experimental tensile strength. This is an important point as PVAc at the strain rate employed in these experiments yields brittle failure well below the yield strength. As the addition of VAE yields "impact modification" of PVAc, the use of yield strength in the calculation is quite logical.

Melt mixing of the PVOH protected PVAc and VAE PVOH emulsions results in a loss of any PVOH continuity as evidenced by the dynamic mechanical data. Melt mixing of the blends yields the same result. Stress-strain data on melt mixed blends clearly demonstrates that the heterogeneous structure of the melt mixed blend yields significant improvement in mechanical compatibility compared to the emulsion cast blend comprised of a more uniform particle array of the constituents of the blend.

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