

# Tensile yield stress of polypropylene composites filled with ultrafine particles

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For polypropylene composites filled with ultrafine or particles of the order of microns, ( $\text{SiO}_2$  and glass, respectively), yield stress was measured as functions of temperature, the rate of strain and filler content. The yield stress of the composites filled with ultrafine particles increased with the filler content and decreased with the filler size, while for the composites filled with glass particles, these relations were reversed. For  $\text{SiO}_2$  filled composites, the tensile yield stress was found to be reducible with regard to temperature, the rate of strain and the filler content. The Arrhenius plot of the shift factors for composing the logarithmic strain rate - temperature master curve formed a single curve irrespective of the filler content and size. The curve comprised three linear regions with breaks appearing at 60 and 110° C, where the transition of the matrix polymer took place. The master curves obtained for different contents of a given size filler could be further reduced into a grand composite curve by shifting them along the axis of logarithmic strain rate, with the logarithmic second shift factors proportional to the square root of the volume fraction of the filler. The dependence of the filler volume fraction on the second shift factor was related to the dispersion state of fillers in PP matrix, namely, the promotion of the aggregation with filler content. The dependences of the yield stress on the filler volume fraction and size were explained by a modified equation based on the dispersion strength theory, with an aggregation parameter incorporated.

## 1. Introduction

In previous papers, we have shown that ultrafine particles have prominent reinforcing effects on the elastic properties of the oriented polymers [1, 2]. The present study describes the effects of ultrafine particles on the yield stress of unoriented polypropylene (PP) composites. The yield stress depends on temperature, the rate of strain and the filler content. At a given temperature and rate of strain, ultrafine particles will cause an increase in the yield stress. This is because the addition gives rise to an effect corresponding to an increase in the stretching rate, which in turn corresponds to the lowering of temperature. The convertibilities among these three factors can be expected to be reduced into some simple relations. Such relations

found were discussed in terms of the physical properties of the PP matrix and the aggregation of fillers.

## 2. Experimental procedure

### 2.1. Polymer and filler

Isotactic PP (melt index = 7 to 8), Shoaromer of Showa Denko Co., was used as matrix polymer.  $\text{SiO}_2$  particles (density,  $\rho = 2.2 \text{ g cm}^{-3}$ ) from Nihon Aerosil Co., and Sodalime glass particles ( $\rho = 2.4 \text{ g cm}^{-3}$ ) from Toshiba Balotini Co., and lead glass particles ( $\rho = 4.35 \text{ g cm}^{-3}$ ) were used as fillers. The moduli of the  $\text{SiO}_2$ , Sodalime glass and lead glass were  $7.0 \times 10^5$ ,  $7.0 \times 10^5$  and  $6.1 \times 10^5 \text{ kg cm}^{-2}$ , respectively. Table I shows average diameters of these particles.

TABLE I Average diameters of filler particles

Particle	Average diameter	
SiO <sub>2</sub>	A300	7 nm
	A130	16 nm
	OX50	40 nm
Lead Glass	Pb	6 μm
Soda-lime Glass	G731	35 μm
Glass	G733	65 μm
	G735	105 μm

## 2.2. Mixing and moulding

The polymer and filler were mixed in a two-roll mill for 15 min at 180°C. The mixing time, 15 min, was chosen because the torque of the composites in molten state became constant in about 10 min. The content of fillers were adjusted to 5, 10, 15 and 20 wt %. Samples loaded more than 20 wt % particles could not be drawn. Films about 0.5 mm thick were moulded from the mixtures at 200°C under a pressure of 100 kg cm<sup>-2</sup>. Since thermal degradation of the matrix polymer took place more or less during the mixing and moulding, films without filler were prepared by the same procedures. It was assumed that the degradation of polymer took place in the composites to the same extent as in the pure polymer sample.

## 2.3. Tensile test

Strips 5.0 cm long and 1.0 cm wide were cut from the composite film and drawn by a Tensilon UTM-III (Toyo Baldwin Co.) equipped with a temperature control bath. The measurements of yield stress were made at temperatures ranging from 30 to 130°C and at strain rates, 20, 200 and 1000 mm min<sup>-1</sup>.

## 3. Results and discussion

Fig. 1 shows stress-strain curves for PP filled with 10 wt % fillers at 30°C and a rate, 20 mm min<sup>-1</sup>. The figure shows that both the yield and necking stresses of samples filled with smaller fillers (7, 16 and 40 nm diameters) are higher than those of non-filled PP. For a sample filled with larger filler (105 μm), the initial Young's modulus is higher than that of non-filled PP, but the yield and necking stresses are lower. Reductions with filler content are known for the yield and stretching strengths of polymer filled with particulates with diameters over some tens of microns order [3-5]. Nicolais and Mashelker [6] have suggested that the major experimental evidence in the literature is

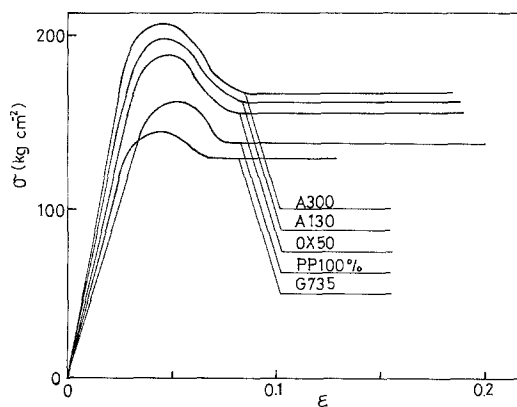


Figure 1 Typical stress-strain curves of PP composites filled with several kinds of filler measured at 30°C and a rate, 20 mm min<sup>-1</sup>.

consolidated in a relation of the type

$$\sigma = \sigma_0 - bV_f^n \quad (1)$$

where  $\sigma$  and  $\sigma_0$  are the strength of the composite and that of the non-filled matrix, respectively.  $V_f$  is the filler volume fraction.  $n$ , which is smaller than 1, is assigned to an appropriate value, and  $b$  is an empirical parameter for which only positive values are admissible. The last condition means that under any conditions, the strength of the composite cannot be greater than the strength of the non-filled one. This is not the case for the composites filled with ultrafine particles. Both the yield and necking stresses of the composites filled with 7, 16 and 40 nm fillers increase with filler content. At a given filler content, the stress decreases with filler size. Figs. 2a and b show yield stresses of composites filled with 20 wt % filler of 7 nm and of non-filled PP, as functions of temperature and logarithmic strain rate. These figures indicate that the yield stresses of both samples increase linearly with logarithmic strain rate. By shifting the lines in Figs. 2a and b along the horizontal axis, master curves, although not smooth but recognizable as single lines, are obtained as shown in Figs. 3a and b. The reference temperature was taken to be 60°C. Figs. 4a and b show the logarithmic plots of the shift factors,  $a_T$ , for the composition of these master curves as a function of reciprocal temperature. These figures show that the plot composes a curve comprising three straight lines with two breaks at 60 and 110°C. Thus, at each linear region,  $a_T$  has the Arrhenius type temperature dependence,

$$a_T = a_T^0 \exp(-\Delta H/RT) \quad (2)$$

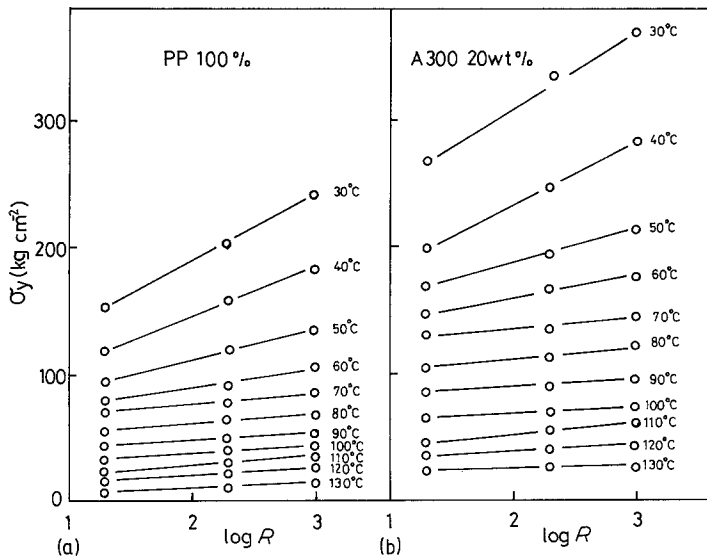


Figure 2 The yield stress of PP composites as function of temperature and strain rate. (a) PP 100%, and (b) 70 nm filler 20 wt %.

where  $a_T^0$  is the frequency factor,  $\Delta H$  the activation energy,  $R$  the gas constant and  $T$  absolute temperature. The activation energies increased with temperature, namely, 50, 78 and 160 kcal\* mol<sup>-1</sup> for the three regions. These values are independent of filler content and size. The breaks, found at the same temperature for filled and non-filled PP, are related with some kinds of transition of matrix PP. The temperature, 60°C, of the first transition is too high to be ascribed to the glass transition. We and many others have shown that some kind of transition in the crystalline region or the crystalline boundary of many crystalline polymers plays an important roll in the drawing property. For example, drawing properties of polyethylene change prominently in the  $\alpha_c$  dispersion region at about 70°C [7, 8]. For PP, Miller [9] and Flocke [10] found the existence of

a very broad dispersion peak at 60°C. Muus *et al.* [11] identified this dispersion with a disorder transition of the crystals. These studies suggests that the transition observed here at about 60°C is closely related with the PP crystalline phase. It has been reported that the compressibility of PP crystal becomes large at about 110 to 120°C in the direction of the *b*-axis [12]. The break found at about 110°C is probably related with another type of transition in the crystalline region. It is interesting to find in Figs. 3a and b that master curves for samples with 0 and 20 wt % filler content have a common feature in their shapes. We tried to synthesize a grand composite curve by shifting these master curves along the horizontal axis. Fig. 5 shows thus synthesized master-master curves for samples filled with 7 nm filler, in which a non-filled PP curve was taken as the reference.

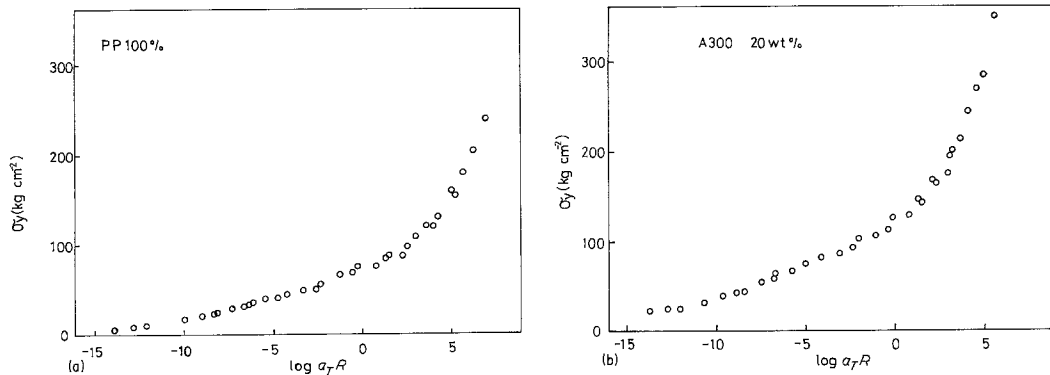


Figure 3 Master curves of the yield stress of PP composites against logarithmic strain rate. The curve was obtained by horizontal shift of curves in Fig. 2.

\*1 cal = 4.184 J.

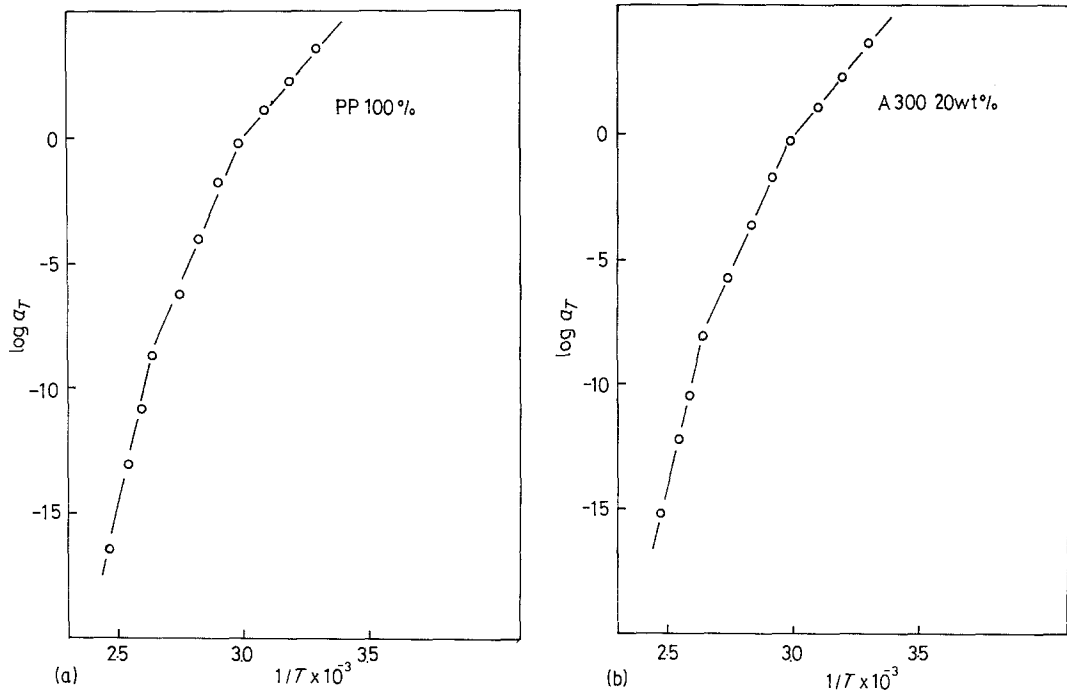


Figure 4 Plot of shift factors for compositions of master curves shown in Fig. 3 against reciprocal temperature.

Figs. 6 and 7 show the master–master curves for the composite filled with 16 and 40 nm fillers, respectively. The composition of single curves indicates that the effect of filler content on the yield stress can be converted into that of the strain rate. The logarithm of the shift factors,  $\log a_c$ , for the synthesis of these grand master curves are proportional to the square root of filler volume fraction,  $V_f^{1/2}$ , as shown in Fig. 8,

$$\log a_c = KV_f^{1/2} \quad (3)$$

$K$  values for 7, 16 and 40 nm fillers were found to be 11.5, 11.0 and 10.1, respectively. It was confirmed that Equation 3 holds for lead glass (6  $\mu\text{m}$ )–PP composites with  $K$  values of about 5 [13]. Many investigators have studied both experimentally and theoretically the filler effect on the viscosity of suspensions [14–16]. However, none

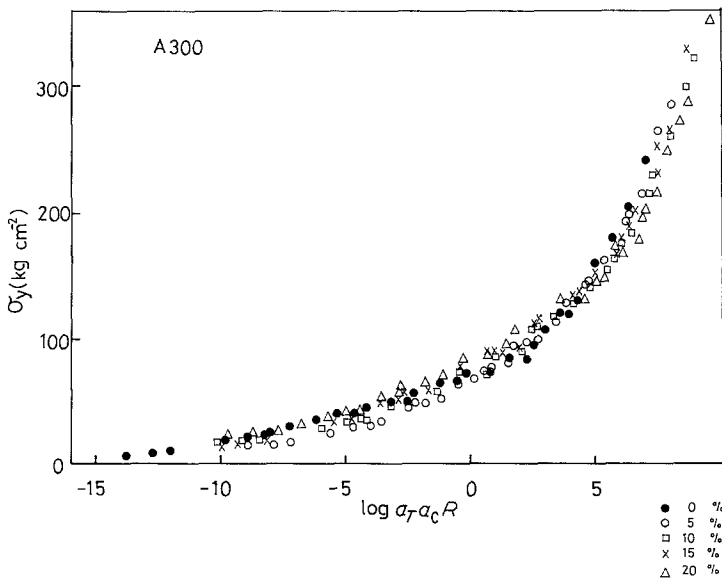


Figure 5 Master–master curve for the yield stress against logarithmic strain rate. The curve was obtained by horizontal shift of master curves shown in Fig. 3. The curve for unfilled sample was taken as reference. Filler size is 7 nm.

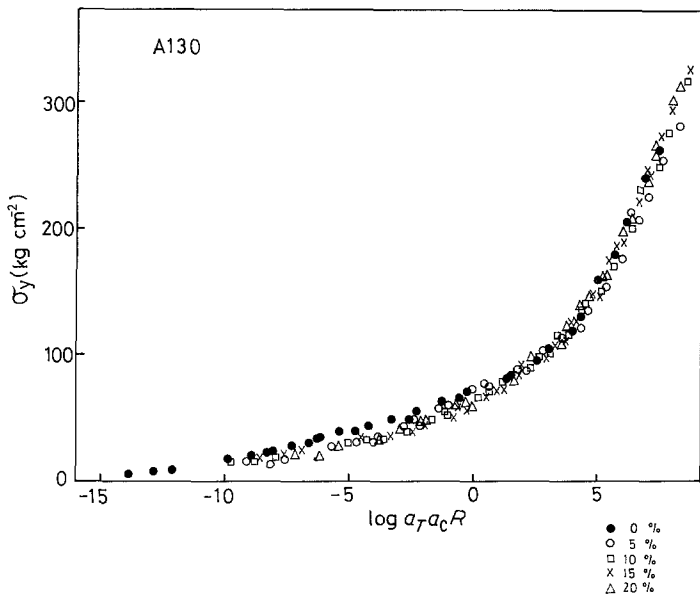


Figure 6 Master-master curve for PP composites filled with 16 nm filler.

of them have commented on the proportionality to the square root of filler volume fraction. Equation 3 shows that the reinforcement of ultrafine fillers becomes less effective with increasing filler content. These effects of filler size and volume fraction on the yield stress of composites are explained based on the dispersion strength theory [17]. Fig. 9 shows the effects of filler size on the shear yield stress,  $\tau_c$ , at a given stretching condition (draw temperature of 60°C, rate of strain 20 mm min<sup>-1</sup>) as a function of filler volume fraction. Values of  $\tau_c$  in Fig. 9 were calculated from the measured ones of tensile yield stress,  $\sigma_y$ , by assuming,  $\tau_c = 1/2\sigma_y$  [18]. Fig. 9

shows values of  $\tau_c$  of the samples filled with ultrafine fillers (7 and 40 nm) increase with filler content and with decreasing filler size. But the  $\tau_c$  value of the samples filled with larger filler (105 μm) decreases with filler content.

These fillers have reinforcing or anti-reinforcing effects depending on their sizes. In analogy to the dispersion strength theory, the  $\tau_c$  of a composite is given by

$$\tau_c = \tau'_m + A/\lambda \quad (4)$$

where  $\tau'_m$  is the shear yield stress of the matrix of the composite and is given by

$$\tau'_m = \tau_m(1 - V_f^{2/3}) \quad (5)$$

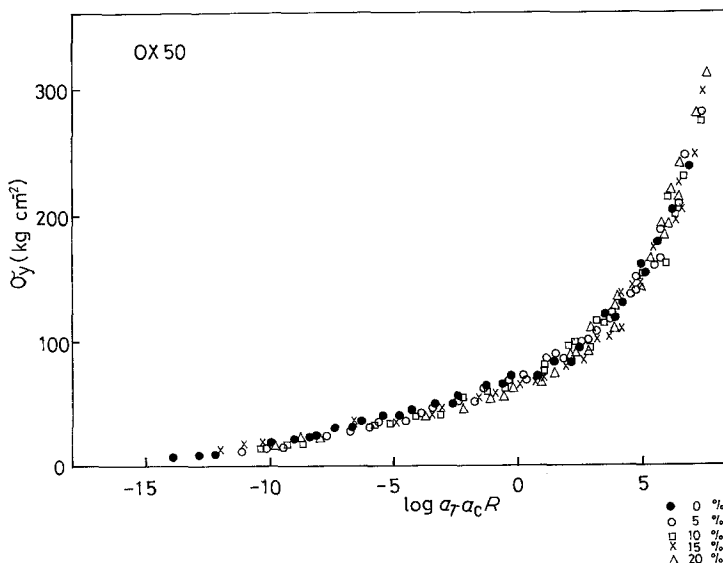


Figure 7 Master-master curve for PP composites filled with 40 nm filler.

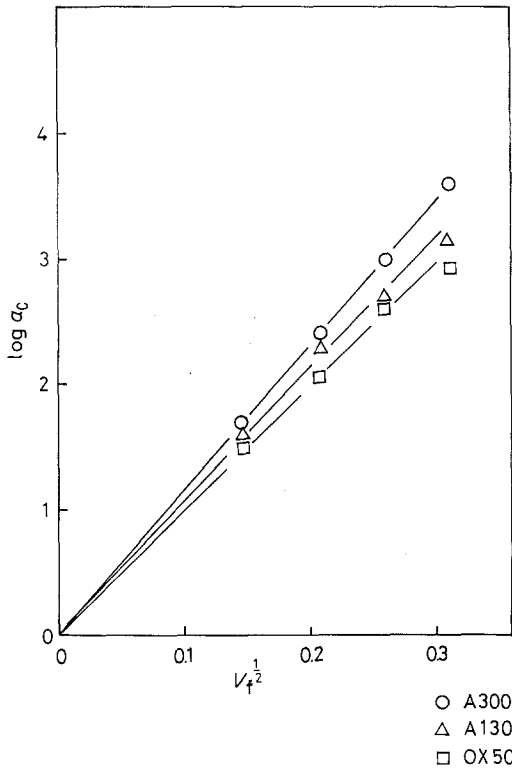


Figure 8 Plot of logarithm of shift factors,  $\log a_c$ , against square root of filler volume fraction.

$A$  is a constant determined by the matrix properties,

$$A = Gb \quad (6)$$

where  $G$  is the shear modulus and  $b$  is the Burger's

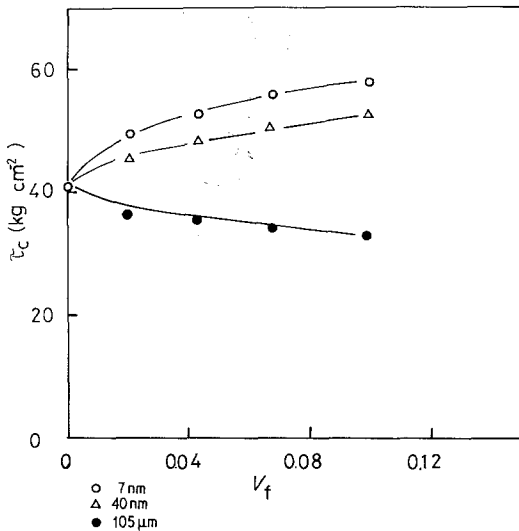


Figure 9 Shear yield stress of PP composites filled with 7, 40 nm and 105  $\mu\text{m}$  fillers against filler volume fraction. Lines are calculated values using Equation 9 with  $Gb/k(d)$  values given in Fig. 10.

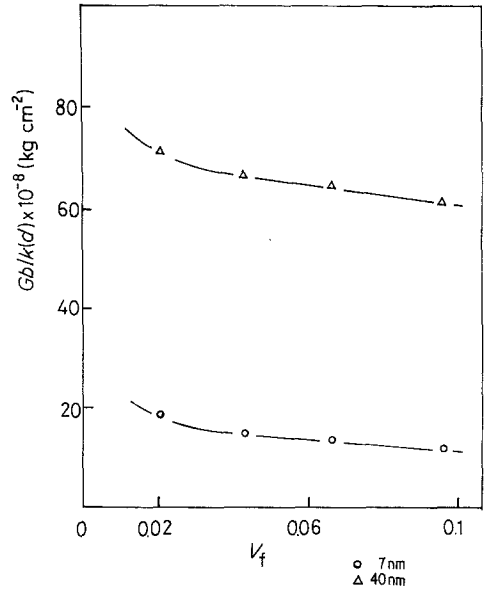


Figure 10 Values of  $Gb/k(d)$  of PP composites filled with 7 and 40 nm filler against filler volume fraction.

vector.  $\lambda$  is the interparticle spacing. For a unit cube containing a particle,  $\lambda$  is given by [19]

$$\lambda = [(4\pi/3V_f)^{1/3} - 2](d/2) \quad (7)$$

where  $d$  is the diameter of a particle. When particles aggregate,  $\lambda$  becomes large. Aggregation of particles modifies Equation 4 to

$$\tau_c = \tau'_m + A/(k(d)\lambda) \quad (8)$$

where  $k(d)$  is an aggregation parameter.

From Equations 6, 7 and 8, Equation 9 is obtained for  $\tau_c$  as a function of  $V_f$ :

$$\tau_c = \tau_m(1 - V_f^{2/3}) + Gb/\{k(d)[(4\pi/3V_f)^{1/3} - 2] \times (d/2)\} \quad (9)$$

By comparing Equation 9 and the yield stress shown in Fig. 9, the values of  $Gb/k(d)$  were determined. For the composites filled with 105  $\mu\text{m}$  filler, the second term of Equation 9 was negligibly small. Fig. 10, which shows a plot of the value of  $Gb/k(d)$  against filler volume fraction, shows slightly decreasing trends of the  $Gb/k(d)$  values. This means  $k(d)$  increases gradually with filler volume fraction, since  $Gb$  is constant for a given matrix. The separate lines for 7 and 40 nm fillers mean that at a given filler volume fraction, the extent of the aggregation of filler particles is larger with 7 nm filler than with 40 nm filler. Lines shown in Fig. 9 represent the values calculated by Equation 9 with  $Gb/k(d)$  values obtained above.

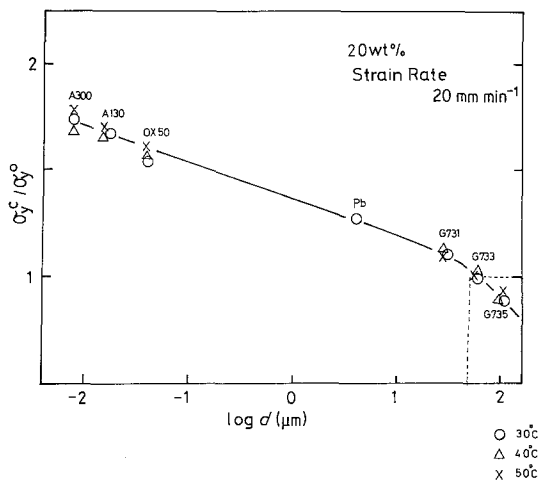


Figure 11 Relationship between  $\sigma_y^c/\sigma_y^0$  and logarithmic filler diameter in  $\mu\text{m}$ .  $\sigma_y^c$  and  $\sigma_y^0$  are tensile yield stresses of the composites and matrix PP, respectively.

Fig. 11 shows the plots  $\sigma_y^c/\sigma_y^0$  against the logarithm of filler diameter in  $\mu\text{m}$  where  $\sigma_y^0$  and  $\sigma_y^c$  are the tensile yield stresses of non-filled and filled PP, respectively. Obviously, the yield stress is higher than that of non-filled PP in the case of  $\sigma_y^c/\sigma_y^0 > 1$  and is lower in the case,  $\sigma_y^c/\sigma_y^0 < 1$ . The data were obtained under the following conditions: the strain rate was  $20 \text{ mm min}^{-1}$ , filler content 20 wt% and draw temperature 30, 40 and  $50^\circ \text{C}$ . A critical filler diameter giving  $\sigma_y^c/\sigma_y^0 = 1$  is about  $50 \mu\text{m}$ . Fig. 11 shows a prominent reduction of the  $\sigma_y^c/\sigma_y^0$  value in the region  $\sigma_y^c/\sigma_y^0 < 1$ , which may be an indication of the occurrence of the drastic stress concentration with fillers having large diameters.

#### 4. Conclusion

The drawing properties of PP composites filled with ultrafine particles have been discussed with regard to the yield stress, and the following conclusions have been obtained.

The yield stress is reducible by the three factors; drawing temperature, strain rate and filler content. The conversion laws are relatively simple.

1. The first shift factor,  $a_T$ , is Arrhenius type for temperature and for strain rate. The activation

energy is not dependent on the filler volume fraction and size.

2. The logarithm of the second shift factor,  $\log a_e$ , for strain rate and filler content is proportional to the square root of the filler volume fraction. The proportionality constant increases with decreasing filler size.

The dependence of the yield stress of PP composites on the filler volume fraction and size are reasonably explained by an equation based on the dispersion strength theory modified by incorporating an aggregation parameter.

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