

Correlation between the Interfacial Tension and Dispersed Phase Morphology in Interfacially Modified Blends of LLDPE and PVC

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ABSTRACT: To study the phase size/interfacial tension relationship for LLDPE/PVC blends over a wide range, three modifiers of widely varying efficacy were chosen based on a cursory analysis of their acid–base interactions with the blend system. The modifiers used were poly(isoprene–4-vinylpyridine) (PIP–P4VP), poly(styrene–acrylic acid) (PS–PAA), and a hydroxyl-terminated polystyrene (PS–Si(CH₃)₂OH). The ternary blend systems were rigorously characterized by tracking both interfacial tension and dispersed phase morphology evolution as a function of percent interfacial modifier. The interfacial tension was measured using the breaking thread technique, and the blends for morphology examination were prepared on a Brabender mixer, a predominantly shear mixing device. Both the interfacial tension and the morphology studies confirm that the best modifier was the PIP–P4VP followed by PS–Si(CH₃)₂OH, and the PS–PAA copolymer did not have any influence on the system whatsoever. The area occupied per molecule at the PVC/LLDPE interface estimated from the emulsification curve (morphology data) for the poly(isoprene–4-vinylpyridine) is approximately 6 nm² per molecule. It is shown that PVC/LLDPE, due to the low interfacial tension of the unmodified blend, represents a case where the dynamic coalescence contribution to morphology development is essentially negligible. This has allowed the relationship between morphology and interfacial tension to be studied in a direct fashion. A comparison of the limiting values of morphology and interfacial tension, in the presence of the modifiers, compared to the unmodified system unambiguously indicates a close 1:1 relationship between the two in the absence of coalescence effects. This direct dependence between dispersed phase size and interfacial tension is observed for all three systems and is independent of the relative efficacy of the modifier itself. These results demonstrate a direct experimental confirmation of the interfacial tension/phase size relationship as predicted by Taylor theory.

Introduction

The blend of poly(vinyl chloride) and polyethylene represents an immiscible system with a discrete dispersed phase. Modification of the interface of a polymer blend with an interfacial modifier serves to reduce the interfacial tension between the parent components,^{1–11} reduce the dispersed phase size,^{6–21} inhibit coalescence,^{5,10,21,22} and improve the adhesion between the constituents in question.²³ This is normally a prerequisite to the obtention of improved mechanical properties.^{18–25}

Taylor^{26,27} studied the deformation and disintegration of the dispersed phase for Newtonian systems in simple shear flow fields in the absence of coalescence effects. He defined a dimensionless parameter E shown in eq 1. Ca represents the ratio of viscous to surface tension forces.

$$E = Ca[(19p + 16)/(16p + 16)] \quad (1)$$

$$Ca = \eta_m \dot{\gamma} a / \sigma \quad (2)$$

η_m is the viscosity of matrix, p is the viscosity ratio of droplet phase to matrix, a is the radius of the droplet, $\dot{\gamma}$ the rate of shear, and σ the interfacial tension. The above equation indicates that viscosity ratio, the shear rate, the droplet diameter, and the interfacial tension

are critical variables to consider in controlling particle deformation and breakup of the dispersed phase during the processing of polymer blends. It can also be seen that the size of the dispersed droplet is directly related to the interfacial tension between the two phases. Although eqs 1 and 2 are cited very frequently, the relationship between interfacial tension and dispersed phase size has not been rigorously demonstrated experimentally for polymer blends.

There is a need to develop strategies to effectively and quantitatively classify the emulsification capability of interfacial modifiers. Recently in this laboratory emulsification curves tracking morphology evolution with modifiers have been used to this effect, and the role of molecular weight of the modifier, its architecture, and chemical composition have been studied extensively.^{5,10–17} The reduction of the dispersed phase size is due to the combined effects of reduced coalescence and reduced interfacial tension. Studying both the reduction of the interfacial tension as well as morphology evolution should therefore not only be effective techniques to analyze emulsification behavior but also help to clarify the fundamental relationship between the two.

In a previous study,¹¹ the breaking thread technique was shown to be applicable to the difficult case of measuring the interfacial tension of PVC/LLDPE blends. By choosing an appropriate molecular weight and reducing the thread size as well as the time of the test in order to minimize thermal degradation, it was shown

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Table 1. Chemical Structures of the Interfacial Modifiers and Their Acid–Base Pair Interaction Parameters

Polymers or segments	Ka/Kb	Kb - Ka
PVC	1.33 (acid)	
LLDPE	≈ 1 (neutral or slightly base)	
PAA		≈ -6 (acid)
PS		2.9 (base)
P4VP		4.9 (base)
PIP		≈ -0.1 (slightly acid)

that the interfacial tension of PVC/LLDPE could be evaluated at 3.4 mN/m. In that paper it was also shown that the PIP–P4VP copolymer was an effective interfacial modifier for that system.

In this paper, quantitative morphology evolution via the emulsification curve as well as the variation of interfacial tension is used to analyze the emulsification capability of three interfacial modifiers of widely varying efficacy for the PVC/LLDPE interface. This study will serve to compare the two techniques as tools for emulsification analysis over a wide range of modifier efficacies. A further objective is to obtain fundamental information concerning the basic relationship between interfacial tension reduction and morphology evolution. Conventionally, copolymer interfacial modifiers are designed based on the zero enthalpy approach, i.e., copolymers possessing different segments chemically identical to the parent components of the blend. In this paper the modifiers were selected based on their varying acid–base interaction potentials for the base materials.

Experimental Section

Materials. The LLDPE (grade HS-7028 Natural, from Union Carbide Chemicals and Plastics Company Inc.) had a melt flow index of 1.0 g/10 min and M_n of 33 000 g/mol and M_w of 115 000 g/mol according to the manufacturer. The PVC (grade SE-950ED) was based on a commercially available sample of PVC with a K value = 51 (M_w = 54 000 g/mol) and supplied by Synergistic Chemicals Inc.; it was stabilized by seven parts liquid methyltin heat stabilizer (Advastab TM-281 SP). Two diblock copolymers—poly(isoprene-4-vinylpyridine) (PIP–P4VP, degree of polymerization, DPn: 256–494) and poly(styrene–acrylic acid) (PS–PAA, DPn: 510–1220)—and a hydroxyl-terminated polystyrene (PS–Si(CH₃)₂OH, DPn: 275) were used as interfacial modifiers. These modifiers were chosen based on their varying potential for acid/base interactions. Their chemical structures and acid/base pair interaction parameters, together with the data of inverse gas chromatography (IGC),^{29–33} are listed in Table 1. A small amount (0.1 wt %) of antioxidant Irganox 1076 from Ciba-Geigy was added to the blends.

Blending. LLDPE/PVC blends in the proportion of 75/25 (by weight) were prepared in a Brabender mixer. Interfacial modifiers, in the desired concentration based on the weight of the dispersed phase, i.e., PVC phase, were added to the blend when both PE and PVC were molten. After blending for 5 min, blends were immediately cooled in cold water and then prepared for the SEM observation. To prepare the sample used in the interfacial tension experiment, the modifier was added in different proportions to the PVC melt immediately after the fusion of PVC. Disklike samples were pressed out of PE and PVC both with and without modifier for rheological measurement.

Rheology. Rheological characterization of PE and PVC with and without modifiers was conducted on a Bohlin constant

Table 2. Zero Shear Viscosities and Viscosity Ratio of Raw Materials and Blends at 200 °C (P4VP–PIP Data Given in Ref 11)

sample	η_0 , Pa s	$\rho = \eta/\eta_m$
LLDPE	8140	
PVC	1940	0.24
PVC + 0.5% PS–PAA	2318	0.28
PVC + 1% PS–PAA	2710	0.33
PVC + 2% PS–PAA	3540	0.44
PVC + 3% PS–PAA	4260	0.52
PVC + 5% PS–PAA	5700	0.70
PVC + 0.5% PS–SiOH	2106	0.26
PVC + 1% PS–SiOH	2433	0.30
PVC + 2% PS–SiOH	2860	0.35
PVC + 3% PS–SiOH	3380	0.41
PVC + 5% PS–SiOH	3800	0.47

stress rheometer in the oscillation mode at the desired temperature. Strain sweeps were performed to define the region of linear viscoelasticity. A parallel plate configuration was used with a gap of about 1.3 mm. Zero shear rate viscosities of the polymers and PVC added with modifiers were extrapolated by using the Cross generalized power law equation.³⁴ These data are reported in Table 2.

Preparation of PVC Thread and PE Film. Threads of PVC and of PVC containing different concentrations of modifiers were produced by drawing out the molten PVC pellets on a hot plate while carefully controlling the heating temperature. The final diameter of the thread varied with the pulling speed. An LLDPE film with a thickness of 0.2–0.4 mm was obtained by compressing LLDPE pellets at 200 °C for 5 min.

Interfacial Tension Measurement. The interfacial tension between PVC and PE melts was measured at 200 °C by the breaking thread method. Details about the experimental and theoretical backgrounds can be found in previous work.^{2,11,35} A Nikon light microscope connected to a CCD-IRIS/RGB video camera was used to observe and record the distortion amplitude of the thread with time at regular intervals. The measurement of the evolution of the distortion amplitude of the thread over time as well as the wavelength was obtained by the Visilog 4.1.3 image analysis software package modified in-house for the breaking thread experiment.

Morphology Analysis. A scanning electron microscope (JSM-T300) was used to examine and record the morphology of the blend. The semiautomatic image analyzer was used for measuring the size of the PVC dispersed phase in the blend from plane faced samples. The number-average diameter d_n and the volume-average diameter d_v were calculated on the basis of more than 500 diameter measurements made on SEM photos taken from different areas of the same blend sample. The Saltikov correction was applied to the diameter determined from SEM micrographs.³⁶ The micrographs displayed in this paper were prepared from cryogenically fractured surfaces.

Results and Discussion

The interfacial tension between PVC and LLDPE melts was measured at 200 °C by the breaking thread method as described in the previous work.¹¹ It was evaluated at 3.4 mN/m.

To be able to test the interfacial tension/phase size relationship over a wide range, it was necessary to use a series of modifiers which would demonstrate widely different efficacies for the interface (ranging from a very poor emulsifier to an excellent one). The three modifiers shown in Figure 1 were chosen based on their varying potential for acid–base interactions. The total interfacial interaction can be estimated from the acid–base pair interaction parameters that are related to their K_a and K_b and the dispersion forces of the individual components.^{37,38} The acid/base interaction constants K_a and K_b are evaluated from inverse gas chromatography

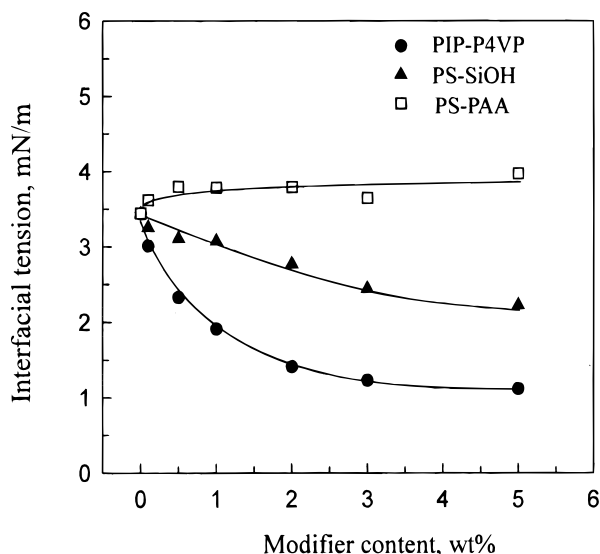


Figure 1. Effect of the concentration of copolymer PIP-P4VP (DPn: 256–494), hydroxyl-terminated polystyrene PS-Si(CH₃)₂OH (DPn: 275), and PS-PAA (DPn: 510–1220) on the interfacial tension between LLDPE and PVC at 200 °C. Percent modifier concentration is based on the weight of PVC.

(IGC) experiments according to Gutmann's theory of acid and bases³⁹ in characterizing the interface in such a system. The K_a/K_b ratio of PVC is 1.33, and it is strongly interactive, acting as an acid. For LLDPE, $K_a = K_b \approx 0$.

A potential strong adsorption exists between the basic P4VP segment in the P4VP-PIP copolymer and the acid PVC (see Table 1). PIP is only slightly acidic, and hence no possibility exists for strong acid-base interactions between it and LLDPE. However, due to their chemical affinity and taking the dispersion forces into account, the LLDPE is more likely to interact with PIP than with PVC.

For PS-Si(CH₃)₂OH, it can be seen from Table 1 that both the PS segment and the hydroxyl functional end group are basic. This specific polymer therefore has the possibility of acid/base interaction with PVC. A specific interaction between chlorine and the oxygen is believed to exist.²⁸ Since the PS segment has a lower surface energy than P4VP,³² a weaker interaction exists between the PE molecules and PS segment than between the PE molecules and the P4VP segment. Furthermore, PS is significantly less basic than P4VP. As well, the hydroxy group terminates the PS chain, and only one hydroxy group is available per PS chain. It is reasonable to assume that the total interfacial interaction between the segment or end group of PS-Si(CH₃)₂OH and each component of the PVC/LLDPE blend is less than that in the PIP-P4VP copolymer compatibilized blends.

The PS-PAA copolymer has the possibility of both acid and base interactions, depending on the relative length of each segment. PAA is a strong acid segment. This segment would not be expected to interact with the PVC and/or LLDPE although the basic PS segment would tend to adsorb to the PVC phase. It should be noted, however, that when the PAA segment is long (1220 units) compared with the PS segment (510 units) as in this case, the main interaction in the blend would be expected to be a repulsive force between the PVC molecules and the PAA segment. This is accentuated by the fact that the PAA is strongly acidic and the PS is weakly basic.

Table 3. Comparison of the Reduction of the Interfacial Tension σ and the Dispersed Phase (PVC) Size in the Blends upon the Addition of Interfacial Modifiers; Ratio of Values at 0% Modifier to the Limiting Values (lv) Are Used

modifier	$\sigma(0\%)/\sigma(lv)$	$d_p(0\%)/d_p(lv)$
PIP-P4VP	3.0	2.7
PS-Si(CH ₃) ₂ OH	1.5	1.6
PS-PAA	0.9	1.0

According to their potential for acid/base pair interactions, the expected interactions between the above modifiers and PVC/LLDPE blend should therefore yield



Effect of Modifiers on the Interfacial Tension.

Figure 1 shows the interfacial tension of the blend as a function of the percentage of the modifier in the PVC phase, for all three modifiers. The modifiers show widely different emulsification capabilities. The PIP-P4VP is clearly the best of the three, and it displays a typical dependence of interfacial tension on modifier concentration. The interfacial tension decreases rapidly and achieves a limiting value at about 3% of modifier (based on the weight of PVC). The approximate reduction of interfacial tension caused by 5% (limiting value of interfacial tension) of PIP-P4VP and PS-Si(CH₃)₂OH is given in Table 3.

From Figure 1 and Table 3, it is evident that the addition of the copolymer PIP-P4VP gives rise to a significant decrease of the interfacial tension. An overall 3 times decrease was observed when 5% of the copolymer was added. The corresponding decrease of interfacial tension caused by the addition of modifier PS-Si(CH₃)₂(OH) was less significant than the PIP-P4VP copolymer. An overall decrease of 1.5 times in interfacial tension was observed. Figure 1 also clearly shows that the interfacial tension between PVC and LLDPE was not reduced by the addition of the copolymer PS-PAA.

These results from the interfacial tension study confirmed the ordering based on the expected acid-base interactions stated above.

Effect of Modifiers on the Morphology. The SEM micrographs for 25/75 PVC/LLDPE blends with 8% copolymers PIP-P4VP and PS-PAA are shown in Figure 2. From these photos, the dispersed phase sizes after compatibilization are clearly seen to be different for the two systems. The effect of the three modifiers on the blend morphology is characterized through the change of the dispersed PVC phase size with the percentage modifier shown in Figure 3a–c and in Table 3. The morphology data in Figure 3a are known as an emulsification curve which is characterized by a rapid drop in the dispersed phase particle size at low concentrations of the interfacial modifier, followed by a leveling off to a constant value at a certain concentration of interfacial modifier. The leveling off of dispersed phase size observed at high block copolymer concentration is an indication of interfacial saturation by the copolymer. This concentration is known as the critical concentration or saturation concentration for emulsification.¹³ Emulsification curves as a tool for studying interfacial modifier efficacy for polymer blends has been used extensively in this laboratory.^{10–17}

In Figure 3a, significant decreases in both the number-average diameter and the volume-average diameter of the PVC dispersed phase can be found when about 8%

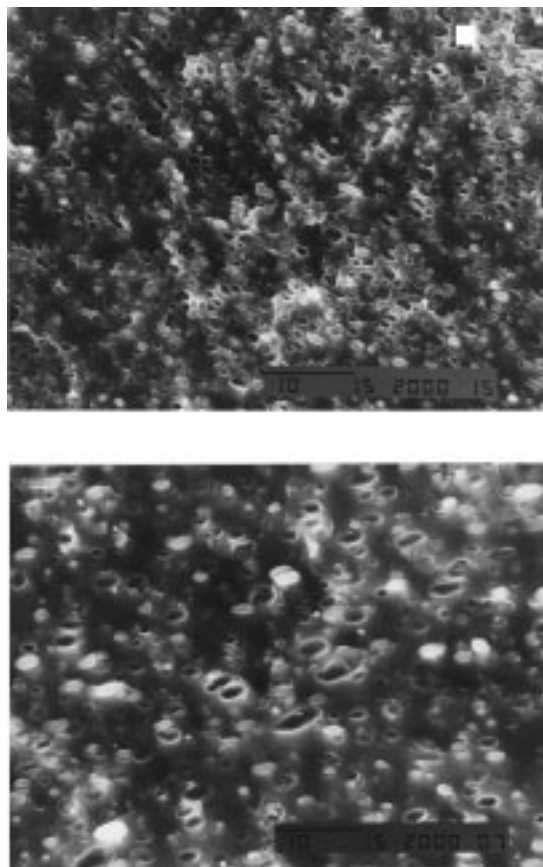


Figure 2. Scanning electron micrographs for 25/75 PVC/LLDPE blends with 8% copolymer (based on the weight of PVC dispersed phase). Blends with PIP-P4VP (above) and PS-PAA (below) were prepared at 200 °C. 1.2 cm equals 10 μm .

copolymer PIP-P4VP (percent based on the weight of PVC dispersed phase) was added. Above this copolymer concentration, there is no further decrease in the particle size. An overall 2.7 times decrease in the volume average diameter was observed at this limiting value of dispersed phase size. It can also be noticed that the relative difference between d_v and d_n becomes narrower with increasing copolymer content, implying a decrease in the dispersity of the PVC domain size.

A similar emulsification curve for the blend with modifier PS-Si(CH₃)₂OH is presented in Figure 3b. It can be seen that although the PVC phase size drops with increasing modifier content, the 1.6 times overall decrease in the volume average diameter brought about by 20% PS-Si(CH₃)₂OH modifier (concentration based on the weight of the dispersed PVC phase) is smaller than with PIP-P4VP modifier. No obvious narrowing in the particle size distribution (d_v/d_n) was observed for this system.

The blend with added PS-PAA copolymer demonstrates no significant changes in the d_v and d_n of the dispersed PVC phase as can be seen from Figure 3c. This indicates that the copolymer was unable to emulsify the LLDPE/PVC system.

In this paper the area occupied per molecule at interfacial saturation for a PIP-P4VP of M_n of 70 000 can be calculated from the emulsification curve in Figure 3a as 6 nm² per molecule. The calculation is only carried out for the PIP-P4VP modifier since it is the only truly effective emulsifier of the three. The area per molecule can be calculated knowing the dispersed phase area and the number of molecules required to saturate

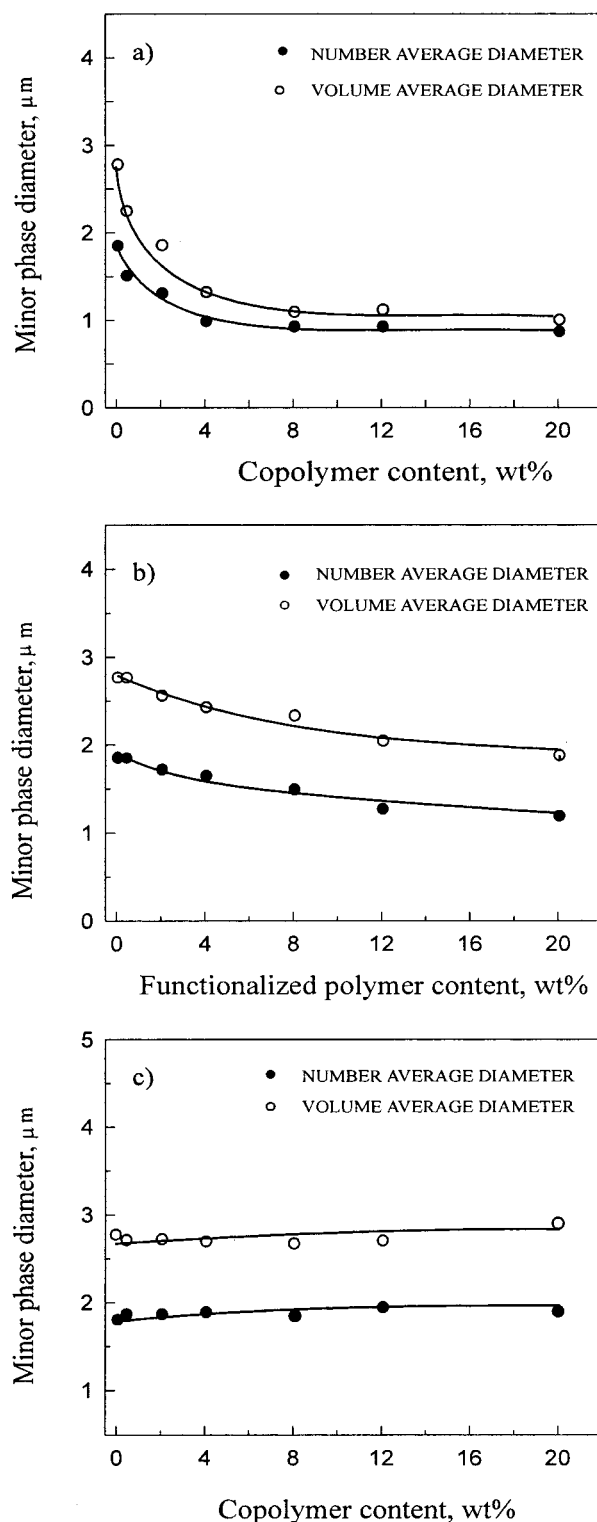


Figure 3. Influence of the concentration of (a) copolymer PIP-P4VP, (b) functionalized polymer PS-Si(CH₃)₂OH, and (c) copolymer PS-PAA concentration on the PVC dispersed phase size in PVC/LLDPE blends (percent copolymer is based on the weight of PVC dispersed phase).

the interface (the critical concentration from the emulsification curve is used for this purpose).^{16,17} This approach assumes that all the modifier has migrated to the interface. Recently, it has been shown that for highly effective modifiers this assumption is not unreasonable.⁴⁰ The area value of 6 nm² per molecule compares closely with that obtained for a block copolymer

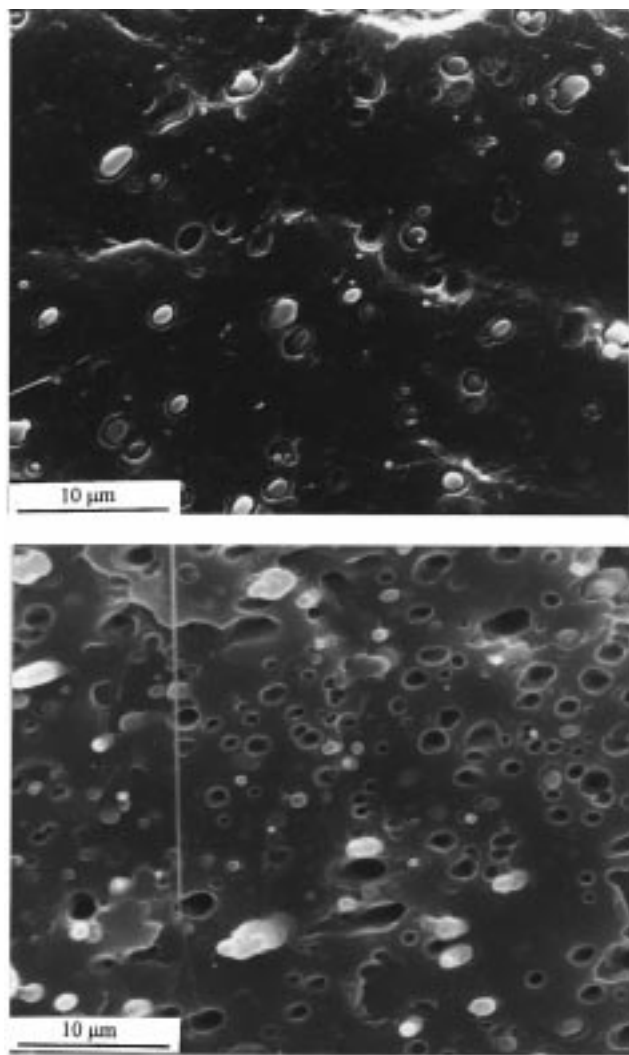


Figure 4. Scanning electron micrographs for 5/95 (above) and 25/75 (below) PVC/LLDPE blends blended in the Brabender mixer at 200 °C.

of similar molecular weight from previous studies where hydrogenated styrene butadiene copolymers were used to emulsify polystyrene/ethylene-propylene blends. It is important to note that despite the fact that the latter work used a compatibilization strategy based on zero enthalpy or like dissolves like and the modifiers in the present work were chosen based on acid–base considerations, the area occupied is very similar. This result may indicate that in melt mixing the nature of the interactions may have less influence on the spatial arrangement of the interfacial modifier, in contrast to the case of polymer solutions.

Interfacial Tension/Morphology Relationship.

From the above work it can be seen that both the interfacial tension and the morphology study clearly demonstrate the widely varying emulsification efficacies of the three chosen modifiers for the PVC/LLDPE system. These two approaches are solid quantitative tools for directly estimating the ability of a given modifier to emulsify a blend system.

Two factors are considered to be responsible for the reduction of the dispersed phase size upon addition of an interfacial modifier: a reduction of the interfacial tension and a reduction of the coalescence of the dispersed phase.¹⁰ To distinguish the relative contribution of these two phenomena in controlling dispersed

Table 4. Dispersed Phase (PVC) Size in the Blends of Different PVC Contents

blend	dn	dv	dv/dn
5/95 PVC/PE	1.6	2.4	1.5
10/90 PVC/PE	1.7	2.5	1.5
25/75 PVC/PE	1.8	2.6	1.5

phase morphology in this system, the morphologies of the 5/95, 10/90, and 25/75 PVC/LLDPE blends in the absence of interfacial modifiers were characterized. The SEM photos of 5/95 and 25/75 PVC/LLDPE blends are illustrated in Figure 4. The average diameters of the dispersed PVC phase in these blends are given in Table 4. It can be seen that there is virtually no increase in the dispersed PVC phase size with its composition in the blend. This indicates that dynamic coalescence of the dispersed phase barely occurs in this system. The decrease of the dispersed PVC phase size upon addition of the interfacial modifier can therefore be almost entirely attributed to the decrease of the interfacial tension. The very low contribution of coalescence can be rationalized by the low interfacial tension of this system at 200 °C compared with other polymer blend systems^{5,10,15}

Since coalescence under dynamic mixing conditions in this system can be considered to be negligible, the relationship between interfacial tension and morphology can be studied directly from Figures 1 and 3. In those figures, the absolute modifier concentration units cannot be compared since one experiment is carried out under dynamic conditions and the other under static conditions. Intuitively, one would expect much more difficulty in migrating the modifier to the interface in the breaking thread experiment. Nevertheless, it is obvious from that data that the interfacial tension and morphology demonstrate identical tendencies. The most rigorous basis of comparing interfacial tension and morphology is to use their plateau values since it can be taken as an indication of interfacial saturation (see Table 3). From those data it can be clearly seen that the reduction in interfacial tension and the reduction in dispersed phase morphology for all three modifiers demonstrate a close direct dependence when the blends are prepared in this predominantly shear mixing device.

In a previous paper,¹⁰ after accounting for coalescence effects, it was also shown that there was a direct dependence between the interfacial tension and morphology for a PET/PP blend prepared in a Brabender mixer. It was demonstrated in that work that the thread in the breaking thread experiment represents a surface area many times lower than the interfacial area of an equivalent volume of 1 μm spheres. This explains the obtention of a limiting value of interfacial tension (as shown in Figure 1) even though the experiment is carried out under static conditions. Evidently, there is sufficient modifier in the direct environment of the thread to saturate that low interfacial area. The present work studying three modifiers as emulsifiers for PVC/LLDPE combined with the previous study on PET/PP indicates unambiguously that a direct relationship exists between morphology and interfacial tension in the absence of coalescence effects for a predominantly shear mixing device. Furthermore, this dependence holds over a wide range of modifier efficacies. These results demonstrate a direct experimental confirmation of the interfacial tension/phase size relationship predicted by Taylor theory.^{26,27}

Taylor theory essentially relates the final particle size to a balance between the shear stress tending to deform and disintegrate the drop and interfacial tension which tends to keep it together. Previous studies^{16,21} have shown that the overall Taylor theory tends to significantly underestimate the actual dispersed phase size in polymer blends. This discrepancy was primarily related to the viscoelastic nature of the droplet. In earlier work⁴¹ it has been shown that blend morphology is not sensitive to 2–3-fold changes in shear stress and shear rate in an internal mixer, despite the fact that Taylor theory predicts a direct relationship between shear stress and particle size. Taken together with the results from this study, it is clearly the overestimation of the influence of shear stress in the Taylor theory which results in its underestimation of the actual particle size for viscoelastic systems. The elastic component of molten polymers allows them to better retain their shape after deformation.⁴²

Conclusions

In this study the emulsification of PVC/LLDPE blends was studied by both interfacial tension and quantitative morphological analysis as a function of interfacial modifier. Three interfacial modifiers of widely different emulsification capabilities were used so that the interfacial tension/dispersed phase size relationship could be studied over a wide range of modifier efficacies. The modifiers were chosen based on a cursory examination of their acid–base interactions with the blend system. The interfacial tension/morphology studies confirmed the expected efficacies of the modifiers. The best modifier was the PIP–P4VP which demonstrated an excellent capability to emulsify PVC/LLDPE. A hydroxyl-terminated polystyrene, PS–Si(CH₃)₂OH, acts less effectively, and the poly (styrene–acrylic acid), PS–PAA, did not emulsify the blend at all.

The dependence of the dispersed particle size as a function of its composition for the uncompatibilized PVC/LLDPE blend revealed virtually no change in particle size with composition. This blend, even in the unmodified state, therefore does not experience significant dynamic coalescence phenomena. This can be rationalized by the low interfacial tension of 3.4 mN/m for PVC/LLDPE. Since coalescence is negligible during melt mixing in this system, the fundamental relationship between interfacial tension and dispersed phase morphology could be studied directly. The results indicate a close 1:1 relationship between particle size and interfacial tension that is independent of the emulsification efficacy of the interfacial modifier in this predominantly shear mixing device. These results demonstrate a direct experimental confirmation of the interfacial tension/phase size relationship as predicted by Taylor theory.

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