Determination of Degree of Compatibility of Novolak-Polybutadiene Blends

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Abstract

Although Polymers have many applications, their shortcoming is that their properties depend on the structure, molecular mass, polymer-polymer and polymer-solvent interactions among others. Hence for a particular use, it is necessary to synthesize a polymer with a particular specification. This is time consuming besides being costly. An alternative to synthesizing the required polymer is to mix or blend two or more polymers. Blending requires knowledge about the miscibility of the two polymers. In this study the compatibility of Novolak-polybutadiene blend as a function of up to 30% rubber concentration, was determined from its theoretical solubility parameters and heat of mixing. The result shows that the degree of compatibility of the two polymers is very low, and the two polymers are thus immiscible above five percent of rubber content.

Keywords: Polymer blend • Compatibility • Miscibility • Polybutadiene • Novolak

Introduction

In recent years there has been considerable interest in polymer blends. This impetus has been due to the ever-increasing need for materials which are superior to any of the individual polymers alone [1-8]. The final properties of the blend system are very much determined by the degree of compatibility of the component polymers. Compatibility here refers to mixing of polymers at molecular level [9,10]. An area in which blending has been widely applied is in the transformation of valuable but brittle low impact strength materials into engineering plastics of high impact strength, by the addition of inexpensive elastomers [11-14].

Since Compatibility contributes to the morphology, properties and performance of polymer bends, it is a topic of great academic and industrial importance. Many studies on the compatibility of two polymers have been reported [1,3-5,9,10,15-19].

Methods and Materials

Two polymers mix completely when the change in Gibb's free energy of mixing, ΔG_m in the expression $\Delta G_m = \Delta H_m - T\Delta S_m$ is negative [1,3,20,21]. ΔH_m and ΔS_m are changes in the heat of mixing and entropy of mixing respectively at temperature T.

Since mixing increases disorder, change in the entropy of mixing is always positive. Hence ΔH_m should either be very close to zero or negative to satisfy the above equation.

Since heat of mixing is a measure of free energy of mixing, its value may be used as an indicator of the degree of compatibility of a system of polymers. It has been argued that the upper limit of compatibility is a value [22] of 4.2×10^{-3} joules of heat of mixing.

Schneier [23] suggested an expression for the change in heat of mixing

ΔH_m of two polymers, given as:

$$\Delta H_m = \left\{ X_1 M_1 \rho_1 \left(\delta_1 - \delta_2\right)^2 \left[\frac{X_1^2}{\left(1 - X_2\right)M_2\rho_2 + \left(1 - X_1\right)\rho_1 M_1}\right]^2 \right\}^{1/2} \quad (1)$$

X, ρ, M and δ are weight fraction of polymer, density of polymer, molecular weight of monomer unit and solubility parameter respectively. The subscripts 1 and 2 refer to the two polymers.

In order to obtain a value for the heat of mixing, the solubility parameters of the two polymers need to be determined.

Determination of solubility parameter δ as given in equation 1 depends on the molecular weights of the polymers involved. For low molecular weight liquids, it is found by the semi-empirical formula put forward by Hildebrand et al. [24], given as;

$$\delta = \left[\frac{\Delta H^v - RT}{V}\right]^{1/2}$$

Where ΔH^v is the latent heat of vaporization of the liquid at temperature T, R is the universal gas constant, and V is the molar volume.

Due to low volatility of high molecular weight polymers, direct experimental determination of ΔH^v in Hildebrand's equation above is difficult, hence the solubility parameter, δ for such system is calculated using other methods. One such method involves calculation of solubility parameter from the addition of the contributions of the different groups of molecules [25,26].

According to Small [25], heat of mixing depends on the cohesive energies of the solution and the unmixed components. For cohesion caused by dispersive forces, Scatchard [27] suggests the equation;

$$\Delta H_{mcc} = \varphi_1 \varphi_2 \left\{ \left(\frac{E_1}{V_1}\right)^{1/2} - \left(\frac{E_2}{V_2}\right)^{1/2} \right\}^2$$

Where ΔH_{mcc} is the change in heat of mixing per cubic centimeter of the mixture, φ, E, V are volume fraction, cohesive energy and molar volume respectively. Subscripts 1 and 2 refer to the two components.

The quantity $\left(\frac{E}{V}\right)$ in equation 2 above is the cohesive energy density and $\left(\frac{E}{v}\right)^{1/2}$ is the solubility parameter δ. The solubility parameter thus reduces to;

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$$\delta = \rho \frac{(EV)^{1/2}}{M} \tag{3}$$

Where M is the mass of the monomer unit and ρ is the density.

Small [25] showed that the quantity $(EV)^{1/2}$ has additive property. A set of additive constants for common groups in organic molecules, which allow the calculation of $(EV)^{1/2}$ have been tabulated [28,29]. These additive constants are called molar-attraction constants and are denoted by the symbol E (or F [26]).

The sum ΣF of all the groups present for one mole of the substance concerned gives the value of $(EV)^{1/2}$. Hence the solubility parameter given as;

$$\delta = \rho \frac{\Sigma F}{M} \tag{4}$$

can be calculated for a polymer of known density and structure, if F is known for every group present in one mole of the substance.

The structures of Novolak and Polybutadiene are given in Figures 1 and 2 respectively.

Results and Discussion

The sum of the molar attraction constants, ΣF for both polybutadiene and Novolak were determined and given on Tables 1 and 2.

Solubility parameter δ_1 for polybutadiene and δ_2 for Novolak were obtained using equation 3 after determining the sum of molar attraction constants ΣF, as in Tables 1 and 2, the density ρ, and the mass M, of the monomer unit as in Table 3.

δ_1=17.6 ($joules/cm^3)^{1/2}$

δ_2=21.7 ($joules/cm^3)^{1/2}$

Having obtained the solubility parameters δ_1 and δ_2 as above, the changes in the heat of mixing ΔH_m with composition of the blend were calculated using equation 1. These values of ΔH_m are shown on Table 4.

The sketch of ΔH_m as a function of rubber concentration is given on Figure 3.
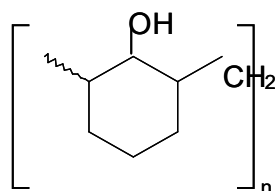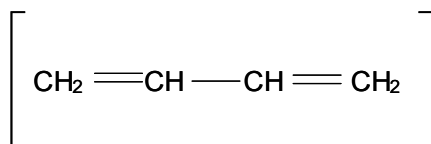

Figure 1. Structure of Novolak [30].

Figure 2. structure of Polybutadiene [31].

Table 1. Molar attraction constants for polybutadiene.

Functional Groups Present in the Monomer Unit*	Number of functional groups present	Molar attaraction constants, F# (Joule-cm3)1/2	Total F (Joule-cm3)1/2
CH2=	2	259	518
-CH=	2	249	498
Conjugation	1	47	47
CIS	1	-14	-14
			ΣF=1049

*The functional groups obtained from the structure of polybutadiene in Figure 2.

#The values obtained from reference [29].

Table 2. Molar attraction constants for Novolak.

Functional groups present in the monomer unit*	Number of functional groups present	Molar attaraction constants, F# (Joule-cm3)1/2	Total F (Joule-cm3)1/2
CH-Aromatic	1	350	350
C= Aromatic	3	200	600
-CH= aromatic	3	239	717
Ortho substitution	1	-19	-19
Para substitution	1	82	82
Six membered ring	1	-48	-48
-CH2=	1	269	269
			ΣF=1951 (joule-cm3)1/2

*The functional groups obtained from the structure of Novolak, Figure 1.

#The values obtained from reference [29].

Table 3. Density and mass of monomer unit for Polybutadiene and Novolak.

Component	Density (g/cm3)	Mass of monomer unit (g)
Polybutadiene	0.91 [32]	54.09 [33]
Novolak	1.19 [33]	107.13

Table 4. Variation of ΔH_m (with rubber concentration) when Novolak is component 1.

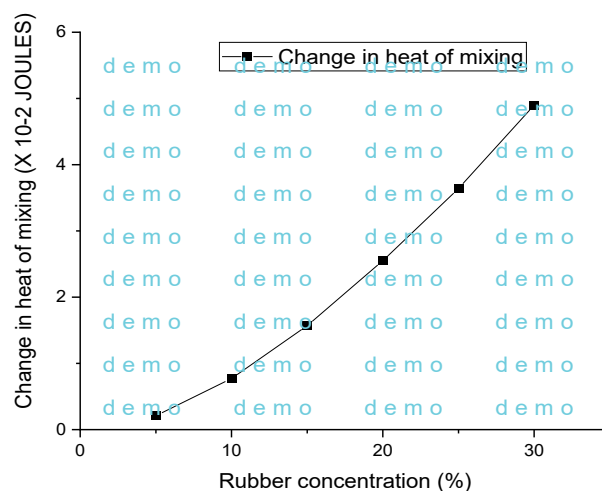| Rubber Concentration %	ΔH_m of mixing (X 10-2 Joules)
5	0.21
10	0.77
15	1.57
20	2.55
25	3.64
30	4.9

Figure 3. Variation of change in heat of mixing with weight fraction of polybutadiene rubber.

The change in the values of heat of mixing for concentrations over 5% weight fraction of rubber are well above the upper limit (of 0.42 x10-2 joules) for compatibility. In fact, the values go farther and farther as the rubber concentration increases. The two polymers are thus incompatible, in the range of composition used in this study. This incompatibility or low compatibility, is brought about by the large difference between the solubility parameters of the two polymers involved (polybutadiene (17.6J/cc)1/2 and for Novolak (21.7J/cc)1/2).

For mixtures of two polymers (without solvent), miscibility over the entire composition range may only occur if the difference in their solubility parameters of the individual polymers does not exceed 0.42-1.47 (J/cc)1/2 [29,30].

For the polymers used in this study, this difference is 4.1 $(J/cc)^{1/2}$, which is quite a large value. This means that the inter-polymer interaction in the blend is much lower than the inter-particle interactions in the individual component polymer. This explains the high values of heat of mixing, hence the low degree of compatibility.

Solubility parameter is a measure of the cohesive energy of the material hence a measure of intermolecular forces. The higher the value of the solubility parameter of a material, the larger the intermolecular forces within the material holding the structure together. Miscibility of two substances occurs if the magnitude of intermolecular forces in the individual components are comparably close.

Conclusion

The following conclusions are drawn from this study;

- The value of the solubility parameters for Polybutadiene and Novolak were very high.

Hence the change in heat of mixing ΔH_m for the two polymers in the range of concentrations studied were very high.

Hence the degree of compatibility of the two polymers is very low.

Limitations and Recommendations for Future Studies

In the determination of degree of compatibility of the Novolak-polybutadiene blends, and generally of polymer blends, the major parameter that needs to be determined is the solubility parameters of the component blends. In this study the solubility parameter one needs to determine the change in heat of mixing, which is difficult for polymers. Hence the need to estimate it from other methods like the one we used. This might have rendered the value obtained as only an estimate. Hence there is need to device methods to determine accurately, the change in heat of mixing for polymers.

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