ELSEVIER

Polymer 40 (1999) 4419–4423

polymer

Polymer Communication

Surface modification strategies for multicomponent polymer systems,VI:acid–base interactions as a strategy for interfacial modification in immiscible polymer blends

H. Liang, Ruijian Xu, B.D. Favis, H.P. Schreiber*

CRASP, Department of Chemical Engineering, Ecole Polytechnique, Box 6079, Stn. Center-Ville, Montreal, H3C 3A7, Que., Canada

Received 4 February 1998; received in revised form 6 October 1998; accepted 14 October 1998

Abstract

Three copolymers with different emulsification efficacies were used as potential interface modifiers for an immiscible blend of linear low density polyethylene (LLDPE) and poly(vinyl)chloride (PVC). The specific interaction between blend components and the modifying copolymers was determined by measurements of interfacial tension and by inverse gas chromatographic (IGC) data, characterizing the acid–base properties of the polymers. Additional information on modifier effectiveness was obtained from blend morphology data. Acid–base pair interaction parameters, computed from IGC results, predicted the modifying potential of the two copolymers which emulsified the system, and were consistent with the morphology and interfacial tension results. IGC, however, did not distinguish between the emulsification qualities of the two good modifiers. The best of the three modifiers (P4VP-PIP) also increased the impact strength of the modified LLDPE/PVC system. The results indicate that specific (acid–base) interactions at component interfaces may represent a promising strategy for the choice of emulsifying agents for some immiscible polymer blends. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymers; Immiscible blends; Interfacial tension

1. Introduction

Most polymer blends, like those of polyvinyl chloride (PVC) and linear low density polyethylene, (LLDPE), are immiscible at the molecular level. Frequently, an interfacial modifier is added in order to improve the compatibility of such blends. The interfacial modifier should have the capacity to locate at the blend interface, reduce the interfacial tension between two phases, inhibit coalescence between domains of the minor phase and improve the adhesion between constituents of the blend. A desirable consequence should be the enhancement of the blend's mechanical properties.

Various strategies may be used to effect the desired interfacial modification. A well-established approach to emulsify polymer blends is based on the zero enthalpy method, that is on the like dissolves like principle. This would involve choosing a block copolymer with different segments that are chemically identical to or miscible with those in the respective phases as indicated by a close match of pertinent solubility parameters. In addition, the copolymer may contain moieties capable of specific physical and/or chemical interactions with the blend components. These interactions may arise from a variety of mechanisms, notably the presence of electron donor and acceptor groups, thus leading to the presence of acid–base interactions. Specific interactions have been cited frequently to account for the miscibility of certain blend systems [1]. Unfortunately, however, these links tend to be qualitative, with little quantitative information available on specific interactions in polymer blend systems. An important objective of this study is to define an approach to the quantification of specific interactions.

An alternative approach to enhanced miscibility has been reported by Tucker et. al [2]. A copolymer where a (PS) block had an exothermic heat of mixing with the homopolymer, poly (2,6-dimethyl-1,4-phenyl oxide) (PEPO), caused a dramatic increase in the degree of miscibility. The negative enthalpy of mixing amounts to an additional driving force for mixing. However, this latter approach is quite limited in terms of an overall strategy for compatibilizing polymer blends.

Recent publications from these laboratories [3–5] have shown the emulsification curve to be an effective assessment of the miscibility enhancement capacity of interfacial modifiers. The curve is characterized by a rapid drop in the

---

* Corresponding author.

PII: S0032-3861(98)00767-8

dispersed phase particle size at low concentration of the interfacial modifier, followed by a levelling off to a constant value at higher concentrations of the modifier. The levelling off in the size of the dispersed phase can be used as an indication of interfacial saturation by the copolymer. In previous work [5–7], efforts were made to link variations in the emulsification curve with modifier concentration to analogous changes in interfacial tension. A direct relationship between the morphology and interfacial properties was confirmed.

Earlier studies in the present series [7] made use of three interfacial modifiers, listed below, with widely different emulsification capabilities with respect to the morphology and interfacial tension of a PVC/LLDPE system. One of the consequences of that work was to underscore the need for a method which could predict the efficacy of proposed emulsifying agents for stated polymer blends. The present work aims to meet that need by attempting to establish a quantitative evaluation of the role played by specific, acid–base interactions in the emulsification process in LLDPE/PVC blends, with the diblock polymers as potential compatibilizers. The current note presents early results, considered to hold sufficient promise to warrant publication in the present form.

The three interfacial modifiers involved in the present exercise were synthesised and described by Yu and Eisenberg [8]. They represent structures combining acidic and basic interaction tendencies. They are:

- PS/PAA - Polystyrene/polyacrylic acid (DPn: 50/1220)
- PS/SiOH - Silyl-hydroxyl terminated polystyrene (DPn: 275)
- PIP/P4VP - Polyisoprene-poly(4-vinyl)pyridine (DPn: 256/494)
- The notation DPn represents degree of polymerization.

2. Experimental

2.1. Inverse gas chromatography

Inverse gas chromatography (IGC) was used to measure the acid–base interaction constants K_a and K_b for each of the diblocks as well as for the blend constituent. The experimental procedures required have been fully described in contemporary literature [9–12]. Briefly, the polymers represent stationary phases which are probed by non-polar and polar vapours injected at extreme dilution. In the present work, carried out in the temperature range 30–60°C, a sample of each of the three polymers was deposited onto Chromosorb G (AW/DMCS, 60/80 mesh), from solutions, to represent about 10 wt% of total solids, and packed in stainless steel chromatographic columns. They were probed initially with vapours of linear alkanes from nC_6–nC_9. These were used to measure dispersion force interactions between polymers and the vapour phase. The specific interaction behaviour of polymers was assessed by measuring their retention characteristics for polar probes, selected on the basis of their electron acceptor and donor numbers, *AN*, *DN*, as given by Gutmann [13]. They included the acids chloroform and dichloromethane, the bases diethyl ether and tetrahydrofuran, and the amphipatic vapours of ethyl acetate and acetone. At least 3 injections of each probe were used in averaging net retention volumes. The standard deviation in these measurements did not exceed 3%. The temperature range investigated was below the T_g for PS/PAA and PS/SiOH, but straddled the T_g for PIP/P4VP. In this case, therefore, vapour absorption could influence the observed retention data. The procedure recently outlined by Mukhopadhyay and Schreiber [14] was used to overcome the problem. The retention of vapors by the polymer is, in this case, equally relevant to interactions occurring at the polymer/mobile phase interface.

2.2. Data processing

The procedures and thermodynamic concepts which link the net retention volume of the IGC experiment with the dispersive surface free energy of the solid, γ_s^d, and its acid and base interaction constants, K_a and K_b, have been fully described elsewhere [8–12,14].Availability of K_a and K_b values for matrix polymers and additives alike allows for the computation of an acid–base pair interaction parameter I_{sp}. In the absence of theoretical guidelines for the calculation, the empirical approaches followed were:

$$I_{sp} = K_{a1}\cdot K_{b2} + K_{a2}\cdot K_{b1} \tag{1}$$

and

$$I_{sp}^{*} = (K_{a1}\cdot K_{b2} + K_{a2}\cdot K_{b1}) - (K_{a1}\cdot K_{a2} + K_{b1}\cdot K_{b2}) \tag{2}$$

Here 1 represents PVC and 2 the block copolymer (the LLDPE phase, of course, has no finite values of K_a and K_b). Expression (2) may be preferred because it takes in account the probability that in a random mixing process for blend preparation acid/acid and base/base moieties will be brought into intimate contact. Clearly, these cannot contribute to acid–base interactions and may indeed diminish them by hindering sufficiently close approach of acceptor and donor groupings in the constituent polymers.

2.3. Blending

Blends were prepared on a Brabender mixer at a roller speed of 50 rpm. Samples used for morphology characterisation were mixed at 200°C; those intended for mechanical property characterisation at 180°C. PVC and LLDPE were introduced into the chamber at the same time. Copolymers were added after the host polymers were molten. Blending was carried out for another 6 min, to the attainment of steady-state torque values.

Table 1
The steady-state (plateau) values of interfacial tension and dispersed phase (PVC) size (characterized by d_v) in the blend upon addition of three interfacial modifiers

Modifiers	σ (5%), (N/m) × 10^3	d_v(20%), µm
PIP/P4VP	1.12	0.99
PS/SiOH	2.23	1.87
PS/PAA	3.97	2.9

2.4. Morphology characterisation

A scanning electron microscope (JSM-T300) was used to examine and record the morphology of cryogenically fractured surfaces of the blends. The semi-automatic image analyser was used for measuring the size of the PVC dispersed phase in plane-faced samples of the blends. The volume average diameter d_v was 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 [15].

2.5. 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 elsewhere [16–18]. 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 evolution of the distortion amplitude of the thread over time and the wavelength was obtained by the Visilog 4.1.3 image analysis software package, modified in-house for the breaking thread experiment.

2.6. Mechanical properties

Only the LLDPE/PVC (75/25) blends with and without the P4VP-PIP copolymer modifier were studied. Specimens were molded using a Carver Laboratory Press at a temperature in the interval 180–190°C. A V-shape notch was introduced according to ASTM D256. Impact strength tests were carried out with an Izod impact tester (CS-137) at room temperature. The quoted results are averaged from at least eight tests, and are presented as the impact energy per unit area of fractured sample (KJ m^{-2}). They are accurate to within ± 7%.

Table 2
Surface characterization of copolymers and homopolymers coated on Chromosorb at mean $T = 50$°C

Sample	γ_s^d, mJ/m^2	K_a	K_b	K_a/K_b
PS/PPA	33.9	0.28	0.53	0.53
PS/SiOH	28.8	0.39	0.84	0.46
PIP/P4VP	30.9	0.25	0.71	0.35
PVC	33.4	0.36	0.27	1.33
LLDPE		~ 0	~ 0	

3. Results and discussion

Previous studies showed [7,17] that of the three diblock polymers designed to modify the PVC/LLDPE blend, copolymer PIP/P4VP was the best performer. It demonstrated excellent emulsification capability, leading to significant reductions in both the interfacial tension between LLDPE and PVC and the dispersed phase size. These parameters attain a steady value after the copolymer concentration exceeds about 4–5 wt.%(based on the PVC weight). The levelling off is an indication of interfacial saturation by the copolymer.

The marked superiority of PIP/P4VP as matrix modifier is documented in Table 1, which compares the steady-state morphology and interfacial tension results for blends using the three diblock additives. These modifiers were chosen because of significant differences in their acid–base interaction potential, as given by IGC results listed in Table 2, and by the pair interaction parameters in Table 3. The sum of these data opens the possibility of seeking the goal of this communication, namely a useful correlation between specific interactions, as given by I_{sp} I_{sp}^*, and the emulsification potential of the copolymers. With reference to Table 2, the acidic behavior of PVC confirms earlier determinations for this polymer [19]. Each diblock registers as a base, the degree of basicity, indicated by K_a/K_b, varying in the sequence PIP/P4VP > PS/SiOH > PS/PAA. Qualitatively, a relationship between emulsifying capability and acid–base interaction seems to be indicated. Of course, basicity would be very dominant in PIP/P4VP,since the latter block is known to be basic, while PIP may be expected to interact primarily by dispersion forces. The other diblocks combine basic (PS) and acidic moieties. Following arguments amply discussed in the literature [19,20], under equilibrium conditions they would orient so as to preferentially place the component with lowest surface free energy into the interface. In the IGC experiment, where the contacting medium is essentially neutral, this would favour the presence of PS groups in the surface layer. Different orientations would be adopted when in contact with the acidic PVC force field [19]. Thus, the interaction parameters in Table 3 should be regarded as approximations and not necessarily as exact representations of the interaction equilibrium in the multi-component blend. Of the two Isp values, it is I_{sp}^* which more closely follows the pattern of morphological parameters in Table 1. This is not surprising, given the greater realism with which this parameter accounts for interfacial interactions.

The principal question posed in this work was a quantification of the possible relationship between acid–base interactions and the compatibilizing capabilities of the modifying copolymers. The matter was studied for

Table 3
Pair interaction parameters for PVC – diblock combinations

PVC and	$I_{sp} \times 100$	$I^*_{sp} \times 100$
PS/PPA	26.64	2.25
PS/SiOH	40.77	4.05
PIP/P4VP	32.31	4.14

LLDPE/PVC (75/25) blends at a copolymer concentration of 5%. This was chosen since it corresponds to steady-state values of the interfacial tension and morphology of these blends and hence to saturated interfaces.

Accordingly, I_{sp} and of I^*_{sp} values were plotted vs. interfacial tension (σ_{12}) and the volume-average phase size of PVC (d_v). The results of this procedure are shown in Fig. 1.

It is evident that a useful correlation is formed by I^*_{sp}, but not by I_{sp}, for reasons already stated. As shown in Fig. 1b, there is a close relationship between acid–base interaction, and the thermodynamic and morphological parameters distinguishing the non-emulsifier from the two emulsifying modifiers. The most effective modifier, PIP/P4VP, also has the highest value of I^*_{sp}, while the non-emulsifier ranks lowest in I^*_{sp}. The correlation in Fig. 1b is not as strong as would be expected, were the orientation of this diblock

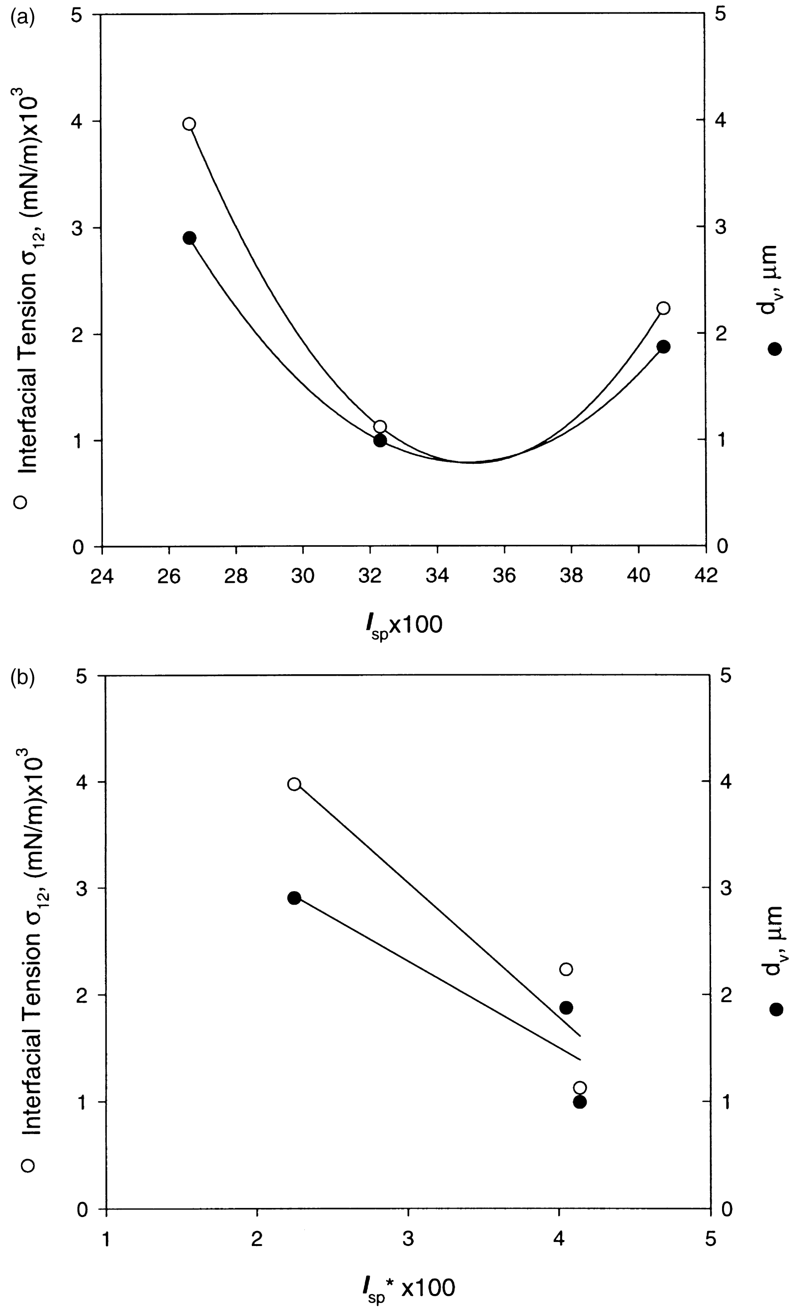

Fig. 1. Plots of (a) I_{sp} and (b) I^*_{sp} against interfacial tension an volume average diameter of the PVC phase size for 5% PIP/P4VP addition to PVC/LLDPE (25/75)

Table 4
The impact properties of the PVC/LLDPE (25/72) blends at room temperature: Impact strengths have uncertainty of ± 7%

Composition	Impact strength, KJ/m^2
PVC/LLDPE (25/75)	12.5
PVC/LLDPE (25/75) + 3% PIP/P4VP	40.7

molecule the same in the IGC as in the morphology experiments. As already suggested, when blended with the molten LLDPE and PVC, the PIP moiety of the diblock is attracted to the LLDPE phase and the P4VP to the PVC. The result would be a more drastic ‘‘segregation’’ of its building blocks than when in the orientational state of the essentially neutral IGC experiment. More fully realistic values of I_{sp}^* would require each constituent of the diblock to be characterized by the K_a and K_b values relating to its equilibrium configuration in the PVC force-field. The I_{sp}^* values show a significant difference between the two copolymers that emulsified PVC/LLDPE as opposed to the PS/PAA, which was a non-emulsifier. However, the difference in Isp^* for the two emulsifying copolymers is slight. Evidently a refinement of the acid–base approach will be needed if it is reliably to demonstrate the subtle differences between varying levels of emulsification. Nevertheless, it is reasonable to conclude that acid–base interaction represents one of the important mechanisms in the capability of copolymers to modify the thermodynamic and morphological states in inherently immiscible polymer blends.

In order to demonstrate that these interactions result not only in emulsification, but also in enhanced adhesion, the impact strength was measured for the blend which contained 3 wt% (based on total blend mass) of the P4VP-PIP copolymer. This formulation ensured saturation of the interface by the copolymer. The PS/SiOH copolymer was excluded from this portion of the study since, at these copolymer concentrations, low level crosslinking effects were observed which would influence the impact results. The blend selected represented the system which was the most effectively emulsified and a copolymer concentration ensuring interfacial saturation. The results are shown in Table 4. The addition of the P4VP-PIP copolymer results in a 3 fold increase in the impact strength, indicative of the expected enhanced interfacial adhesion. Evidently specific, acid–base interactions can exert considerable influence on adhesion in immiscible blend systems [21]. The use of I_{sp}^* for the predictive selection of emulsifiers for given immiscible polyblends, while as yet tentative, holds promise. An elaboration of the potential usefulness of acid–base interactions in this context, through the study of a wider range of polymer blend systems, is an indicated objective for forthcoming studies.

Acknowledgements

Support for this research was obtained from a Cooperative Research Grant of the N.S.E.R.C. Canada and from Operating Grants, also from the N.S.E.R.C., awarded to B. D. Favis and H. P. Schreiber.

References

[1] Paul DR. In: Paul DR, Newman S, editors. Polymer blends, New York: Academic Press, 1978 Chapter 1.
[2] Tucker PS, Barlow JW, Paul DR. Macromolecules 1988;21:2794.
[3] Favis BD. Polymer 1994;35:1552.
[4] Matos M, Favis BD, Lomellini P. Polymer 1995;36:3899.
[5] Cigana P, Favis BD, Jérôme R. J Polym Sci Polym Phys Ed 1996;34:1691.
[6] Lepers JC, Favis BD, Tabars RJ. J Polym Sci Polym Phys Ed (in press).
[7] Liang H, Favis BD, Yu YS, Eisenberg A. (in preparation).
[8] Wang W, Schreiber HP, Yu YS, Eisenberg A. J Polym Sci Polym Phys Ed 1997;35:1793.
[9] Lloyd DR, Ward TD, Schreiber HP, editors. Inverse Gas Chromatography *ASC Symposium series*, 391. Washington: Am Chem Soc, 1989.
[10] Gray DG. Prog Polym Sci 1977;5:1.
[11] Schultz J, Lavielle L, Martin CJ. J Adhesion 1987;23:45.
[12] Panzer U, Schreiber HP. Macromolecules 1991;25:3633.
[13] Gutmann V. The donor-acceptor approach to molecular interactions. New York: Plenum Press, 1983.
[14] Mukhopadhyay P, Schreiber HP. Colloids Surf A Physicochem Engng Aspect 1995;100:47.
[15] Saltikov SA. Stereometric metallography, 2nd ed., Metallurgizdat, Moscow, 1958.
[16] Tomotika S. Proc Roy Soc Lond 1935;A150:322.
[17] Elemans PHM, Janssen JMM, Meijer HEH. J Rheol 1990;34:1311.
[18] Liang H, Favis BD. Ind Engng Chem Res 1997;36:1211.
[19] Deng Z, Schreiber HP. In: Culberston BM, editor. Contemparary topics in polymer science, 6. New York: Plenum Press, 1989. pp. 385.
[20] Lipatov Yu S. In: Ishida H, editor. Controlled interphases in composite materials, New York: Elsevier, 1990. pp. 599.
[21] Fowkes FM. J Adhesion Sci Technol 1987;1:7.