CHAPTER V

RESULTS & DISCUSSIONS

Polymer blends of styrene-acrylonitrile copolymer (SAN) and poly (methyl methacrylate) (PMMA) were used in this work. Five solvents which are methylene chloride (MC), acetone (AC), tetrahydrofuran (THF), methyl ethyl ketone (MEK) and 1,2-dichloroethane (DC) were chosen to study the effects of these small molecular solvents on the phase diagrams, tensile strength and glass transition temperatures of the polymer blend.

The experiments performed in this work are divided into three parts as follows.

Part I The Studies of Phase Diagrams

In this part, two methods of blend preparation as mentioned, solvent casting from different solvents and melt mixing, were used. The preparation of blend and the determination of phase diagram of blend were described in Chapter 4 section 4.3. Phase diagrams of solvent casting blends from different solvents were compared in order to study the effects of different solvents and the amount of the solvent retained in the blends at various drying times.

Besides, phase diagrams of solvent casting blends were compared with phase diagrams of melt mixing blends to study the effects of blend preparation on the phase diagrams.

Part II The Studies of Tensile Strength

In this part, only the melt mixing blend was used. The preparation of the specimens for tensile testing and the experimental procedure of the tensile testing were mentioned in Chapter 4 section 4.4. To study the effects of various solvents on tensile strength of the blends, the tensile strength of blends containing different solvents is compared with the tensile strength of blends without solvent. Blends containing solvent was prepared by suspending the melt mixing SAN/PMMA blends in the vapor of each solvent for 20 min and left to dry for 1 hr prior to the tensile testing.

Part III The Studies of Glass Transition Temperatures

In this part, the glass transition temperatures of the blends without solvent and blends containing different solvents obtained from Part II were examined using DSC technique. The experimental procedure of the studies of glass transition temperatures was described in Chapter 4 section 4.5. The comparisons between the glass transition temperatures of blends without solvent and those of blends with different solvents were made in order to study the effects of various solvents on the glass transition temperatures of the SAN/PMMA blends.

5.1 The Studies of Phase Diagrams

The polymer blend of styrene-acrylonitrile copolymer (SAN) and poly (methyl methacrylate) (PMMA) was used in this study due to the fact that it is miscible at all compositions at room temperature and can exhibit lower critical temperature solution (LCST) behavior, i.e. the blend can transform from clear to cloudy state on heating. The cloud point temperatures of SAN/PMMA blends prepared from solvent casting from different solvents and melt mixing, were observed as aforementioned in Chapter 4 section 4.3.2.

The cloud point temperatures of blends at various compositions of SAN and PMMA cast from five solvents, which are methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane, and dried at a period of time of 1 to 7 days are respectively listed in Tables A.1, A.2, A.3, A.4, and A.5. While the cloud point temperatures of blends prepared from melt mixing were tabulated in Table A.6. These tables were shown in the Appendix.

From the obtained cloud point temperatures, the phase diagrams of SAN/PMMA blends can be constructed by plotting the cloud point temperatures against blend compositions.

5.1.1 Discussions

5.1.1.1 Comparisons of the Phase Diagrams of SAN/PMMA Blends Cast from Different Solvents

Considering the phase diagrams of the blends cast from different solvents at the same period of drying time from 1 to 7 days as shown in Figures 5.1 to 5.7, it is seen that all the constructed phase diagrams of the blends are in the same trend, i.e. the phase separation of blends with low weight percent of SAN occurs at the lower temperatures than blends with high weight percent of SAN. This is consistent with the phase diagrams of SAN/PMMA blends reported in many works [Chiou, Paul and Barlow, 1982; Kressler, Kammer and Klostermann, 1986; Lyngaae-Jørgenson and Søndergaard, 1987; Suess, Kressler and Kammer, 1987; Fowler, Barlow and Paul, 1987]. For example, Kressler et al. [1986] studied the phase diagram of the blends of PMMA and SAN copolymer containing the acrylonitrile (AN) content of 9.5 to 28 wt%. They found that the phase separation of the SAN/PMMA blends occurred at the higher temperature when the weight percent of SAN in blends increased. They also found that the lower the AN content in SAN, the higher the temperature that the phase separation of the SAN/PMMA blends took place.

When considering all the phase diagrams of blends at drying time of 1 day (Figure 5.1), 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 chioride 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 observed phase diagram of the SAN/PMMA blends.

The similar results are also observed in the phase diagrams of SAN/PMMA blends at other drying time period as shown in Figures 5.2, 5.3, 5.4, 5.5, 5.6 and 5.7. 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. It is supposed to be caused by the complete removal of the solvents retained in blends after drying in a vacuum oven for 7 days.

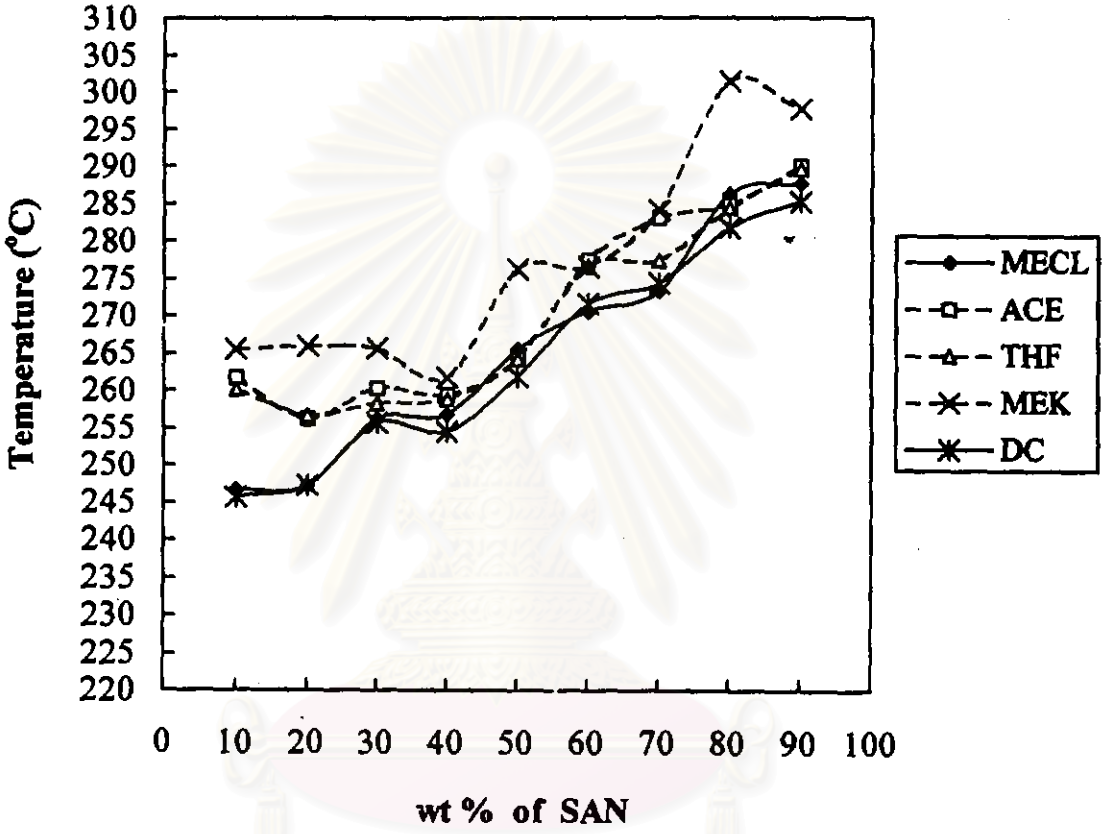

Figure 5.1 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 1 day.

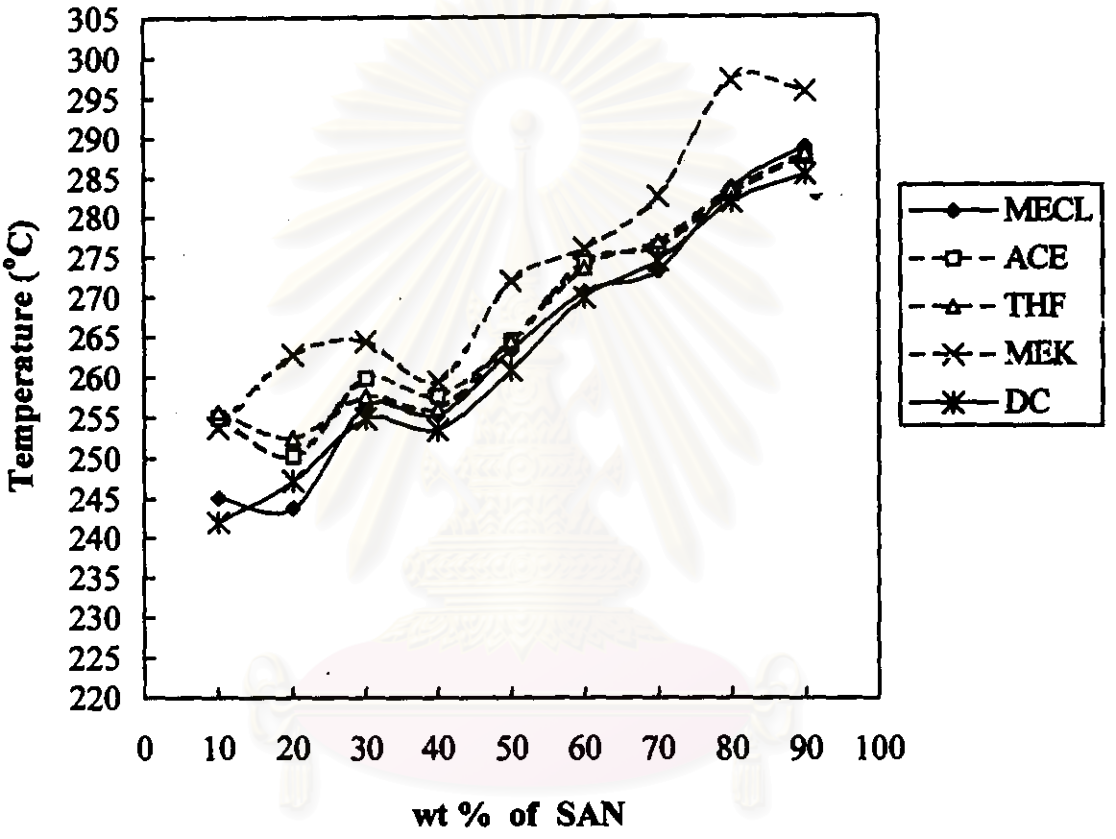

Figure 5.2 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 2 days.

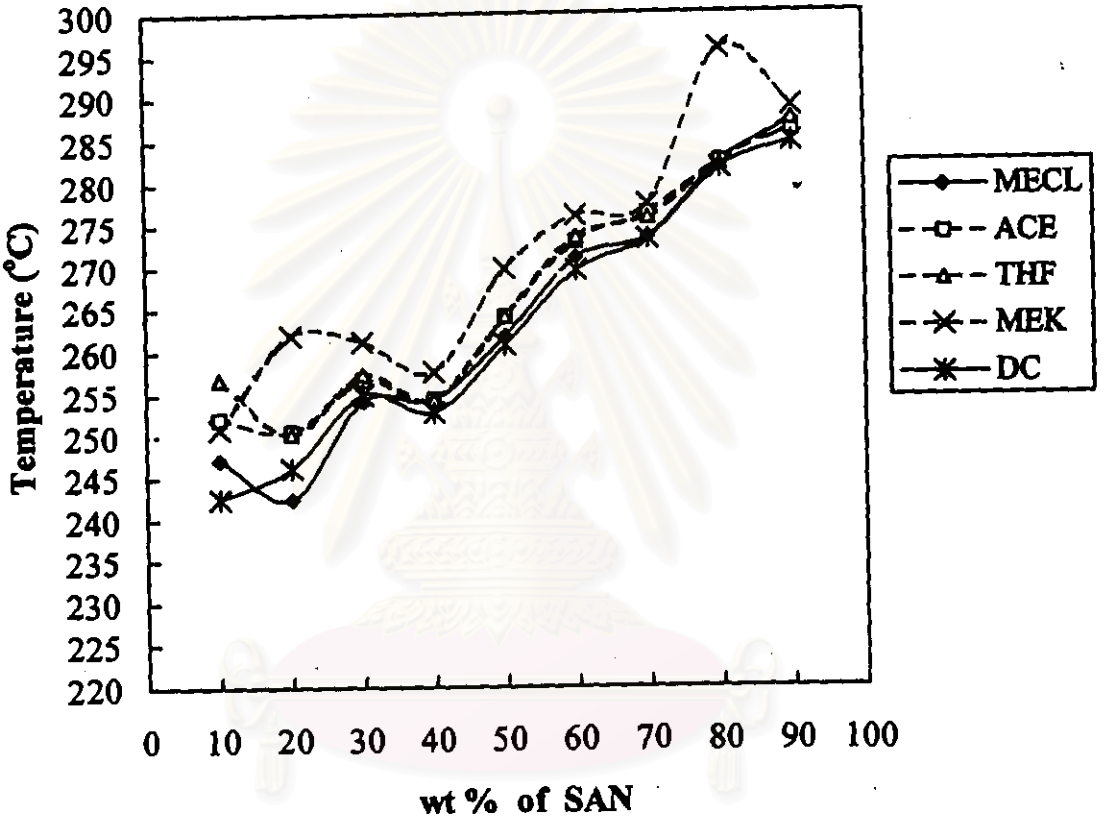

Figure 5.3 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 3 days.

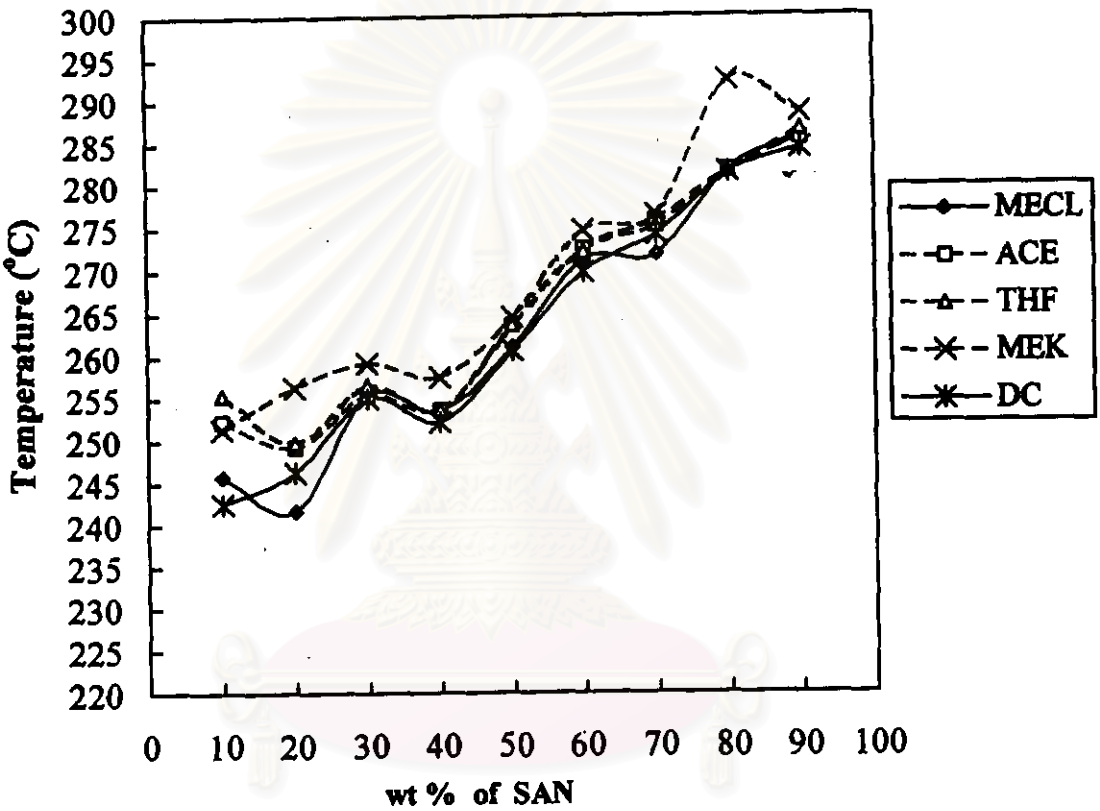

Figure 5.4 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 4 days.

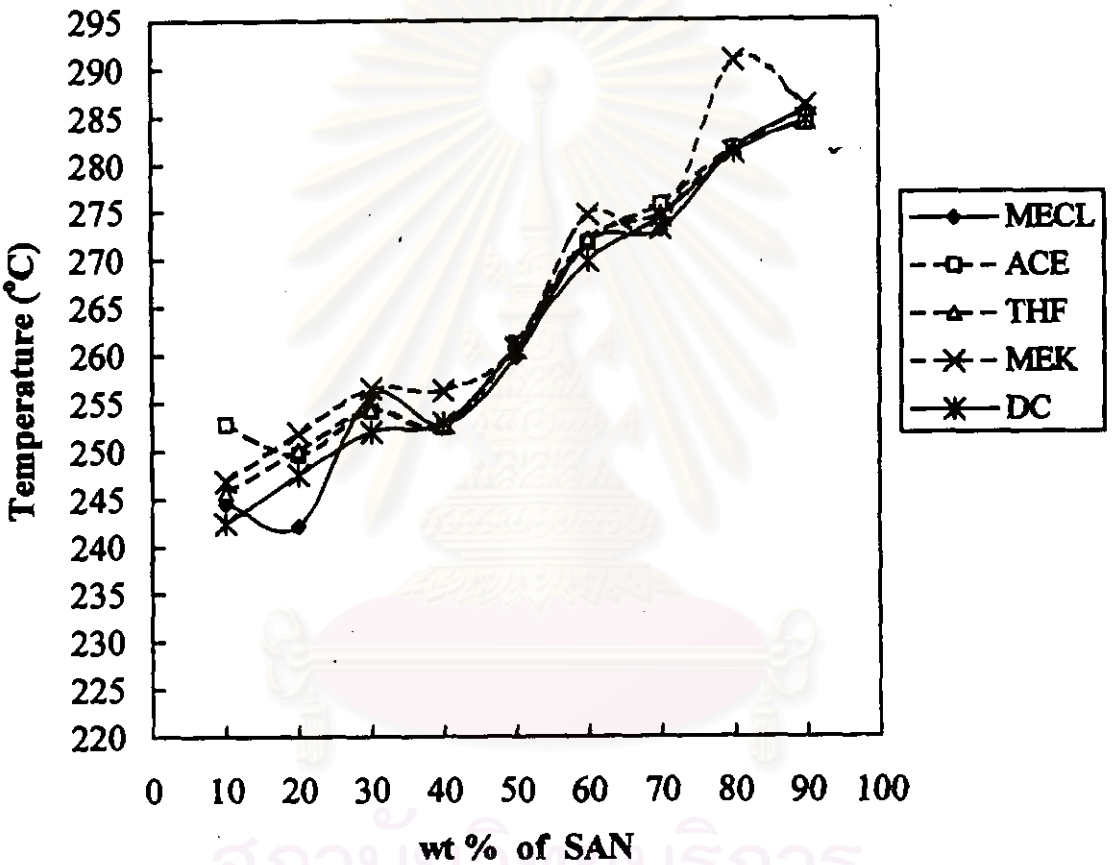

Figure 5.5 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 5 days.

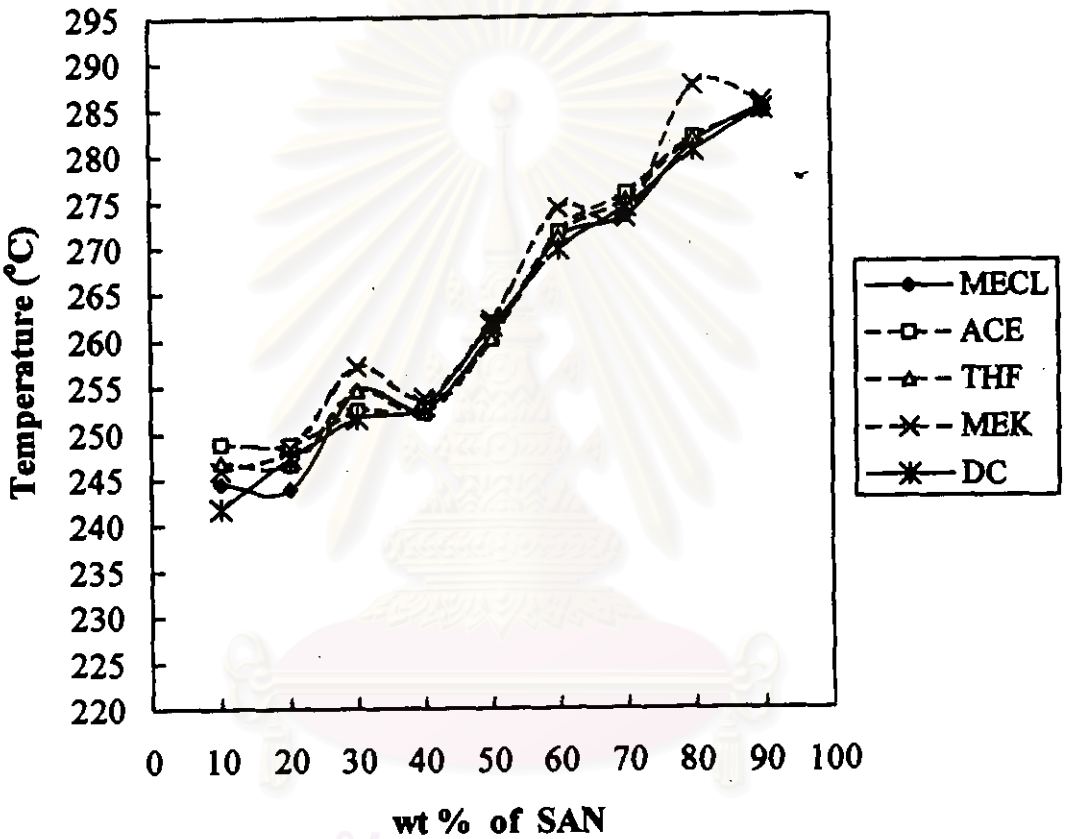

Figure 5.6 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 6 days.

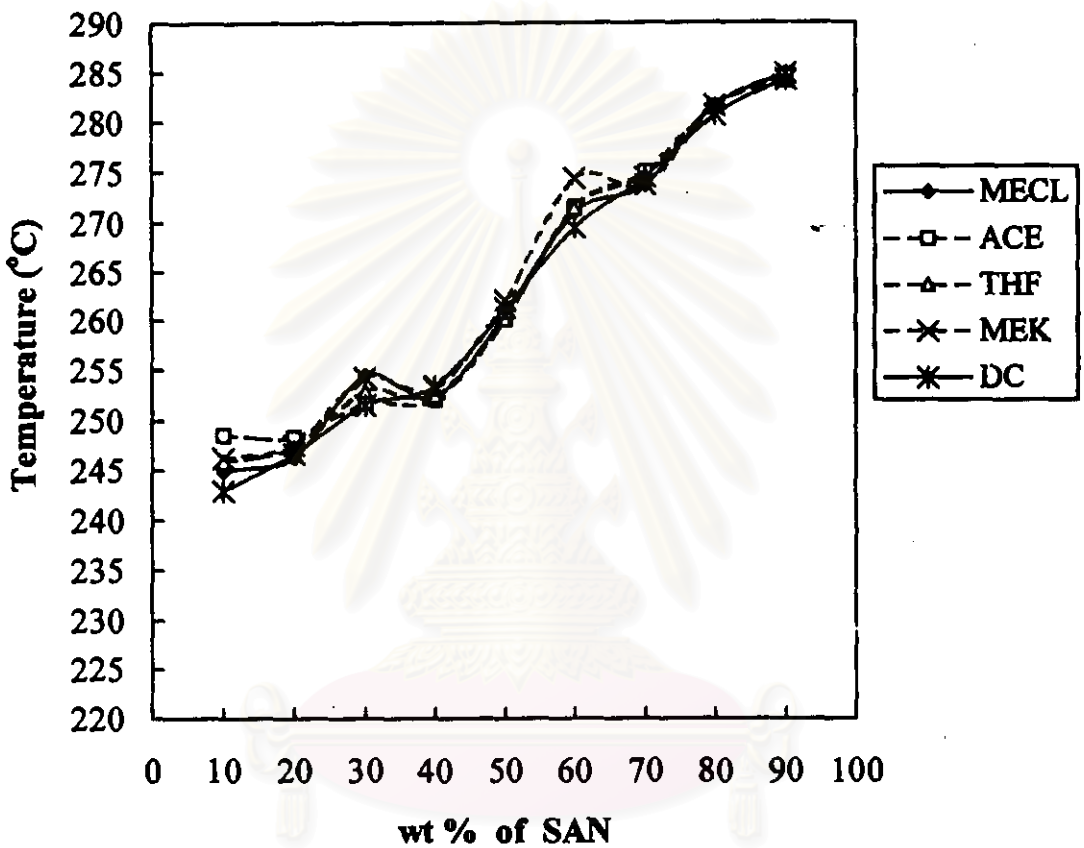

Figure 5.7 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 7 days.

The effects of the type of solvents on the phase separation of blends as discussed above can also be demonstrated by plotting the cloud point temperatures of the blends versus drying times and keeping weight percent of SAN constant, for example as shown in Figures 5.8 to 5.12.

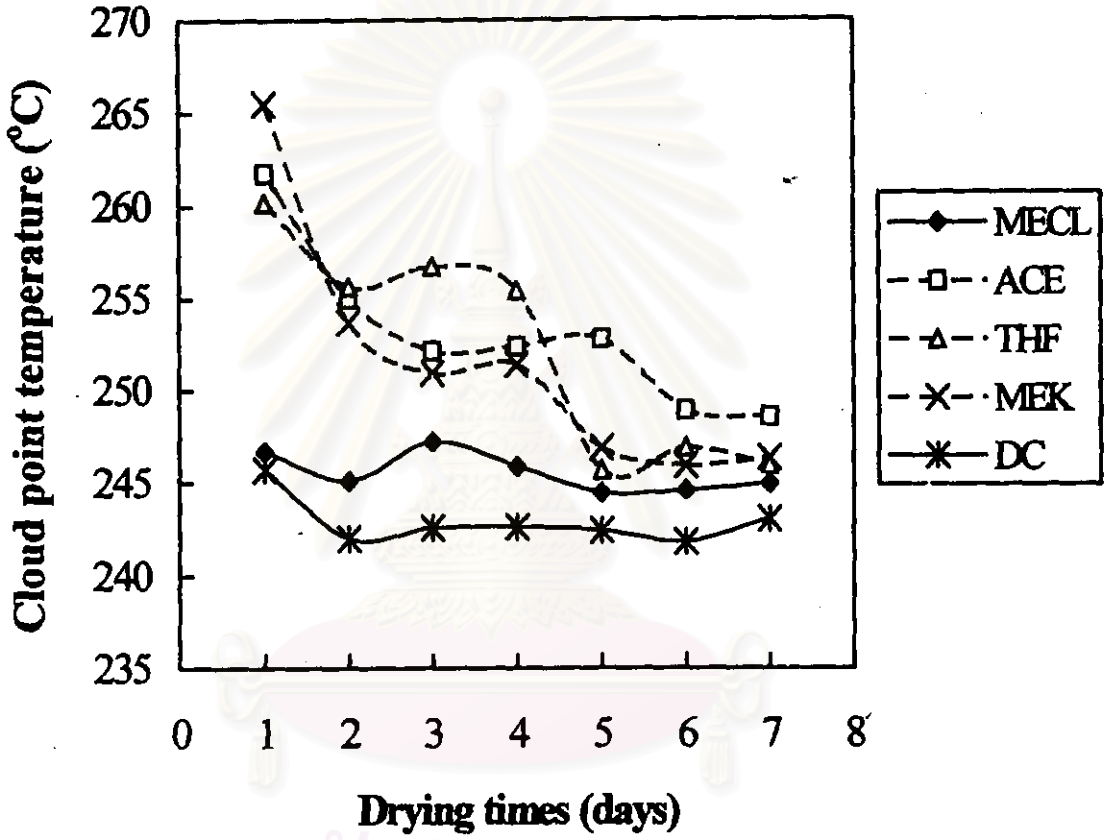

Figure 5.8 Cloud point temperatures of SAN/PMMA blends at 10 wt% of SAN cast from different solvents at the drying time of 1 to 7 days.

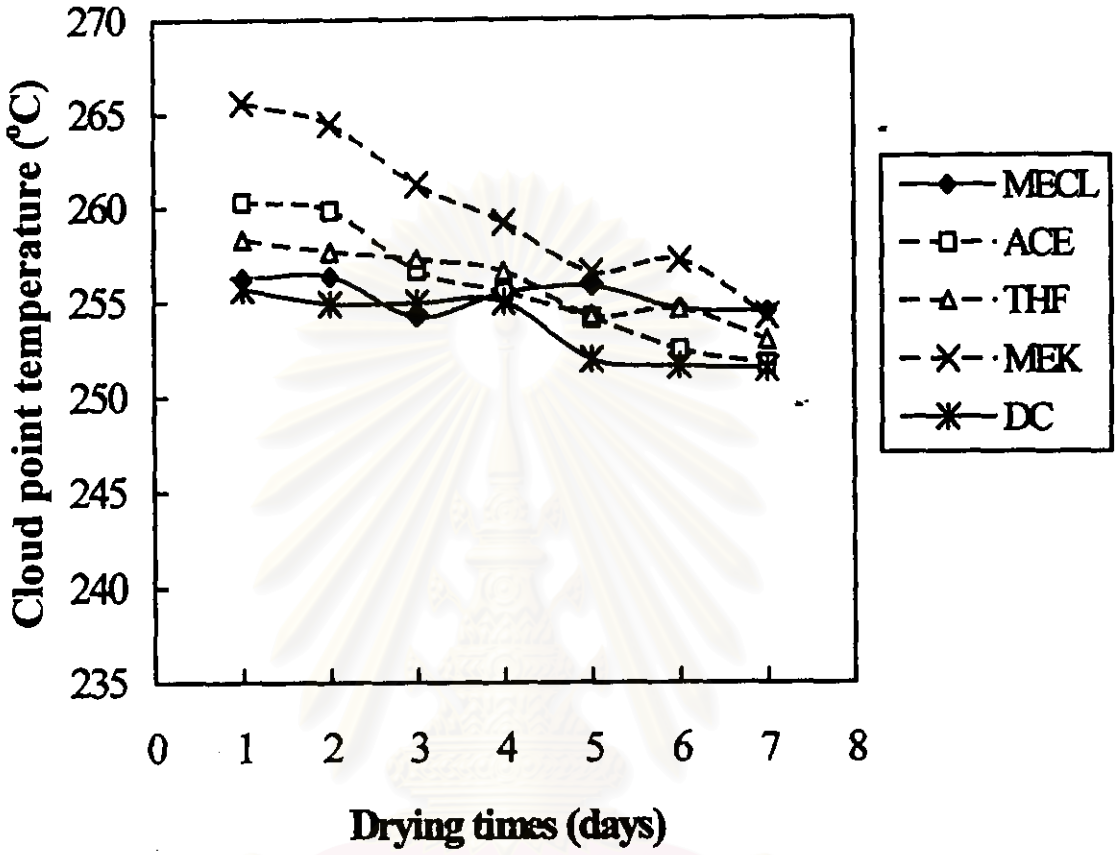

Figure 5.9 Cloud point temperatures of SAN/PMMA blends at 30 wt% of SAN cast from different solvents at the drying time of 1 to 7 days.

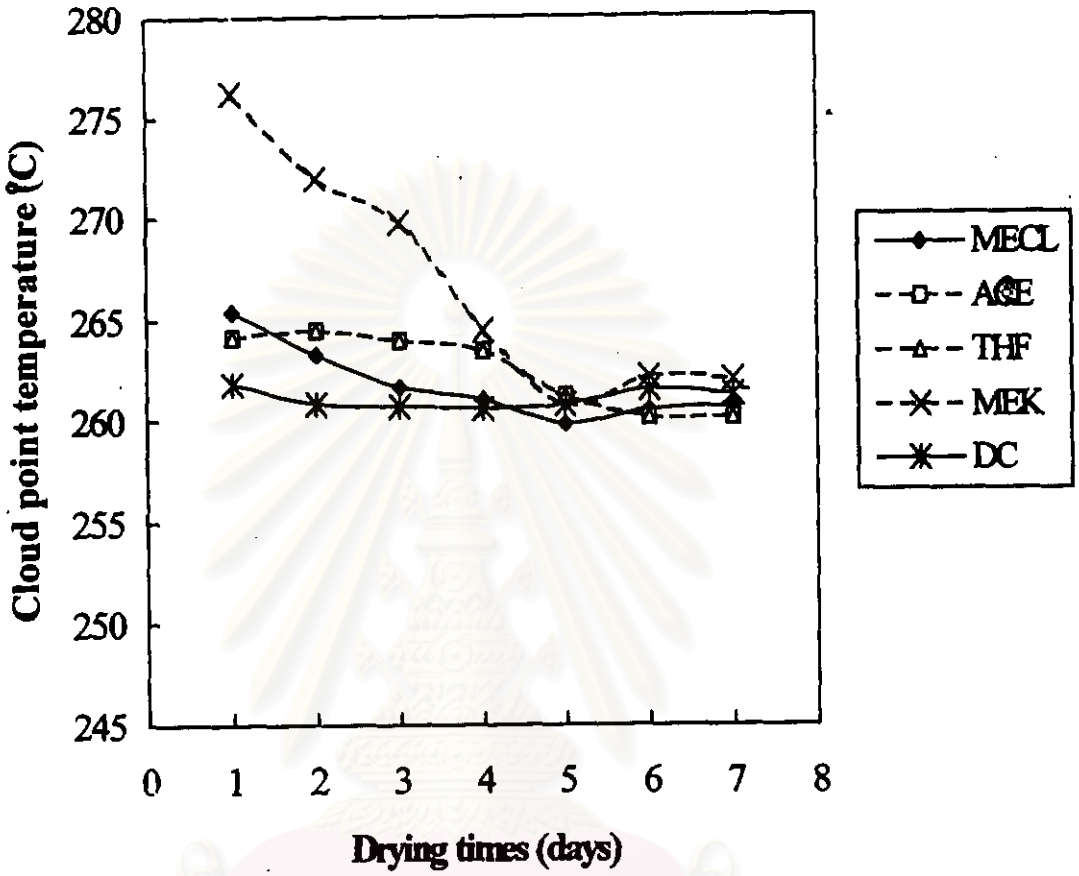

Figure 5.10 Cloud point temperatures of SAN/PMMA blends at 50 wt% of SAN cast from different solvents at the drying time of 1 to 7 days.

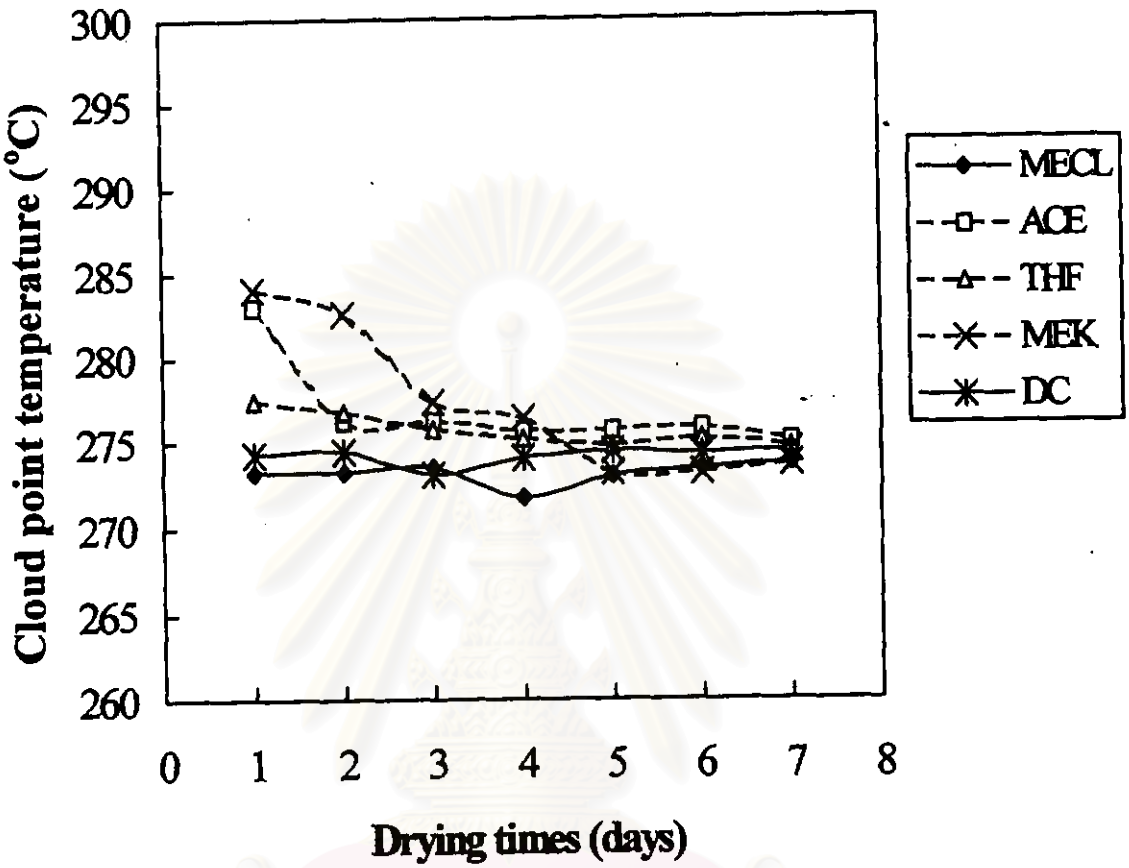

Figure 5.11 Cloud point temperatures of SAN/PMMA blends at 70 wt% of SAN cast from different solvents at the drying time of 1 to 7 days.

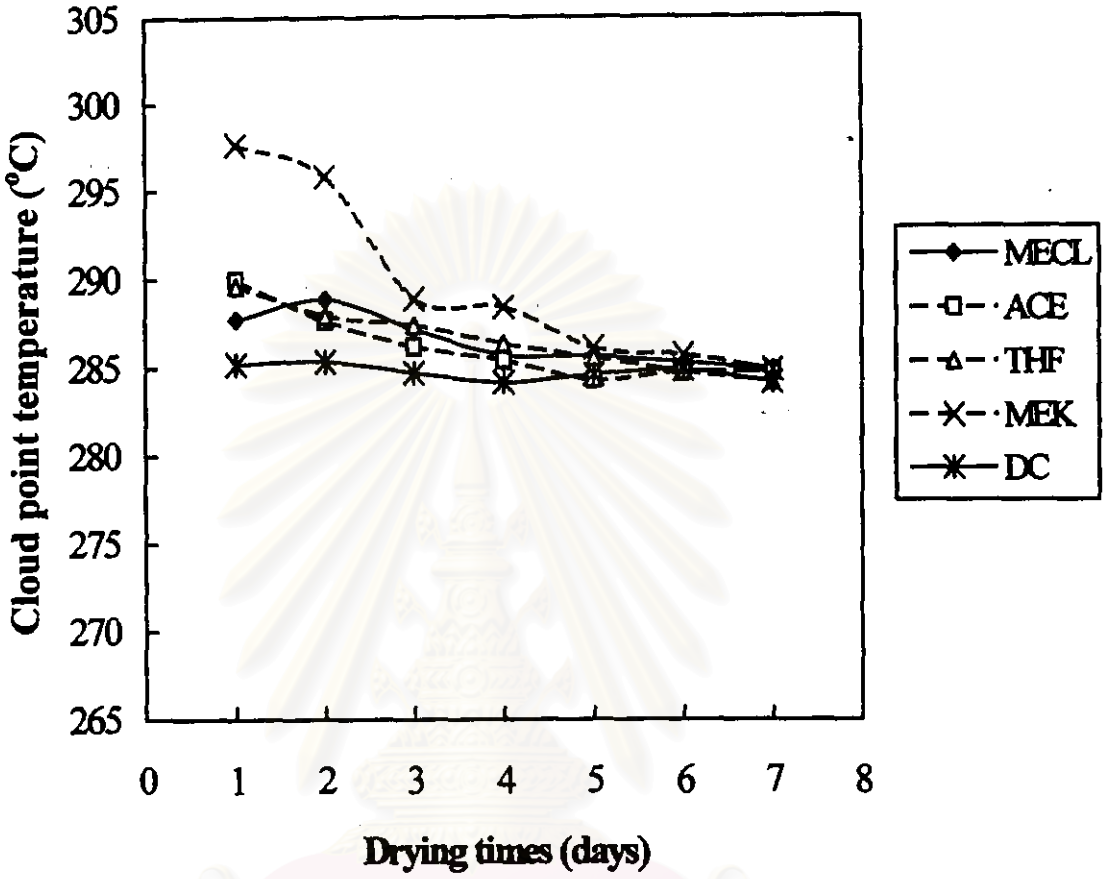

Figure 5.12 Cloud point temperatures of SAN/PMMA blends at 90 wt% of SAN cast from different solvents at the drying time of 1 to 7 days.

5.1.1.2 Comparisons of the Phase Diagrams of SAN/PMMA Blends Dried at Different Drying Times.

In order to study the effects of the amount of solvent remained in blends at different drying time, the phase diagrams of the SAN/PMMA blends cast from different solvents are replotted as shown in Figures 5.13 to 5.17.

As shown in Figures 5.13 to 5.17, 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 increases, 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, because the remained solvents in blends are completely removed.

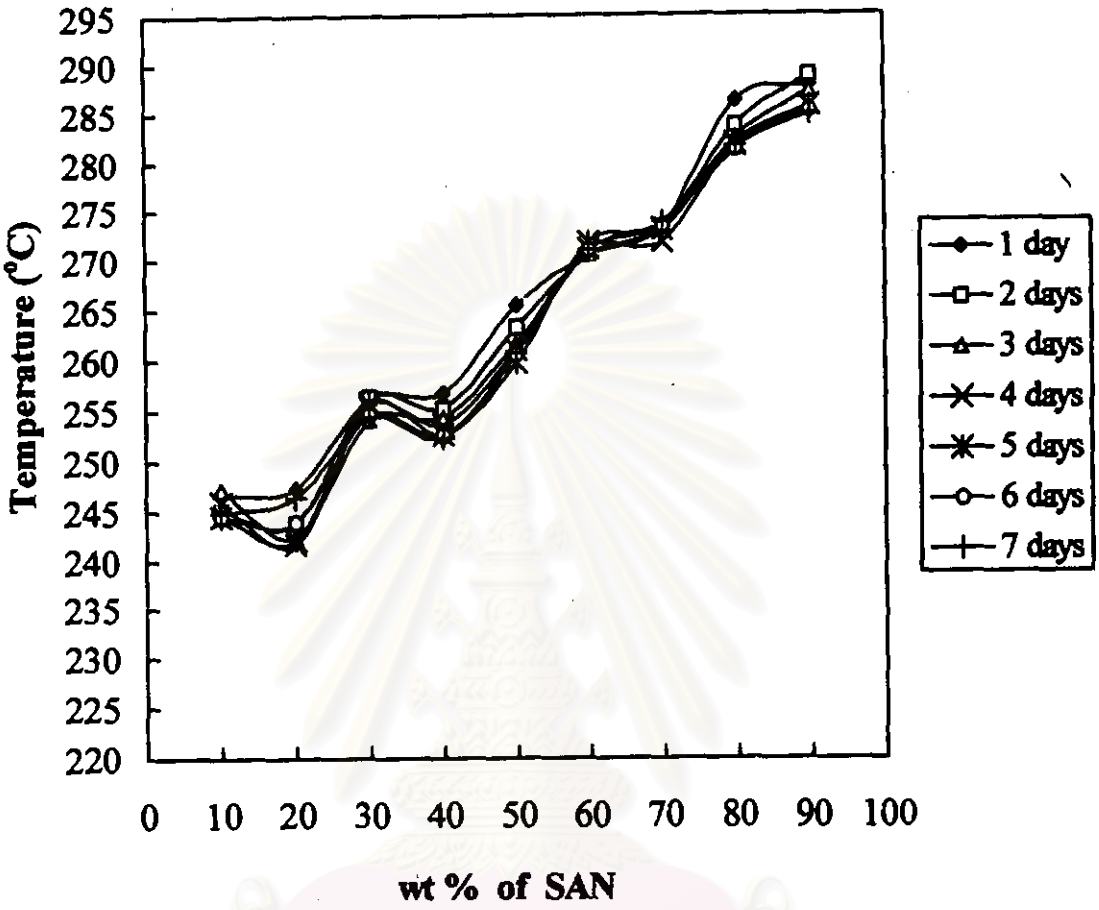

Figure 5.13 Phase diagrams of SAN/PMMA blends cast from methylene chloride at the drying time of 1 to 7 days.

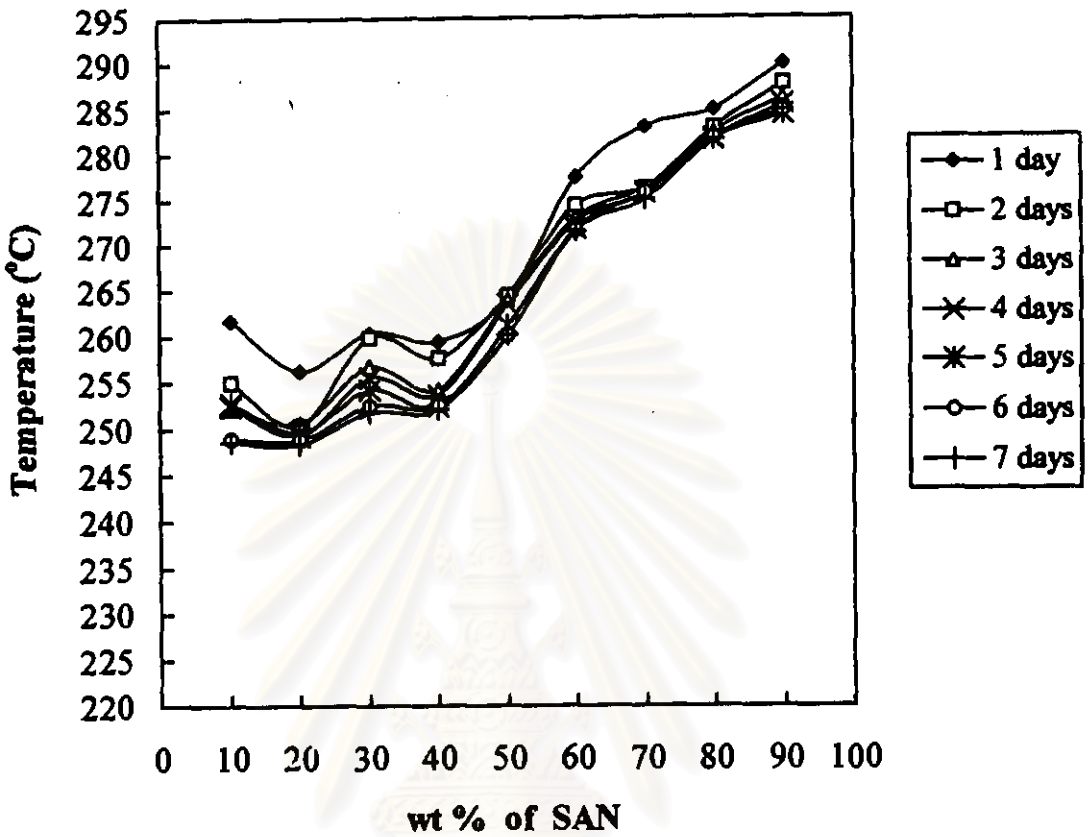

Figure 5.14 Phase diagrams of SAN/PMMA blends cast from acetone at the drying time of 1 to 7 days.

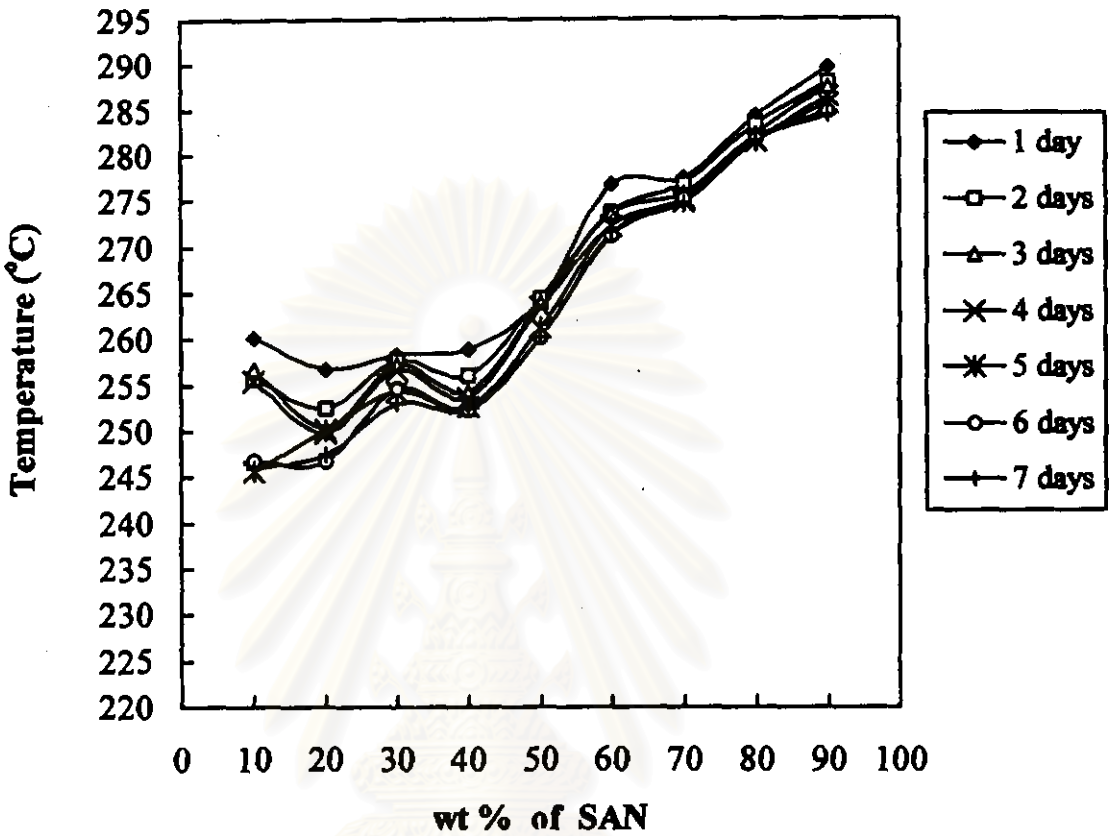

Figure 5.15 Phase diagrams of SAN/PMMA blends cast from tetrahydrofuran at the drying time of 1 to 7 days.

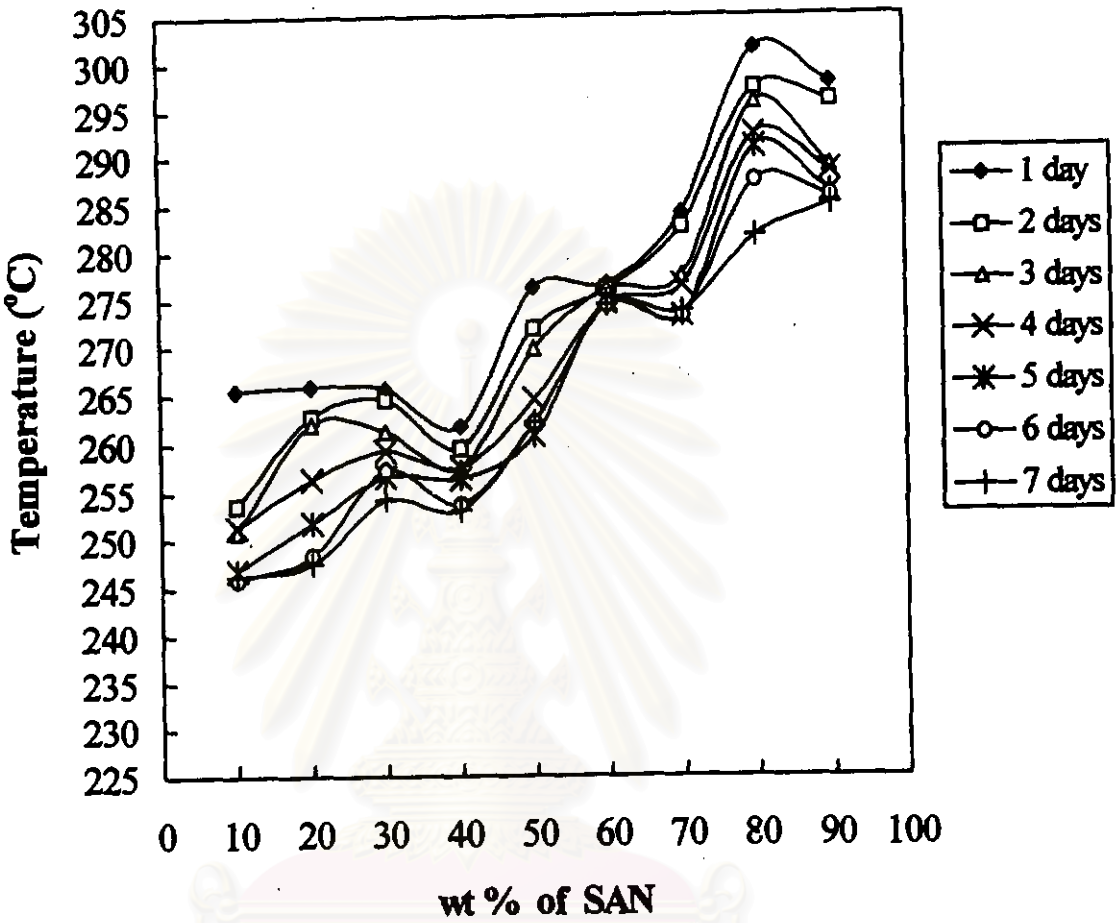

Figure 5.16 Phase diagrams of SAN/PMMA blends cast from methyl ethyl ketone at the drying time of 1 to 7 days.

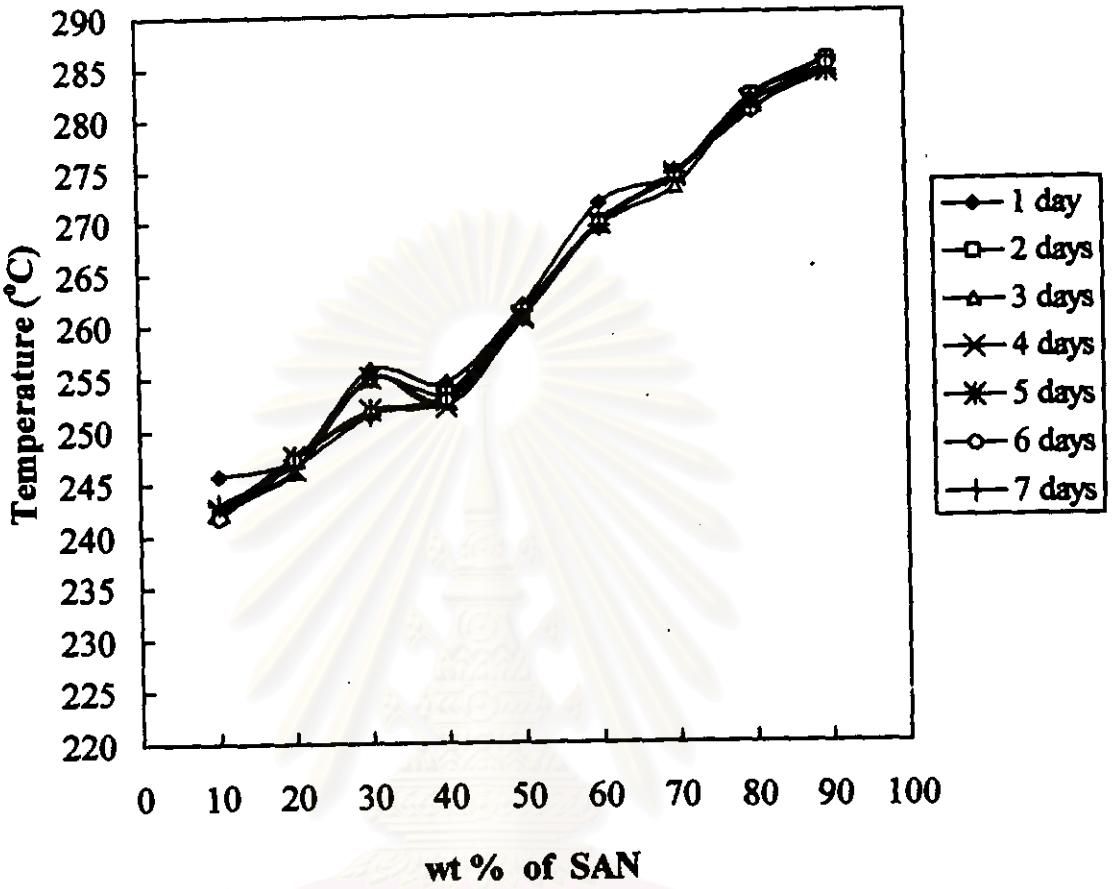

Figure 5.17 Phase diagrams of SAN/PMMA blends cast from 1,2-dichloroethane at the drying time of 1 to 7 days.

5.1.1.3 Comparisons of the 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 5.18. 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 5.18 showed that the phase diagrams of the blends prepared from solvent casting method occur at much higher temperatures than the phase diagram of the blends prepared from melt mixing. This is supposed to be originated from the differences of blend morphology between the two methods of blend preparation.

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.

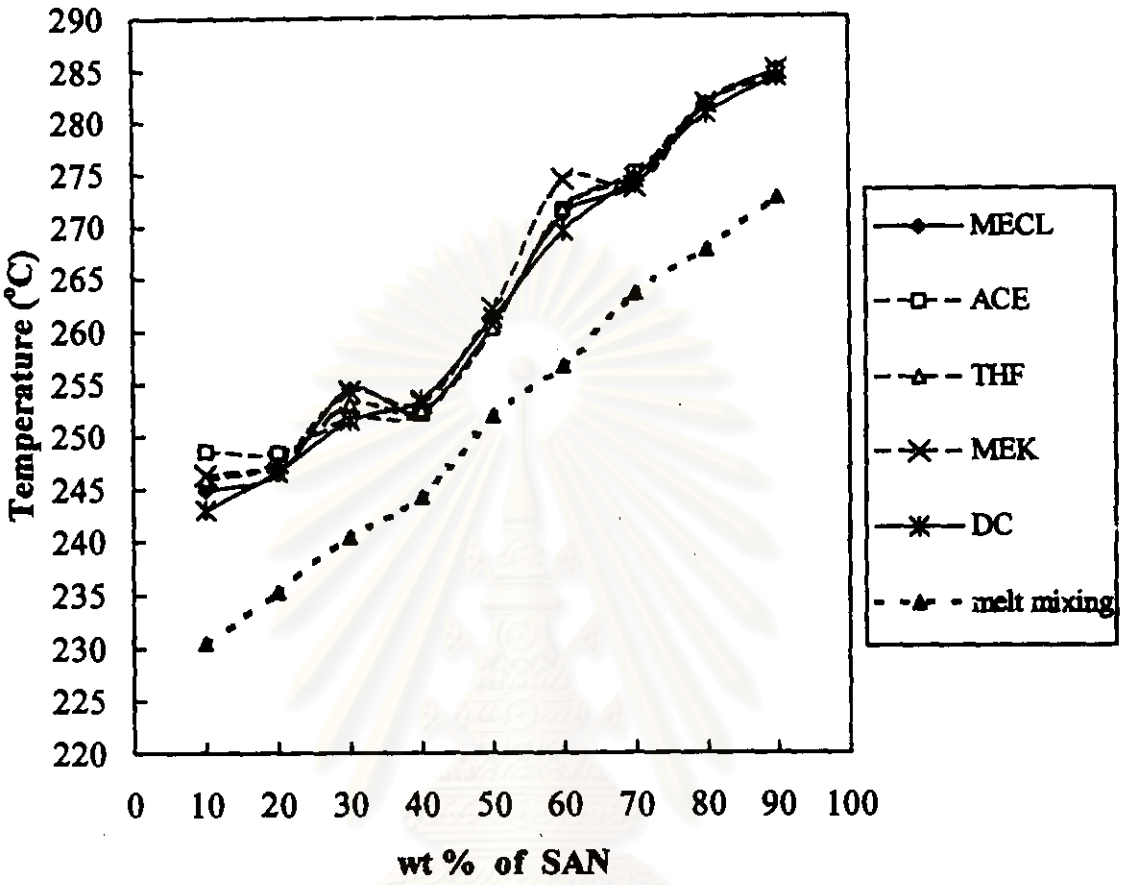

Figure 5.18 Phase diagrams of SAN/PMMA blends cast from different solvents at a drying time of 7 days and phase diagram of SAN/PMMA blends from melt mixing.

5.2 The Studies of Tensile Strength

Tensile testing on a series of SAN/PMMA blends prepared from melt mixing was performed as described in Chapter 4 section 4.4.2. The tensile strength at break of the blends was calculated by dividing the maximum load at break by the original minimum cross-sectional area of the specimen. Twenty specimens of each blend formulation were tested and only the average value of the tensile strength of each blend formulation is tabulated in Table B.1.

For the blends containing solvent, 20 specimens of each blend formulation were suspended in the vapor of the solvent according to the procedures described in Chapter 4 section 4.4.2 before performing tensile test. In this part, the five different solvents which were methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane were also used. The tensile strength of the blends with solvent was calculated in the same way as mentioned above. The average tensile strength of each blend containing methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane were listed in Tables B.2, B.3, B.4, B.5 and B.6, respectively. Tables B.1 to B.6 were shown in the Appendix.

The comparisons between the tensile strength of blends without solvent and blends with methylene chloride, acetone, tetrahydrofuran, methyl ethyl ketone and 1,2-dichloroethane were plotted in Figures 5.19 to 5.23.

5.2.1 Discussions

As seen in Figures 5.19 to 5.23, it is found that the tensile strength of SAN/PMMA blends is not much changed by suspending in the vapor of different solvents. The tensile strength of blends without solvent is in the same order of magnitude as the tensile strength of blends with solvents. The tensile strength of the blends with and without solvents ranges from 31 to 42 N/mm^2. The differences of tensile strength of the blends with and without solvents as calculated from equation 5.1 are shown in Figures 5.24 to 5.28. Overall, it can be seen that the differences of tensile strength were within $\pm 6\%$.

$$\%DTS = \frac{TS_w - TS_{wo}}{TS_{wo}} \times 100 \qquad (5.1)$$

where %DTS is the percent difference of tensile strength, TS_w and TS_{wo} are tensile strength of the blends with and without solvents.

This is supposed to be a result of traces of solvent absorbed by the blends at the room temperature. Because the room temperature is lower than the glass transition temperature of the blends, hence, the segments of amorphous polymer have very little mobility and there are fewer voids between polymer molecules for the small molecular solvents to diffuse into the SAN/PMMA blends [Brydson, 1995]. The traces of solvents in the blends, then, can hardly change the glass transition temperatures of the blends. This implies that the modulus of the blend is also not changed very much. Therefore, the measured tensile strength of the blends does not vary much.

The detail of the glass transition temperatures of SAN/PMMA blends with solvents is discussed in the next section.

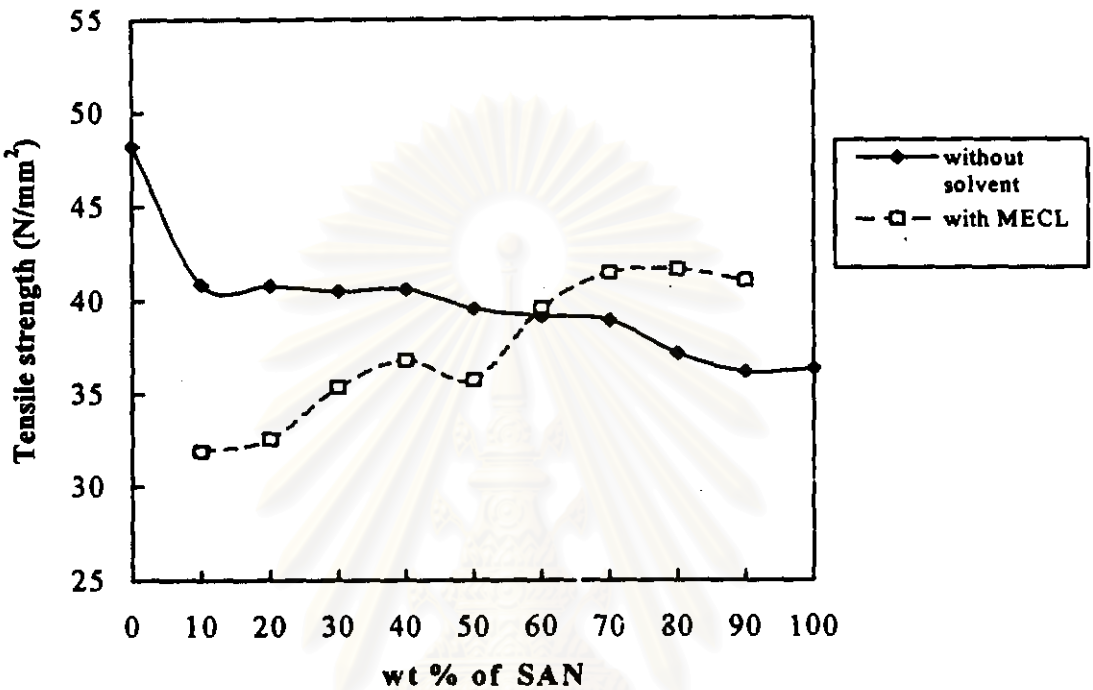

Figure 5.19 Tensile strength of SAN/PMMA blends without solvent and with methylene chloride.

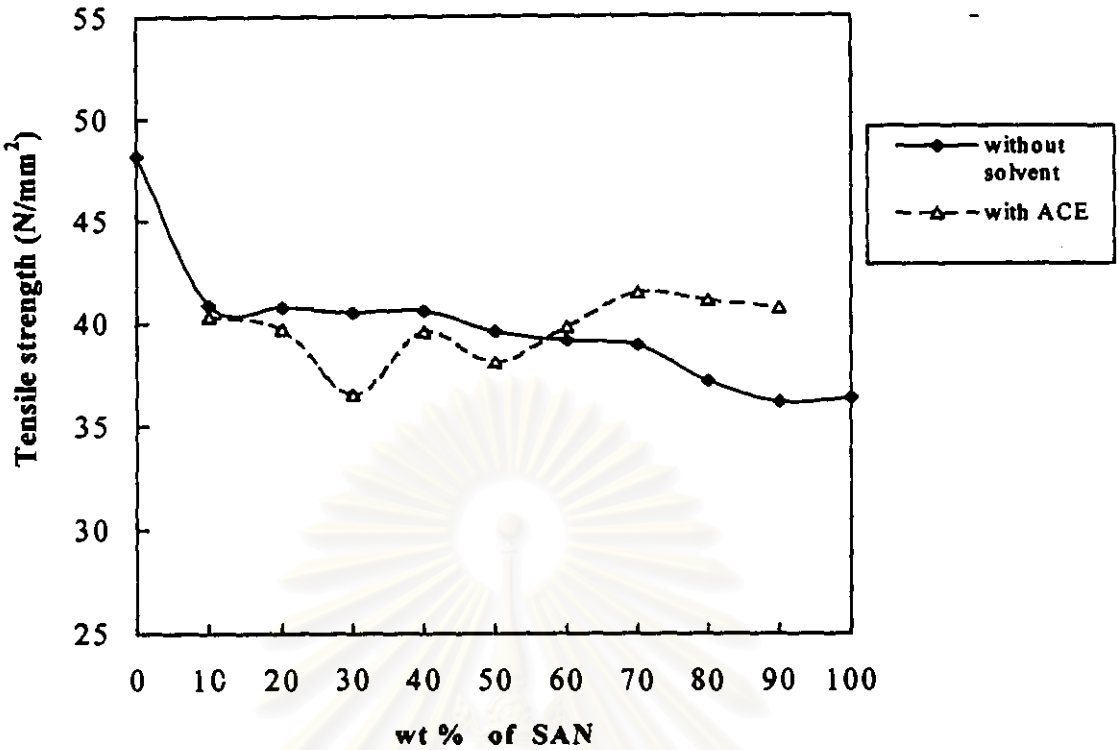

Figure 5.20 Tensile strength of SAN/PMMA blends without solvent and with acetone.

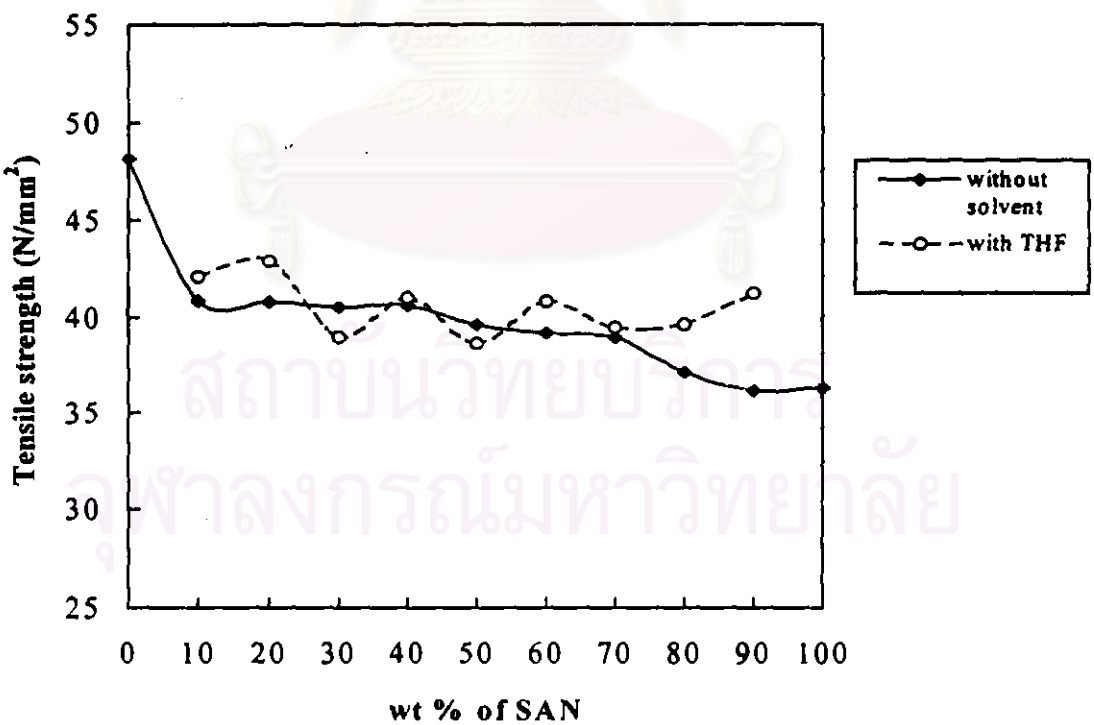

Figure 5.21 Tensile strength of SAN/PMMA blends without solvent and with tetrahydrofuran.

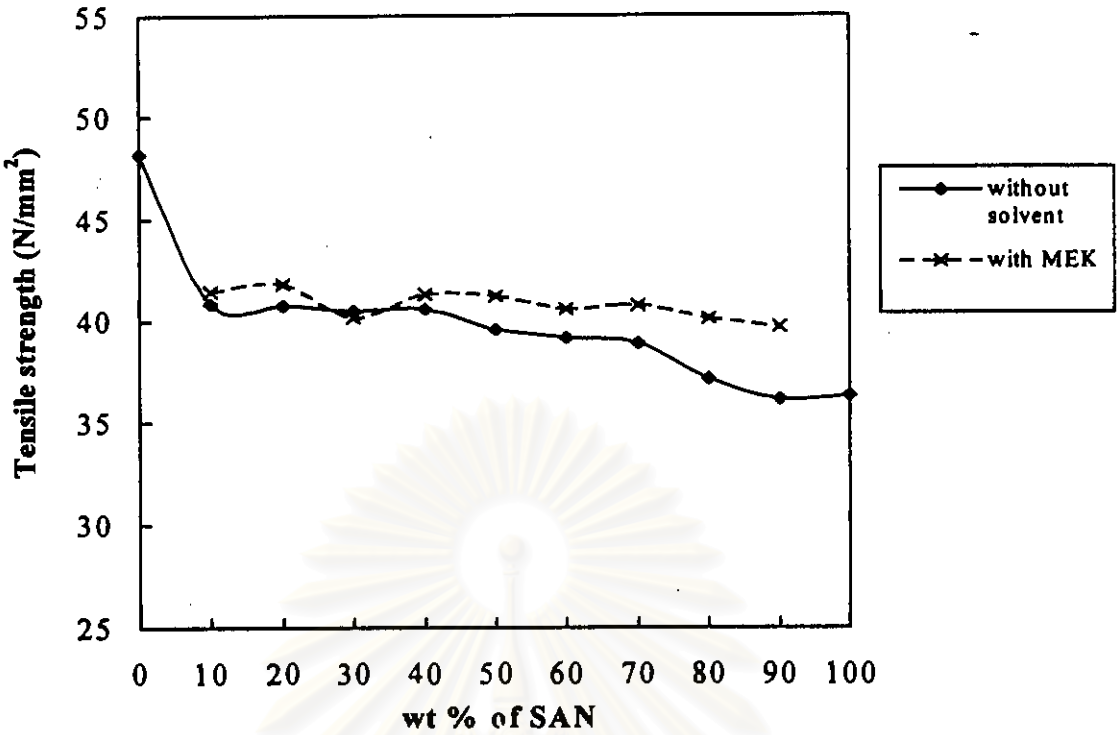

Figure 5.22 Tensile strength of SAN/PMMA blends without solvent and with methyl ethyl ketone.

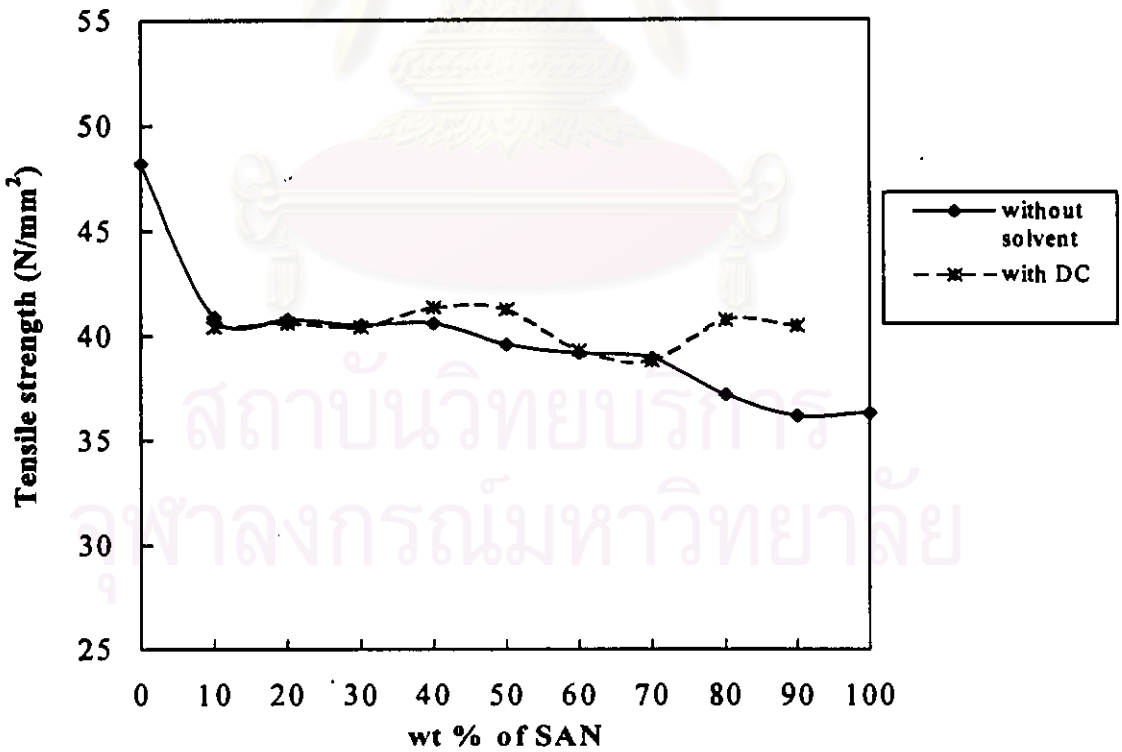

Figure 5.23 Tensile strength of SAN/PMMA blends without solvent and with 1,2-dichloroethane.

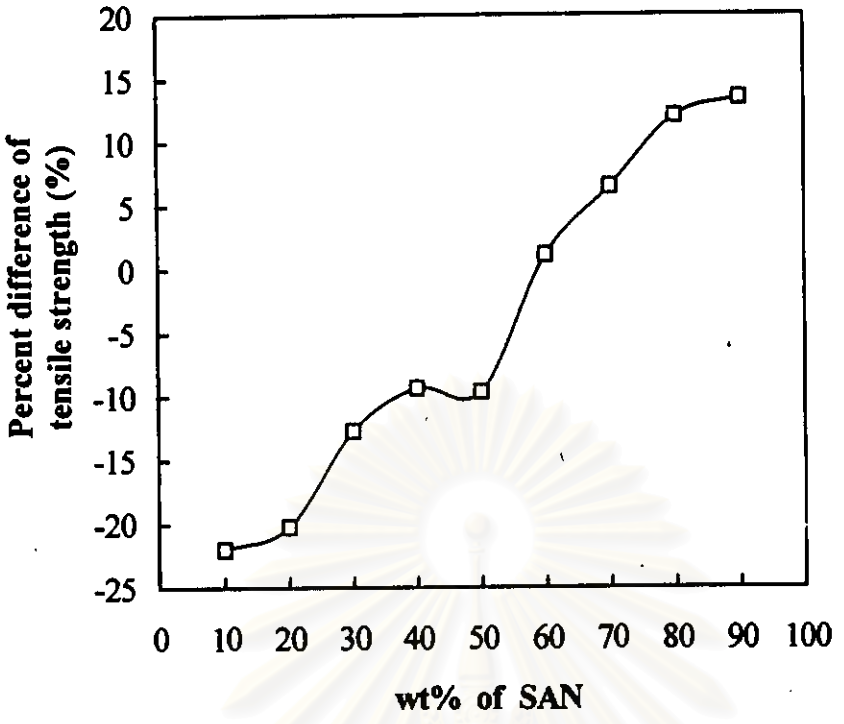

Figure 5.24 Percent difference of tensile strength of SAN/PMMA blends without solvent and with methylene chloride.

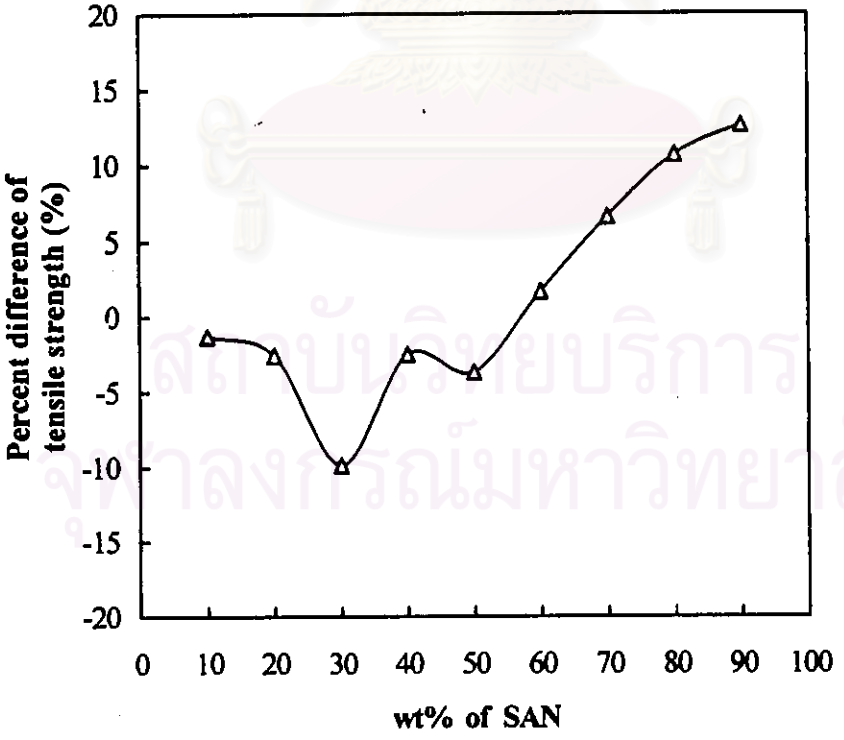

Figure 5.25 Percent difference of tensile strength of SAN/PMMA blends without solvent and with acetone.

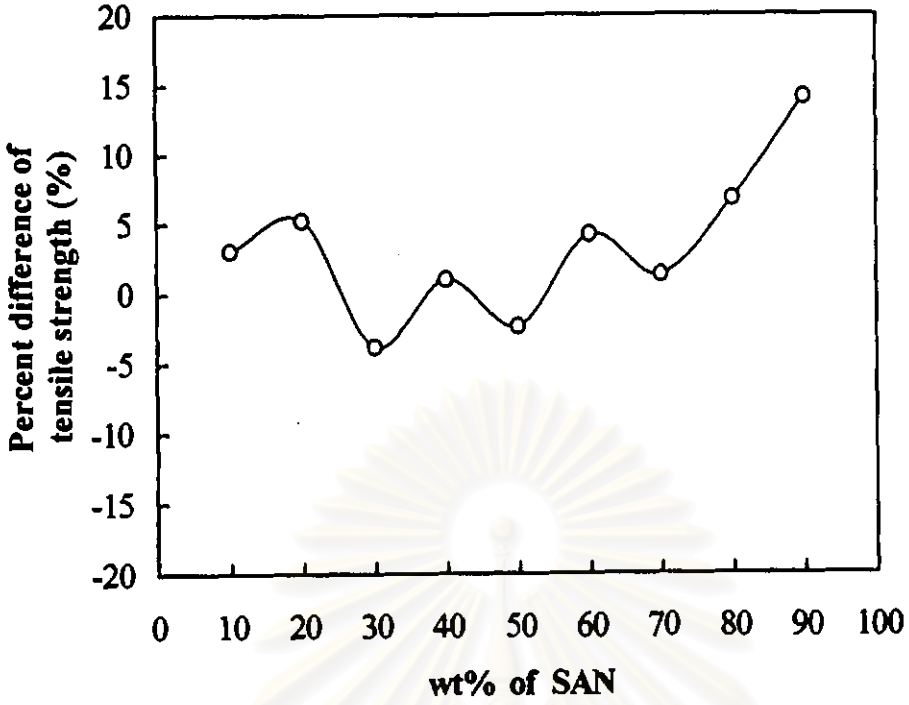

Figure 5.26 Percent difference of tensile strength of SAN/PMMA blends without solvent and with tetrahydrofuran.

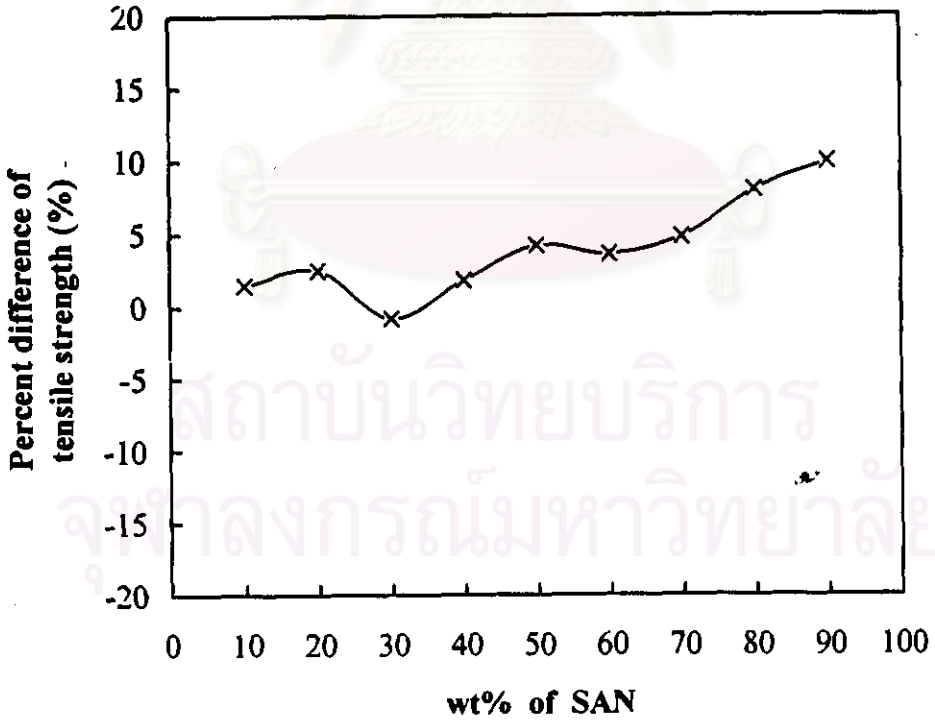

Figure 5.27 Percent difference of tensile strength of SAN/PMMA blends without solvent and with methyl ethyl ketone.

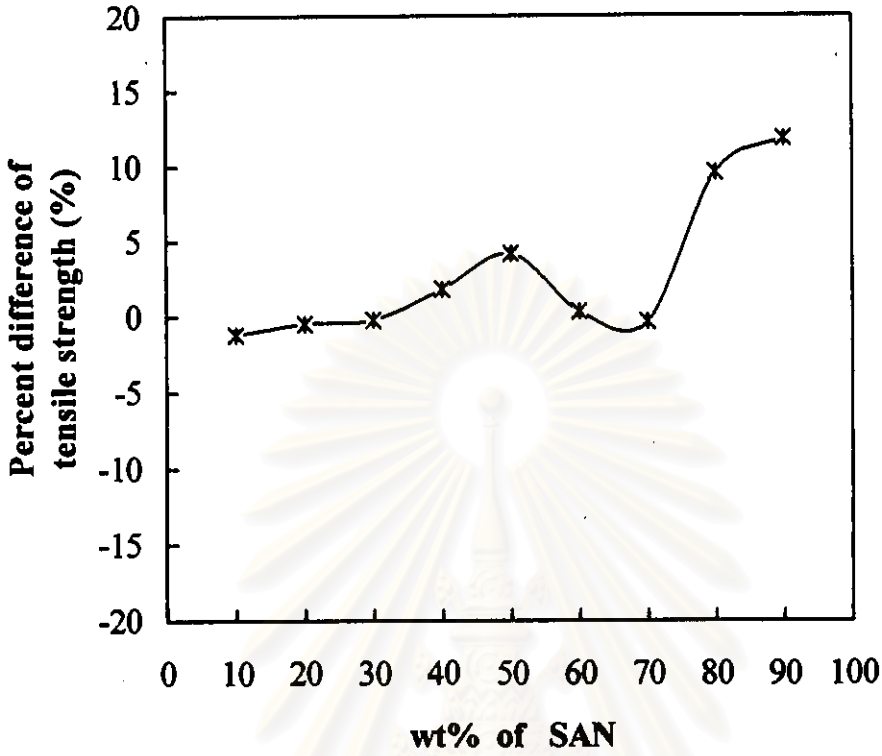

Figure 5.28 Percent difference of tensile strength of SAN/PMMA blends without solvent and with 1,2-dichloroethane.

5.3 The Studies of Glass Transition Temperatures

The glass transition temperatures of SAN/PMMA blends without solvent and with solvents were examined by DSC in this part. The glass transition temperatures of blends without solvent and blends with five different solvents were listed in Tables C.1 to C.6 and shown in the Appendix. The comparisons of the glass transition temperatures of the blends without solvent and blends with solvents were plotted in Figures 5.29 to 5.33.

5.3.1 Discussions

Figures 5.29 to 5.33 show that the glass transition temperatures of blends with various solvents are closely to those of blends without solvent. That is to say, the traces of solvents vapor in the blends of SAN and PMMA are not enough to plasticize the blends to such an extent that the significant reducing of the glass transition temperatures of the blends can be noticed. This corresponds to the inability of solvents to significantly lower the tensile strength of the blends in section 5.2.

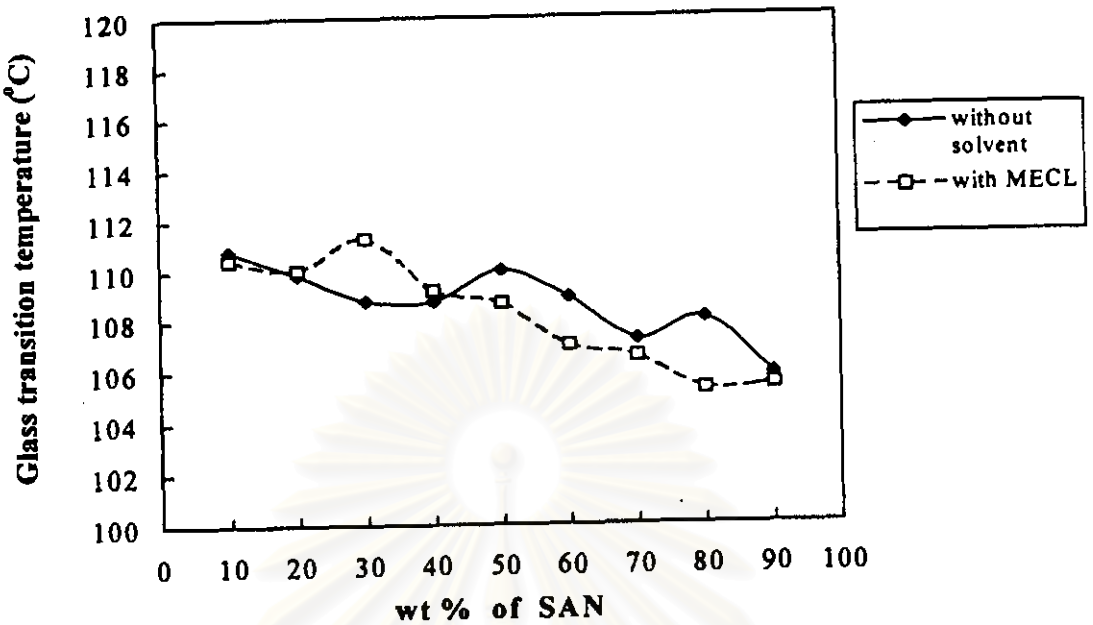

Figure 5.29 The glass transition temperatures of SAN/PMMA blends without solvent and with methylene chloride.

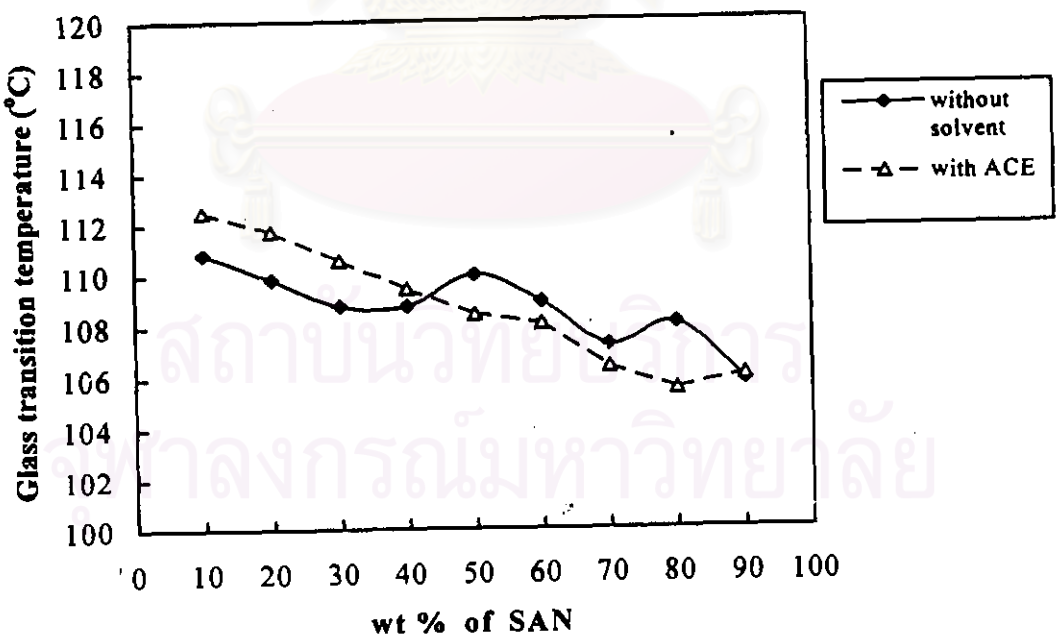

Figure 5.30 The glass transition temperatures of SAN/PMMA blends without solvent and with acetone.

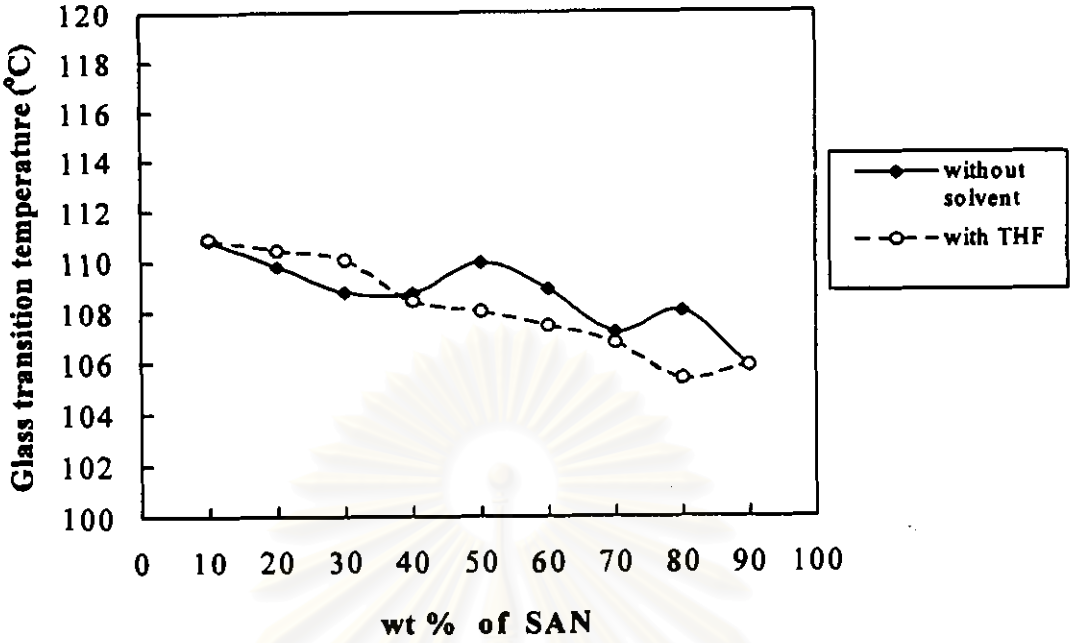

Figure 5.31 The glass transition temperatures of SAN/PMMA blends without solvent and with tetrahydrofuran.

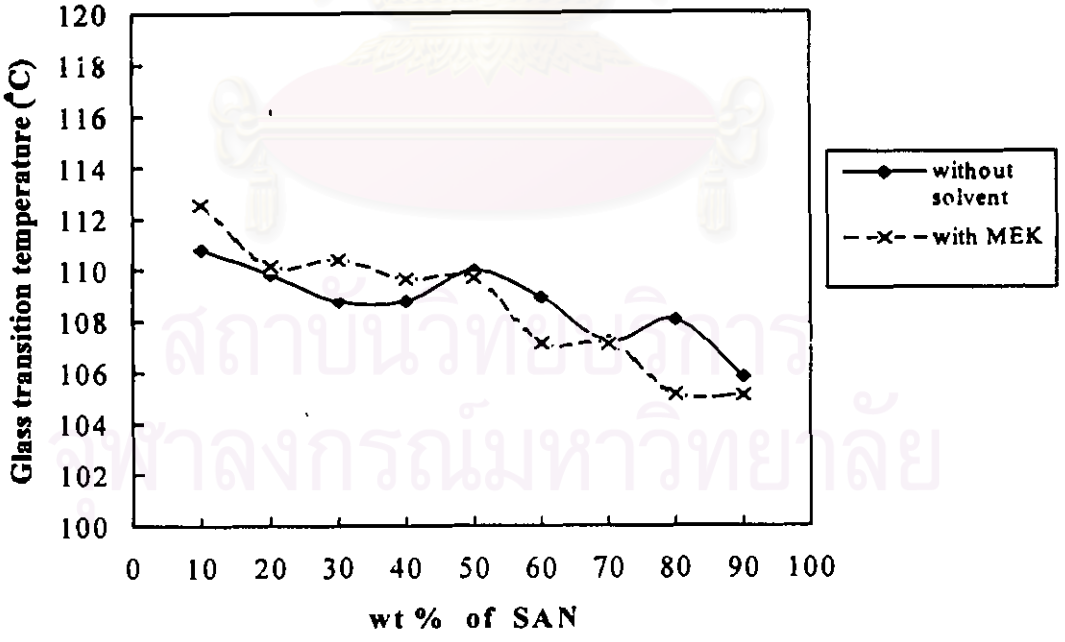

Figure 5.32 The glass transition temperatures of SAN/PMMA blends without solvent and with methyl ethyl ketone.

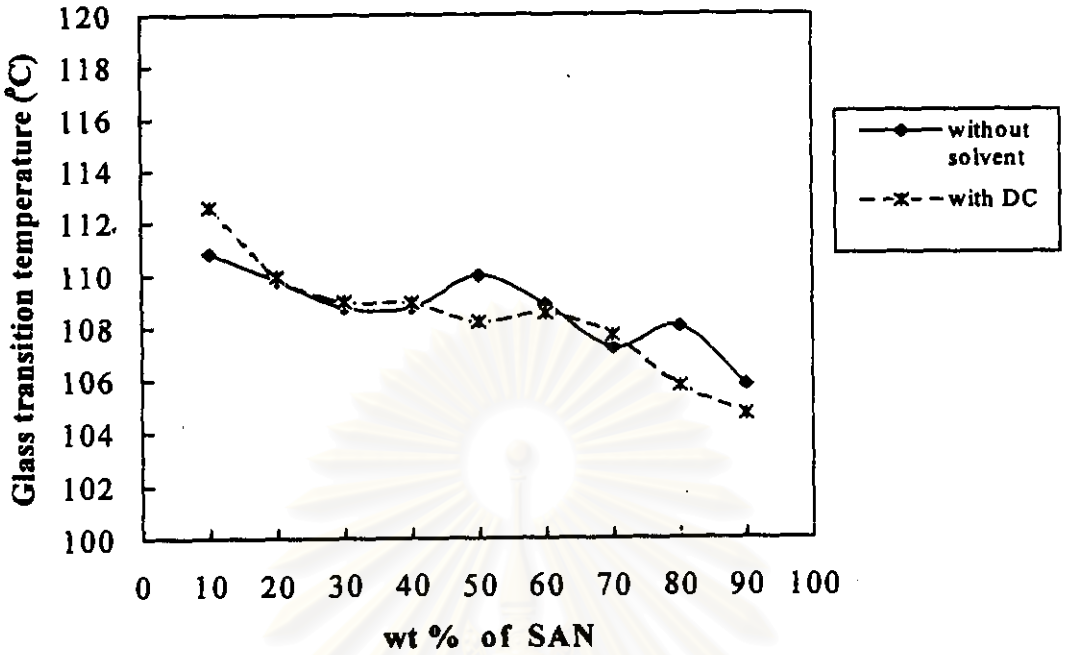

Figure 5.33 The glass transition temperatures of SAN/PMMA blends without solvent and with 1,2-dichloroethane.