

## Effect of Acrylonitrile Content on the Glass Transition Temperature and Melt Index of PVC/SAN Blends

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(Received August 9, 2005; Revised January 27, 2006; Accepted February 23, 2006)

**Abstract:** PVC and SAN are often mixed to compensate for the disadvantages of each polymer. Miscibility and thermal stability of PVC/SAN blend were investigated in this study by blending SAN polymer having 20, 24, 28, 32 % of acrylonitrile contents. Two polymers were mixed using a melt blending method with a single screw extruder. DSC thermogram was used to evaluate miscibility of the two polymers. SAN having 24 % of acrylonitrile showed the best miscibility with PVC. In order to evaluate degradation behavior, blended polymer was heat treated in DSC furnace and glass transition temperature was measured consecutively. Glass transition temperature increased continuously with annealing time due to degradation and cross-linking of polymer chains. Melt index of blended polymer was always higher than that of PVC.

**Keywords:** PVC/SAN blend, Melt blending, DSC, Melt index, Acrylonitrile content

### Introduction

A polyvinylchloride (PVC) and poly(styrene-co-acrylonitrile) (SAN) blend is widely used for commercial applications to improve the physical properties of PVC and SAN. The mixtures of PVC with SAN have considerable technological importance. For example, SAN can be used as an additive to raise the heat distortion temperature of PVC and latex rubbers with grafted SAN shells are used as impact modifiers for PVC [1].

PVC is neither miscible with polystyrene [2] nor with polyacrylonitrile [3]. However, there are many reports concerning the miscibility of PVC and SAN. These studies reported many conflicting results on the miscibility of PVC and SAN. Deanin and Moshar [4] reported that PVC was well mixed with SAN, and Breuer *et al.* [5] also concluded that the SAN of ABS had high compatibility with PVC. Conversely, Pavan [6] and Congdon [7] reported that PVC and SAN were not miscible based on the observation of two glass transition temperatures ( $T_g$ ) of their blends. Due to the conflicting reports regarding the phase behavior of PVC-SAN blend that appeared in the literature, Kim *et al.* [8] prepared blended samples using several methods, including solution cast, melt mixing and precipitation of solution by a non-solvent. They observed different miscibilities according to the blending method, and concluded that PVC was miscible with SAN having acrylonitrile contents from 11.5 to 26 %.

In order to improve the miscibility of PAC and SAN,  $\alpha$ -methyl SAN was used by several researchers [9-12]. Park *et al.* [9] showed that the compatibility of PVC/ $\alpha$ -SAN blend was determined to be better than that of PVC/SAN blend. Rink *et al.* [10] concluded that an  $\alpha$ -methyl styrene/acrylonitrile copolymer containing 32 percent of acrylonitrile was miscible with PVC based on the observation of a single composition dependent  $T_g$ .

It was reported that the  $T_g$  of the PVC phase was raised slower during degradation in the PVC/PS-blend due to a negative influence of the double bonds and the nitrile groups on the thermal stability of PVC [13]. Jin [14] also described the raising of  $T_g$  of PVC due to cross-linking of the polymer chains during the thermal degradation. Since the cross-linking is directly connected to the mechanical properties of PVC, the increase of  $T_g$  can be used to study the influence of a second polymer on the degradation of PVC in heterogeneous polymer blends [13].

The purpose of this study is to investigate the miscibility of PVC and SAN based on a practical extrusion process (melt blending), and to study the effect of acrylonitrile content in SAN on the miscibility of blending. Blending ratios of PVC and SAN were altered, and thermal and rheological properties were investigated.

### Experiments

#### Materials

PVC pellets were supplied by Unofiber Co. Ltd. PVC (LG, LS080) was used as the main material, and organo-tin thermal stabilizer, wax lubricant, and processing aids were added to make compounded pellets.

SAN was supplied from Cheil Industries. Four different grades having 20 %, 24 %, 28 %, 32 % of acrylonitrile contents were chosen to investigate an influence of acrylonitrile content on the miscibility between PVC and SAN polymers. Polymers used in this study were listed in Table 1.

#### Blending

Blends of PVC with various SANs were prepared by using a single screw compounder.

The processing conditions of the compounder were as follows: The extruder temperatures of cylinder 1 and cylinder 2 were 190 °C and 185 °C respectively. A die with one hole of 2.5 mm diameter was used, and the die temperature was

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**Table 1.** Polymers used in this study

Polymer	Commercial name	Maker	Molecular weight	Acrylonitrile content (%)
PVC	LS1000	LG	62,000	--
SAN	HC5920	Cheil Industries	135,000	20
	HF5661	Cheil Industries	140,000	24
	HR5330	Cheil Industries	120,000	28
	CR5381	Cheil Industries	145,000	32

**Table 2.** Denotation of the samples used in this study

	SAN20	SAN24	SAN28	SAN32
PVC20%	P20S20	P20S24	P20S28	P20S32
PVC40%	P40S20	P40S24	P40S28	P40S32
PVC60%	P60S20	P60S24	P60S28	P60S32
PVC80%	P80S20	P80S24	P80S28	P80S32

200 °C. The extruded polymer was cooled down in a water tank and it was cut into pellets using a pelletizer.

The SAN samples composed of 20 %, 24 %, 28 % and 32 % of acrylonitrile were labeled as SAN20, SAN24, SAN28 and SAN 32 respectively. Compounded mixtures of PVC/SAN were labeled as follows; when 20 % of PVC and 80 % of SAN20 were mixed, it was named as P20S20. When the amount of PVC was 20 % and that of SAN was SAN24, SAN 28 and SAN 32, they were named as P20S24, P20S28 and P20S32 respectively. Complete sample names used in this study are summarized in Table 2.

### Differential Scanning Calorimetry (DSC)

Glass transition temperature was determined by using DSC (TA Instruments, DSC 2010). Temperature calibration was carried out with indium reference prior to main tests. About 7 mg of each sample was heated at a heating rate of 10 °C/min up to 200 °C, and then rapidly quenched to room temperature. The sample was reheated with a heating rate of 10 °C/min up to 200 °C and  $T_g$  was measured during the second heating process.

### Determination of $T_g$ Increase

The thermal degradation behavior of PVC and PVC/SAN blend were studied by DSC. The sample was thermally degraded and  $T_g$  was measured in DSC cell by the following method. About 7 mg of sample was heated from room temperature to 200 °C at a heating rate of 10 °C/min and the first  $T_g$  value was determined. The sample was thermally degraded by maintaining it at 200 °C for 20 min, and then it was cooled down to room temperature. Again, temperature was raised to 200 °C at a heating rate of 10 °C/minute and the second  $T_g$  was determined. The sample was thermally degraded again by keeping it at 200 °C for 20 minutes. Those processes were repeated to determine the  $T_g$ s of the third, the fourth and so on.

### Melt Flow Index

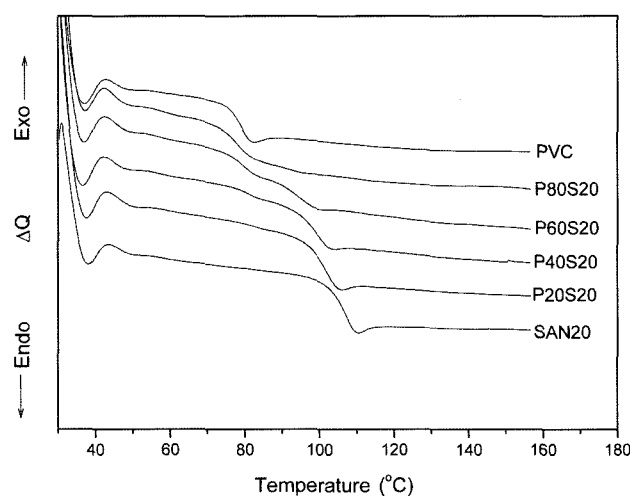
Melt index (MI) was measured by using Kayeness MFI Model 7050. The sample was dried in a vacuum oven at 80 °C for 4 h before MI was measured. The dried sample was placed in the bowl of the melt flow indexer nozzle and was heated at 200 °C for 5 min. Then 5.86 kg of weight was loaded and the mass flow rate during 10 min was measured.

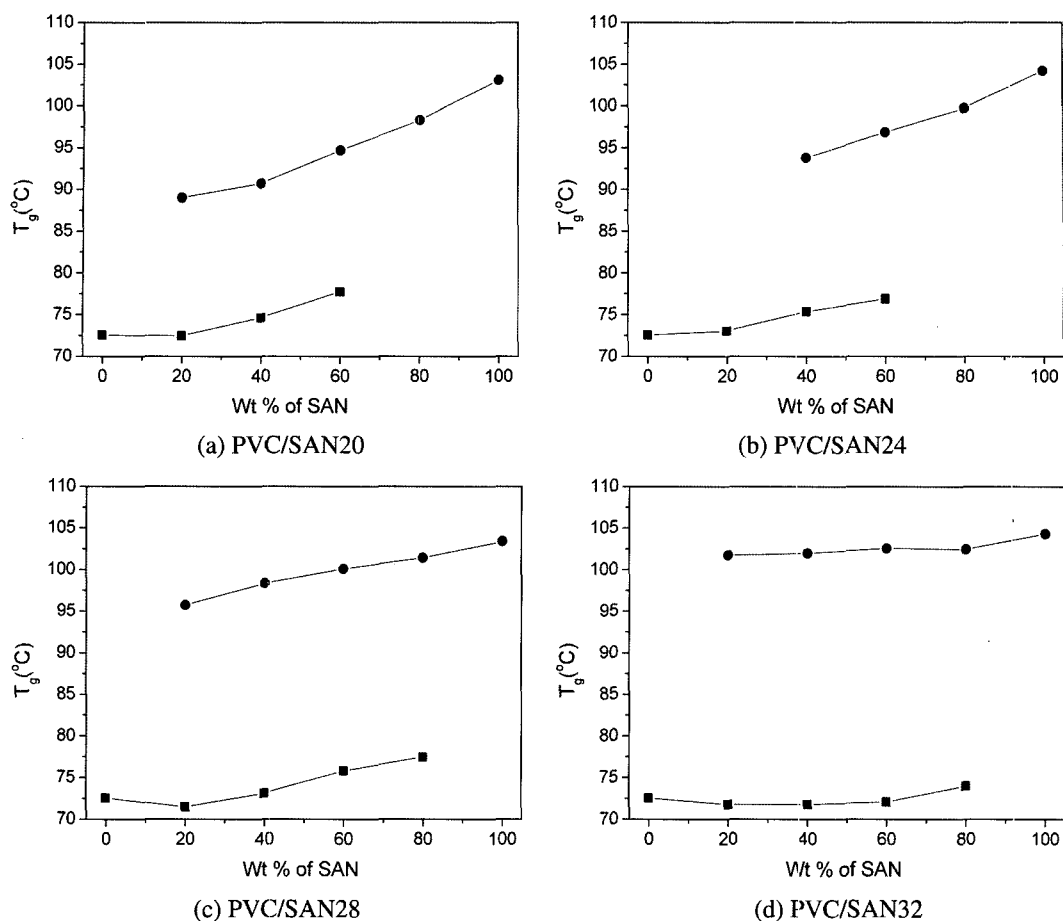
## Results and Discussion

### Miscibility of PVC and SAN

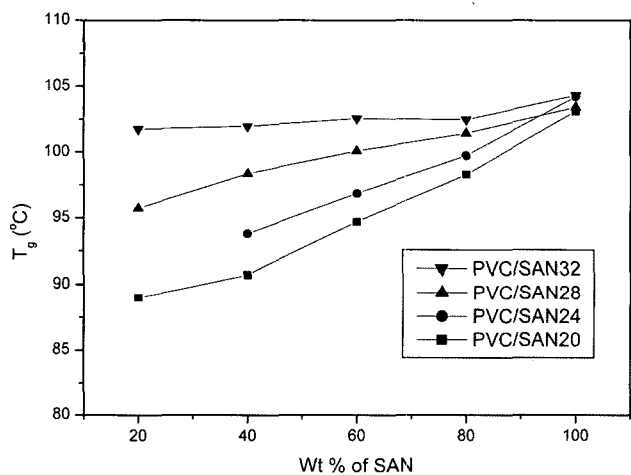
DSC thermograms of the blends containing PVC and SAN20 were shown in Figure 1. PVC showed one  $T_g$  (82.5 °C). When 20 % of SAN20 was mixed with PVC, the mixture presented two  $T_g$ s. As the content of SAN20 increased to 40 % and 60 %, two  $T_g$ s were also identified due to the immiscibility of the two polymers. When the content of SAN20 was increased further, up to 80 %, only one  $T_g$  was identified.

In Figure 2,  $T_g$  was plotted against the blending ratio of SAN having different acrylonitrile contents. It is known that there is only one  $T_g$  when the two polymers are miscible, while there are two peaks when they are immiscible. In the case of SAN20, the blends containing 20 %, 40 % and 60 % of SAN showed two  $T_g$ s, while the blend containing 80 % of SAN showed only one  $T_g$ . One  $T_g$  was observed when SAN24 contents were 20 % and 80 %, which meant they were miscible at those blending ratios. However, two  $T_g$  was shown when SAN24 contents were 40 % and 60 %, which meant they were immiscible at those blending ratios. This suggested that SAN rich phase or PVC rich phase presented excellent miscibility while the PVC/SAN equal phase did failed to exhibit desirable miscibility. In the case of SAN28 and SAN32, all the blends presented two  $T_g$ s regardless of blending ratios. This meant that they were not miscible in all blending ratios.

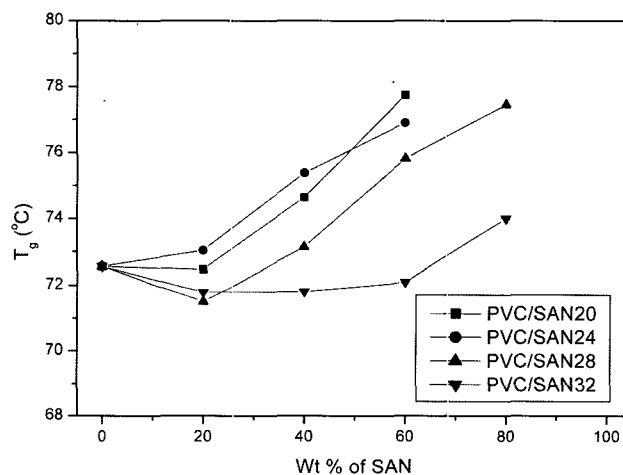
**Figure 1.** DSC thermograms of PVC and SAN20 blends.



**Figure 2.** Glass transition temperature of the PVC/SAN blends having different acrylonitrile contents in SAN.



**Figure 3.** Change of  $T_g$  caused by SAN in PVC/SAN blend.



**Figure 4.** Change of  $T_g$  caused by PVC in PVC/SAN blend.

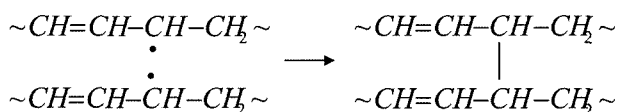
In the DSC curve, there were two  $T_g$ s in the blend of PVC and SAN. One  $T_g$  was caused by PVC, and the other  $T_g$  was caused by SAN. Figure 3 is a plot of  $T_g$  caused by SAN. As the weight percent of PVC increased,  $T_g$  of SAN decreased. An interesting fact was that when acrylonitrile content in the

SAN was higher, the decrease of  $T_g$  was smaller. In case of SAN 32,  $T_g$  was almost unchanged with the blending ratio of PVC. The degree of  $T_g$  change in a mixture might be affected by an interaction between two polymers, and acrylonitrile content in SAN might affect on the interaction.

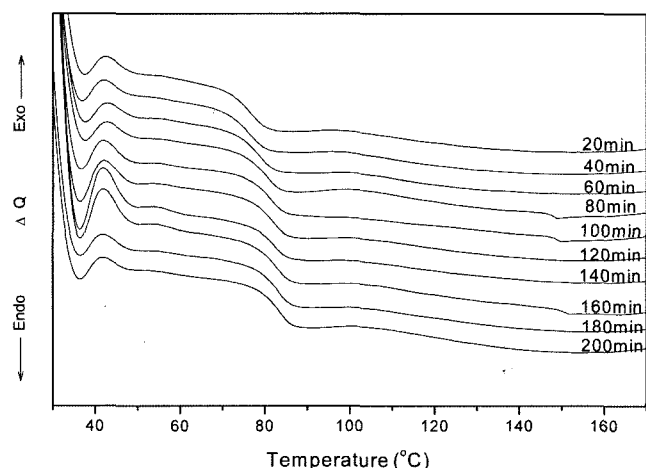
Figure 4 shows a plot of  $T_g$  caused by PVC in PVC/SAN blend. As the weight percent of SAN increased,  $T_g$  of PVC increased. However, increase of  $T_g$  became smaller when acrylonitrile content in the SAN was higher. Combining the result of Figure 3, changes of both  $T_g$  of PVC and  $T_g$  of SAN were smaller when acrylonitrile content in SAN was greater.

**Thermal Degradation Behavior**

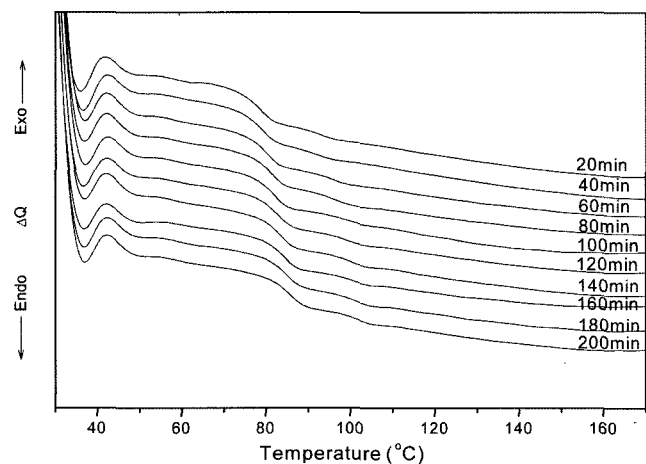
Braun [13] investigated the thermal degradation of PVC in blends with many polymers using DSC. He described the raising of  $T_g$  of PVC due to cross-linking of the polymer chains during thermal degradation. When PVC is thermally



**Figure 5.** Mechanism of cross-linking between dehydrochlorinated PVC chains.



**Figure 6.** DSC curves of PVC during sequential decomposition.



**Figure 7.** DSC curves of P80S20 during sequential decomposition.

degraded, HCl is initially removed from main chain and a double bond is formed as a result. As thermal degradation progresses, cross-linking is formed between the double bonds of two molecular chains. When such cross-linking occurs, glass transition temperature of PVC is increased due to cross-linking (Figure 5).

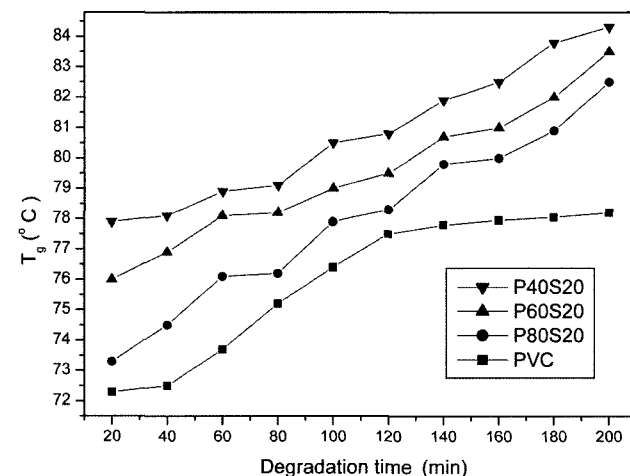
Figure 6 is a DSC thermogram which shows the change in glass transition temperatures of PVC due to thermal degradation in a DSC furnace.  $T_g$  increased continuously as degradation time increased.

Figure 7 is a DSC thermogram which shows the change of  $T_g$  with degradation time in PVC/SAN20 blend containing 80 % of PVC and 20 % of SAN20. Two glass transition temperatures were observed. Lower  $T_g$  came from PVC and higher  $T_g$  came from SAN20. Glass transition temperature caused by PVC could be seen clearly because the amount of PVC was greater. Both  $T_g$  increased with degradation time.

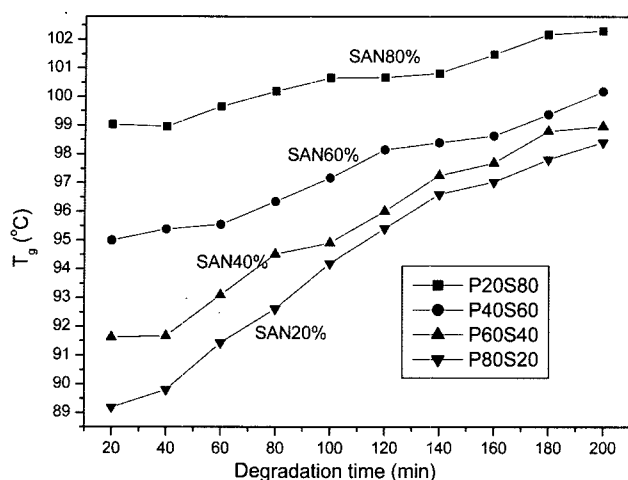
Figure 8 is a plot showing a relationship between degradation time and  $T_g$  of PVC. As degradation time increased,  $T_g$  of PVC increased gradually. Degradation caused cross-linking formation between PVC molecular chains and, as a result,  $T_g$  was increased.

When SAN polymers were mixed with PVC,  $T_g$ s were also increased. The slope of an increasing  $T_g$  was similar in all the cases. That is, even though the blending ratio of SAN20 increased to 20 %, 40 % and 80 %, the increasing ratio of glass transition temperature were similar. It implied that SAN20 mixed with PVC did not affect to the degradation of PVC polymer.

Figure 9 presents the relationship between degradation time and  $T_g$  of SAN20. When the degradation time increased, the  $T_g$  increased in all the SAN20 blending ratios. The slope of an increasing  $T_g$  decreased gradually when the SAN20 blending ratio increased to 20 %, 40 %, 60 % and 80 %. PVC affected to a degradation of SAN, because  $T_g$  of SAN



**Figure 8.** Increase of  $T_g$  of PVC with annealing time in PVC/SAN20 blend.



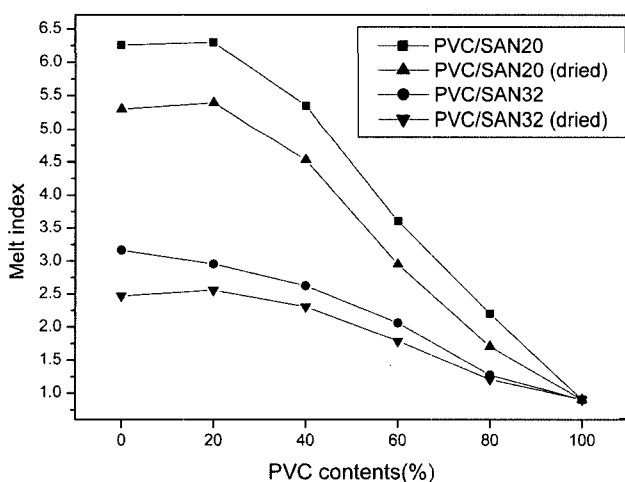
**Figure 9.** Increase of  $T_g$  of SAN with annealing time in PVC/SAN20 blend.

increased in the blend. When blending ratio of PVC decreased, PVC affected less to the degradation of SAN, hence, the slope of an increasing  $T_g$  decreased. From Figures 8 and 9, SAN20 did not affect the degradation of PVC, but PVC accelerated to the degradation of SAN20.

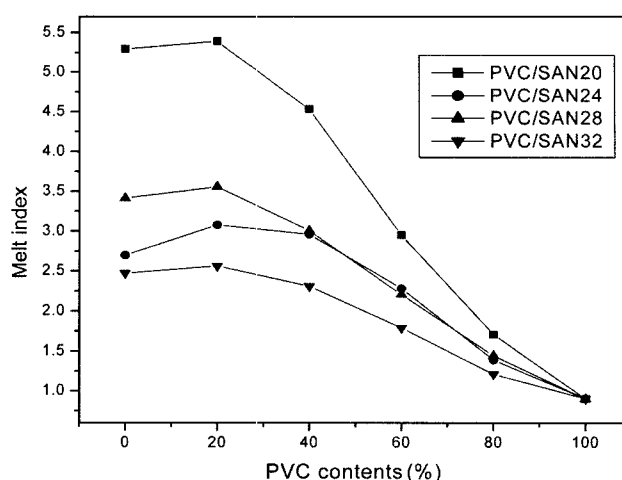
#### Melt Flow Index Behavior

During the extruding or spinning processes, melt viscosity is an important factor to establish process conditions. PVC and SAN have different melt viscosities, so melt flow property of PVC/SAN blend was investigated using a melt flow indexer.

The moisture content of PVC or SAN is almost zero; however, they are sometimes dried to remove the moisture on the surface of the pellet. In order to determine the moisture effect on MI (melt index), MIs of dried sample and undried sample were measured and compared.



**Figure 10.** Comparison of melt index of dried sample and undried sample.



**Figure 11.** Melt index with the PVC blending ratio.

Figure 10 presents the result of MI measurement for PVC/SAN20 and PVC/SAN32 blends before and after the sample was dried. In both blends, MIs of dried samples were lower than that of undried samples. This meant that the moisture on the surface of the undried sample facilitated the degradation of polymer in melt state. As a result, melt viscosity was decreased and MI was increased.

Figure 11 shows MI of melt blend of PVC and SAN. All the samples were dried prior to MI test because moisture might affect the MI value. MI of SAN was higher than that of PVC because SAN was less viscous and easier to flow than PVC. As the content of PVC increased, the MI decreased in all blends.

In Figure 11, MI of 20 % of PVC mixture was slightly higher than that of pure SAN. In fact, SAN had more fluidity, so volumetric flow amount of pure SAN was visually greater than that of 20 % of PVC mixture. However, the mass flow amount of SAN was lower than that of 20 % of PVC mixture because the density of SAN was smaller (1.07) and that of PVC was greater (1.4). Since MI is defined as a weight of output through MFI nozzle during 10 minutes (g/10 min), MI of pure SAN was lower even though the volumetric flow amount was greater due to lower density.

#### Conclusion

The glass transition temperature of PVC/SAN blend increased after increasing the SAN content. Miscibility of SAN24 was better than the SAN containing other acrylonitrile contents. Both the PVC rich phase and SAN rich phase presented excellent miscibility, while the PVC/SAN24 equal phase exhibited poor miscibility. There were continuous increases of  $T_g$  with annealing time at 200 °C. An increase of  $T_g$  was due to the cross-linking of double bond formed by dehydrochlorination in PVC chain. Fluidity(MI) of blend decreased after increasing PVC content in the PVC/SAN blend.

### Acknowledgement

This work was supported by the Research Center of Industrial Technology at CBNU.

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