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Determination of Kneading Temperature in Continuous Kneading of Composite Conductive Plastics

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The torque-temperature curve is used to determine the optimum kneading temperature to obtain composite conductive plastics of high electric conductivity and shielding effectiveness. The effect of the kneading temperature on the dispersion state of fillers is discussed. The dispersion state of the filler is evaluated by three parameters, namely, the variance of the residence time distribution, the ratio of specific resistivities of the composite along perpendicular directions, and the breakage of the fillers.

1. Introduction

In precision electronic instruments like computers, troubles occasionally arise due to noise of electromagnetic waves intruding through their plastic housings. This phenomenon, called electromagnetic interference (EMI), has become an important problem in this industry in recent years. The use of electroconductive plastic housings prevents to a high extent the occurrence of EMI. Kneading is one of the usual methods for the preparation of composite conductive plastics because of its simplicity and the durability of the shielding effect of the obtained composites. However, further investigations concerning the influence of the kneading variables on the properties of the product is required.

Concerning the kneading technique, a few works have appeared in the literature up to the present¹⁻⁴⁾. In previous papers, kneading of composite conductive plastics with fibrous fillers under different operating conditions have been reported⁵⁻⁹⁾. In the present work, a method for determining the proper kneading temperature to obtain composite conductive plastics of high electric conductivity and shielding effectiveness is suggested. The dispersion state of filler within the matrix resin as a function of the kneading temperature is also evaluated.

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2. Experimental

2. 1. Equipment and materials

The continuous twin-shaft kneader and the measurement system are depicted in Fig.1.

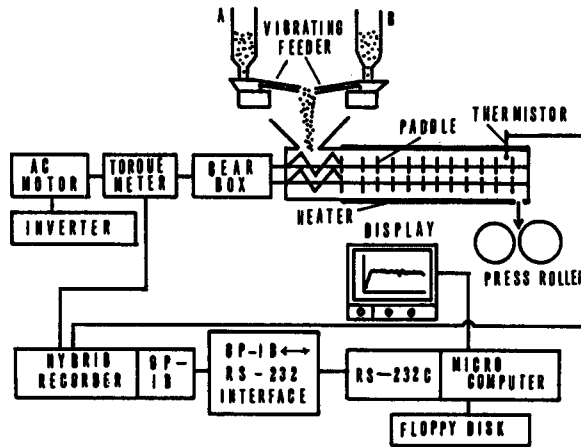


Fig. 1 Skeleton diagram of the kneading apparatus and measurement system.

The kneading chamber consists of two overlapped cylinders, each one 0.025m in diameter and 0.165m long. The volume of the chamber is $1.4 \times 10^{-4} \text{m}^3$ and the effective volume (excluding paddles and shafts) is $8.84 \times 10^{-5} \text{m}^3$. The two shafts, one in each cylinder, rotate at the same speed and in the same direction. The lenticular paddles are disposed in such a way that their tips form a helix around the shafts. While rotating, the paddles of one shaft are kept in contact with the paddles of the other one as well as with the wall, so that the sticked material can be continuously removed. In this manner, kneading and (self-) cleaning are simultaneously performed. The kneader is heated by a band-heater equipped with an on-off controller to keep a constant temperature during the operation. The temperature was measured by a thermistor inserted into the kneading chamber.

Once the paddles are rotating at a prescribed speed (set by an inverter), the raw materials are charged into the kneader at a determined rate by means of a vibrating feeder. The changes of the temperature and the torque during kneading were monitored and recorded by a microcomputer.

The powders employed in the kneading experiments were ABS resin as the matrix resin and stainless steel fiber as the conductive fillers. Their properties are listed in Table 1.

Table 1 Properties of materdilo vnسد in kneading.

	ABS resin	Stainless stell fiber
softening point 〔 K 〕	373	1673~1723
specific gravity 〔 - 〕	1.04	7,9
specific resistvitx 〔 Ω·m 〕	1~5 ×10 ¹⁴	7,2×10 ¹⁷
size 〔 mm 〕	φ 2.5×3	φ 0.008×5
shape	pellets	bundles of 5000 chops

2. 2 Kneading experiment

ABS resin from the hopper A was firstly fed to the kneader and heated upto 543K. At this point, the feeding was switched to the matrix/filler mixture of the hopper B. When the melting state of the mixture attained a stable state (constant torque), the heater was turned off and, as a result, the temperature of the mixture decreased gradually. At fixed time-intervals of 30 seconds, samples of the kneaded materials were taken. The samples were moulded with a press roller (thickness, 5 mm), cut into 20x20mm rectangular pieces, and their specific resistivities measured.

During the kneading, the torque change was also continuously monitored and recorded. From these data, the characteristics of the torque change and the specific resistivity change with temperature decrease could be classified into three regions. With the purpose of investigating the relationship between the electric conductivity and the dispersion state of the fillers in these regions, continuous kneading experiments were carried out at constant temperatures selected from each one of them. The purpose of these experimens at constant temperatures was to enhance the reliability of the experimental data by taking the statistical averages of the values obtained for several samples (in the experiment described above, only one sample was taken at a time).

2. 3 Specific resistivity and shielding effectiveness

The specific resistivity, ρ_v [Ω·m], of the each sample is calculated by the formular,

$$\rho_v = (S/l) \cdot R \quad (1)$$

where S is the area of the electrode, l the distance between the electrodes, and R is the measured resistivity.

The mean specific resistivity $\bar{\rho}_v$ is calculated from the resistivities of the samples obtained in a continuous kneading experiment.

The shielding effectiveness, SE [dB], is calculated from the Schelkunoff's equation⁹⁾,

$$SE = 50 + 10 \log (\rho_v \cdot f)^{-1} + 1.7d (f/\rho_v)^{1/2} \quad (2)$$

where the specific resistivity, ρ_v [Ω·cm], has been substituted for the mean specific resistivity, $\bar{\rho}_v$ [Ω·cm]. The frequency of the electromagnetic wave, f , and thickness

of the shield material, d , were assumed to be 1000 MHz and 0.2cm, respectively.

2. 4 Dispersion, direction and length of fillers

In the plastic composite, electricity flows through the network of conductive paths formed by the filler dispersed within the matrix resin. Therefore, the degree of dispersion should be evaluated according to whether the conductive paths are formed or not. In case of fibrous filler, it is considered that formation of the conductive paths depends on three parameters, namely, the dispersion state of the filler within the matrix resin, the directions of the individual fillers and the lengths of the fillers.

The dispersion state is evaluated by the variance, σ_θ^2 , of the dimensionless residence time distribution of filler, calculated by the equation,

$$\sigma_\theta^2 = \int \theta^2 E(\theta) d\theta, \quad (3)$$

where θ is the dimensionless time (t/\bar{t}) and $E(\theta)$ is the dimensionless residence time distribution function.

The direction of the filler within the matrix resin is estimated by the ratio of the specific resistivities, $\rho_{v,r}$, measured in the directions A and B of the rectangular samples as shown in Fig. 2(B). From the values of the $\rho_{v,r}$ the mean ratio of the specific resistivities, $\overline{\rho_{v,r}}$, is calculated.

The mean length of the filler dispersed within the matrix resin after kneading, L_{F0} , is measured as follows. The composite conductive plastic is dissolved in a solvent (methyl ethyl ketone:toluene=1:1), the fillers are separated from the matrix resin and their length measured. The mean value is calculated from above 400 fillers. The ratio of the average length of the fillers before kneading to that after kneading, L_{F0}/L_{F1} , is used as a measure of the breakage of the filler during kneading.

3. Results and Discussion

3. 1 Characteristics of torque change with temperature

Examples of the torque change and the specific resistivity change with temperature decrease are shown in Fig. 2(A) and (B), respectively. As shown in Fig. 2, the curves of the torque change and the specific resistivity change can be divided into three regions.

In the region I ($T > 473\text{K}$), the kneading torque increases slowly with temperature decrease. This behavior is believed to be caused by the increase in the viscosity of the melted matrix resin as the temperature decreases. Since the value of the torque in this region is comparatively low, it is inferred that the matrix resin is sufficiently melted during this kneading stage, thus promoting the dispersion of the filler. Therefore, the composite conductive plastics kneaded in this region present good conductivity as shown in Fig. 2(B). The specific resistivity change shows the same trend as the torque, that is, increases slowly with temperature decrease.

The kneading torque diminishes with temperature decrease in the region II ($453\text{K} < T < 473\text{K}$). It is considered that this phenomenon results from an insufficiently melted state of the matrix resin. The resin pellets are partially melted in the

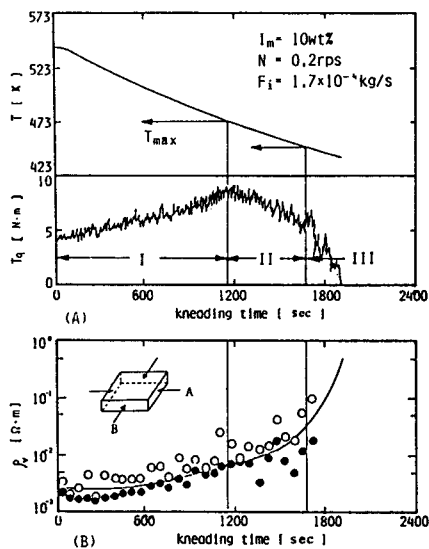


Fig 2 An illustration of the torque-time curve(A) and the change of specific resistivity (B)with the kneading temperature sweeping

temperature range of this region, and the melted fraction decreases as a consequence of the temperature decrease. The decreasing viscous resistance resulting from the gradual solidification of the matrix resin leads to a decrease in the torque. In this situation, the filler can not be properly dispersed within the matrix resin and the resulting composites show much higher specific resistivities than the corresponding to region I.

In the region III ($T < 453\text{K}$), the kneading torque shows irregular and large fluctuations, falling down sharply to $T_q = 0$. In this temperature range, the coagulation of the superficially melted resin pellets alternates with the break up of these so-formed coagulates. The successive occurrence of these two phenomena may explain the oscillating pattern of the torque curve. In this region, the melting state of the matrix resin makes impossible the dispersion of the filler and the composites obtained under this condition present the resistivities falling out of the measuring range ($2\Omega \sim 2\text{M}\Omega$) of the ohmmeter used in this work.

The description of the results presented in the preceding paragraphs may be summarized as follows. The melting state of the matrix resin, which depends on the kneading temperature, plays a fundamental role in the dispersion state of the filler. Composites of high electric conductivity are obtained when the resin is completely melted. The dispersion state of the filler according to the kneading temperature will be later discussed in detail.

Fig. 3, where the relationship between the temperature T_{max} at the maximum torque (see Fig.2(A)) and the revolution speed of paddles and the feeding rate, shows that the torque-time curves shift as the operating conditions are changed. In other words, the melting state of the matrix resin depends not only on the kneading

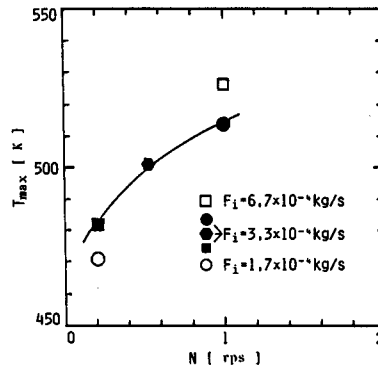


Fig.3 Relationship between the temperature presented maximum torque, T_{max} , and the operating condition.

temperature but also on the other operation conditions such as revolution speed of paddles and feeding rate of the raw materials. Therefore, the suitable kneading temperature can be selected from the characteristics of torque change curve (region I) for given feeding rate and revolution speed of paddles.

3. 2 Evaluation of dispersion state of fillers

As it is well known, the variance of the dimensionless residence time distribution, σ_{θ}^2 , is usually the parameter employed in the evaluation of the axial mixing in a continuous plug reactor¹⁰⁾. In this work, since the dispersion of the filler takes place along the axial direction, σ_{θ}^2 can be used to assess the degree of dispersion of the filler within the matrix resin. The relationship between σ_{θ}^2 and the kneading temperature, T , is plotted in Fig. 4. This figure shows that σ_{θ}^2 increases, that is, the degree of dispersion of the filler within the matrix increases as the temperature increases.

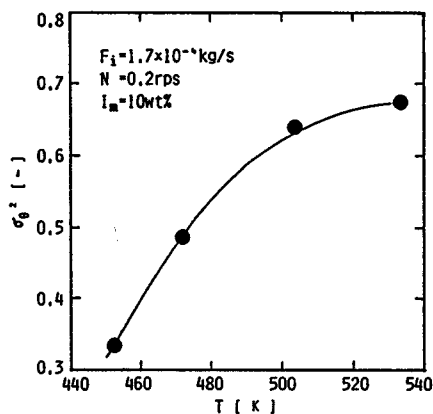


Fig 4 Relationship between the variance of dimensionless residence time distribution, σ_{θ}^2 , and the kneading temperature, T .

The dispersion state is particularly good in the range of temperature corresponding to region I shown in Fig. 2. This result is also confirmed by the electron microscopy photographs of the cross sections of the composites shown in Fig. 5. The photograph of region I (Fig. 5(A)) demonstrates that the fillers (white spots in the photographs) are homogeneously dispersed within the matrix resin (black parts).

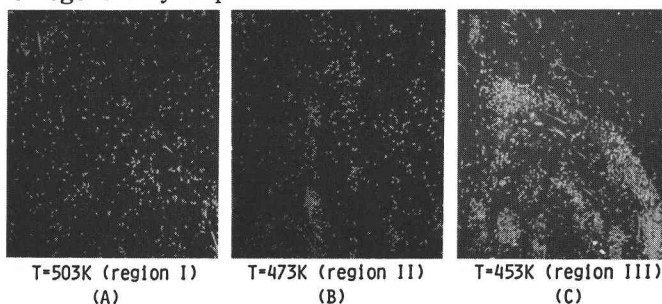


Fig 5 Photographs of electron microscopy of the samples kneaded under different kneading temperature.

As mentioned in the experimental section, the degree of randomness of the filler's orientations is estimated by the ratio of the specific resistivities measured along perpendicular directions, $\overline{\rho_{v,r}}$. When the fillers are randomly oriented, the conductive paths are not disposed along any predominant direction and, accordingly, $\overline{\rho_{v,r}}$ takes on the value 1⁸⁾. The relationship between $\overline{\rho_{v,r}}$ and the kneading temperature, T , is illustrated in Fig. 6. In the temperature range of region I ($T > 473\text{K}$), the values of $\overline{\rho_{v,r}}$ are lower and closer to 1. On the contrary, $\overline{\rho_{v,r}}$ is relatively high in the temperature range of the region II ($453\text{K} < T < 473\text{K}$). From these results, it is concluded that the fillers become more randomly oriented when kneading is carried out under the temperature range of region I, where the melting state of the matrix resin is more favorable.

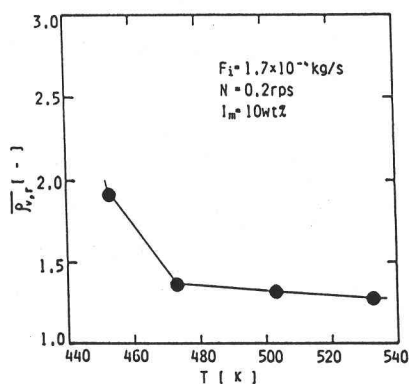


Fig. 6 Relationship between the ratio of specific resistivity along perpendicular direction, $\overline{\rho_{v,r}}$, and the kneading temperature, T

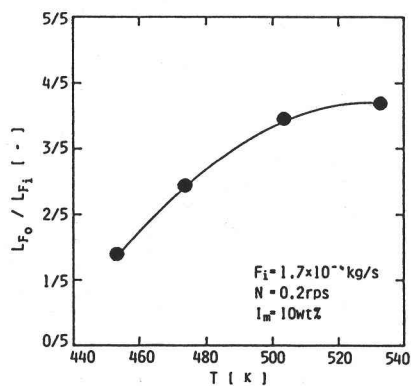


Fig. 7 Relationship between the breakage of fillers during kneading, L_{F_0}/L_{F_1} , and the kneading temperature, T .

Fig. 7 shows the effect of the kneading temperature, T , on the breakage of fillers during kneading, L_{F0}/L_{F1} . The breakage of fillers is markedly high at the kneading temperature of region II. It is believed that this considerable breakage of fillers is caused by the coagulation of the matrix resin pellets insufficiently melted. Under these circumstances, the kneaded material resides for a long time in the kneader because it is jammed in the kneading chamber. And the longer the residence time of the filler in the kneader, the more likely is its breakage by the paddles' rotation.

The results shown in Figs. 4 through 7 indicate that the extent to which the filler is dispersed, the degree of randomness of its orientation and its breakage, are all temperature-dependent variables. Under the kneading temperatures of region I, the fillers are more homogeneously dispersed, their orientation takes place at random and the magnitude of their breakage is lower. Since all these conditions are favorable, it is considered that region I constitutes the optimum temperature range for the compounding of conductive plastics.

3. 3 Conductivity and shielding effectiveness

The specific resistivity of the composite conductive plastic, $\bar{\rho}_v$, as a function of the kneading temperature for several revolution speeds of paddles is plotted in Fig.8.

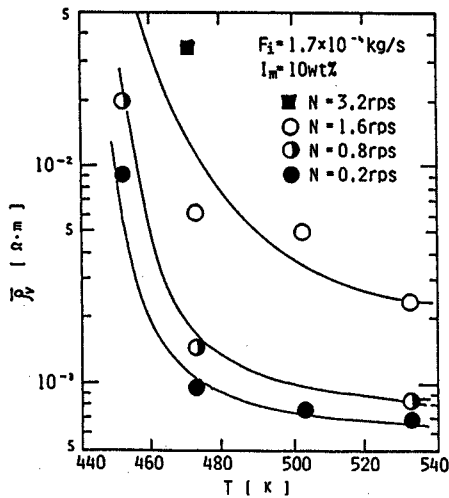


Fig. 8 Relationship between the mean specific resistivity $\bar{\rho}_v$, and the kneading temperature, T

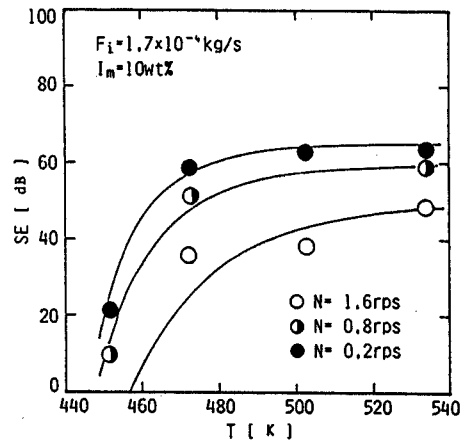


Fig. 9 Relationship between the shielding effectiveness, SE, and the kneading temperature, T .

The composites kneaded under the temperature range of region I present excellent conductivities ($\overline{\rho_v}$ is in the $10^{-4} \Omega \cdot m$ level) in comparison with those of region II. Their shielding effectiveness, shown in Fig.9, is also satisfactory, meeting the standard specifications required for EMI shield materials (40 dB). Figs.8 and 9 also show that the composite conductive plastics kneaded under high revolution speed of paddles such as $N=1.6$ rps or $N=3.2$ rps, present comparatively high specific resistivity and low shielding effectiveness even though the kneading temperature is high. This is caused by the shift of the torque change curve to higher temperatures as the revolution speed increases.

This result confirms the usefulness of the torque-time curve in the selection of the temperature range at which the composite conductive plastic of optima properties may be obtained.

4. Conclusion

The torque-temperature curve has been suggested as a method to determine the optimum kneading temperature to obtain composite conductive plastics of high electric conductivity and shielding effectiveness to be used as a preventive measure against EMI. The electrical properties of the kneaded composite depend on the dispersion state of the fillers within the plastic matrix. In turn, the degree of dispersion of the fillers has been shown to be influenced by the kneading temperature. This effect has been evaluated in terms of the residence time distribution of the material in the kneader, the ratio of specific resistivities of the composite along perpendicular directions, and the breakage of the fillers. It has been demonstrated that for given values of the revolution speed of paddles and the feeding rate, the optimum temperature range can be selected directly from the torque-temperature curve.

Nomenclature

d	: distance between electrodes	[cm]
f	: frequency	[MHz]
F_i	: feeding rate of raw materials	[kg/s]
l	: distance between electrodes	[m]
L_{Fi}	: length of filler before kneading	[m]
L_{Fo}	: mean length of filler after kneading	[m]
N	: revolution speed of paddles	[rps]
R	: resistivity	[Ω]
S	: section area of electrode	[m ²]
t, \bar{t}	: residence time and mean residence time, respectively	[s]
$\rho_v, \overline{\rho_v}$: specific resistivity and mean specific resistivity, respectively	[$\Omega \cdot cm$] or [$\Omega \cdot m$]

σ_s^2	: variance of dimensionless residence time distribution	[—]
θ	: dimensionless time ($=t/\bar{t}$)	[—]

References

- 1) N. Sakai, Gousei Jushi, **24**(11), 7 (1978)
- 2) N. Sakai, Koubunshi Ronbunshi, **38**(4), 279 (1981)
- 3) M. Eyrich, The 3th Reactive Processing of Polymer Preprint, 165 (1985)
- 4) J. M. Mckelvey, "Polymer Processing", John & Wiley, (1962)
- 5) P. J. Lyoo, K. Terashita, Y. Mizuno and K. Miyanami, Bull. of the Univ. of Osaka Prefecture, Series A, **37**(1), 43 (1988)
- 6) P. J. Lyoo, K. Terashita, M. Mitsui and K. Miyanami, J. of Soc. of Powder Technology, Japan, **26**(9), 64 (1989)
- 7) K. Terashita, M. Mitsui, P. J. Lyoo and K. Miyanami, Zairyou, **38**(435), 81 (1989)
- 8) P. J. Lyoo, K. Terashita and K. Miyanami, to be published in J. of Soc. of Powder Technology, Japan
- 9) K. Yoshino, K. Kaneto, M. Tabata and T. Ohsawa, J. of Che. Soc., Japan, (3), 342 (1986)
- 10) K. B. Bischoff and E. A. McCracken, IEC, **58**(7), 18 (1966)