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Effects of Small Molecular Solvent on Phase Diagram of Polymer Blends

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Abstract

This work involved the studies of the effects of small molecular solvent on the phase diagrams of polmer blend of styrene-acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (PMMA). For the studies of the effects of solvent on the phase diagrams, SAN/PMMA blends were prepared by solvent casting and melt mixing at the weight percent of SAN at 10, 20, 30, 40, 50, 60, 70, 80 and 90. The phase diagrams of SAN/PMMA blends were constructed by plotting the cloud point temperatures occurred on heating against blend compositions. It was found that the phase diagrams of the blends cast from five different solvents; methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane, were different depended on the type of solvent, the boiling point of solvent and the period of drying time in a vacuum oven. Moreover, the phase diagrams of the SAN/PMMA blends prepared from solvent casting occurred at the higher temperatures than that of the blends prepared from melt mixing.

Introduction

Nowadays polymeric materials can be considered to be one of the essential components in varieties of products, for example, household appliances, toys, automobiles. These products require different physical, chemical, mechanical, and other properties from polymeric materials. The ability to improve these properties of polymeric materials to meet the current and future demand is still the important research and development activities in both academic and industrial sectors.

New properties of polymeric materials can be obtained in several ways (Brydson, 1995). The synthesization of new types of homopolymers and copolymers is always an option; however, the cost and time needed is quite substantial. Another way is to use proper additives to improve processing and service properties of polymeric materials. Still another way is to form polymer blends by blending or mixing existing polymeric materials together to obtain new properties. Polymer blends have been of interests from both academic and industrial sectors in the past few decades because of their

relatively minor capital investment and shorter period of time needed with respect to synthesization. In addition, polymer blends can fill the deficiency in price/performance of the existing homopolymers and copolymers (Paul and Newman, 1978).

The preparation of polymer blends can be accomplished by several methods such as melt mixing, solvent casting, freeze drying. Each method can influence the resulting properties of polymer blends (Walsh, *et al.* 1985). Solvent casting has been widely used in many academic studies of polymer blends due to its simplicity. The solvent casting parameters, such as casting temperature, the type of solvent used, the evaporation rate of solvent, can affect several properties, e.g. mechanical properties, crystallinity, and miscibility of polymer blends (Hirschbuehler and Thies, 1975; Runt and Rim, 1982; and Eastmond and Haraguchi, 1983). However, the effects of these parameters have still not been clearly understood. Thongyai (1994) has reported the effects of solvent casting on the phase diagrams of polymer blends of tetramethyl-bisphenol-A polycarbonate (TMPC) and polystyrene (PS) that the phase separation behaviour of the blends of TMPC and PS prepared by solvent casting method occurred at higher temperature than that of blends prepared from melt mixing. That is to say that the miscibility of the blends of TMPC and PS was improved by solvent casting method. However, only the blend at 50 wt% of PS was examined in his research. Other workers had also reported the effects of solvent on the resulting properties of polymer blends obtained from solvent casting method (Varnell, *et al.* 1981; Semerak and Frank, 1987; and Lu, *et al.* 1995).

It is therefore very interesting to study the effects of small molecular solvents on the phase diagrams of other polymer blends to better elucidate the effects of solvents on the properties of polymer blends obtained from solvent casting method. The polymer blend of styrene-acrylonitrile copolymer (SAN) and poly(methyl methacrylate) (PMMA) was chosen in this work because this polymer pair can be prepared by both melt mixing and solvent casting methods. Its phase diagram exhibits the lower critical solution temperature (LCST) behaviour, i.e. the polymer blend transforms from transparent to cloudy state upon heating (Chiou, *et al.* 1982). Two classes of solvents; weak hydrogen bonding solvent and moderate hydrogen bonding solvent, were used to prepare SAN/PMMA blends.

Experimental Procedure

MATERIALS

Styrene-acrylonitrile copolymer (SAN)

From Mitsubishi Corporation, Japan, under the trade name of "SANREX" was used in this study. Its viscosity-average molecular weight (M_v)

determined in tetrahydrofuran (THF) at 25 °C is 165,200 and the acrylonitrile content examined by elemental analysis is 25.74 % by weight.

Poly (methyl methacrylate) (PMMA)

Under the trade name of "Acrylic Resins" manufactured by Thai Petrochemical Industry, Co. Ltd., was used to blend with SAN. The viscosity-average molecular weight (M_v) of PMMA in THF is 108,600.

Solvents

Used in this study were methylene chloride (MC), acetone (AC), tetrahydrofuran (THF), methyl ethyl ketone (MEK) and 1,2-dichloroethane (DC). All are reagent grade solvents. The properties of the solvents are summarized in Table 1.

SAMPLE PREPARATION

Two methods, solvent casting and melt mixing, were used to prepare SAN/PMMA blends.

Solvent Casting

SAN and PMMA were weighed to desired compositions at following SAN/PMMA weight ratio: 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10. 17 ml of solvent was added to 0.85 g of the total solid weight of the polymers to form 5% (w/v) solution. The mixture was stirred at 400 rpm by digital hotplate/stirrer at room temperature until all polymers were dissolved and continuously stirred overnight to ensure complete miscibility. Methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1, 2-dichloroethane were used as common solvents.

The solution was cast onto 22x22 mm coverslips placed in petri dishes. Each coverslip contained about 0.15 ml of solution. The petri dishes were covered and the solvent was allowed to slowly evaporate at room temperature in a fume cupboard for 24 hr. The resulting clear films with 0.05 mm thickness were further dried under reduced pressure of-30 inch Hg in a vacuum oven at 75 °C for 1 to7 days.

Melt Mixing

The desired weight ratio (10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10) of SAN and PMMA was weighed to 1 kg. Pellets of the weighed composition were dry-blended in a v-shaped mixer at 32 rpm for 10 min before continuously melt mixing in a twin screw kneader. Melt mixing was performed at 200 °C, 100 rpm screw speed and the feed rate was kept constant at 0.36 kg/hr. The blends came out from the kneader in molten and unshaped form, so the scissors were used to take samples every 30 seconds and then the cut samples were calendered by a press roller to make small pieces of samples with smooth surfaces. Each piece of sample was about 3 to 4 g.

Pieces of blends were compressed at 200 °C under a pressure of 300 kg/cm^2 into thin sheets by a hot press. The sheet at the thickness of 0.1 mm was used to study the phase diagram.

DETERMINATION OF PHASE DIAGRAMS

In this study the phase diagrams of polymer blends both cast from various solvents and melt mixing were constructed by plotting the cloud point temperature against the blend compositions. The cloud point temperatures at which phase separation occurred on heating for each blend formulation were determined as follows.

For the solvent casting blends, two pieces of films with 0.05 mm thickness were attached together to form the 0.1 mm thick film sandwiched between two coverslips. The 0.1 mm thick film was then placed on a covered hot plate. Prior to the observation, the surface of the hot plate was covered by a blackened aluminum foil to make the cloud point more easily judged by eyes.

Table 1 The properties of solvents

Solvent	Boiling Point (°C)	Solubility Parameter $(\delta, MPa)^{1/2}$	Hydrogen Bonding Interaction
Methylene chloride	39.50	19.8	Weak
Acetone	56.24	20.3	Moderate
Tetrahydrofuran	64-65	18.6	Moderate
Methyl ethyl ketone	79.60	19.0	Moderate
1,2-Dichloroethane	83.50	20.1	Weak

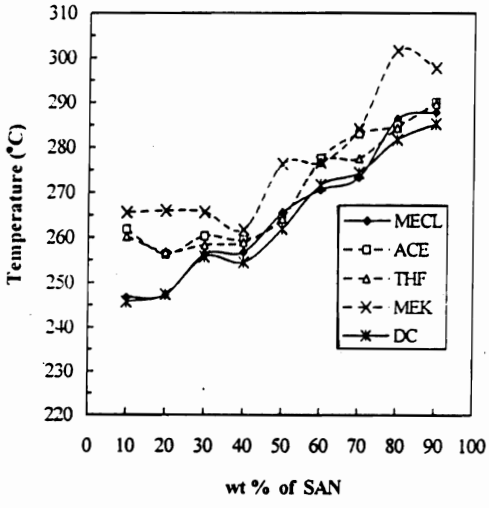

Figure 1 Phase diagrams of SAN/PMMA blends Cast from different solvents at a drying time of 1 day

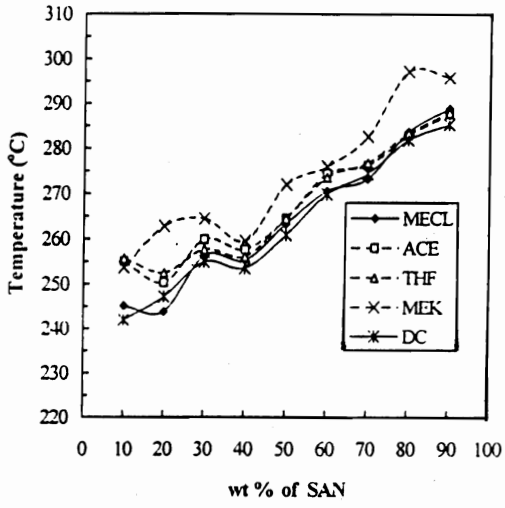

Figure 2 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 2 day

The film was heated from 200 °C at a heating rate of 5 °C/min until the first cloudiness was occurred. The cloud point temperature was taken as the temperature where the blend started to turn from clear to cloudy. For the melt mixing blends, the 0.1 mm thick film was cut to a size of 10 mm x 10 mm and was sandwiched between two coverslips. It was then placed on the covered hot plate. The cloud point temperature was observed in the similar way as mentioned for the solvent casting blends.

Results and Discussions

PHASE DIAGRAMS OF SAN/PMMA BLENDS CAST FROM DIFFERENT SOLVENTS

When considering all the phase diagrams of blends at drying time of 1 day (Figure 1), it is found that the phase diagrams of SAN/PMMA blends cast from methyl ethyl ketone (MEK) takes place at the highest temperatures, while those from other solvents occur at the lower temperatures corresponding to the lower boiling points of the solvents. The boiling points of methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane are 39.50, 56.24, 64-65, 79.60 and 83.50 °C, respectively (Brandup and Immergut, 1989). Due to the fact that methyl ethyl ketone has the higher boiling point than other solvents except 1,2-dichloroethane, it is more difficult to remove methyl ethyl ketone from the blends. This could result in enhancing the miscibility of the blends.

However, this is not found in the case of blends cast from 1,2-dichloroethane, which has the highest boiling temperature at 83.5 °C, the phase diagram of blends cast from 1,2-dichloroethane occurs at the lowest temperature and is nearly the same temperature as one from methylene chloride which has the lowest boiling temperature at 39.50 °C.

Five solvents used in this work can be classified into two classes: weak or poor hydrogen bonding and moderated hydrogen bonding solvents. Methylene chloride and 1,2-dichloroethane which are chlorinated hydrocarbon belong to the class of weak hydrogen bonding solvent, whereas acetone, methyl ethyl ketone and tetrahydrofuran which are ketone and ether belong to the class of moderated hydrogen bonding solvent. It is believed that those moderated hydrogen bonding solvents which are oxygen containing solvents are capable of more effectively producing solute-solvent bonds than chlorinated hydrocarbons. This could cause a better solvation and hence result in a good solubility of the blends. The greater the solvation of polymer molecules in solvent, the harder the polymer molecules to disengage themselves from the solvent (Dack, 1976). As a result of the stronger interaction between the polymers and those moderated hydrogen bonding solvents, the phase separation of the blends cast from acetone, tetrahydrofuran and methyl ethyl ketone takes place at the higher

temperatures than those from methylene chloride and 1,2-dichloroethane.

It is apparent that not only the boiling point of solvents, but also the type of solvents are responsible for the phase diagram of the SAN/PMMA blends.

Similar results are also observed in the phase diagrams of SAN/PMMA blends at different drying time period as shown in Figures 2, 3, 4, 5, 6 and 7. Nevertheless, the effects of the type of solvents on the observed phase diagrams of blends seem to be decreased as the drying time in a vacuum oven increases and almost disappear at the drying time of 7 days. This might be caused by the complete removal of the solvents retained in blends after drying in a vacuum oven for 7 days.

PHASE DIAGRAMS OF SAN/PMMA BLENDS DRIED AT DIFFERENT DRYING TIME

In order to study the effects of the amount of solvent remained in blends at different period of drying time, the phase diagrams of the SAN/PMMA blends cast from different solvents are replotted as shown in Figures 8 to 12.

As shown in Figures 8 to 12, it is found that only the phase diagrams of the blends cast from moderated hydrogen bonding solvents, which are acetone, tetrahydrofuran and methyl ethyl ketone, are affected by the amount of the solvent retained in blends. The longer the period of drying time in a vacuum oven is, the lower the cloud point temperatures occur. In other words, the phase separation of the blends cast from those moderated hydrogen bonding solvents takes place at the lower temperature when the amount of solvents retained in blends decreases. At the drying time of 7 days, the phase diagrams of the blends cast from the moderated hydrogen bonding solvents are almost the same as those from the weak hydrogen bonding solvents, methylene chloride and 1,2-dichloroethane. This should be because of the complete removal of solvents in the blends.

PHASE DIAGRAMS OF SAN/PMMA BLENDS PREPARED FROM DIFFERENT METHODS

The phase diagrams of solvent cast blends at the drying time of 7 days were compared with one prepared from melt mixing as shown in Figure 13. Though the interactions between solvents and polymers in solvent cast blends seem to be negligible at the drying time of 7 days, there was still a difference between the phase diagrams of the blends prepared from solvent casting and melt mixing methods. Figure 13 showed that the phase diagrams of the blends prepared from solvent casting method occur at much higher temperatures (15-20 $^{\circ}$C) than the phase diagram of the blends prepared from melt mixing. This is supposed to be originated from the differences in the morphology of the blends prepared from two different methods.

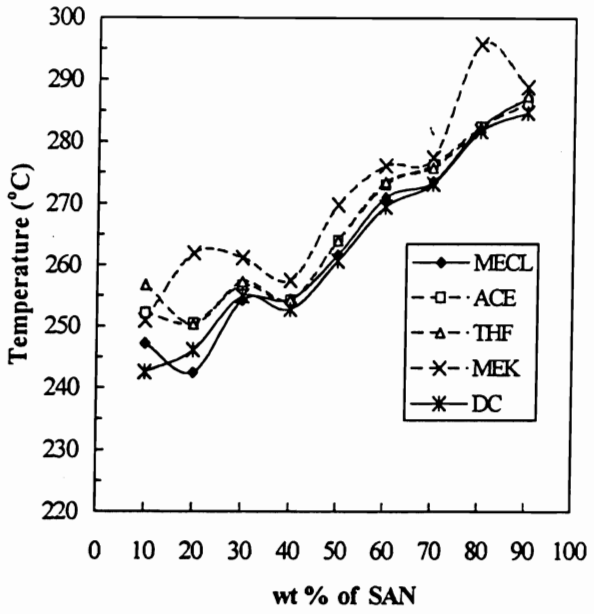

Figure 3 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 3 day

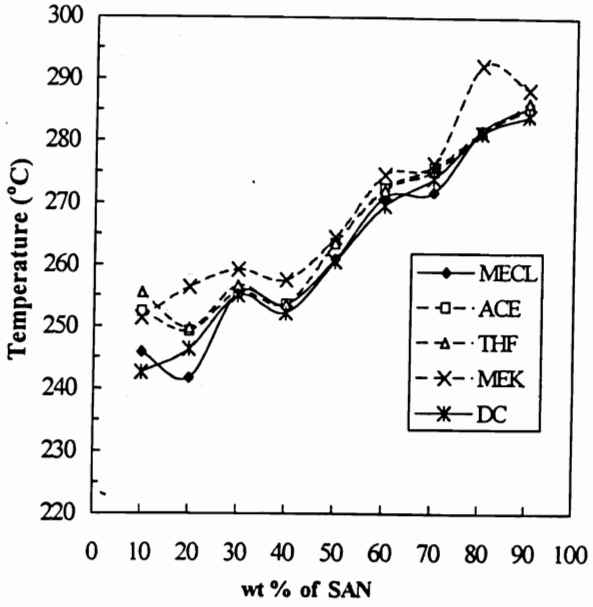

Figure 4 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 4 days

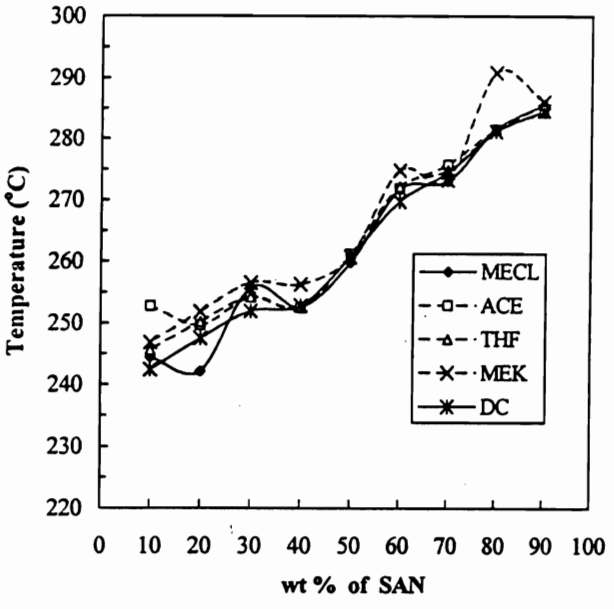

Figure 5 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 5 days

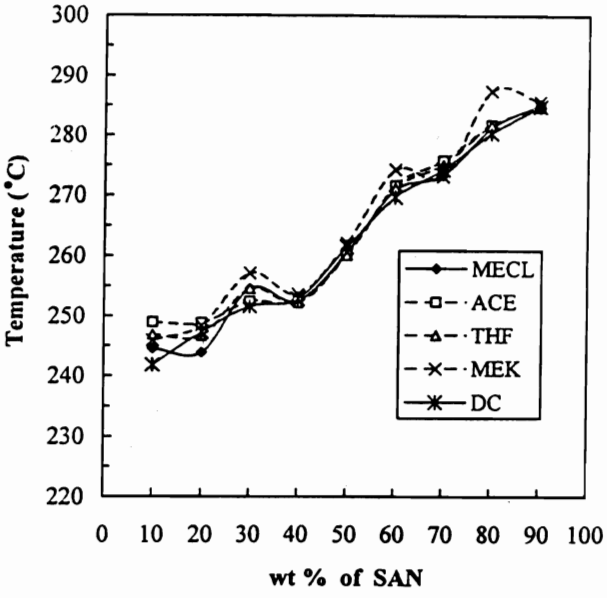

Figure 6 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 6 days

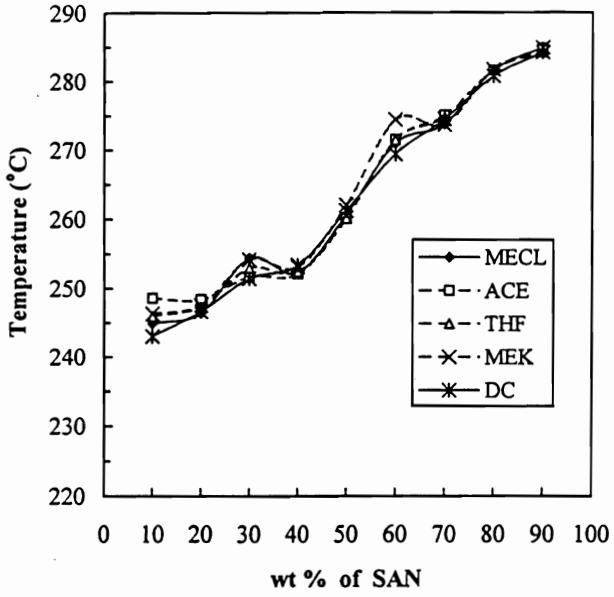

Figure 7 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 7 days

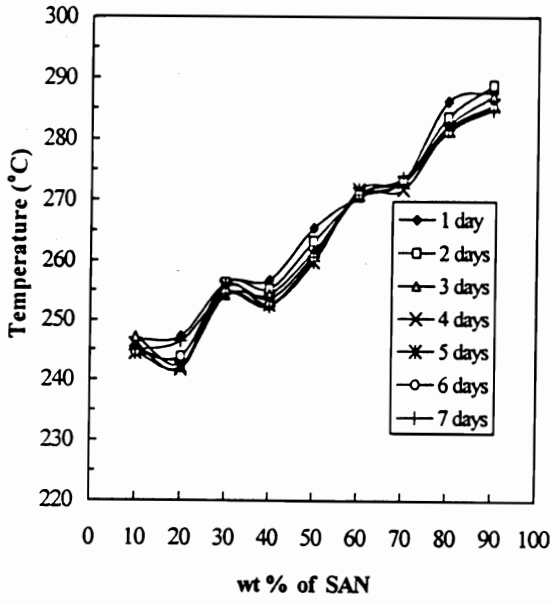

Figure 8 Phase diagrams of SAN/PMMA blends cast from methylene hloride at a drying time of 1 to 7 days

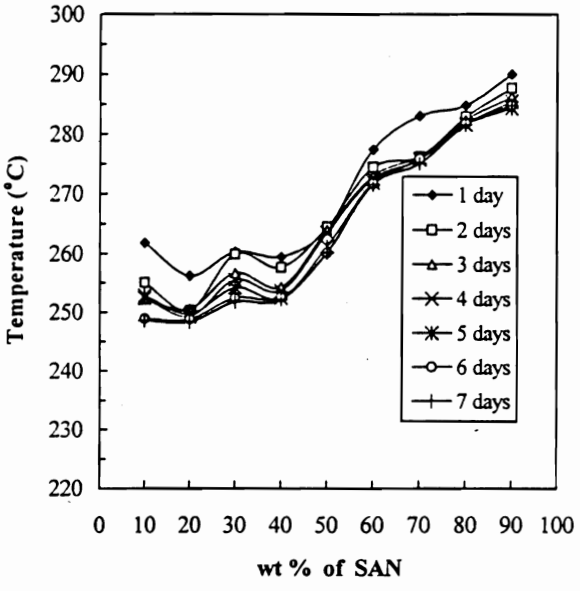

Figure 9 Phase diagrams of SAN/PMMA blends cast from acetone at the drying time of 1 to 7 days

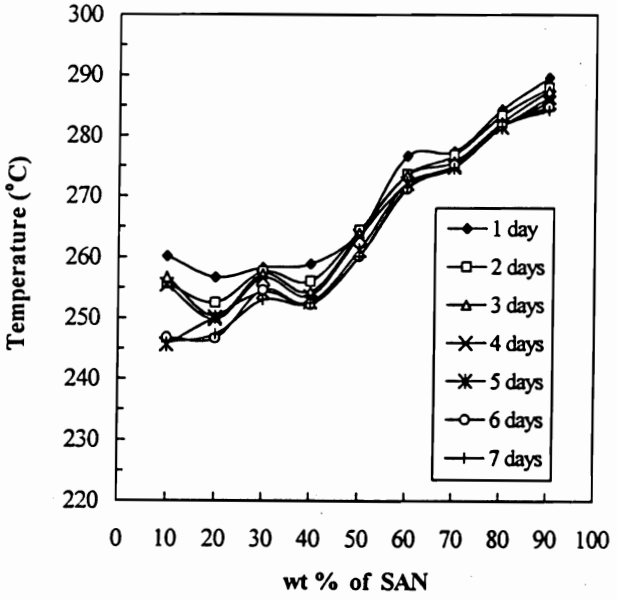

Figure 10 Phase diagrams of SAN/PMMA blends cast from tetrahydrofuran at the drying time of 1 to 7 days

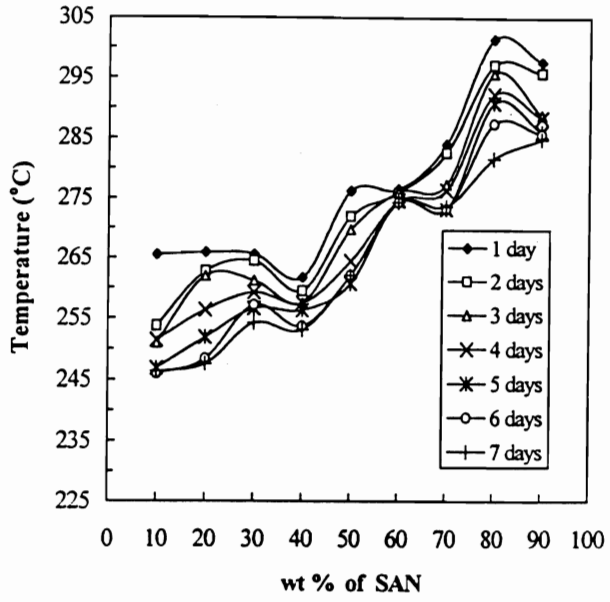

Figure 11 Phase diagrams of SAN/PMMA blends cast from methyl ethyl ketone at the drying time of 1 to 7 days

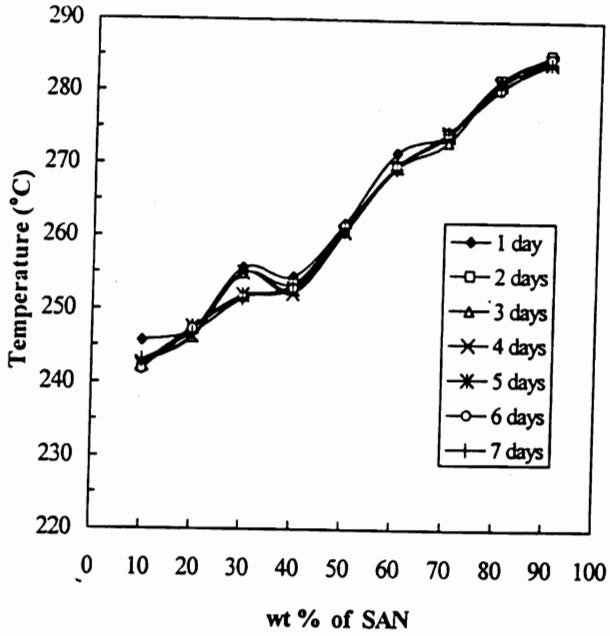

Figure 12 Phase diagrams of SAN/PMMA blends cast from 1,2-dichloroethane at the drying time of 1 to 7 days

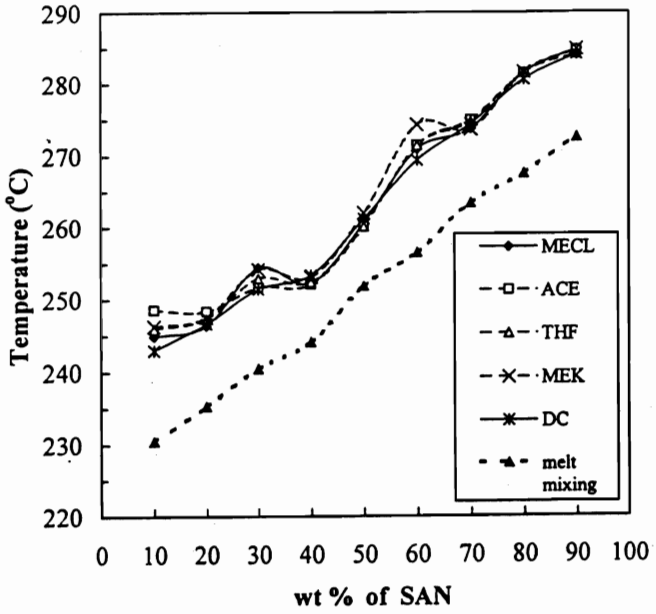

Figure 13 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 7 days and phase diagram of SAN/PMMA blends from melt mixing

Solvent casting is believed to provide the vehicle for dispersion of the multicomponent system (Semerak and Frank, 1987) because the method of solvent casting is performed by dissolving polymers in solvent and then casting the films of blend from the solution. Dissolving polymers in solvent is expected to reduce the high viscosity of polymers more efficiently than applying heat to molten polymers in melt mixing method. The reducing of polymers viscosity results in improving the blend miscibility which relates to the dispersion of blends. From this reason, the solvent casting can provide the finer dispersion morphology than the melt mixing method. Therefore, solvent cast blends can undergo phase separation at higher temperatures.

Conclusions

The conclusions from this work can be summarized as follows:

1. The phase diagrams of the blends of SAN and PMMA are affected by different type of solvents used in preparation. The phase separation of the blends cast from moderated hydrogen bonding solvents which are acetone, tetrahydrofuran and methyl ethyl ketone occurs at higher temperatures than blends cast from weak hydrogen bonding solvents that are methylene chloride and 1,2-dichloroethane. Appropriate solvents can therefore be used in solution casting method in order to improve the miscibility of SAN/PMMA blends.

2. The amount of the solvents remained in the blends of SAN and PMMA cast from moderated hydrogen bonding solvents can enhance the miscibility of the blends. The higher the amount of so0lvent remains in the blends, the higher the cloud point temperatures of the blends occur.

3. The phase diagrams of blends cast from acetone and tetrahydrofuran take place at the lower cloud point temperatures than one cast from methyl ethyl ketone owing to the lower boiling points of acetone (56.24 °C) and tetrahydrofuran (64-65°C) compared with methyl ethyl ketone (79.60 °C).

4. There is a difference in the phase separation of SAN and PMMA blends prepared from solvent casting and melt mixing. The phase separation of solvent cast blends, which are expected to have the finer morphology, occurs at much higher temperatures than that of melt mixing blends.

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