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Estimation of flocculation structure in filled polymer composites by dynamic rheological measurements

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Abstract The frequency and concentration dependences of the storage modulus (G') for carbon black and short-carbon-fiber-filled polymer composites were investigated by means of dynamic rheological measurements. It was found that G' at low frequencies and amplitudes could be used as a sensitive experimental parameter for detecting the flocculation structure of the ultra-fine-particle-filled polymer composites. Correlation of electrical resistivity of the composites to the relative storage modulus, $G'_r(=G'_c/G'_p)$, revealed that the three-dimensional interparticle networks start to construct through the matrix when G'_r increases to 7 regardless of the composite systems. Quantitative calculations in order to determine the flocculation structure were carried out by means of the modified Kerner equation. A plot of the calculated value, defined as the floc index A, dependence of electrical resistivity for various systems was found to be a universal curve. Accordingly, we suggest that A might universally correspond to the flocculation structure of the filler, which is independent of the nature of the filler, the molecular weight, the chemical composition of the polymer and the temperature at which the measurement is made. This method is particularly effective for estimating the flocculation structure of ultra-fine-particle-filled polymer composites no matter whether the filler is conductive or not.

Key words Dispersion · Flocculation · Rheology · Carbon black · Filled polymer composites

Introduction

It is well known that the morphology and properties of filled polymer composites are greatly influenced by the state of filler dispersion [1]. Usually, scanning electron microscopy (SEM), transmission electron microscopy (TEM), as well as optical microscopy are used to characterize the distribution of filler particle size and interparticle distance in the matrix. However, independent means of assessing the dispersion are unsatisfactory for ultra-fine-particle-filled composites (such as carbon black, silica gel and recently developed TiO_2, Al_2O_3, and $CaCO_3$, etc. fine powders). Due to the small size and the high specific surface, these fillers are favorable to self-aggregation and easily form three-dimensional networks in a polymer matrix. In other words, they are apt to form a three-dimensional flocculation structure [2]. SEM and TEM observations only reflect the dispersion localized within a two-dimensional microscopic site and thereby are easily misinterpreted [3]. Even for the quantitative information obtained by digital image analysis [4, 5] and small-angle X-ray scattering measurements [6–8], the data are still ambiguous with regard to correlating the information to the real dispersion space and its contribution to the target properties [9, 10].

In this report, we try to evaluate the filler dispersion by means of dynamic rheological measurements. Although it is not correlated directly with the distribution of interparticle distance, the rheological properties of highly filled polymer composites may provide essential information about the flocculation structure of the filler, which corresponds not only to the dispersing state of the filler but also to the physical properties of composites, such as mechanical strength, electrical resistivity, heat conductivity, etc. [11]. Much work has been performed in order to elucidate the effects of filler geometry and structure on the rheological properties. Early in the 1960s, Payne [12] found that the three-dimensional structure networks constructed by the aggregation of carbon black substantially alter the dynamic viscoelastic properties of rubber mixtures. A semiquantitative theory based on Payne's results was latter developed by Kraus [13] concerning the contribution of carbon black specific surface area and structure, as well as concentration, to the dynamic storage and the loss modulus. Nielsen [14] demonstrated that the dynamical mechanical properties of polymer composites incorporating various fillers including spheres with permanent aggregates ranging from doublets and triplets to clusters and fibers with different aspect ratios could be well described by a modified Kerner equation.

Recently, rheological experiments [15–17] have shown that polymer compounds filled with high concentrations of ultrafine particles always exhibit a well-defined yield stress, i.e., a stress below which there is no flow. It was reported that the yield stress only depends on the concentration and the nature of the filler but is independent of the type of polymer and the temperature at which the measurement is made [16–20]. The existence of yield stress in its physical meaning is correlated with the density and strength of a structure formed by the interaction between the particles of the filler. This characteristic provides an important clue that the yield stress might be used as an experimental parameter sensitively related to the flocculation structure of the filler and is less influenced by the behavior of the matrix and the measurement conditions.

Two types of carbon black with different characteristics and a short carbon fiber were used as model fillers. They were mixed with various polymer matrices including high-density polyethylene (HDPE), polypropylene (PP), and poly(methyl methacrylate) (PMMA). These composites were interesting not only because of the presence of the feature behavior (i.e., the yield behavior) in the rheological properties but also due to their conductivity. Generally, the electrical resistivity of such composites decreases with an increase in the filler concentration. A drastic reduction in the resistivity can be observed at the percolation threshold when the three-dimensional conductive networks are formed in the polymer matrix [21]. Since the resistivity is directly related to the density of the conductive networks, it was regarded as a reference to inspect the results evaluated from the dynamical rheological measurements.

Experimental

Sample preparation

Six matrices of the three kinds of polymers having the characteristics listed in Table 1 and three kinds of carbon fillers having the characteristics listed in Table 2 were used in this study. Each polymer was mixed with a certain amount of the carbon particle in a two roll mill for 10 min at the temperatures listed in Table 1. Prior to mixing, both the polymers and the carbon particles were dried at 80 °C for 24 h under vacuum. Films with thickness of about 1.0 mm were compression-molded from the polymer–carbon mixtures at the temperatures listed in Table 1 for 10 min under a pressure of 20 MPa, followed by quenching in cold water.

Dynamic rheological measurements

The dynamic storage moduli of filled and pure polymers were determined with a universal dynamic spectrometer (Physica UDS200, Physica Messtechnik). A cone-and-plate fixture, with a cone angle of 4° and a diameter of 25 mm, was used at angular frequencies from 0.1 to 100 rad/s. In the case of low viscosity samples, another type of cone-and-plate fixture, with a cone angle of 2° and a diameter of 50 mm, was used in order to obtain more data. For all the experiments, the strain amplitude was maintained at 0.5%. The measurement temperature is also listed in Table 1.

Electrical resistivity measurements

The electrical resistivity was measured in the thickness direction of the composite films. Silver paste was used to ensure good contact of the sample surface with the copper electrodes. A Keithley 487 picoammeter equipped with a direct current voltage source was employed for the resistivity measurements. Prior to the measurements, all the samples were kept in a vacuum at 20 °C for 24 h. The resistivity was measured at room temperature after 2 min in order to obtain the stationary value. Due to no observable deviation from the four-terminal measurements, the data in this work were

Table 1 Characteristics of matrices used: high-density polyethylene (*HDPE*), polypropylene (*pp*), poly(methyl methacrylate) (*PMMA*)

Matrices	Melt flow rate[a] (g/10 min)	Density (g/cm^3)	Temperature[b] (°C)
HDPE1	20	0.95	190
HDPE2	12	0.95	190
HDPE3	0.05	0.95	190
PP1	25	0.90	190
PP2	0.3	0.90	190
PMMA		1.15	220

[a] Data obtained from company
[b] Temperature for mixing, pressing and measurement

Table 2 Characteristics of fillers used

Fillers	Diameter (nm)	N_2 surface area (m^2/g)	Density (g/cm^3)
Ketjenblack	30	1000	1.86
Seast 300	27	84	1.86
Vapor-grown carbon fiber	200	11	2.0

measured using a two-terminal technique under direct current conditions.

Results

Yield behavior

Figure 1a–c shows typical plots of the angular frequency dependence of the storage modulus, G' for HDPE2, PP2, and PMMA, respectively, containing various contents of carbon black, including Ketjenblack (KB) and Seast 300, at the temperatures indicated. As shown in this figure, G' increases with increasing KB content and frequency. At high loading, G' begins to level off and exhibits a plateau in the low-frequency range. A similar tendency was observed for carbon-black-filled HDPE1, HDPE3, PP1, and PMMA composites and this was in agreement with previous results [16–20]. The appearance of a plateau at low frequencies is undoubtedly due to the presence of fillers in the system and is assumed to be the result of forming the three-dimensional carbon black network structure.

The yield behavior is also observed in vapor-grown carbon-fiber (VGCF)-filled HDPE2 and PMMA melts, as shown in Fig. 2a and b, respectively. These data are important because little has been reported about the yield behavior of fiber-filled polymer composites [17]. The VGCF used is a newly developed vapor-grown short carbon fiber with a diameter of about 0.2 μm and an aspect ratio of about 50. Compared with traditional carbon fiber (diameter about 10 μm), the extremely small carbon fibers might result in strong fiber–fiber interactions and thus form the strong interparticle networks [22–25].

The formation of interparticle networks might be also detected by the frequency and concentration dependences of the loss angle, δ, where $\tan\delta = G''/G'$. A typical plot is shown in Fig. 3 for HDPE2/KB composites. It is observed that when the concentration of filler is higher than a certain value via $\phi^* = 2$phr, a peak angle is observed. The magnitude of the peak angle decreases with an increase in the filler concentration, whereas the relevant peak frequency increases with the filler concentration as indicated by the arrows in Fig. 3. The existence of the peak angle is a result of the breaking down and the re-formation of carbon black networks, according to Payne's explanation [11], and, therefore, it is related to the existence of interparticle networks.

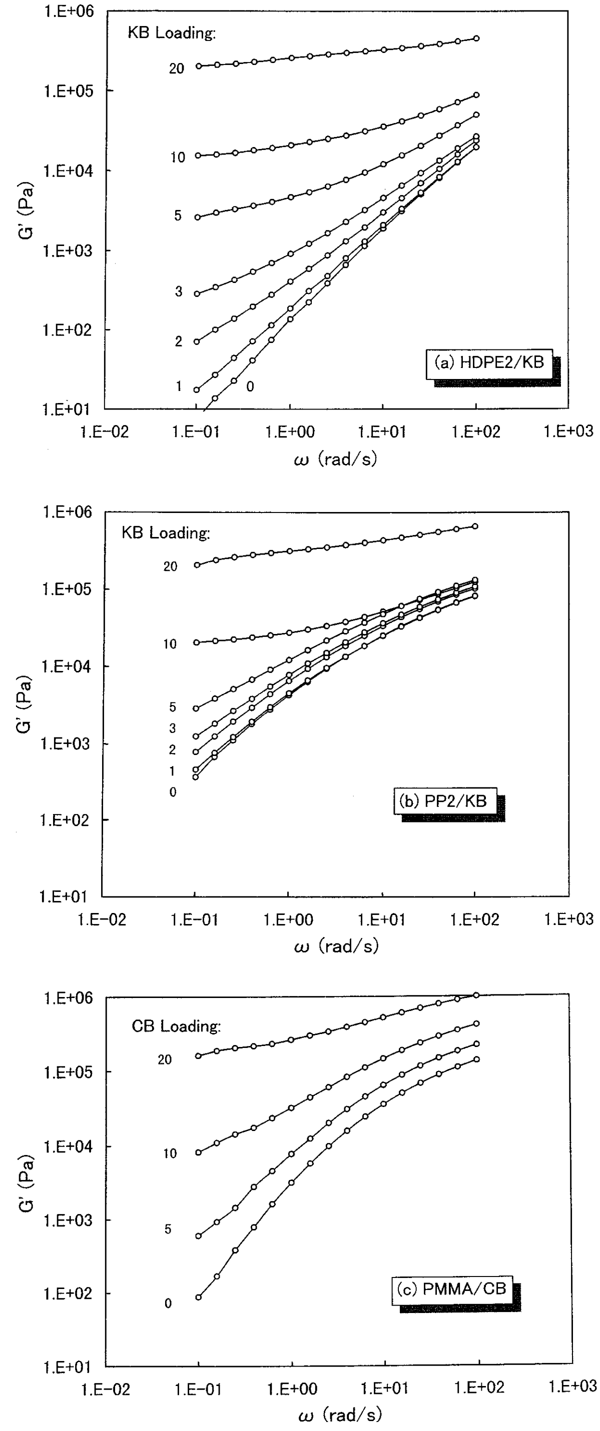

Fig. 1 Frequency and concentration dependences of the storage modulus, G', for **a** high-density polyethylene (*HDPE*)2/Ketjenblack (*KB*) at 190 °C, **b** polypropylene (*PP*)2/KB at 190 °C and **c** polymethyl methacrylate (*PMMA*)/Seast 300 (*CB*) at 190 °C

Concentration dependence

Figure 4 shows the dependence of KB concentration on the storage modulus at a frequency of 0.1 rad/s in various polymer matrices. In this figure, samples, which exhibit the peak angle in the plot of the frequency dependence of the loss angle, are marked with filled symbols. It is observed that G' increases greatly with

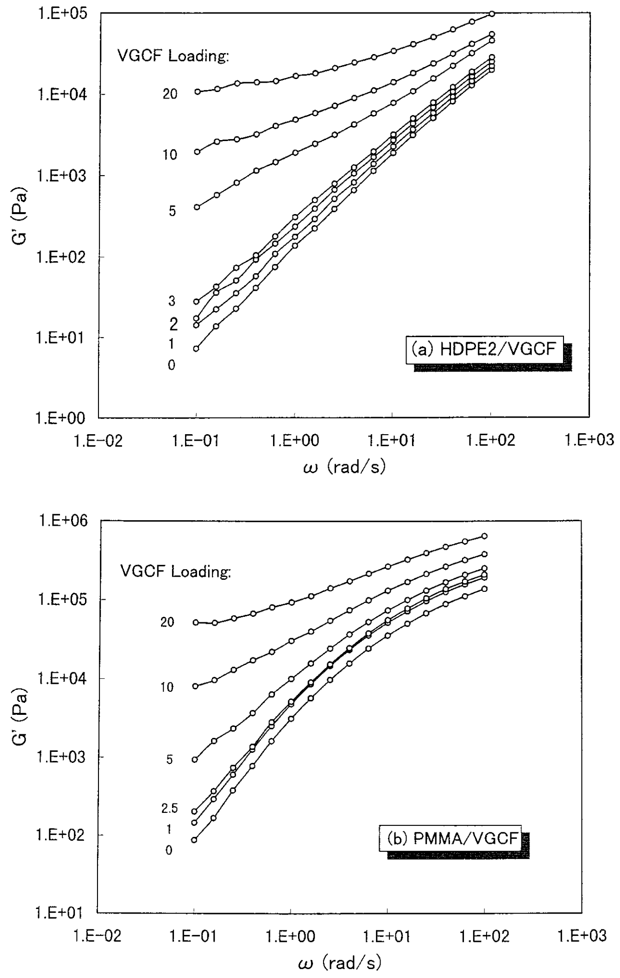

Fig. 2 Frequency and concentration dependences of G' for **a** HDPE1/vapor-grown carbon fibers (*VGCF*) at 190 °C and **b** PMMA/VGCF at 220 °C

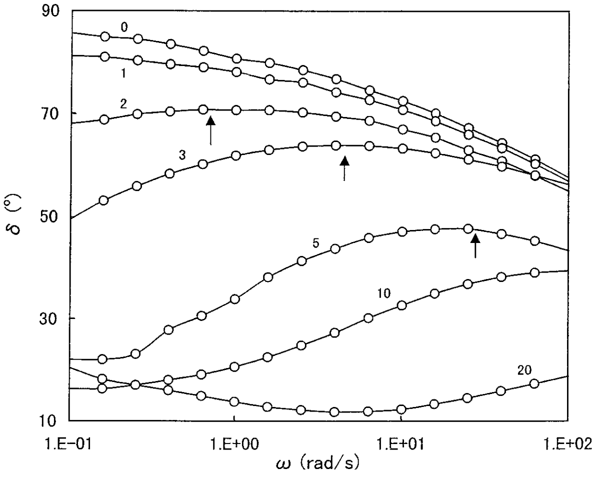

Fig. 3 Loss angle versus frequency of HDPE2/KB composites at 190 °C

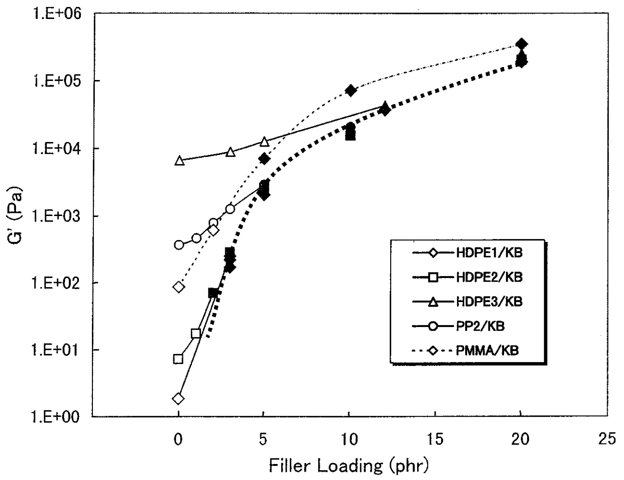

Fig. 4 Concentration dependence of G' at a frequency of 0.1 rad/s for various systems

filler concentration. Meanwhile, all the filled data points in Fig. 4 are found to be located on one curve, except for the PMMA composites. These results demonstrate that G' is very sensitive to the filler concentration and it is less dependent on the polymer matrix, especially for polyolefin composites. The higher storage modulus for PMMA composites might be ascribed to the effect of the matrix; this will be discussed later.

In order to normalize the effect of the polymer matrix on the experimental value, the ratio of the storage modulus of the composites, G'_c, to the storage modulus of the neat polymer, G'_p, at a frequency of 0.1 rad/s is expressed as a function of the filler concentration (Fig. 5).

It should be pointed out that both the viscosity and the loss modulus also depend on the concentration of filler with a similar tendency; however, they were found to be less prone compared with the storage modulus and, therefore, we only consider the results of the storage modulus.

Electrical resistivity correlation

Electrical conductivity is of great interest in correlation with dynamic rheological properties since both phenomena involve the carbon particle network. The network structure formed by carbon particles transmits force under a stress field and it also conducts electrons under an electrical field. The high density of the network usually results in both a high storage modulus and high electrical conductivity.

The electrical resistivity of various filled polymer composites is shown as a function of $G'_r(=G'_c/G'_p)$ in Fig. 6. The melt flow rate of the polymer matrix, the type of filler, and the percolation threshold (Φ_c) of the related composites are also listed in the figure. It is observed that

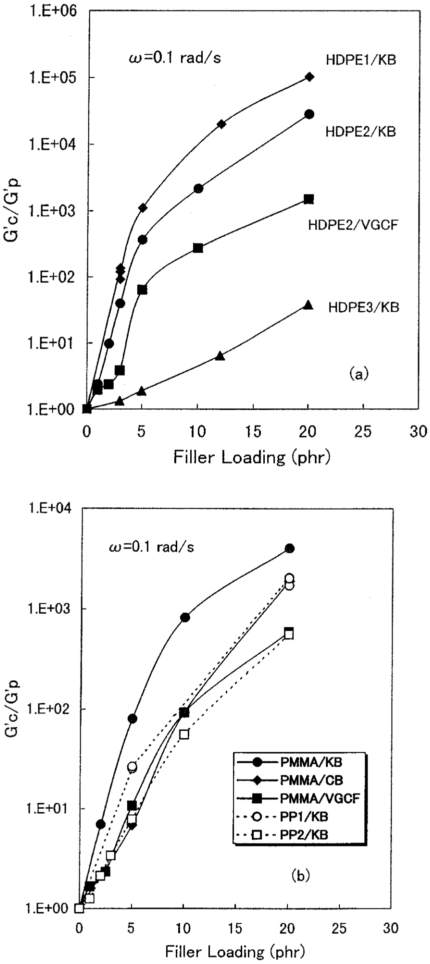

Fig. 5a, b Concentration dependence of the relative storage modulus, G'_c/G'_p, at a frequency of 0.1 rad/s for various systems

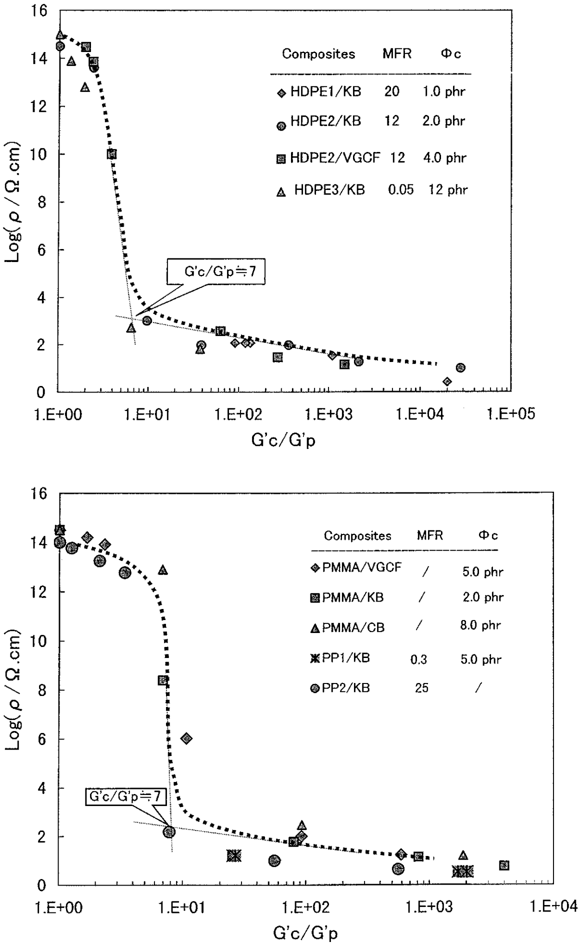

Fig. 6 Correlation of G'_c/G'_p with the electrical resistivity for **a** HDPE/carbon particle systems and **b** filled PP and PMMA composite systems. The inset shows the melt flow rates (*MFR*) and the percolation thresholds (Φ_c) of the composite systems

the relative storage moduli, G'_r, obtained at a frequency of 0.1 rad/s and a strain amplitude of 0.5% are well correlated to the electrical resistivity for the various composites. The electrical resistivity decreases with an increase in G'_r, slightly at first and then abruptly when a critical range of G'_r is reached, i.e., an insulator-to-conductor transition takes place. A further increase in G'_r is found to only cause a slight decrease in the resistivity, suggesting that G'_r is more sensitive to the density and the strength of the interparticle networks compared with the electrical resistivity at a high loading of filler. Traditionally, the percolation threshold is defined at a filler concentration where the first conductive network is formed [26]; however, we observed that the critical filler concentration, ϕ^*, which was detected by the dynamic rheological measurements (according to the plot of the frequency dependence of the loss angle, see Fig. 3) always appeared near the higher end of the percolation range. This may be due to the low density of interparticle networks at the percolation threshold and it is difficult to identify the contribution of the interparticle networks from the whole storage modulus of the composites. Accordingly, we designate the percolation threshold to another critical point – the higher end of the percolation range where the electrical resistivity becomes saturated.

It is interesting to find in Fig. 6 that G'_r at the percolation threshold is close to $G'_c/G'_p = 7$ for various systems though their percolation thresholds vary greatly from 1 to 12 phr. This means that the conductive network starts to construct through the matrix when the storage modulus of the composites increases up to about 7 times that of the pure matrix, regardless of the various systems.

Quantitative estimation of flocculation structure

The majority of the theories describing the concentration dependence of rheological properties of diluted and moderately concentrated filled systems are based on the hydrodynamic approach developed by Einstein. One quite useful equation was proposed by Kerner and was generalized by Nielsen [14]:

$$\frac{G'_\mathrm{c}}{G'_\mathrm{p}} = \frac{1 + AB\phi_\mathrm{f}}{1 - B\psi\phi_\mathrm{f}} \;, \tag{1}$$

where

$$B = \left(\frac{G'_\mathrm{f}}{G'_\mathrm{p}} - 1\right) \Big/ \left(\frac{G'_\mathrm{f}}{G'_\mathrm{p}} + A\right)$$

$$\psi = 1 + \left(\frac{1 - \phi_\mathrm{m}}{\phi_\mathrm{m}^2}\right)\phi_\mathrm{f} \;.$$

Here G'_c, G'_p, and G'_f are the storage moduli of the composite, the polymer matrix, and the filler, respectively. ϕ_f is the volume fraction of the filler and ϕ_m is the maximum packing fraction of the filler. The constant A was reported to be a coefficient sensitive to the aggregate number and the geometry of the filler.

Usually, like many other expressions, Eq. (1) is not suitable to describe the relative modulus when the concentration is higher than the critical value. This is because at the critical point, the carbon particles are coagulated to form the networks and the suspension experiences a transition from liquidlike behavior to solidlike behavior, as marked by the appearance of a yield stress. Though such kinds of transition might be better described by percolation theory, as suggested by some researchers [27, 28], both in its concept and data treatments, one may lose the information about the flocculation structure of the filler without the aid of SEM and TEM observations [28]. As a matter of fact, the process of agglomeration of carbon particles may be traced by the modified Kerner equation if the parameter A is regarded as a variant.

The concentration dependence of A and the electrical resistivity for HDPE2/KB composites are depicted in Fig. 7. Here, A was calculated from Eq. (1) assuming $\phi_\mathrm{m} = 0.637$ and $B = 1$. As shown in the figure, the increase in A with concentration corresponds well to the decrease in electrical resistivity, implying that A is sensitive to the density of the interparticle conductive networks. Since A in its physical meaning is related to the aggregate number and the geometry of the filler, the great increase at the percolation threshold can be regarded as an increase in the effective contact number of carbon particles that take part in the conductive networks; therefore, it can be used to estimate the flocculation structure of the filler. For convenience, we define the coefficient A as the floc index, a term with a similar meaning to the degree of agglomeration.

All the experimental and calculated results are listed in Table 3. A plot of the electrical resistivity as a function of A for the various composite systems studied in this work is shown in Fig. 8. It is found that the percolation threshold of these systems takes place at one floc index A near to 400. All the data plotted in Fig. 8 seem to form a single curve despite representing various systems. These results strongly suggest that A calculated from G'_r reflects a general state of the flocculation structure of the filler which is independent of the nature of the carbon particles, the molecular weight, the chemical composition of polymer, and the temperature at which the measurement is made.

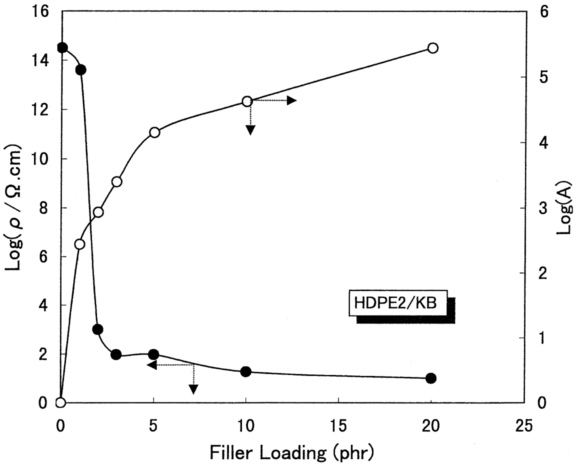

Fig. 7 Concentration dependence of the floc index, A, and the electrical resistivity for HDPE2/KB composites

Discussion

The yield behavior has been reported to be the most typical feature of rheological properties of highly filled polymer composites [17]. The presence of a plateau at low frequencies as shown in Figs. 1–2 confirmed this argument. By means of correlation of the electrical resistivity to the relative modulus, G'_r, it was verified that the yield behavior arises from the formation of three-dimensional interparticle networks through the matrix.

It should be pointed out that the storage modulus at a frequency of 0.1 rad/s is certainly different from the yield stress determined from shear stress–shear rate curve ("stationary" method) and from the exact value determined from the "dynamic" approach. The latter approach requires a sufficiently low frequency where the storage modulus is completely leveling off; however, this would take a long time. The self-agglomeration of carbon particles during measurements at a high temperature would develop the additional networks [29, 30], resulting in a deviation from the as-produced sample; therefore, the lowest angular frequency in this work was limited to 0.1 rad/s so as to reduce the measuring time.

Generally, the contribution of filler to the storage modulus can be analyzed in terms of three effects: a

Table 3 Experimental and calculated data: fillers Ketjenblack (*KB*), Seast 300 (*CB*), vapor-grown carbon fibers (*VGCF*)

Mixture	Cont. (phr)	G'_c (Pa)	G'_c/G'_p	Log(ρ)	Log(A)
HDPE2/KB	0	7.22	1	14.5	0
Melt flow rate = 12	1	17.3	2.396122	13.6	2.435104
	2	70.3	9.736842	5.41	2.931561
	3	283	39.19668	1.97	3.396427
	5	2610	361.4958	1.97	4.149441
	10	15500	2146.814	1.27	4.622405
	20	204000	28254.85	1	5.43814
HDPE1/KB	0	1.85	1		0
Melt flow rate = 20	3	249.6	134.9189	2.06	3.94137
	3	169.5	91.62162	2.06	3.771736
	3	219.4	118.5946	2.06	3.884908
	5	2042	1103.642	1.53	4.634996
	12	37070	20037.84	0.42	5.513058
	20	190400	102918.9	−0.15	5.999554
HDPE3/KB	0	6603	1	15	0
Melt flow rate = 0.05	3	8853	1.340754	13.9	1.326757
	5	12590	1.906709	12.8	1.537345
	12	42970	6.507648	2.72	2.207067
	20	250400	37.92216	1.81	2.553036
HDPE2/VGCF	1	14.1	1.952909	14.47	2.300169
Melt flow rate = 12	2	17.1	2.368421	13.85	2.15541
	3	27.8	3.850416	10	2.298811
	5	457.1	63.30861	2.56	3.418501
	10	1970	272.8532	1.46	3.756724
	20	10800	1495.845	1.16	4.193627
PP2/KB	0	368	1	14	0
Melt flow rate = 0.3	1	461	1.252717	13.77	1.709464
	2	780	2.119565	13.24	2.059451
	3	1250	3.396739	6.37	2.215016
	5	2890	7.853261	2.18	2.450406
	10	20600	55.97826	1	3.054194
	20	207000	562.5	0.64	3.760177
PP1/KB	0	102.9	1		0
Melt flow rate = 25	5	2614	25.4033	1.21	3.003088
	5	2741	26.6375	1.21	3.034536
	20	211000	2021.38	0.53	4.322543
	20	177010	1720.21	0.53	4.246214
	20	208000	1049.563	0.53	4.316321
PMMA/KB	0	87	1	14.5	0
	2	606	6.965517	8.39	2.682463
	5	7000	80.45977	1.77	3.409458
	10	71500	821.8391	1.15	4.121637
	20	350000	4022.989	0.76	4.420659
PMMA/VGCF	1	145	1.666667	14.2	2.060447
	2.5	203	2.333333	13.92	1.962483
	5	936	10.75862	6.02	2.529124
	10	8080	92.87356	2	3.20202
	20	51600	593.1034	1.24	3.706972
PMMA/CB	5	597	6.862069	14	2.275175
	10	8120	93.33333	2.46	3.172465
	20	165000	1896.552	1.2	4.180167

hydrodynamic effect (G'_h), a viscoelastic (G'_p) effect, and the interparticle network (G'_n) [11],

$$G'_c = G'_h + G'_p + G'_n \qquad (2)$$

Here, the hydrodynamic term contains the effect of the filler geometry and filler–polymer interactions. The viscoelastic term refers to the frequency dependence of the matrix itself. According to Eq. (2), G'_c is dominated by G'_n only when G'_n is much larger than ($G'_h + G'_p$). This is the reason why the yield behavior always appears at low frequencies and high concentrations of ultrafine filler (the ultrafine fillers are necessary because of their strong particle–particle interactions). Otherwise, the G'_h and G'_p items may influence the results. The higher

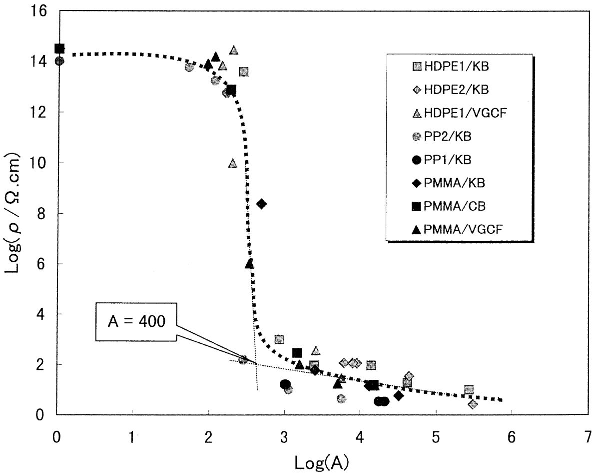

Fig. 8 Electrical resistivity versus A for various systems

storage modulus of PMMA/KB composites compared with polyolefin/KB in Fig. 4 might be ascribed to two reasons: one is that a frequency of 0.1 rad/s is not low enough to obtain the exact yield value, as mentioned previously. The other is the special interaction between KB and PMMA, which may weaken the strength of the particle–particle interactions.

Equation (2) can be changed into the following form:

$$\frac{G'_c}{G'_p} = \frac{G'_p + G'_h}{G'_p} + \frac{G'_n}{G'_p} \quad . \tag{3}$$

G'_c/G'_p might be estimated by Mooney's equation [14] if one neglects the effect of interparticle networks. In this case, the relative storage modulus was found to be less than 3 even if the carbon particle loading is up to 20 phr and the aggregate number is infinitively large [14]. The higher relative storage modulus should be ascribed to the effect of interparticle networks. Our result that percolation takes place at $G'_c/G'_p = 7$ for various systems is therefore reasonable.

A theory of Kraus [13] describing dynamic mechanical properties of filled rubbers in terms of an interparticle network states that the increase in the number of contacts per unit volume should be the main contribution to the augmentation of the storage modulus. Accordingly, the increase in the floc index, A, evaluated from the storage modulus can be interpreted as an increase in the contact number. Our findings that the percolation takes place near $A = 400$ for various composites may originate from the statistical results. According to percolation theory [31] and experimental verification [32], the percolation threshold generally takes place when the average contact number of each particle in the three-dimensional network equals a universal value, 1.5, regardless of the composite systems. Computer simulation is needed to further understand the critical value of A.

Discussions about the physical meaning of A can also be extended to composites filled with very fine fibers. In fact, highly structured carbon black (such as KB) aggregates have a nodular-like individual shape with an aspect ratio of more than 20 [33]. The VGCF filaments can be regarded as the aggregated particles. Since A correlates directly to the contact number, it is easy to understand in this way that the higher value of A results from the higher aspect ratio of the filler. For VGCF-filled composites with concentrations lower than their percolation thresholds, we observed that A was near to 100 (log A = 2.0) both in HDPE and in PMMA matrices and was less related to the concentration (see Table 3). This value was found to correspond to the geometry of VGCF (aspect ratio about 50) [14].

Some caution should be emphasized in view of the different mechanisms of the conductivity versus the dynamic modulus. Conductivity is high within each aggregate, so the resistivity is essentially determined by the nature of the surface and by the barrier between aggregates [26]. Conduction between two aggregates by electron tunneling does not require "contact" between two aggregates, but only close proximity of the order of a few nanometers [26]. Thus, while the "through-going path" responsible for the conductivity of the specimen may be equivalent to the network which contributed to the augmentation of the dynamic modulus, the gap width between the aggregates may have a quantitatively different effect on the tunneling versus interaggregate attractive force. Because of different interfacial structures between filler and matrix and/or barrier between fillers, we observed in Fig. 8 that the resistivity was different between systems though their floc index might be the same. Another possibility for the fluctuation of the resistivity is the different states of the matrix during the measurements, i.e., in the melting state for rheological measurements and in the solid state for resistivity tests. Since the crystallization of the matrix often reduces the resistivity of composites, a different crystallinity of the matrix might also lead to a variation of the room-temperature resistivity.

More precise measurements by in situ detection of the electrical resistivity during the measurement of the storage modulus are under consideration.

Conclusions

1. The storage modulus at low frequencies and strains can be used as a sensitive experimental parameter reflecting the flocculation structure of the ultra-fine-particle-filled polymer composites. Correlation of electrical resistivity of the composites to the relative storage modulus, G'_r, revealed that the three-dimensional interparticle networks start to construct through the matrix

when G'_r of the composites increases to 7 regardless of the type of system.

2. Based on the fact that the augmentation of the storage modulus is responsible for the contact number of the filler, the flocculation structure was estimated by means of the modified Kerner equation. The plot of the floc index dependence of the electrical resistivity was found to be a universal curve irrespective of the composite systems studied. It was suggested that the flocculation structure estimated by dynamic rheological measurements is a universal value, which is independent of the nature of the filler, the molecular weight, the chemical composition of polymer, and the temperature at which the measurement is made.

3. Since the result of dynamic rheological measurements is well correlated to interparticle networks, the estimation of the flocculation structure of filled polymer composites is supposed to be more attractive for nonconductive ultrafine particles, such as TiO_2, Al_2O_3, $CaCO_3$, etc.

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