

## Self-compatibilization of polymer blends via concentrated emulsions

Eli Ruckenstein\*, Hangquan Li\*\*

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, NY 14260, USA

Received: 5 May 1995/Accepted: 18 May 1995

### Summary

A novel approach to the formation and compatibilization of polymeric blends is suggested, namely the self-compatibilization via concentrated emulsions. In this method, two concentrated emulsions are prepared from different monomers and subjected to partial polymerization; at least one concentrated emulsion contains also some di-vinyl-terminated macro-monomers. A blend is formed by mixing the partially polymerized latexes and subjecting the mixture to complete polymerization. Some AB networks, with the macro-monomers as chains A and the homo- and co-polymers generated from the other monomers as chains B, are formed, which ensure the self-compatibilization of the resulting blend. Blends of styrene-co-methyl methacrylate and poly (vinyl acetate) were prepared and investigated as a model system.

### Introduction

Polymer blending is one of the most important pathways to the development of new polymeric materials. However, in such blends, the problem of compatibility may arise, since satisfactory physical and mechanical properties are related to a fine dispersion of one phase in the other one and to the resistance to gross phase segregation. For this reason, the compatibilization of immiscible polymers has received increasing interest in recent years<sup>(1-3)</sup>.

The compatibility of a blend can be promoted through copolymers which have segments capable of specific interactions and/or chemical reactions with the blend components<sup>(4-7)</sup>. The copolymer compatibilizers can be either added to or formed *in situ* in the blend during melt-mixing and processing. Being a convenient and fast way to produce polymer blends, the reactive extrusion<sup>(8,9)</sup> has been widely used in commercial manufacturing. However, it has some limitations<sup>(10)</sup>, such as the short residence time in the equipment, heat generation, and the need for special design for reactant feeding and volatile removing<sup>(11)</sup>. For

\* Corresponding author

\*\* Permanent address: Beijing University of Chemical Technology, Box 61, Beijing 100029, People's Republic of China

these reasons, an alternative approach to the formation and compatibilization of blends of immiscible polymers, namely self-compatibilization<sup>(12,13)</sup> via concentrated emulsion polymerization<sup>(14,15)</sup>, was developed by this group. In the present paper, two concentrated emulsions of different monomers or monomer mixtures, in which at least one concentrated emulsion contains a small amount of di-vinyl-terminated macromonomer (DVTM), are prepared and subjected to partial polymerization. A blend is formed by mixing the partially polymerized concentrated emulsions instead of the melts. Further, the mixture is subjected to complete polymerization. Both before and after the two concentrated emulsions have been mixed, AB networks will be formed, with the DVTM as chain A and the homo- or co-polymers of the other monomers as chain B. Such AB networks constitute good compatibilizers between the two components. Since the formation of the network occurs independently in each latex particle, the crosslinking is limited to each latex, and the latexes have flowability. A distinctive feature of this method is that the polymers which are blended and the compatibilizers are generated simultaneously. In other words, a compatibilized blend is produced via a single polymerization.

In this paper, blends from styrene-co-methyl methacrylate (SM) and poly (vinyl acetate) (PVAc) were chosen as model systems. They were chosen not only because the flexible PVAc can toughen the brittle SM, but also because the copolymerization between styrene (St) and vinyl acetate (VAc) and between methyl methacrylate (MMA) and VAc occurs with difficulty and hence little copolymer is generated. Indeed their copolymerization parameters are<sup>(16)</sup>:  $r_1=0.01$  and  $r_2=56.0$  for VAc and styrene and  $r_1=0.03$ , and  $r_2=26.0$  for VAc and MMA. Vinyl-terminated polycaprolactone (VTPCL) was selected as the precursor of the network compatibilizer, because it possesses some compatibility with MMA<sup>(17)</sup>.

The effect of compatibilization is evaluated in this paper via the measurement of tensile properties. For a partially compatible blend, the higher the compatibility, the better the tensile properties. If the compatibility is lower than a certain level, a catastrophic fall in those properties will occur. Since both components, SM and PVAc, are transparent materials, the transparency of the products can be used as a criterion of compatibility as well.

## Experimental

### *Materials*

Azobisisobutyronitrile (AIBN, Kodak) was recrystallized from methanol. Other chemicals were purchased from Aldrich. Styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc) were filtered through an inhibitor removal column before use. The other compounds were used as received.

### *Preparation of Vinyl-terminated PCL (VTPCL)*

Preparation of VTPCL was described in a previous paper<sup>(17)</sup>. In this paper, it was used in the form of a solution (0.2g/ ml toluene).

### *Concentrated Emulsion Polymerization*

A mixture was first prepared from a monomer (styrene/MMA or VAc), an initiator azobisisobutyronitrile (AIBN, 0.005g/g of monomers) and a VTPCL solution. The mixture thus prepared was used as the dispersed phase of a concentrated emulsion. An aqueous solution of SDS (10wt.%) was first placed in a flask provided with a magnetic stirrer. The mixture was added dropwise with vigorous stirring into the flask with a syringe, until the volume fraction of the SDS aqueous solution became 0.2. The whole addition process lasted about 15 minutes, and took place at room temperature. The paste-like concentrated emulsion thus formed was additionally stirred for 15 min under a flow of nitrogen. Two concentrated emulsions of different monomers were prepared and introduced into a water bath at 50°C to carry out the partial polymerization of each until a 20% conversion was achieved (about 3h). Subsequently, the two concentrated emulsions were mixed with magnetic stirring. The mixture of concentrated emulsions thus obtained was further heated at 60 °C for 48h for completing the polymerization. The product thus obtained was washed three times with 2-propanol and dried in a vacuum oven for 24h. The blend product of the concentrated emulsion polymerization was obtained as a white powder, which will be denoted as concentrated emulsion blend (CEB). The ratio of the weight of the powder to the original weight of the reactants was considered as the conversion.

For comparison purposes, SM, PVAc and copolymers from styrene/MMA/VAc were also prepared via the concentrated emulsion polymerization.

### *Preparation of Solution Blends*

By “solution blend” we denote a blend obtained via casting a solution containing both polymers. In this paper a SM/PVAc blend was obtained by casting the solution of SM and PVAc in chloroform on a glass plate and evaporating the solvent.

### *The Tensile Testing*

The powders of the CEBs or of the solution blends were thermo-pressed with a Laboratory Press (Fred S. Carver INC.) at 150°C for 3-5 min, and then cooled to room temperature. The sheets thus obtained were cut to the size required by the ASTM D.638-58T. The tensile testing was conducted at room temperature, with an Instron Universal Testing Instrument (Model 1000). The elongation speed of the instrument was 20 mm/min.

### *Solubility Measurements*

A pre-weighed blend sheet prepared as for tensile testing was washed with methanol in an extractor for 12h. The remaining sheet was retrieved and dried in a vacuum oven for 24h to remove the solvent. The ratio of the weight lost during washing to that of the original

sheet represents the content of methanol soluble species (CMSS) and was taken as the content of VAc homopolymer (in percentage). The sheet remaining after methanol washing was further washed with chloroform for 12h. The weight percentage of the remaining sheet to the original weight was considered as the gel content (the crosslinked part of the blend).

## Results and discussions

### *Solution Blends*

Data for the solution blends and pure SM (styrene/MMA wt ratio=1/1) and PVAc are listed in Table 1. The solution blends are milk opaque materials. Compared with the pure SM and PVAc, the mechanical properties of these blends exhibit a dramatic decrease. Both the appearance and the mechanical properties indicate a complete incompatibility. The solution blends represent an extreme case in which no copolymers are present. From the content of methanol soluble species one can conclude that the method employed in this paper to evaluate the content of VAc homopolymer is a suitable one.

**Table 1: Properties of the Solution Blends**

| wt. Ratio of SM/PVAc | Tensile Strength (MPa) |            | Elongation at Break (%) |            | Content of Methanol Soluble Species (%) |
|----------------------|------------------------|------------|-------------------------|------------|---|
|                      | Average                | Std. Error | Average                 | Std. Error |   |
| 1/0                  | 65.5                   | 3.2        | 10.2                    | 1.3        | 0                                       |
| 1/0.5                | 16.2                   | 1.0        | 10.3                    | 0.4        | 64.6                                    |
| 1/1                  | 7.2                    | 0.5        | 26.7                    | 1.6        | 48.9                                    |
| 1/2                  | 6.0                    | 0.4        | 65.4                    | 5.4        | 31.7                                    |
| 0/1                  | 15.1                   | 1.6        | 350                     | 19.5       | 100                                     |

### *Copolymers*

The properties of the copolymers are listed in table 2. As mentioned in the Introduction, the copolymerization between either styrene and VAc or MMA and VAc occurs with difficulty. For this reason the "copolymerization" of VAc with either styrene or MMA does not lead to copolymers only, but to mixtures of homopolymers and copolymers. This is clearly shown by the content of PVAc in Table 2, which indicates that only about 50% of VAc monomer was combined with styrene or MMA as copolymers, which do not dissolve in methanol. One can also note that the conversions are relatively low. A large fraction of the monomers remain unreacted or form only oligomers after 48h of polymerization. However, because of the presence of the copolymer chains, the mechanical properties are generally better than those of the solution blends.

**Table 2: Properties of the Copolymers**

| wt. Ratio<br>of<br>St/MMA/VAc | Tensile Strength (MPa) |            | Elongation at Break (%) |            | Conversion<br>(%) | Content of<br>Methanol<br>Soluble<br>Species (%) |
|-------------------------------|------------------------|------------|-------------------------|------------|-------------------|--|
|                               | Average                | Std. Error | Average                 | Std. Error |                   |  |
| 1/1/1                         | 21.1                   | 2.4        | 13.2                    | 0.8        | 84                | 15.6   |
| 1/1/2                         | 12.5                   | 0.6        | 29.8                    | 2.8        | 83                | 24.5   |
| 1/1/4                         | 8.8                    | 0.6        | 61.4                    | 5.9        | 81                | 34.0   |

*Concentrated emulsion blends without VTPCL*

The data for the concentrated emulsion blends (CEBs) without VTPCL are presented in Table 3. One may note that the contents of homo-PVAc in the CEBs are higher than those in solution blends. This is a result of the preparation methodology. As described in the Experimental section, in the preparation of CEBs, each concentrated emulsion was first partially polymerized until a 20% conversion was achieved and subsequently the two were mixed. At that conversion, each concentrated emulsion acquires a high viscosity, which delays the transfer of the monomers and oligomers from one latex to another, thus inhibiting copolymerization. However, still about 10% of the VAc monomer was involved in copolymerization. One should also note that the conversions of the CEBs are higher than those of the copolymers; this probably occurs because of the homopolymerization of VAc. The mechanical properties of the CEBs are comparable to those of the copolymers; because of the higher contents in homo-PVAc of the CEBs, the tensile strengths are somewhat lower but the elongations at break are somewhat higher. Both the copolymers and the CEBs are translucent, which indicates that the compatibility in both systems is somewhat improved.

**Table 3: Properties of the Concentrated Emulsion Blends without VTPCL**

| wt. Ratio<br>of<br>St/MMA/<br>VAc | Tensile Strength<br>(MPa) |          | Elongation at<br>Break (%) |          | Conversion<br>(%) | Content of<br>Methanol<br>Soluble<br>Species (%) | Content of<br>Chloroform<br>Insoluble<br>Species (%) |
|-----------------------------------|---------------------------|----------|----------------------------|----------|-------------------|--|--|
|                                   | Average                   | Std. Err | Average                    | Std. Err |                   |  |  |
| 1/1/1                             | 20.5                      | 0.5      | 14.1                       | 2.5      | 92                | 27.3   | 0  |
| 1/1/2                             | 11.4                      | 0.8      | 32.7                       | 1.7      | 91                | 41.7   | 0  |
| 1/1/4                             | 8.5                       | 0.7      | 62.2                       | 3.8      | 89                | 57.6   | 0  |

*Concentrated emulsion blends with VTPCL*

In order to strengthen the compatibilizing effect, small amounts of VTPCL were introduced. The reactions among VTPCL and styrene, MMA and VAc generate AB networks, with PCL as chains A and the copolymer and homopolymers of those monomers as chains

B. Because the network contains chains of both SM and PVAc, it compatibilizes the two. This function of the network is similar to that of a block copolymer. It should be emphasized that the network compatibilizer is not added, but is formed during polymerization. For this reason we call such a methodology self-compatibilization. All the CEBs with VTPCL possess a transparent appearance, which indicates an improved compatibility. The effect of self-compatibilization is also made clear by Table 4. The tensile strength and elongation at break increase simultaneously, in contrast to what happens in Tables 2 and 3. Of course, the PCL chains themselves can improve to some extent the mechanical properties. Indeed, it was noted in a previous paper<sup>(17)</sup>, that PCL can toughen PMMA when the weight ratio of PCL/PMMA is higher than 20/100. However, this kind of improvement differs from that caused by compatibilization. Comparison between different contents of VTPCL indicates that a content of 0.05 g/g of the other monomers is enough for self-compatibilization. A higher content of VTPCL results in a lower tensile strength and a higher elongation at break.

Another advantage brought by the network is a higher conversion. One can see from Table 4 that the higher the content of VTPCL, the higher the conversion.

**Table 4: Properties of the Concentrated Emulsion Blends without VTPCL**

| wt. Ratio of St/MMA/VAc            | Tensile Strength (MPa) |          | Elongation at Break (%) |          | Conversion (%) | Content of Methanol Soluble Species (%) | Content of Chloroform Insoluble Species (%) |
|------------------------------------|------------------------|----------|-------------------------|----------|----------------|---|---|
|                                    | Average                | Std. Err | Average                 | Std. Err |                |   |   |
| VTPCL = 0.05 g/g of other monomers |                        |          |                         |          |                |   |   |
| 1/1/1                              | 46.6                   | 5.8      | 20.7                    | 4.1      | 93             | 19.6                                    | 18.2  |
| 1/1/2                              | 42.7                   | 3.7      | 43.0                    | 1.6      | 94             | 30.3                                    | 17.1  |
| 1/1/4                              | 35.1                   | 2.6      | 61.4                    | 5.4      | 91             | 42.7                                    | 15.2  |
| VTPCL = 0.1 g/g of other monomers  |                        |          |                         |          |                |   |   |
| 1/1/1                              | 36.8                   | 3.3      | 23.6                    | 3.1      | 94             | 18.0                                    | 32.7  |
| 1/1/2                              | 30.4                   | 1.6      | 50.9                    | 5.4      | 92             | 28.8                                    | 30.6  |
| 1/1/4                              | 26.5                   | 3.6      | 67.5                    | 3.3      | 91             | 33.4                                    | 29.3  |

#### *Effect of the Distribution of VTPCL*

In the preparation of the samples of Table 4, VTPCL was equally distributed between the two concentrated emulsions. CEBs in which only one concentrated emulsion contained VTPCL were also prepared, and the results are listed in Table 5. One can see that if VTPCL is introduced only in VAc, comparable mechanical properties are obtained as when VTPCL is introduced in both concentrated emulsions. When, however, VTPCL is

added to styrene/MMA only, lower mechanical properties are achieved. This can be ascribed to the decrease in compatibility. Indeed, to be a good compatibilizer, both SM and homo-PVAc chains should be present in the network. Because of the copolymerization parameters, styrene and MMA are more easily included in the network than VAc after the concentrated emulsion containing styrene, MMA and VTPCL is mixed with that containing VAc alone. The homo-PVAc has the opportunity to combine with VTPCL only when VTPCL is present in the VAc containing concentrated emulsion.

**Table 5: Properties of the Blends<sup>a</sup> with Different VTPCL Distributions**

| VTPCL containing conc. emul. | Tensile Strength (MPa) |          | Elongation at Break (%) |          | Conversion (%) | Content of Methanol Soluble Species (%) | Content of Chloroform Insoluble Species (%) |
|------------------------------|------------------------|----------|-------------------------|----------|----------------|---|---|
|                              | Average                | Std. Err | Average                 | Std. Err |                |   |   |
| St/MMA                       | 23.3                   | 0.5      | 32.1                    | 2.5      | 92             | 32.4                                    | 16.6  |
| VAc                          | 40.7                   | 1.9      | 42.2                    | 3.9      | 94             | 29.6                                    | 16.2  |
| both                         | 42.4                   | 3.7      | 43.0                    | 1.6      | 94             | 30.3                                    | 15.0  |

<sup>a</sup> St/MMA/VAc wt ratio=1/1/2, Content of VTPCL=0.1 g/g of other monomers

#### *Effect of the Styrene/MMA wt Ratio*

The nature of the system affects the self-compatibilization. Indeed, Table 6 shows the effect of the styrene /MMA wt ratio on the mechanical properties. The elongation at break decreases with increasing styrene/MMA ratio, while the tensile strength exhibits a maximum. This behavior can be explained on the basis of the difference in the polarities of the components, which are reflected in the solubility parameters. The solubility parameters<sup>(16)</sup> of PS, PMMA and PVAc are 17.5-18.5, 18.5-19.5 and 19-21 (MPa)<sup>1/2</sup>, respectively. The polarity of PVAc is closer to that of PMMA than to that of PS. In other words, the compatibility between PVAc and PMMA is higher than that between PVAc and PS. For this reason, PVAc has a stronger effect on the blends with higher MMA content. Therefore, the higher the MMA content, the higher the elongation at break and the lower the tensile strength. For the samples free of MMA, the compatibility is very low, and both the elongation at break and the tensile strength are poor.

#### **Conclusion**

While the solution blends of SM and PVAc are incompatible, the compatibility of the blends generated from the same components via concentrated emulsions is greatly improved because of the self-compatibilization. The former are opaque and the latter are transparent; the mechanical properties of the former are poor while those of the latter are excellent. This study shows that the methodology of self-compatibilization constitutes an alternative approach to the reactive melt-processing to prepare blends from incompatible polymers.

Table 6: Properties of the Blends with Various St/MMA wt Ratios

| wt. Ratio of St/MMA              | Tensile Strength (MPa) |          | Elongation at Break (%) |          | Conversion (%) | Content of Methanol Soluble Species (%) | Content of Chloroform Insoluble Species (%) |
|----------------------------------|------------------------|----------|-------------------------|----------|----------------|---|---|
|                                  | Average                | Std. Err | Average                 | Std. Err |                |   |   |
| 100/0                            | 24.5                   | 0.6      | 28.9                    | 3.6      | 81             | 22.1                                    | 33.3  |
| 25/75                            | 38.2                   | 0.8      | 43.3                    | 2.7      | 85             | 24.9                                    | 30.4  |
| 50/50                            | 30.4                   | 1.6      | 50.9                    | 5.4      | 92             | 28.3                                    | 29.4  |
| 75/25                            | 24.5                   | 0.8      | 67.6                    | 4.1      | 95             | 27.6                                    | 32.2  |
| 0/100                            | 19.5                   | 0.7      | 100.5                   | 6.8      | 97             | 28.4                                    | 31.7  |
| VTPCL= 0.1 g/g of other monomers |                        |          |                         |          |                |   |   |

## References

1. Utracki LA (1987) *Inter Polym Proc* 2: 3
2. Paul DR (1992) Phase coupling and morphology generation in Engineering polymer alloys. In Choy CL, Shin FG (ed) *Proc Inter Symp on Polym Alloys & Composites*. Hongkong p21
3. Keskkula K, Paul DR (1994) Toughening agents for engineering polymers. In Collyer AA (ed) *Rubber toughened Engineering plastics*. Chapman & Hall New York p136
4. Xanthos M, Dagli SS (1991) *Polym Eng Sci* 31:929
5. Xanthos M (1988) *Polym Eng Sci* 28:1392
6. Gaylord NG (1989) *J Macromol Sci Chem* A26:1211
7. Kreisher K (1989) *Plastics technol* 35:67
8. Brown SB (1989) *Reactive Extrusion, course notes*, Polymer Processing Institute, Hobken NJ
9. Tzoganakis C (1989) *Adv Polym Technol* 9:321
10. Todd DB (1988) *Am Chem Soc Polym Prepr* 29:563
11. Lambla M (1987-88) *Polym Proc Eng* 5:297
12. Ruckenstein E and Park JS. (1990) *Polymer* 31:2397
13. Ruckenstein E and Li H. (1994) *Polymer* 35:4343
14. Ruckenstein E and Park JS. (1988) *J Polym Sci Chem Lett Ed* 26:529
15. Ruckenstein E and Kim KJ. (1988) *J Appl Polym Sci* 36:907
16. Brandrup J, Immergut EH (ed) (1989) *Polymer Handbook*. 3rd Ed. John Wiley & Sons New York
17. Li H, Ruckenstein E (1995) *Polymer* 36:2281