Physical Properties and Adhesion of the Polymer/Metal Composites

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Abstracts: The effects of the shape and the surface state of the metallic particles on the electrical, mechanical and thermal properties of metal filled polymeric composites and on the adhesion between metallic filler and polymeric matrix were studied. It was found that there was a marked change of the properties of the composites at a critical volume percent of the metallic particles. The ordinary spherical nickel particles, having bumpy and equiaxed granuled type of surface, showed a strong adhesion to the PVC matrix and increased the mechanical strength of the composites up to a maximum value at a critical volume percent of metallic particles. However, the irregular plate-like copper particles, having even and flat type of surface, showed no adhesion to the polymeric matrix and decreased the mechanical strength and flexibility of the composites remarkably. In the electrical properties, the nickel particles formed an aggregated continuous conductive metallic network structure in the polymeric matrix at about 5 V/O of metal loading and gave a drastic fall in electrical resistivity, but the copper particles formed a conductive network structure at below 2 V/O of metal loading, even if the same metallic particles size of 7μm was used. The linear thermal expansion coefficients of the composites agreed relatively well with the values predicted by Turner, who suggested a concept of the segregated metallic network formation in metal filled polymeric composite. The metallic particles in the polymeric composite system gave a shift of the glass transition temperature of polymer matrix to a higher temperature in proportion to the surface area of the metallic filler. The SEM study of the fracture surface of the composites manifested the adhesion between the metallic filler and the polymeric matrix.

1. INTRODUCTION

When metallic particles are dispersed into polymeric matrix, the properties of the metal filled polymeric composite are influenced by the size, shape, volume fraction and nature of the metallic particles, in general.

Landon et. al[1]. suggested the importance of the adhesion between filler and matrix phase on the mechanical properties of the compos-

ites. Similar observations were made by Brassell and Wischmann[2].

Nielsen[3,8] and others[4,5] put emphasis on the volume fraction of the particle filler and the mode of packing to explain the experimental results of the mechanical properties of the particle filled polymeric composites.

A concept of segregated network formation in metal filled polymeric composite systems was introduced by Turner and coworkers[6,7],

and the effect of segregated distribution of nickel particles on the electrical properties of Poly(vinyl chloride) was observed.

The influence of the particle size ratio of poymer/filler on the continuity of aggregates, or the network structure formation, could be explained by a model suggested by Kusy[9].

Since it was recognized that the continuity of the aggregates could be formed by the particles of the dispersed phase that cover the small portion of the primary matrix surface, Kusy set up an equation that involved a critical volume fraction of the filler, Vc, for the continuity. Kusy's[9] and Turner's[6,7,13] model for metal filled polymeric composites are usually applied to the explanation of the electrical resistivity of these composites in terms of the filler concentration. Many reporters[12,14,24] verified that these models generally well agreed with the PVC/metal composite system manufactured by solid-solid compacting. On the other hand, Nielsen[23] suggested another model for conductive filler dispersed polymeric composites; it does not agree with the solid-solid compacted composite system, but agreed relatively well with the conductive filler dispersed polymeric composites prepared by filler particles dispersed in polymeric melts

Thermal characteristics of the PVC/metal composites were studied by previous workers [8,10~12,17,19,23] and the effect of filler on the change of the thermal characteristics, which are glass transition temperature, Tg, thermal expansion and thermal conductivity, etc., were shown to be dependent on the volume fraction of filler.

Thus, the mechanical, electrical and thermal properties of the filled polymeric composites were measured and studied. However, no systematic explanation on the strength of the interfacial adhesion between the metallic filler

and polymeric matrix phase has been provided, since no direct method to determine the strength of mechanical or chemical adhesion between these two phases is known as yet.

In this study the interfacial adhesion between the metallic filler Ni or Cu and the polymeric matrix PVC as a function of metal concentration was studied indirectly by the measurements of mechanical, thermal properties and the SEM (Scanning Electron Microscopy) study. The effects of filler contents, size and shape on the mechanical, electrical, thermal properties and the mobility of the polymer chains were measured.

2. EXPERIMENTALS

2-1. Materials

The matrix polymer used in this experiment was Poly (vinyl chloride) (PVC; Korea Plastic Co., Ltd. P-1700) and its average degree of polymerization was 1700. The density of the polymer was 1.38g/cm³ at 25°C. The glass transition temperature (Tg), as determined by a quartz tube dilatometer, was 78°C, and the particle shape, as determined by an Inverted Metallurgical Microscope (Olympus, Japan, Model; PME), was spherical type. The particle size distribution range, as measured by X-ray image analyzer (Nireco, Japan), was from 100 μm to 325μm, and 165μm was the average size. The linear thermal expanison coefficient, αp, as measured by a quartz tube dilatometer, was 8.333$\times$10^{-5}cm/cm°C at the temperature below glass transition temperature, and the electrical specific resistivity, as measured by Keithley 610c solid-state electrometer, was 9.25$\times$10^{13} Ω-cm at 14°C.

The filler particles employed, in this work were nickel (Kanto Chemical Co., Japan) and copper (Junsei Chemical Co., Japan) powders. The nickel powder was regular and spherical

shape when it was measured by the inverted metallurgical microscope. Its surface was not even and it was equiaxed granuled type. The nickel powder had a particle size ditribution ranging from $1\mu m$ to $31\mu m$, and its mean particle size was $7\mu m$. The particle size was also measured by X-ray image analyzer. The density of nickel powder was $8.90g/cm^3$ at $25°C$.

The copper powder was irregular and plate shape and its surface was smooth and flat. The particle size was distributed from $2.7\mu m$ to $21\mu m$ and the mean particle size was $7\mu m$. The particle size was determined by Sedigraph (Micrometritics, U.S.A. model; 5000D). The density of copper powder was $8.94g/cm^3$ at $25°C$.

All the powders used in this experiment were not treated in any way.

2-1. Preparation of Composites

A desired amount of each powder was mixed by tumbling using V-type mixer giving a homogeneous mixture after 48 hrs. The homogenity of the mixture was checked under a microscope.

The mixture and steel moulds(or die) were preheated at $140°C$ for 30 minutes, and the mixture was compacted in various type of steel moulds at $450kg/cm^2$ and a temperature of $140°C$ for 10 minutes. Then the mixture was cooled in mould to $60°C$, and ejected out from the mould for cooling to room temperature. In the last procedure, the specimen was annealed for 3 hours at $50°C$ in an air oven. After the annealing, the precipitation of metallic particles was checked by Rockwell hardness test (R Scale).

2-2. Measurements

2-2-1. Electrical Resistivity

Samples were prepared by using a cylindrical steel die of diameter 12mm. The thickness of the specimen was controlled to be 2-3mm

with an accuracy of 0.01mm. Silver paste was coated onto the surface of specimen. The contact resistivities with electrodes and samples were reduced as well as the space charges[6,16].

Measurements of high resistivity were made using a Keithley 610c solid-state electrometer. Mearsurements of low resistivity were made using an universal bridge (Meguro electronics, Japan, Model; MZ827). During measurements at room temperature, electrodes were shielded from the external electrical fields and other conditions were kept constant as much as possible.

2-2-2. Mechanical Properties

Tensile tests: Dumbbell shaped samples for tensile tests were prepared according to ASTM D638-77a (type-I). Tensile tests on dumbbell shaped specimens were carried out using an Instron Universal Testing machine (Model; 11 23, 2.5ton capcity). The cross-head speed used on a nominal cross-sectioned area of $13mm \times 3mm$ was 5mm/min., and the chart speed was 50mm/min.. Fracture surfaces of the specimens were examined with an electron scanning electron microscope (Zeol, Japan).

Flexural tests: Bar shaped samples for flexural tests were cut from the molded sheet into $25 \times 3.2 \times 80mm^3$ test bars, and tested in 3-point flexural loading using an Instron Universal Testing Machine(Model 1123, 2.5ton capacity) according to ASTM D790-71(Method I, procedure A). The cross head speed was 1.3mm/min., and the chart speed was 50mm/min.

2-2-3. Other Properties

The dilatation tests were carried out using a quartz tube dilatometer between room temperature ($14°C$) and $70°C$, and the heating rates were approximately $2°C/min$. The dimension of specimen was $5 \times 5 \times 55mm$ according to ASTM D696-79.

The dynamic mechanical properties and glass transition temperature of the composite materials were determined by RMS tester(Rheometric Inc., U.S.A., Model; RMS-605). Measuring conditions were as follow;

Heating rate=3°C/min.

Frequency=1 Herz.

In dynamic mechanical tests, G', tan δ, and Tg were obtained.

3. RESULTS AND DISCUSSION

The change of log (electrical specific resistivity) of the PVC/Ni and PVC/Cu composites as a function of metal concentration was shown in Fig.1. At low concentration of the nic-
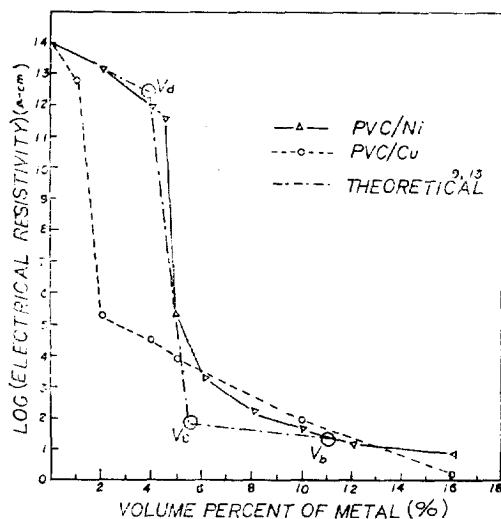
kel particles, the electrical specific resistibity of the PVC/Ni composite was essencially that of the insulating polymer ($10^{13}-10^{14} \Omega$-cm). A drastic fall of the electrical specific resistivity in the neighborhood of 5 volume percent of nickel particles loading was found due to the formation of a segregated network structure (a continuous network). Thereafter, at high concentraton of the nickel particles, the change in the electrical specific resistivity was relatively small.

The experimental values for Va, Vb and Vc of the PVC/Ni composited were found to agree fairly well with the theoretical values calculated by Kusy and Turner, as shown in Table 1. Va, and Vb are the volume percent of metallic filler particles for formation of the metallic monolayer and the double layer, respectively.

However, as shown in Fig.1, the rapid fall of the electical specific resistivity of the PVC /Cu composites was found at 2 volume percent of the metal loading, even if the same metallic particle size of 7μm was used. It is believed to be due to the shape of the copper particles. The copper particles, irregular and plate-like,

Fig. 1. Log(electrical specific resistivity) of PVC/ Ni and PVC/Cu composites as a function of metal content.

Table 1. The Values of ϕ and Pc for Various Planar Lattice.

	C.N.*=6	C.N.=4	C.N.=3
ϕ	1.110	1.27	1.375
Pc	1/3	1/2	2/3

*C.N. ; Coordination number.

(a) 2 v/o of Ni (×100)　　(b) 5 v/o of Ni (×100)　　(c) 16 v/o of Ni (×100)
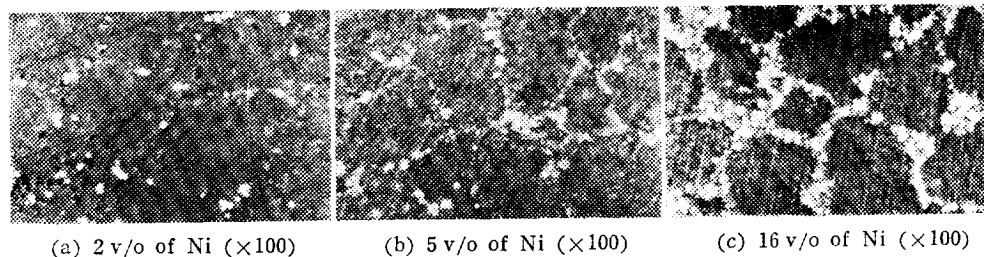
Fig. 2. Micro-photographs of the PVC/Ni composites.

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(a) 2 v/o of Cu (×100)   (b) 5 v/o of Cu (×100)   (c) 16 v/o of Cu (×100)

Fig. 3. Micro-photographs of the PVC/Cu composites.

have a large surface area than the spherical neckel particles and form a conductive path or conitinuous network easily.

The procedures of the conductive or continuous network formation were manifested by the photo-micrographs of Fig.2 and Fig.3. Fig. 2(a)-(c) showed that of the spherical nickel particles in the PVC matrix and Fig.3 (a)-(c) also showed that of the irregular and plate-like copper particles in the PVC matrix. In Fig.2 and 3, the dark region was a PVC matrix and the white region was the metallic filler particles. As shown in Fig.2, the complete continuous network was formed in the neighborhood of 5 volume percent of the nickel particles in the PVC/Ni composite, thereafter a thickening of the conductive network was found with increasing the concentration of nickel particles. However, the conductive network was already formed below 2 volume percent of the copper particles loading, as shown in Fig. 3. The formation of a continuous metallic network was very much dependent on the shape of the metallic filler particles as seen from the photographs of Fig.2 and 3. Thus, the effect of the shape of the metallic filler particles on the electrical resistivity of the metal filled polymeric composite was found to be very important as much as the effect of the size of the metallic filler particles.

A strengthening effect of the PVC matrix due to the introduction of the nickel particles
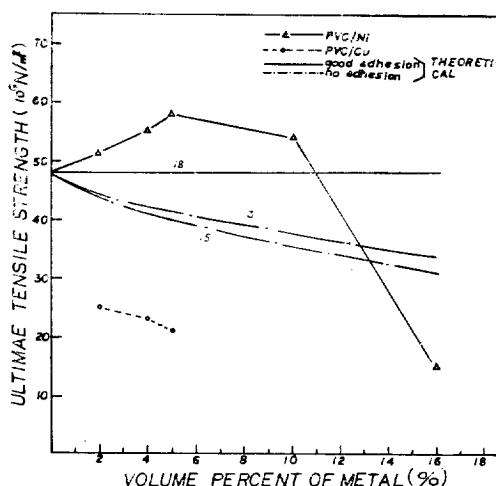
Fig. 4. Ultimate tensile strength of the PVC/N and PVC/Cu composites.

was evident from the fact that the values of the tensile and flexural strength increased with increasing the nickel particles concentration and up to a maximum at a particular volume percent of nickel particles loading as shown in Fig.4 and 6. This particular volume percent of the nickel particles loading occurred at almost the same value as where the sudden fall in the electrical specific resistivity was observed. The maxima in the tensile and flexural strengths and the drastic fall in the electrical specific resistivity at a particular nickel particles loading were believed to be due to the formation of continuous network of the metallic filler particles in the PVC matrix. Beyond the particular volume percent of nickel

particles, the tensile and flexural strengths of the PVC/Ni composites decreased with increasing the nickel particles loading. However, the tensile and flexural strengths of the PVC /Cu composite always decreased with increasing the copper particles loading, because the formation of the continuous copper particles network was already observed below 2 volume percent of the copper particles.
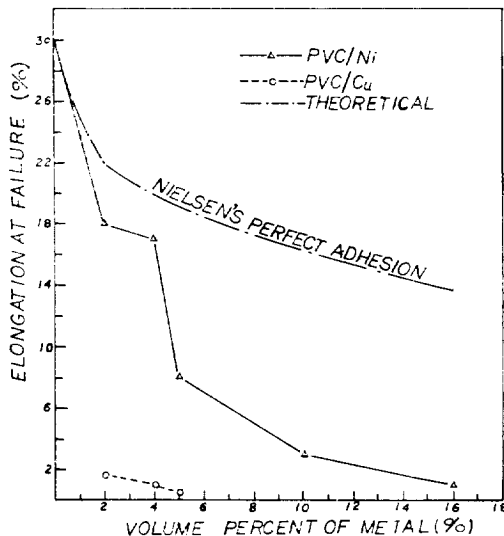
The differences in the tensile and flexural

strengthes between the PVC/Ni and the PVC/ Cu composites were due to the difference in the adhesion between the metallic filler particles and the polymeric matrix phases. Fig.7 represents the scanning electron photo-micrographs at the fracture surface of the two composite systems. The fracture surface of the PVC/Ni composite, as shown in Fig.7 (a), proved that the nickel particles tend to lie away from the fracture surface and to retain some adherent poly(vinyl cholide) matrix, while the fracture surface of the PVC/Cu composite, as
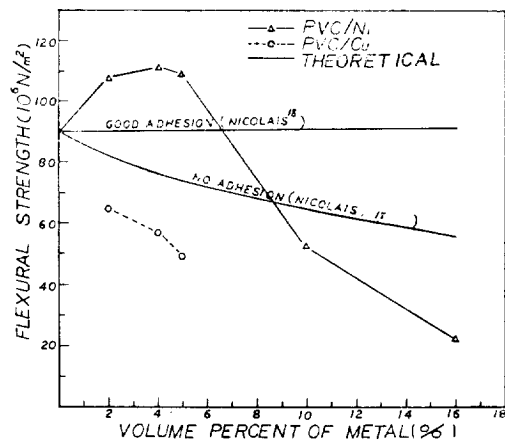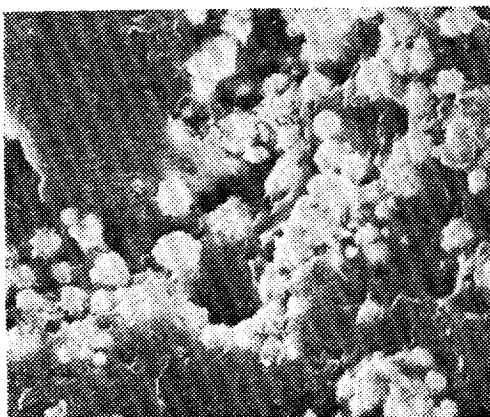

Fig. 5. Percent elongation at failure of the PVC/ Ni and PVC/Cu composites.

Fig. 6. Flexural strength of the PVC/Ni and PVC /Cu composites.

(a) 10 v/o of Ni (×1,500)   (b) 4 v/o of Cu (×1,000)

Fig. 7. Scanning electron micrographs of the PVC/Ni and PVC/Cu composites.

shown in Fig.7 (b), proved that the copper particles tend to pull out clearly from the poly (vinyl chloride) matrix. Hence there was an adhesion between the nickel particles and the PVC matrix phase in the PVC/Ni composite, but in the PVC/Cu composite, there was no adhesion between the copper particles and the PVC matrix phase. In the case of the PVC/Ni composite, the surface state of nickel particle was bumpy and equiaxed granuled state, therefore this state caused an adhesion between filler and matrix phases by sliding the polymeric matrix phase into the crevice of the nickel particles during compacting for the sample preparation. However, in the case of the PVC/Cu composites, the surface state of copper particle was smooth and even, so there was no motive of a mechanical adhesion between the filler and the matrix. The adhesion between the metallic filler particles and the PVC matrix was dependent on the surface state of metallic particles.

The elongation at failure was plotted against the concentration of metallic filler particles in Fig.5. The percent elongation at failure fall drastically, even though a small percents of metallic filler particles were introduced into the polymeric matrix. The degree of elongation drop of the PVC/Cu composite was larger than that of the PVC/Ni composite, therefore one could say that the Cu particles made a composite of a more brittle material than the Ni particles.

Comparing the experimental values of the tensile strength and percent elongation at failure of the composites with the calculated values from the theoretical equations,[3,4,15] a great discrepancy could be found. Nielsen[3], Nicolais[15] and Kerner[4] explained the composite that the rigid filler particles were dispersed randomly in the polymeric matrix. But in this experi-

ments, the rigid metallic filler particles were in the polymeric matrix phase with forming a segregated continuous network.

In the case of good adhesion between filler particles and the polymeric matrix, some workers[3,4,15] predicted that the filler particles act as a reinforcing material in all the volume percent of metal loading. However, the curves of the PVC/Ni composite having good adhesion between filler and matrix showed that the metallic filler particles contribute to the weakening of the metal filled composite beyond the critical volume percent of the nickel particles (or after the formation of continuous network), and it was believed due to the fact that the fracture path tended to pass through the continuous metallic network.

The experimental results of the linear thermal expansion coefficient of the metal filled polymeric composite in the glassy region(below glass transition temperature; Tg) was shown
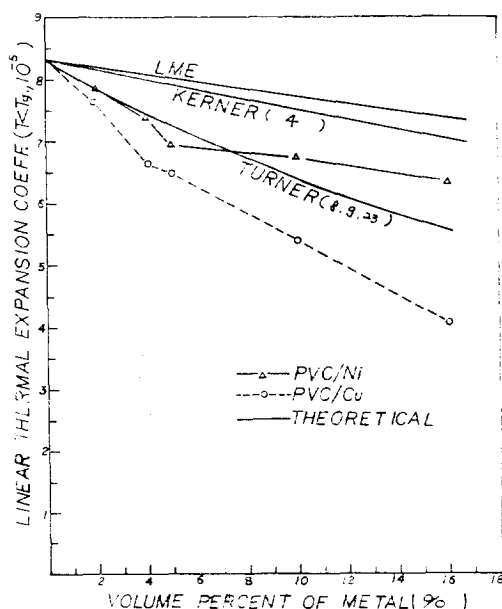

Fig. 8. Linear thermal expansion coeff. of the PVC /Ni and PVC/Cu composites.

in Fig. 8 and the respective values predicted by various theories were also plotted for comparison.

Examination of Fig. 8 revealed that the linear thermal expansion coefficients of the metal filled polymeric composited fell below the straight line of the rule of mixture (LME). The experimental results of the PVC/Ni composite agreed relatively well with the predicted values by Turner.[8,9,19] Turner derived an equation* based on the assumption of substantial residual microstresses resulting from the restriction of each phase on cooling for sample preparation, But, the thermal expansion coefficients of the PVC/Cu composite fell well below the curve of Turner's equation. The diffierent behavior of the two composites in thermal expansion should be explained by the adhesion between metallic filler and polymeric matrix phase, as shown in Fig. 7(a) and (b), and the microstructure of the two composites.

With the copper paritcles, there was poor n between the metallic particles surface and the polymeric matrix due to the surface state and the shape of the metallic filler particles.

In the case of nickel particles, individual nickel particles were surrounded by the polymeric matrix with good adhesion due to the surface state and the shape of the nickel particles.

$$*\alpha c = \frac{\alpha p \ Vp \ Kp + \alpha m \ Vm \ Km}{Vp \ Kp + Vm \ Km} \quad \text{if } \nu m \neq \nu p$$

Where V, α, and K are volume fraction, thermal expansion coeff. and bulk modulus of the materials, respectively. Subdescription of p, m, and c represent polymer, metal and composite, respectively.

In the PVC/Cu composite, as the matrix phase of the poly(vinyl chloride) expanded faster than the copper particles, it tended to occupy

existing voids of the copper particles, having larger surface area than the Ni particles seemed to restrain the expansion of polymeric phase more, so that the thermal expansion coefficient of the composite was much lower than that of the PVC/Ni composite. According to the experimental results of Papinicolaou, Paipetis, and Theocaris[20], the same phenomena were observed in the thermal expansion properties above glass transition temperature($T >$ Tg) of the epoxy/aluminium composite system.

The glass transition temperature, Tg, obtained in this experiment was plotted as a function of metallic filler concentration in Fig. 9. The results of Fig.9 showed an increase in the glass transition temperature with increasing the concentration of each filler particles. The increment in the glass transition temperature are attributed to the change in the segmental mobility of the metal filled polymeric composite, due to the restriction of the motion of the polymer chain. The restriction was due to the adsorption of the polymer onto the filler surface. The adsorbed polymer would then restricted the motion of polymer adjacent to it.

The values of glass transition temperature observed with the PVC/Ni and PVC/Cu composites were significantly different. In spite of
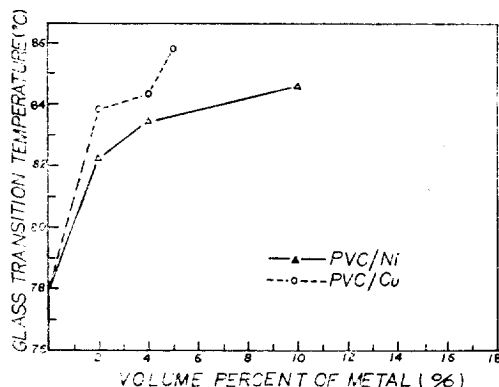

Fig. 9. The glass transition temperature of the PVC/Ni and PVC/Cu composites.

the poor adhesion between filler and matrix, the PVC/Cu composite showed higher glass transition temperature than that of the PVC/ Ni composite with increasing the metallic filler concentration.

To explain this unexpected result, one should consider the surface area of the metallic filler particles in the polymeric composites. The plate-like copper particles in the PVC/Cu composite had a larger surface area than the spherical nickel particles in the PVC/Ni composite. Therefore, the plate-like copper particles were more effective to the restriction of the segmental motion of polymer chain in the metal filled polymeric composite. As a result of the experimental values of glass transition temperature, one could note that the effect of the surface area of the filler particles was more important factor to increase the glass transition temperature than that of the adhesion between filler and polymeric matrix.

The effects of metallic fillers on the dynamic mechanical properties of metal filled polymeric composites were illustrated in Fig.10, and 11. The filler gave a larger effect, as shown in Fig.10(a) and (b), in raising the elastic shear modulus of the composite at above glass transition temperature than at below the glass transition temperature. The main reason was the smaller elastic shear modulus of the polymeric matrix phase of the metal filled polymeric composite, when the polymeric phase was in the rubbery state (above glass transition temperature) compare to the rigid glassy state (below glass transition temperature). Therefore, the elastic shear modulus of the metallic filler proved to be more significant factor to determine the elastic shear modulus of the metal filled polymeric composite at above glass transition temperature.

Less important factors contributing to this
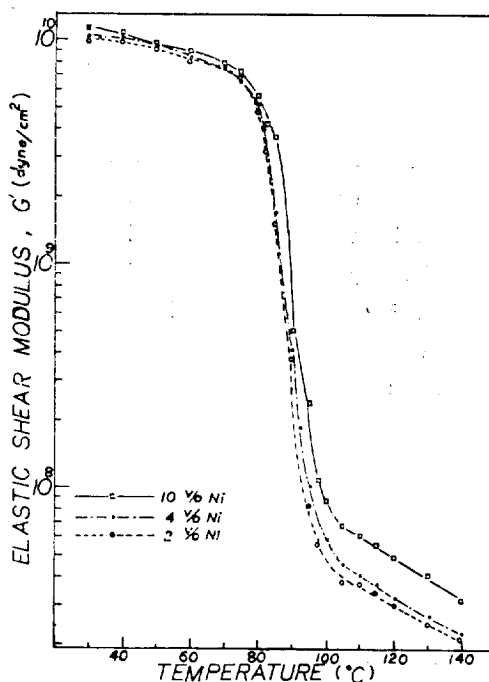
(a) PVC/Ni composites
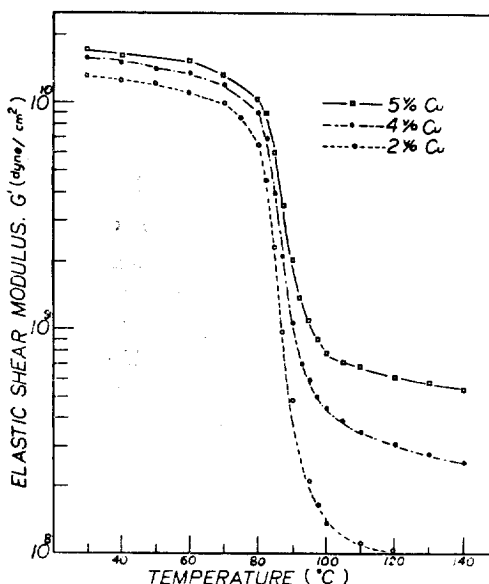
(b) PVC/Cu composites

Fig. 10. Elastic shear modulus of the PVC/Ni and PVC/Cu composites

effect was the presence of induced thermal stresses which were caused by the negative mismatch in the coefficient of the thermal expansion($\alpha p > \alpha m$) below glass transition temperature.

However, the effects of nickel particles on raising the elastic shear modulus of the composite were smaller than the effects of copper particles. These were believed to be due to the surface area of the metallic filler particles. The plate-like copper particles had a larger surface area than the spherical nickel particles. Previous workers[21] showed an increase in modulus as the surface area of the filler particles increased.

In Fig. 11(a) and (b), the damping, $tan\delta = G''/G'$, was plotted against the temperature change for the PVC/Ni and PVC/Cu composites, where, G' and G'' refer to the elastic shear modulus and the loss modulus, respectively.
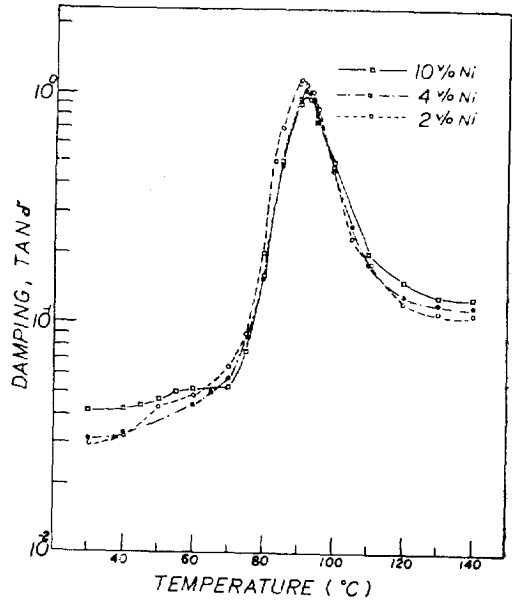
The damping of PVC/Cu composite decreased, as shown in Fig.11(b), with increasing the concentration of copper particles through out the temperature range examined.

In the case of no adhesion between filler and matrix, Gray, McCrum[22] and Nielsen[25] explained the damping by,

$$(tan\delta)c = (G''/G')c \cong (G''/G')pVp + (G''/G')mVm$$

where subscript c,p and m referred to composite, polymer matrix and metallic filler, and V represented the volume fraction, respectively.

The damping of the most rigid fillers in the case of no adhesion between filler and matrix was very low compared to that of the polymer, so $(G''/G')m$ was merely zero and could be neglected. Therefore, the damping of rigid filler filled polymeric composite could be expressed as follow,

(a) PVC/Ni composites
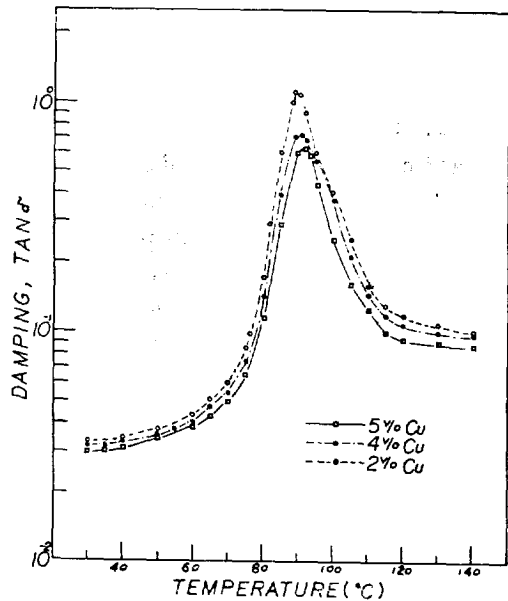
(b) PVC/Cu composites

Fig. 11. Damping of the PVC/Ni and PVC/Cu composites.

$$(tan\delta)c = (G''/G')c \cong (G''/G')pVp = (G''/G')p(1-Vm)$$

Hence, the damping of the composite decre-

ased with increasing the rigid filler concentration.

However, the damping of the PVC/Ni composite as shown in Fig.11(a) increased with increasing the metal concentration: Friction between metallic filler particles in the segregated network structure and an adhesion betweenmetallic filler particles and polymeric matrix were considered to be the causes of the damping.

In Fig.11(a) and (b), the maxima in damping curves shifted to higher temperature as the metallic filler concentration increased and the temperature at the maxima in damping was the glass transition temperature. Since the shift in glass transition temperature was proportional to the surface area of the metallic filler particles, the effect increased with the concentration of metallic filler particles increased. The shift in glass transition temperature was due to the adsorption of polymer onto the metallic filler surface. Since the adsorption restricted the molecular motion of polymer chain and changed the packing density of polymer chains, the conformation and orientation of polymer chain segments in the neighborhood of the filler surface were modified in the same way.

4. CONCLUSIONS

The electrical specific resistivities of the spherical metallic particles filled polymeric composite were agreed well with the equations of the models suggested by Kusy and Turner. The critical volume percent of metallic filler, where a segregated network was formed, was the crisis in the electrical and thermal conductivities and tensile and flexural strength of the composites.

A strengthening effect of the polymeric matrix due to the introduction of metallic particles was maximum just before the continuous metallic network formation and the strengthening effect was verified by the tensile and flexural tests.

The particle shape of the filler was an important factor to determine the thermal and mechanical properties of the metal filled polymeric composites and to determine the critical volume percent of metallic particles at which the continuous metallic network was formed. The large surface area of the irregular and plate-like copper particles gave rise to h: higher values in the shift of glass transition temperature than the shift caused by the nickel particles which were regular and spherica type in shape and had a small surface area.

At about 2 volume percent of the metallic particles loading, the plate-like copper particles made the continuous network in the PVC/Cu composit system, but in the PVC/Ni composite system, the continuous metallic network was formed at about 5 volume percent of nickel particles loading, in spite of the same metallic particle size of $7\mu m$ was used.

Even if a small amount of plate-like copper particles were introduced into the polymeric matrix, the polymeric material became brittle one. The plate-like metallic particles increased the tensile and flexural modulus magnificantly and decreased the flexibility and elongation at yield point sharply of the metal filled polymeric composites with increasing the metal loading.

The nickel particles having bumpy and equiaxed granuled surface state provided an adhesion between filler and matrix, but the copper particles having smooth and flat surface state provided no adhesion between metallic filler and polymeric matrix phases. Hence, the surface state of metallic filler was an important factor to produced the adhesion between

two phases, and the adhesion was also an important factor to determine the various mechanical properties of the metal filled polymeric Composites. The adhesion between metallic filler and polymeric matrix was produced by the mechanical compacting for sample preparation and this adhesion was clearly revealed by the SEM study and by the damping curves, tanδ, of the dynamic mechanical test.

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