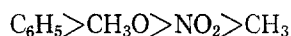


factors in stabilization of the nematic phase<sup>6</sup>. The above order is in fair agreement with those observed for other types of compounds.

### Conclusions

The following conclusions can be drawn from this study:

- (1) The compounds with  $n=2, 3, 7, 9$  and  $10$  of Series I were monotropic, while the others were enantiotropic.
- (2) As the polymethylene spacer becomes longer, the compound tends to form a smectic phase.
- (3) The melting and isotropic transition temperatures of the compounds of Series I decreased with the central spacer length. The decrease showed an odd-even relationship.
- (4) Only the compounds with phenyl, nitro, methoxy and methyl substituent of Series II exhibited mesophases. The monotropic compounds formed only nematic phase. However, the phenyl substituted compound was enantiotropic and formed both smectic A and nematic phases.
- (5) The ability of the substituent to stabilize the mesophase of Series II compounds was in the following order;



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## The Thermal Properties of PVC-Ni Composite Materials

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The glass transition temperature, dynamic shear moduli, and bulk viscosities of PVC, filled with nickel particles, were investigated. The glass temperature of the composite increased with increasing filler concentration. The data were interpreted by assuming that the interaction between filler particles and the polymer matrix reduces molecular mobility and flexibility of the polymer chains in the vicinity of the interfaces. The relative modulus for the PVC/Ni composite system followed the Kerner equation. The relative viscosities were strongly temperature dependent and did not agree with the conventional viscosity predictions for suspensions. It is suggested that the filler has a twofold effect on the viscosity of the composite materials; one is due to its mechanical presence and the other is due to modification of part of the polymer matrix caused by interaction. This phenomenon is approximately bounded by Kerner's predictions for suspensions.

### 1. Introduction

The glass transition temperature,  $T_g$ , of metal-filled polymers, the extent of interaction between polymeric matrix

and metallic filler and its effect on the thermal property of the composite materials were investigated to pursue the mechanism of the composite formation.

Since the thermal property, especially the glass transition

temperature, is very important in the processing and manufacturing polymer materials, a lot of attempts to increase or decrease the glass transition temperature by an addition of some inorganic fillers were made previously.

Some changes in thermodynamic and mechanical properties in filled thermoplastic materials were reported by Ragai<sup>1</sup>, Theocariss<sup>2</sup>, Nielson<sup>3</sup>, Kwei<sup>4</sup> and others. In general, the mechanical properties or the glass transition temperature of the matrix increase as the filler concentration increases.<sup>7</sup>

However, Van der Wal *et al.*<sup>5</sup> observed no changes in the glass transition temperature of sodious chloride-filled polyurethanes and Kumin and Roteman<sup>6</sup> indicated a decreases of  $T_g$  of  $TiO_2$ -filled poly (vinyl-acetate).

The thermal expansion properties of particulate-filled composites have been studied by numerous authors<sup>7-11</sup>, and fairly good experimental results for nylon-silica system were presented by Holliday and Robinson<sup>7</sup>.

Theoretical explanation for thermal expansion coefficients has been given by Levin and Schapery<sup>9</sup>, Thomas<sup>10</sup>, and Turner<sup>11</sup> *et al.*

It was reported by Landel and Smith<sup>12</sup>, Turner<sup>11</sup> and others<sup>13</sup> that the concentration, surface area and surface treatment of the inorganic filler influenced the thermal and mechanical properties of the composites.

It is suggested that the filler has a twofold effect of the viscosity of the composite materials; one is due to modification of part of the polymer matrix caused by interaction, and the other is due to its mechanical presence. This phenomenon is approximately explained by Kerner's<sup>14</sup> predictions for suspensions.

## 2. Experimentals

**Materials.** The matrix polymer used in this experiment was poly (vinylchloride) (PVC: Korea Plastic Co., Ltd. Item No. P-1700) and its average degree of polymerization was 1700. The density of the polymer was 1.38 g/cm<sup>3</sup>. The glass transition temperature ( $T_g$ ) was 79.4°C, and the particle shape was spherical.

The particle size distribution range was from 100  $\mu$ m to 325  $\mu$ m, and 165  $\mu$ m was the average size. The linear thermal expansion coefficient,  $\alpha_p$ , as measured by Thermomechanical Analyser (TMA: Du Pont Instruments, Model No. 943), was  $5.6 \times 10^{-5}$  cm/cm°C.

The filler particle employed in this work was nickel powder (Junsei Chemical Co., Ltd. chemical pure, Lot No. 471221). The nickel powder was regular and spherical in shape and its picture was taken by the Scanning Electron Microscope (SEM: Akashi, JAPAN, ISI, DS-120). The shape of Ni powder was a lump of several small spherecal particles, its surface was constructed with many meniscuses. Nickel powder was sieved with fritsch seive shaker (Fritsch analysets, GERMANY, Type; 03501 No. 4632), and the particle size distribution was ranging from 38  $\mu$ m to 75  $\mu$ m. The Ni powder used in this experiment was not treated in any way.

**Preparation of Composites.** A desired amounts of Ni powder were weighed and mixed with PVC, and Ba-stearate and Cd-stearate were used as stabilizers. The amounts of stabilizers

were 1 part per hundred resin (phr), respectively. The mixture of PVC, Ni powder, Ba-stearate and Cd-stearate was rolled in a two-roll mill (Toyoseiki Seisakusho Ltd. Diameter 8-in., Length 12-in.) at a temperature of 170°C for 15 min.. The rpm (round per minute) of front roll was set at 12 and the rpm of rear roll at 10, respectively. The 0.5 mm thick sheets prepared by rolling were cut in the size of 220mm  $\times$  120 mm, and the cut sheets were pressed in an electric heating press (Toyoseiki Seisakusho Ltd.) at a temperature of 170°C and a pressure of 100Kg/cm<sup>2</sup> for 10 minutes.

The final product was a 220 $\times$ 220 $\times$ 2 mm plate.

**Testing.** The glass transition temperature of PVC-Ni composites was tested on the Differential Thermal Analyzer (DTA: Rigaku, JAPAN Model No. 8078BI). The heating rate of sample in DTA was 5°C/min. from room temperature to 120°C. CaCO<sub>3</sub> powder was used as standard sample.

The thermal expansion coefficient of PVC-Ni systems was detected by using Thermomechanical Analysis (TMA: Du Pont Instruments, Model No. 943) at temperature between -80°C and 110°C. The temperature was dropped to -100°C by using liquid nitrogen. The heating rate was set at 5°C/min to maintain the same condition with DTA. The sample was prepared as, 5 mm diameter and 2.5 mm thickness, and pressed by 10g metal weights.

The rheological properties of PVC-Ni systems were experimented by using Rheometric Dynamic Spectrometer (RDS: Rheometrics Inc., U.S.A., Model No. 7700). The type of sample holder was constructed with torsion-bar shape. The shape of sample was rectangular with the dimension of 12.5 $\times$ 47 $\times$ 2.5 mm.

## 3. Results and Discussion

The glass transition temperature of PVC-Ni composites,  $T_{gc}$ , as a function of metal concentration is shown in Figure 1. The glass transition temperature of pure polymer,  $T_{go}$ , was approximately 78.4°C, and  $T_{gc}$  increased as the filler concentration increased. The increment of  $T_{gc}$  ceased at 20v/o Ni and no change has been observed afterwards. Applying the concept of free volume, it is reasonable to say that the free volume decreases when the polymer is adsorbed on the filler surfaces, and the measured glass temperature should increase with increasing filler concentration. The polymer matrix portion under the influence of the filler surfaces,  $V_A$ , can be expressed by<sup>15</sup>

$$V_A = V_T \phi_f s \delta \quad (1)$$

$V_T$ : Total volume of the composite

$\phi_f$ : The volume fraction of filler

$s$ : The specific surface area of the filler (cm<sup>2</sup>/cm<sup>3</sup>)

$\delta$ : "zone of influence" around each filler particle (cm<sup>3</sup> polymer/cm<sup>2</sup> filler)

When  $V_A = (1 - \phi_f)V_T$ , all of the polymer phase in the composite is exposed to the influence of the filler. Qualitatively, one would expect the glass temperature will increase with  $\phi_f$ , reaching a constant value as the volume fraction of filler approaches to  $1/(1 + s\delta)$ . It was suggested by Dibenedetto<sup>15</sup> that the "zone of influence" is probably a monolayer of polymer molecules. Therefore, the glass transition temperature

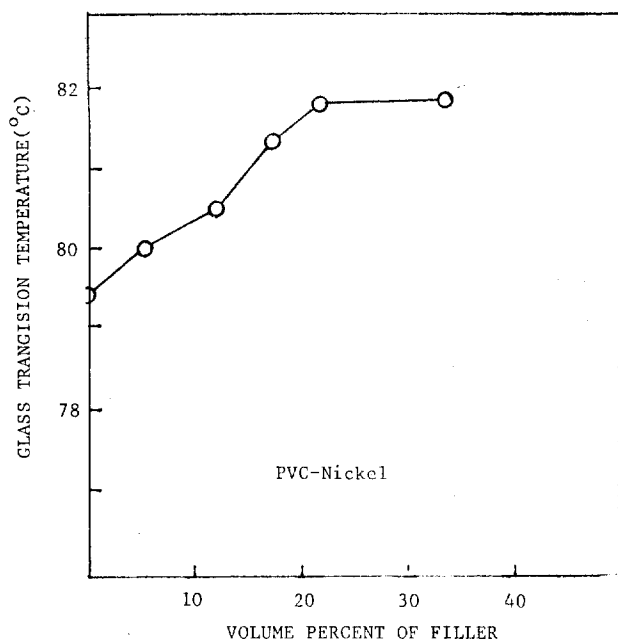


Figure 1. The glass transition temperature of PVC/Ni composites as a function of metal content.

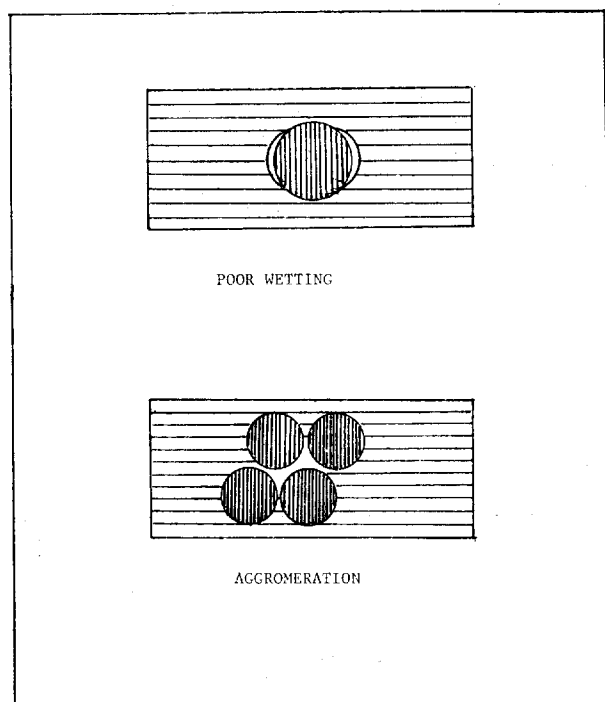


Figure 2. A schematic diagram of poor wetting and agglomeration of particles.

of composites,  $T_{gc}$ , is the sum of those in the influence region and uninfluenced polymer matrix, since the filler has no glass transition,

$$T_{gc} = F(T_{gi}, T_{go}, V_i, V_m, \dots)$$

$V_i$  : Volume fraction of influence region  
 $V_m$  : Volume fraction of uninfluence region

There are some contradictory data concerning the glass transition temperature; Papanicolaou<sup>2</sup> reported drops in  $T_g$  with increasing filler concentration in iron-epoxy composites.

TABLE 1: Summary of the Factors Affecting the Glass Transition Temperature of Composites

residual compressive stress	increase $T_g$
dispersion	increase $T_g$
wettability	increase $T_g$
voids	decrease $T_g$

Van der Wal *et al*<sup>5</sup>, observed no change in  $T_g$  of sodium chloride-filled polyurethanes and Dibenedetto<sup>15</sup> indicated an increase of  $T_g$  of glass beads-phenoxy system. It implies that the glass transition of composites is a complex phenomenon.

The other factor which also influences glass transition in particulate-filled composite is the difference in the thermal expansion coefficient between polymer matrix and filler materials. Most of the composite materials are prepared far above the glass transition temperature. When cooled, each phase will shrink, but the shrinkage of the matrix will be restrained by the particles, thus providing compressive stresses across the interface and residual strain energy near filler surfaces. The compressive stresses thus formed make a good adhesion between polymer matrix and filler surfaces, causing an increase in glass transition temperature around the filler surfaces.

However, the residual strain energy decreases the activation energy of large chain movement of polymer, causing a decrease in glass transition temperature, therefore,  $T_{gc}$  must be accounted by both effects.

If a wettability between matrix and filler surfaces is poor, the reinforced polymers will retain a certain amount of voids at the interfaces. Some voids between the agglomerated filler particles may be present if the filler particles do not disperse evenly in the polymer matrix. These voids have the same effect as the free volume in the polymer matrix, thus decreasing the glass transition temperature of composite systems, as illustrated in Figure 2.

All of the above mentioned factors affecting the glass transition temperature of composite systems are summarized in Table 1.

It may be suggested from this experiment that the adhesion between PVC and Ni particles is fairly good, which is considered as the main cause of increasing  $T_{gc}$  in this composites, and the increment of  $T_{gc}$  goes through a constant value, about 82°C, as was expected by Dibenedetto.

The dispersion of Ni particles in PVC matrix as a function of filler concentration is shown in Figure 3. Ni powder was dispersed very evenly up to 34 v/o of filler concentration. The filler particles were treated at high shear stresses in the processing of two-roll mill blending, because the speeds of the front and rear roll were set at 12 and 10 rpm, respectively. Thus the agglomerates of Ni particles were broken by the shear stresses, and the particles had more effective surface area which crucially influenced the glass transition temperature of composites, as mentioned in equation 1.

The bulk viscosities and storage moduli in PVC/Ni composite systems were illustrated in Figures 4 and Figure 5, respectively, as a function of temperature. The transition region of the two diagrams was shifted slightly to higher

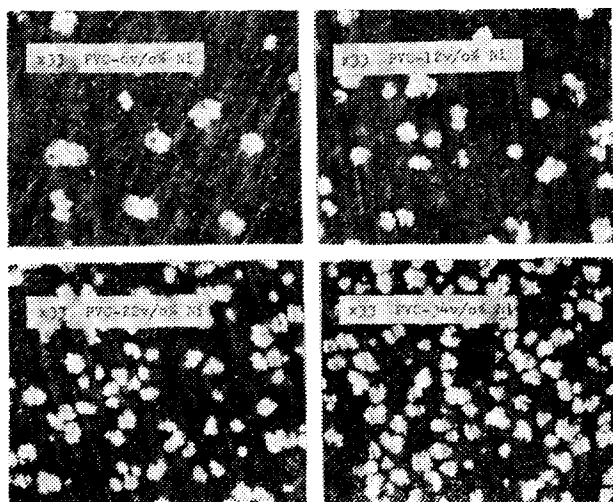


Figure 3. Micro-photographs of the PVC/Ni composites.

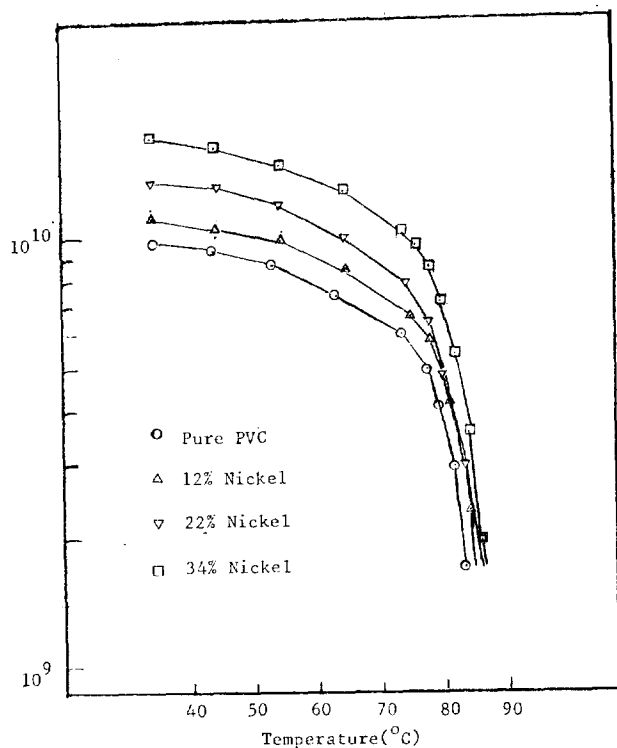


Figure 4. Viscosity of PVC/Ni composites as a function of temperature.

temperature with increasing filler concentration. It is evident that the shift noticed in the dynamic mechanical response in Figure 5 coincided with the same increment of the glass temperature in Figure 1. The shift of the glass transition temperature and the decrease in viscous dissipation per unit volume of polymer lead one to believe that the longer-range chain flexibility and mobility are inhibited by the presence of the filler.

Since modulus means the response of materials for the imposed stresses, the increment of modulus can be interpreted as the evidence of good stress transfer in the interfaces of polymer matrix and rigid metallic fillers. Turner<sup>11</sup>, Kerner<sup>14</sup> and Thomas<sup>10</sup> suggested that the stress transfer is created by

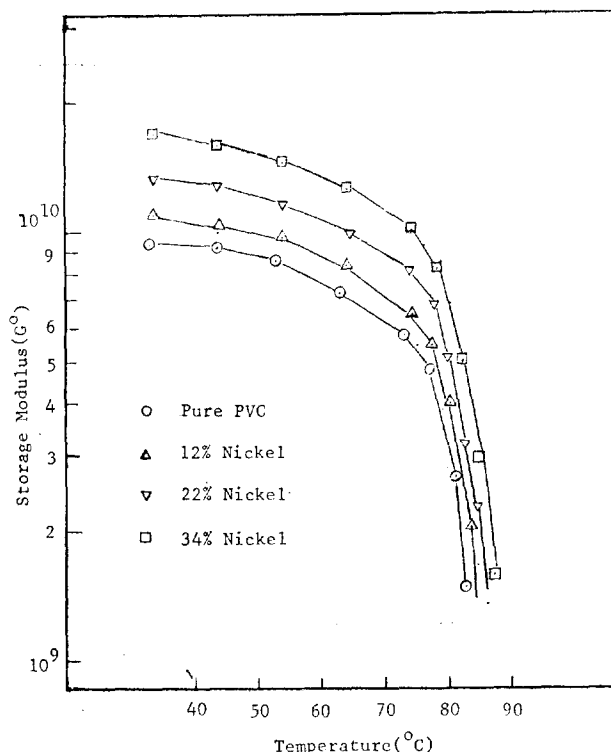


Figure 5. Storage Modulus of PVC/Ni composites as a function of temperature.

the residual compressive stresses around filler particles.

The relative modulus,  $G_c/G_{m0}$  (i.e., the ratio of the modulus of the PVC/Ni composite to the modulus of pure PVC) was depicted in Figure 6. The experimental values are compared with the theoretical predictions developed by Kerner<sup>14</sup> and Hashin<sup>16</sup>. The relative modulus of PVC-Ni systems was well explained by the Kerner equation. It is assumed in Kerner equation that the ratio of shear modulus of rigid filler to that of matrix polymer,  $G_f/G_m$ , is infinitive and Poisson's ratio of matrix polymer is about 0.33. The calculated value of  $G_f/G_m$  for the systems was very large and Poisson's ratio of PVC was 0.38.

Since Kerner assumed a good adhesion between the two phases, one would expect a "good adhesion" between PVC matrix and Ni particle surfaces from Figure 6.

The logarithmic decrement of PVC-Ni composites was illustrated in Figure 7. Logarithmic decrement is defined as the ratio of loss modulus to that of storage modulus. Although the shift of glass transition temperature was very difficult to detect in damping curves, the damping peaks are dropped with increasing filler concentration. So, it is easily understood that the viscous flow of polymer matrix was restricted by the filler presence.

As the case of bulk moduli and viscosities, the mechanical presence of rigid-filler materials and residual thermal stresses in the composite inhibited the flexibility and mobility of polymer chains near the filler surfaces.

The volumetric thermal expansion coefficients of PVC/Ni composite systems,  $\gamma_v$ , were calculated in Table 2, and plotted in Figure 8 as a function of filler concentration. Since the thermal expansion coefficient is a temperature dependence function, the adjustable temperature range of the data in

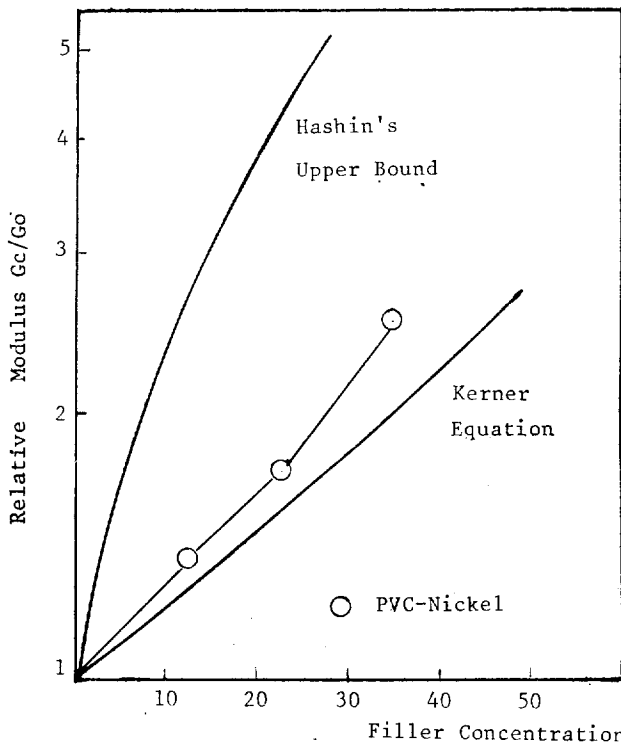


Figure 6. Relative Modulus of the PVC/Ni composites as a function of metal content.

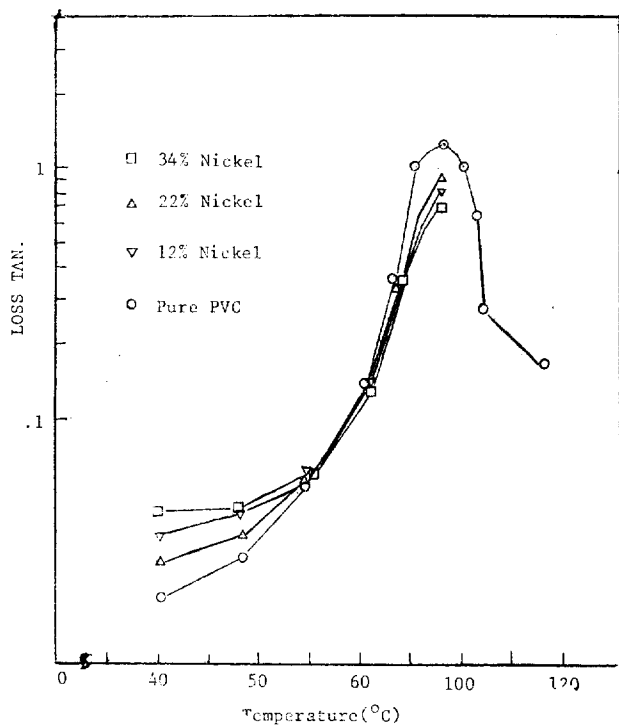


Figure 7. Loss Tangent of PVC/Ni composites as a function of temperature.

Table 2 expanded to 30°C from -80°C. In this range, the volumetric thermal expansion coefficient of pure PVC,  $\gamma_0$ , was detected as 20.16 cm/cm°C, and that of Ni particle as 3.99 cm/cm°C, respectively.

There were certain declines of  $\gamma_c$  as the amount of filler particles increased.

Several approaches have been made to the theoretical study of the thermal expansion of particulated filled polymer

TABLE 2: Volumetric Thermal Expansion Coefficient of PVC/Ni Composite

PURE PVC	$20.16 \times 10^{-5}/^{\circ}\text{C}$
12% NICKEL	$16.56 \times 10^{-5}/^{\circ}\text{C}$
22% NICKEL	$14.04 \times 10^{-5}/^{\circ}\text{C}$
34% NICKEL	$12.6 \times 10^{-5}/^{\circ}\text{C}$

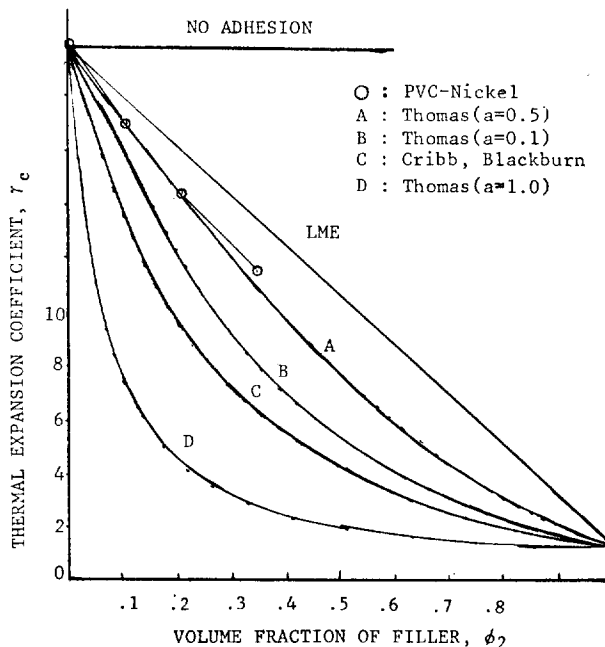


Figure 8. Thermal Expansion Coefficient of PVC/Ni composite as a function of metal content.

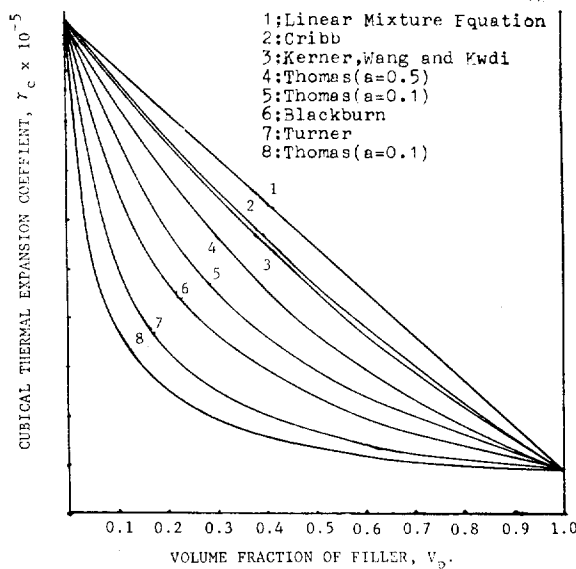


Figure 9. Theoretical graphs of  $\gamma_0$  versus  $V_p$  for a hypothetical composite.

as in Figure 9 for a hypothetical composite, assumed that

$$\begin{aligned} \gamma_m &= 20 \times 10^{-5} \text{ } ^{\circ}\text{C}^{-1} & \gamma_p &= 1 \times 10^{-5} \text{ } ^{\circ}\text{C}^{-1} \\ K_m &= 4 \times 10^4 \text{ bar} & K_p &= 4 \times 10^5 \text{ bar} \\ \nu_m &= 0.33 & \nu_p &= 0.17 \end{aligned}$$

All of the equations in Figure 9 were based on the assumption that there is good stress transfer at the interfaces. If there are

**TABLE 3: Summary of Available Data on Thermal Expansion Behaviour of Polymer-based Composites**

Matrix material	Filler	Slope(LME)	Slope(EXP)	S(EXP) S(LME)
PMMA	Calcium Carbonate	-0.26	-0.61	2.3
Polyester	Calcium Carbonate	-0.32	-0.67	2.1
Epoxy	Calcium Carbonate	-0.28	-0.42	1.5
PMMA	Silica	-0.39	-0.40	1.0
PVC	Nickel	-16.17	-7.85	0.48
PTFE	iron	-0.76	-0.15	0.20

no adhesion between the polymer matrix and filler surfaces, the thermal expansion coefficient of composites shows exactly the same values as pure polymer independent of composition, which is depicted as the line 1 in Figure 9.

Linear Mixture Equation (LME) was applied only, as mentioned in the expansion theories, in a specific case that the two phases had no interaction in expanding like liquids. The thermal expansion coefficients of PVC/Ni composite systems agreed well with the line 4 in Figure 9, and the unknown variable "a" in Thomas's equation is 0.5 in the case of PVC/Ni system.

As mentioned before, LME implies no interaction between the two phases, the deviation from LME is considered as a result of interaction between the filler surface and polymer matrix. This interpretation was suggested by Holliday and Robinson<sup>17</sup>.

The derivation of thermal expansion coefficient in low filler concentration ( $0 < V_f < 0.2$ ) was approximately constant and it was the characteristic slope of the composite. Deviding the slopes of various composites by the slope of the corresponding LME, the interaction between the two phase can be calculated qualitatively, and this ratio varied from -0.64 to +4.6, which was reported by Holliday and Robinson<sup>17</sup> for various composite systems.

In PVC-Ni systems, the slope of LME was -16.17, and the characteristic slope was -7.85, and the ratio, Slope(PVC/Ni)/Slope(LME), was calculated as 0.49, as in Table 3.

\*(The other values in Table 3 were quoted from the reference 7). Contraty to other values in the Table 3, the interaction between Ni particle and PVC matrix is considered to be relatively weak.

#### 4. Conclusion

The glass transition temperature of Ni-filled PVC composites was increased with increasing filler concentration up to 0.2% volume fraction of Ni. No further change of  $T_g$  by the addition of more filler over 20 % Ni was detected, and the results were well agreed with the predictions of Dibenedetto about the glass transition temperature of rigid-particulate filled polymers.

The dispersion of filler particles was an important factor to effect the glass transition temperature and the mechanical properties of the composite materials. Nickel particles were dispersed very evenly in the PVC matrix, providing good properties. Since the thermal expansion coefficient of composite materials plays a crucial role to determine the glass

transition temperature of amorphous materials, many workers have studied on  $\gamma$ , and yet no adequate equation has been obtained.

The volumetric thermal expansion coefficient of PVC/Ni composites was concurred accurately with the predictions of Thomas.

The variable factor "a" in the Thomas's equation was determined to be 0.5 for PVC/Ni system.

The relative modulus,  $G_c/G_{mo}$ , of PVC-Ni composites was agreed approximately with the equation of Kerner for the suspensions.

The slight deviation from the equation was considered as the difference in Poisson's ratio of the matrix in Kerner's prediction and that of PVC in this sysyem.

All of the above mentioned factors were closely related with the adhesion between filler surface and PVC matrix. The Thomas's equation and Kerner's prediction assumed good stress transfer between the two phases, and the stress transfer was withstood by the adhesion between the polymer matrix and rigid-filler surface. The adhesion of the interface was checked indirectly by the glass transition temperature, the thermal expansion coefficient, and the relative modulus of PVC-Ni composite systems. It was revealed from those experiments that the adhesion between PVC-Ni surface was fairly good and the adhesion was caused by the residual compressive stress around the Ni surface, which was induced by the difference in thermal expansions of the rigid filler and the polymer matrix.

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