

Dynamic Mechanical Properties of Poly(vinyl Chloride)–Xonotlite Composite System

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Synopsis

The filler effect of xonotlite ($6\text{CaO}\cdot 6\text{SiO}_2\cdot \text{H}_2\text{O}$; needle-shaped) on dynamic mechanical properties, such as storage modulus (E'), loss modulus (E''), and $\tan \delta$ was studied for the PVC–xonotlite composite system. And the properties of the system containing mechanically or chemically disaggregated particle of xonotlite were compared with those of the system-filled aggregates. The dynamic mechanical properties obviously depends on the dispersion condition of xonotlite particle. The aggregates of xonotlite produces a remarkably high modulus, an increase in T_g , and a decrease in mechanical damping near T_g in the system. On the other hand, the disaggregates, especially the chemical disaggregate one, bring softer or more rubbery properties in these systems. The interaction between matrix and filler was the strongest in the aggregates system and decreases in the order, mechanical disaggregates system, chemical disaggregates system.

INTRODUCTION

This paper describes dynamic mechanical properties of poly(vinyl chloride)–xonotlite composite system. Xonotlite is a needle shaped calcium silicate ($6\text{CaO}\cdot 6\text{SiO}_2\cdot \text{H}_2\text{O}$) is shown in Figure 1. The crystal structure was revealed through the study of Mamedov and Belov.¹ That is a double “Drierkette” of SiO_4 and is a kind of inorganic polymer. Author has developed xonotlite as a new functional filler for plastics. Xonotlite shows various functional effects on plastics, especially polyvinyl chloride (PVC), such as the fire-, smoke-, and HCl-retarding effect,² the crosslinking effect,^{3,4} the thermal stabilizing effect,⁵ and the damping effect. Besides these effects, xonotlite shows also a superior reinforcing effect on plastics. For these reasons, xonotlite has attracted interest as a filler for mechanical and thermal improvement of PVC window flame, damping materials, cable, and so on.

Xonotlite synthesized by hydrothermal reaction of $\text{Ca}(\text{OH})_2$ and SiO_2 is usually obtained as aggregated particles. However, it is hard to make a well-dispersed condition of xonotlite in a matrix with only mixing roll or extruder. Therefore, a disaggregation treatment of xonotlite particles is desirable for it to obtain good properties of the composites, while it is very hard to disaggregate the particles with an ordinary mill, such as a grinding mill or ball mill. Then, two methods for the disaggregation were applied. The one was a mechanical atomization by jet air mill. The other was an addition of hexamethyl disiloxane (HMDS) to the reaction system when xonotlite was synthesized. Though the later is not mechanical, xonotlite-containing HMDS is well dispersible. In this paper, effects of the disaggregation of xonotlite particles on the dynamic modulus of the PVC–xonotlite system are compared, and, also, an interface interaction between filler and matrix is discussed for the systems.

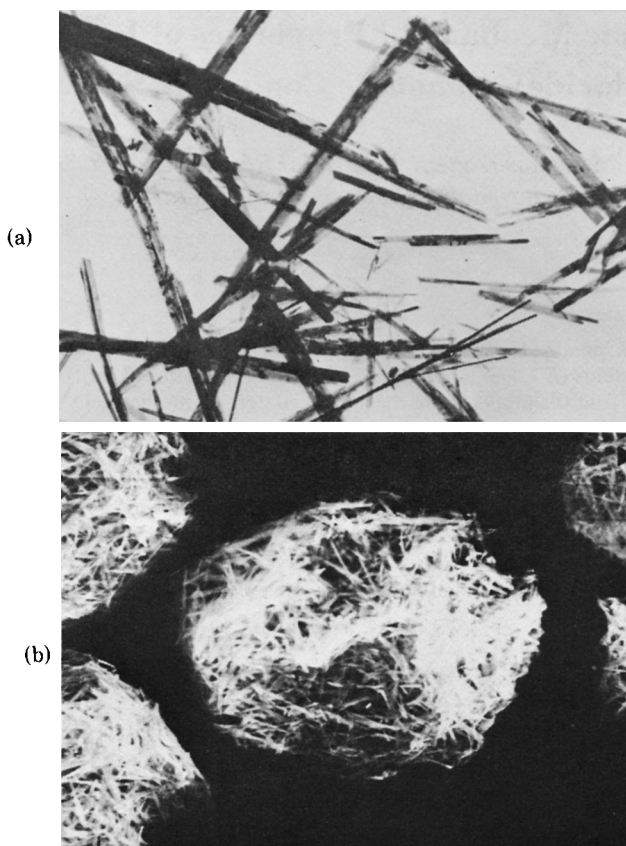


Fig. 1. (a) SEM photograph of xonotlite crystal (crystal length: about 5μ). (b) SEM photograph of aggregates of xonotlite (particle size: about 60μ).

EXPERIMENTAL

Preparation of Xonotlite

Xonotlite was prepared by a hydrothermal reaction of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and pure silica powder (SiO_2). The calcium hydroxide was made by adding H_2O to CaO rebaked at 950°C . The reaction temperature was 240°C . After reaction, the reaction mixture was dried by a spray method. This powder of aggregated particles was abbreviated as X in this paper. The one of disaggregated xonotlite, which was abbreviated as X(JA), was prepared by a jet air mill atomization. Another was prepared by adding 10 wt % of HMDS to the mixture of $\text{Ca}(\text{OH})_2$ and SiO_2 in the autoclave before the reaction. This was also abbreviated as X(HMDS). The properties of these xonotlite are tabulated in Table I.

Preparation of Testing Materials

The xonotlite were mixed with PVC (NIPPON ZEON 103EP8; \bar{P} : 800) with a heating roll. The content of xonotlite was varied from 20 to 150 PHR (per hundred resin) for the aggregates system (PX system), and was 40 and 100 PHR for the disaggregates systems [PX(JA) and PX(HMDS) systems]. The sheets

TABLE I
Properties of Xonotlite

Materials	Crystal size (μm)	Aspect ratio	BET surface area (m^2/g)	DOP ^a absorptive power (mL/g)	Average ^b particle size (μm)
X	4-6	20-30	26.2	2.50	40-100
X(JA)	4-6	20-30	24.8	3.07	5-15
X(HMDS)	3-5	15-20	26.9	2.83	5-20

^a By Brabender Absorpt Meter.

^b By Coulter Counter TA II.

obtained from the roll were hot-pressed to 3 mm of thickness. The materials were unplasticized except for adding small amounts of stabilizer and lubricant. The preparing conditions of these materials are tabulated in Table II.

Measurements of Dynamic Mechanical Properties

TOYO-BAWLDWIN RHEOVIBRON DDV-3ATP was used for the measurements. A vibration frequency of 110 Hz was applied to the materials from room temperature to 150°C with rising speed of 1°C/min. The amplitude (rheovibron strain) was 25 μm . The linear viscoelasticity was kept for these materials in the strain. The test pieces were 0.5 cm wide by 10 cm long by 0.3 cm thick. The output data from the apparatus were recorded on tapes and calculated with a computer.

RESULTS AND DISCUSSION

Storage Modulus (E')

The temperature dependence of storage modulus (E') for PX is shown in Figure 2. The curves of PX(JA) and PX(HMDS) are also shown in Figure 3. As seen from these figures, the modulus (E') increased with increase of filler content. The increase of the modulus was more remarkable at high temperature (rubbery region) than at room temperature (glassy region). This means that

TABLE II
Preparing Conditions of Materials

Filler content (PHR)	Stabilizer ^a (PHR)	Rubricant ^b (PHR)	Mixing		Press		
			Temp (°C)	Time (min)	Temp (°C)	Time (min)	Pressure (kg/cm^2)
0 (unfilled)	2	1	165	5	170	10	100
20 (PX-20)	3	1.5	165	5	170	10	100
40 (PX-40)	3	1.5	165	5	170	10	100
60 (PX-60)	4	2	165	5	170	10	100
100 (PX-100)	4	2	165	6	170	10	100
150 (PX-150)	6	4	165	7	170	10	100

^a Dibutyl tin-malate + dibutyl tin-mercaptide (1:1).

^b Butyl stearate + stearic glyceride (1:2).

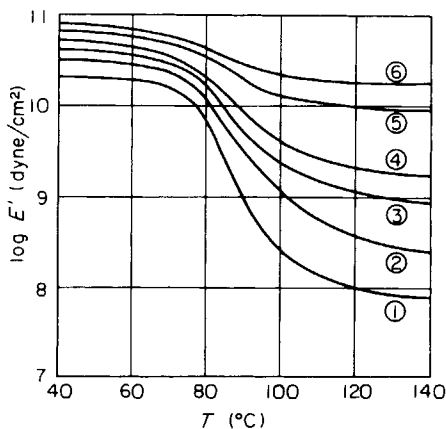


Fig. 2. Temperature dependence of storage modulus (E') for PX. ① Unfilled PVC, ② PX-20, ③ PX-40, ④ PX-60, ⑤ PX-100, ⑥ PX-150.

xonotlite improves the heat resistance of PVC. Such a large increase of elastic modulus in rubbery region has been also observed by Lewis and Nielsen on an epoxy-glass beads system.⁶

Relative moduli (E'/E'_0) in glassy region for PX, PX(JA), and PX(HMDS) are shown in Figure 4. The effect of the disaggregation on E' showed at relatively high content. Among these systems, PX(HMDS) had the lowest modulus. Next, a relative magnitude of transition in the modulus for these systems is shown in Figure 5. Here, D is a magnitude of the transition in modulus from glass state to rubbery state. Namely, the D value is termed as the difference of modulus between glass state and rubbery state. D_0 is for unfilled polymer, and also the broken line in the figure is the theoretical curve, which is connected between 1 of D/D_0 and 1 of ϕ_f . Namely, the broken line is that of an ideal condition in which any slip or restraint does not exist on the interface between filler and matrix. When a slip exists on the interface, the curve of D/D_0 vs. ϕ_f comes above the broken line. A polystyrene-aluminum powder system is a typical example.⁷ On the contrary, when free motion of matrix molecules is restrained by filler, the curve comes under the broken line. As shown in the figure, the D values of the PVC-xonotlite system became small with increase of filler content and the D/D_0

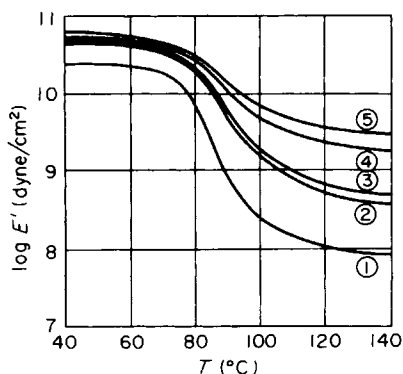


Fig. 3. Temperature dependence of storage modulus (E') for PX(HMDS) and PX(JA). ① Unfilled PVC, ② PX(HMDS)-40, ③ PX(JA)-40, ④ PX(HMDS)-100, ⑤ PX(JA)-100.

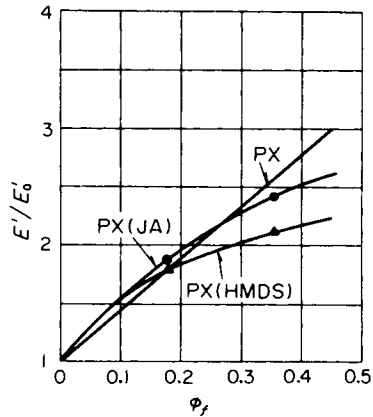


Fig. 4. Effect of filler content on relative modulus (E'/E_0) for PX, PX(JA), and PX(HMDS).

curves came under the broken line. Therefore, it is evident that PVC molecules are restrained by xonotlite. The curves of PX(JA) and PX(HMDS) were closer to the broken line than that of PX. The fact is explained by that an interaction between matrix and filler decreased because of more improved dispersion condition than PX. Among them, PX(HMDS) had the smallest interaction. It is also considered that an improvement of wettability of filler to matrix by HMDS contributes to the decrease of the interaction.

A sharpness of the transition in E' is shown in Figure 6. The sharpness of the PX(JA) and PX(HMDS) were larger than that of PX. Usually, the sharpness decreases with increases of filler content and of interaction between filler and matrix. From the results of temperature dependence of storage modulus, it was confirmed that the disaggregates systems, especially PX(HMDS), had a weaker interaction than the aggregates system.

Loss Modulus (E'')

Temperature dependence of the loss modulus (E'') for PX, PX(JA), and PX(HMDS) is shown in Figures 7 and 8. The loss modulus increased with increase of filler content. At the same time, the peak (α -peak) of the curves shifted

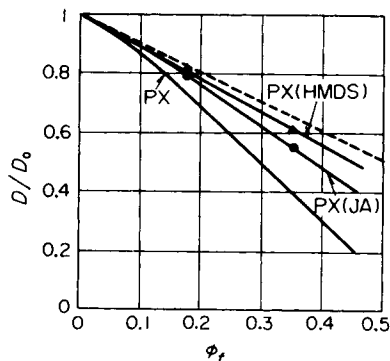


Fig. 5. Effect of filler content on relative magnitude of transition of E' (D/D_0) for PX, PX(JA), and PX(HMDS). Broken line is that of an ideal condition in which any slip or restraint does not exist on the interface between filler and matrix. D is the difference of modulus E' between glassy state and rubbery state. D_0 is of unfilled polymer.

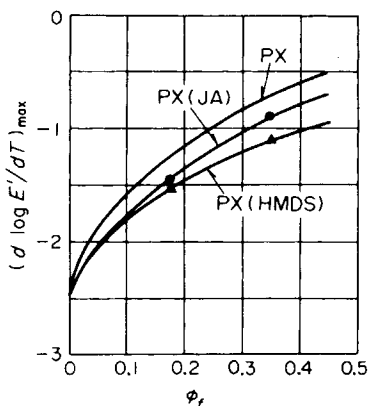


Fig. 6. Effect of filler content on sharpness of transition of E' for PX, PX(JA), and PX(HMDS).

to higher temperature side. The α -peak temperature (T_α) of these systems are plotted against filler content in Figure 9. A logarithmic increase of T_α was observed with increase of filler content, and PX had higher T_α than PX(JA) and PX(HMDS). The increase of T_α is due to the restraint of free motion of matrix molecules. Therefore, the volume of polymer restrained by filler can be estimated by a degree of the increase of T_α . Droste and Dibendetto presented the following equation⁸:

$$T_{g_c} - T_{g_0} = \Delta T_{g_\infty} [1 - \exp(-B\phi_f)] \quad (1)$$

Here, T_{g_c} and T_{g_0} are the T_g of composites and unfilled polymer, respectively. ΔT_{g_∞} is the maximum increase of T_g of the composites, and B is a constant. Equation (1) can be transformed into

$$\log(\Delta T_{g_\infty} - \Delta T_g) = \log \Delta T_{g_\infty} - B\phi_f \quad (2)$$

Here, $\Delta T_g = T_{g_c} - T_{g_0}$. Namely, there exists a linear relation between $\log(\Delta T_{g_\infty} - \Delta T_g)$ and ϕ_f . The relation of the equation was applied to these systems. But in this paper, the value of T_α was used in place of T_g . The results are shown in

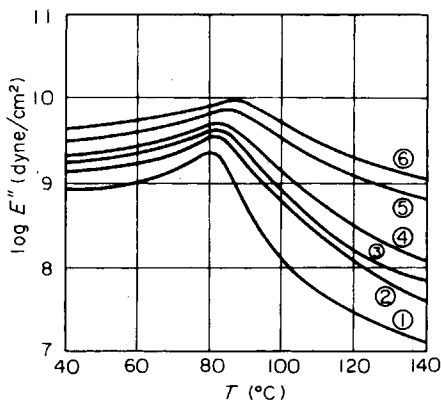


Fig. 7. Temperature dependence of loss modulus (E'') for PX. ① Unfilled PVC, ② PX-20, ③ PX-40, ④ PX-60, ⑤ PX-100, ⑥ PX-150.

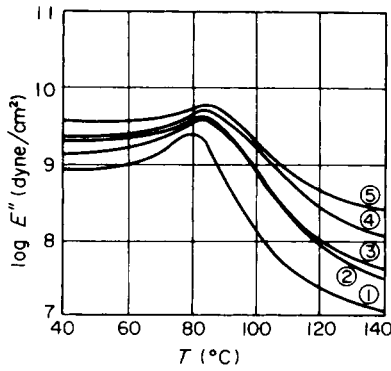


Fig. 8. Temperature dependence of loss modulus (E'') for PX(HMDS) and PX(JA). ① Unfilled PVC, ② PX(HMDS)-40, ③ PX(JA)-40, ④ PX(HMDS)-100, ⑤ PX(JA)-100.

Figure 10. Each system had a linear relation between $\log(\Delta T_{g\infty} - \Delta T_g)$ and ϕ_f . It was confirmed that eq. (2) could be applied well to these systems.

And also, the volume (V_A) of the matrix restrained by filler is obtained from the following equation:

$$V_A = V_T \cdot \phi_f \cdot \bar{S} \cdot \delta \tag{3}$$

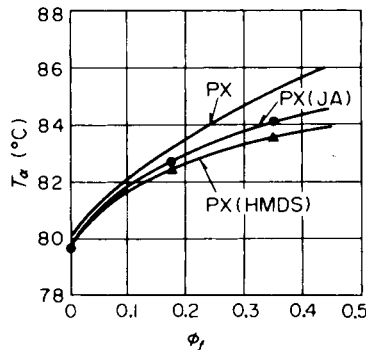


Fig. 9. Effect of filler content on T_α (temperature at a peak of E') for PX, PX(JA), and PX(HMDS).

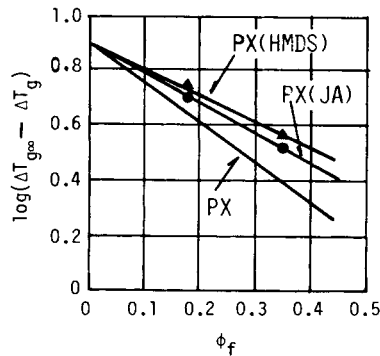


Fig. 10. Relationship between $\log(\Delta T_{g\infty} - \Delta T_g)$ and ϕ_f for PX, PX(JA), and PX(HMDS). $T_{gc} - T_{go} = \Delta T_{g\infty} [1 - \exp(-B\phi_f)]$ and $\log(\Delta T_{g\infty} - \Delta T_g) = \log \Delta T_{g\infty} - B\phi_f$. Here, $\Delta T_g = T_{gc} - T_{go}$, T_{gc} : T_g of composites, T_{go} : T_g of matrix (PVC).

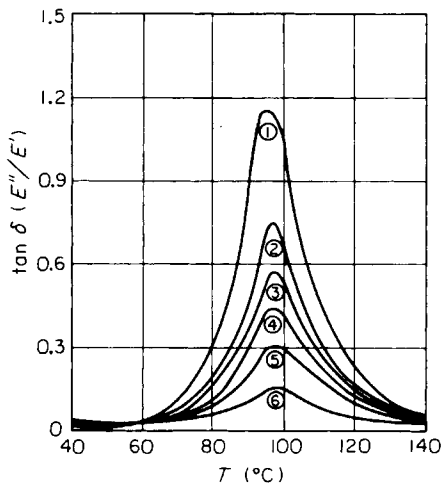


Fig. 11. Temperature dependence of $\tan \delta$ for PX. ① Unfilled PVC, ② PX-20, ③ PX-40, ④ PX-60, ⑤ PX-100, ⑥ PX-150.

Here, V_T is the total volume of composites. \hat{S} is the specific surface of filler (cm^2/cm^3), and δ is the volume of matrix under the influence of unit surface of filler (cm^3 polymer/ cm^2 filler). Now, at $V_A = (1 - \phi_f)V_T$, namely $\phi_f = 1/(1 + \hat{S}\delta)$, whole volume of matrix polymer is influenced by the filler. The influence exerts when the increase of T_g halts. Therefore, δ can be calculated from the equation $\phi_{f(\max)} = 1/(1 + \hat{S}\delta)$. Here $\phi_{f(\max)}$ is the ϕ_f at which T_g of the composites reaches maximum. In this paper it was obtained by extrapolation of the T_g vs. ϕ_f curve. However, a problem of how to estimate \hat{S} of filler in matrix arises. In the case of aggregated particle, the filler particle in matrix usually dispersed insufficiently. Therefore, the effective surface area (\hat{S}_{eff}) of such a filler in matrix is considered to be smaller than the specific surface area of the filler, such as the BET surface area. However, it is impossible to know the effective surface area. Then, in this paper, \hat{S}_{eff} for each system was estimated by the following process:

- (1) Specific surface area ($\hat{S}_{\text{specific}}$) = (BET surface area) \times (true density).
- (2) (\hat{S}_{eff}) = ($\hat{S}_{\text{specific}}$) \times (factor).

The true density of xonotlite is 2.78. Here, the factor was estimated from the B value, which is considered a parameter of the strength of interaction between filler and matrix. The B values calculated from Figure 10 decreased in the order PX, PX(JA), PX(HMDS). Then, the factor of PX(HMDS) which had the smallest B value was given as 1. And the factor of PX or PX(JA) was given as the ratio of each B value to that of PX(HMDS). Namely,

$$\text{factor}_{\text{PX or PX(JA)}} = B_{\text{PX(HMDS)}}/B_{\text{PX or PX(JA)}}$$

The calculated results are tabulated in Table III. The values of δ obtained for PVC—xonotlite system is 15–79 Å. The order in the δ value was the same as that of B value. In the case of phenoxy—attapulgite clay system, the δ value is 35–100 Å.⁸

TABLE III
Measurement of Thickness (δ) of Matrix Polymer Restrained by Filler

Materials	B	Factor	$\phi_{f(\max)}$	S_{specific} (m^2/cm^3)	S_{eff} (m^2/cm^3)	δ (A)
PX	3.7	0.57	0.75	73	42	79
PX(JA)	2.5	0.84	0.85	69	58	30
PX(HMDS)	2.1	1	0.9	75	75	15

Tan δ

The temperature dependence of $\tan \delta$ for PX is shown in Figure 11. Those of PX(JA) and PX(HMDS) are also shown in Figure 12. The $\tan \delta$ increases with a rise of temperature and shows a maximum near T_g or at a somewhat higher temperature. The $\tan \delta$ maximum value for these systems is plotted against filler content in Figure 13. The $\tan \delta$ maximum decreased with increase of filler content. If the mechanical damping comes from only the matrix polymer, the relative damping is roughly equal to the volume fraction of the polymer.^{9,10} Namely, $\tan \delta$ maximum decreases monotonously against ϕ_f like the broken line in Figure 13. In the case of the PVC-xonotlite system, the curves of $\tan \delta$

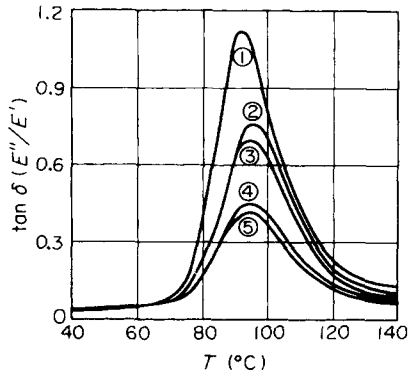


Fig. 12. Temperature dependence of $\tan \delta$ for PX(HMDS) and PX(JA). ① Unfilled PVC, ② PX(HMDS)-40, ③ PX(JA)-40, ④ PX(HMDS)-100, ⑤ PX(JA)-100.

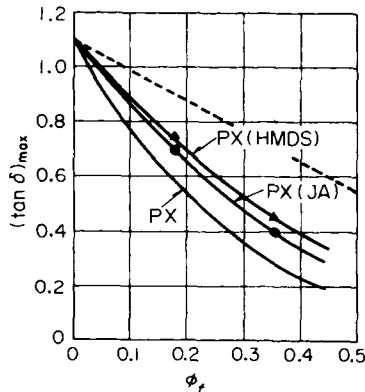


Fig. 13. Effect of filler content on $\tan \delta$ maximum for PX, PX(JA), and PX(HMDS). Broken line is the theoretical curve when all mechanical damping come from the matrix polymer.

maximum value vs. ϕ_f came under the broken line. It is because of a strong interaction between PVC and xonotlite. Generally, the interaction between matrix and filler decreases at a higher temperature, because the polymer becomes soft and a motion of the polymer on the interface becomes easier. Therefore, the mechanical damping increases with decrease of the interaction. As shown in the figure, PX showed a lower value in $\tan \delta$ maximum than PX(JA) and PX(HMDS). And also, the $\tan \delta$ maximum peak of PX remarkably shifted to higher side of temperature. Therefore, these results also indicate that the aggregates system had a stronger interaction than the disaggregates system.

The interaction of xonotlite to PVC results from an electrical attraction between calcium in xonotlite and chlorine in PVC. However, as shown from these results, the strength of the interaction obviously depends on the dispersion condition of particle. For this reason, it is thought that the aggregated particle produces a complex and/or a rigid structure in the matrix, and such a structure restricts free motion of PVC molecules. On the other hand, the disaggregated particle has a more homogeneous structure or simple interface structure, and the structure gives more rubbery or softer properties to the system. In the case of the unaggregated particle, an effect of the particle size on elastic modulus is essentially negligible.^{11,12} However, the aggregated particle brings remarkably high modulus in the system compared with the disaggregated particle. Moreover, it is noted that the aggregated particle produces more increase in T_g and decrease in mechanical damping near T_g .

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