Polypropylene–Carbon Black Interaction in Conductive Composites

ZORAN S. PETROVIĆ,* BRATISLAV MARTINOVIĆ,[1] VLADIMIR DIVJAKOVIĆ,[2] and JAROSLAVA BUDINSKI-SIMENDIĆ[1]

[1]Faculty of Technology, University of Novi Sad, Novi Sad, Yugoslavia; and
[2]Institute of Physics, University of Novi Sad, Novi Sad, Yugoslavia

SYNOPSIS

Interaction between polypropylene matrix and carbon black was examined by measuring physical, mechanical, and electrical properties. It has been shown that presence of carbon black influences the morphology and crystallinity of the matrix. Strong interaction was observed directly by electron microscopy and indirectly by the rise of the modulus of elasticity. The effect of carbon black on strength and physical properties of the composites is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Preparation of electroconductive composites based on a polymer and carbon black involves mixing and dispersion of the filler in the polymer matrix. Electroconductivity and other physical properties are dependent both on the properties of each component and the degree of dispersion, but also on the interaction between components.[1-10] In this work, the results of the study of the interaction between isotactic polypropylene (PP) and very fine particle, electroconductive carbon black and its effect on properties is discussed. The influence of concentration on electrical and mechanical properties of the compounds was modelled using various approaches in order to obtain at least qualitative estimation of the interaction component. In the absence of interaction between the components, many properties of a mixture satisfy the linear mixture equation (LME), stating that property of a composite, P_c, is a linear combination of properties of the matrix and filler, P_m and P_f, and their volume fractions, ϕ_m and ϕ_f, that is,

$$P_c = P_m\phi_m + P_f\phi_f. \tag{1}$$

However, the property/mixture composition relationship may also be described by other, very different relationships. Carbon black is added to PP in order to obtain a certain degree of conductivity that is required for specific applications. The conductivity of the compound depends not only on the carbon black concentration but also on the morphology of the mixture, which depends on the mixing conditions. In this work, mixing conditions were kept constant and the effect of the concentration of carbon black on density, melt index, thermal expansion, crystallization of the matrix, static and dynamic mechanical properties as well as conductivity of the mixtures was examined.

EXPERIMENTAL

Materials

Polypropylene "Hipolen MA-3" produced by Hipol-Odzaci, Yugoslavia, was used as the matrix. It is characterized by melt flow rate (MFR) = 11 g/10 min, M_w = 284,000, and M_n = 39,400. Ketjen Black EC is a carbon black produced by Akzo. Its iodine number is 950 mg/g, its specific area according to the BET method is 1000 m²/g, and the DBP number is 340 mL/g.

Methods

The components were compounded in a Haake Rheomix laboratory mixer at 180°C for 5 min. The

Table I   Designation of PP/Carbon Black Samples

Designation	I	II	III	IV	V	VI
Wt. conc. of carbon black (%)	5	10	15	20	25	30
Volume fraction of carbon black	0.026	0.053	0.081	0.111	0.143	0.176

mixture was then compression molded for 2 min at 230°C, then cooled under pressure of 120 atm to room temperature in 2 min to obtain plates either 0.5-mm or 3-mm thick. The plates were used for preparation of the test specimens. Six samples were prepared with varying carbon black concentration from 5 to 30 wt %. A description of samples is given in the Table I. Samples with 20 wt %, 25 wt %, and 30 wt % of carbon black were difficult to mix since the resultant compound was in the form of a powder that would not flow. However, it could be compression molded under the same conditions as the other samples.

Density was measured by immersion in alcohol, using a Mohr balance. This method gives precision to two significant figures, which was considered satisfactory for our purposes.

The linear coefficient of expansion was measured from the slope of thermal expansion curves, using a Du Pont Thermomechanical Analyzer, model 981. Measurements were carried out at the heating rate of 5°C, from −60° to 100°C, using sample thickness of 3 mm. Dynamic mechanical tests were carried out using a Polymer Laboratories DMTA apparatus at the heating rate of 2°C and frequencies of 1 Hz and 10 Hz. Tensile properties were measured with an Instron 1122 Tensile Tester, employing a gauge length of 50 mm and extension rate of 50 mm/min. Specimens 0.5-mm thick and 6–8-mm wide were cut from the molded sheets. MFR was measured using a Ceast Melt Indexer at 230°C under a 2-kg load according to ASTM D 1238. Notched Izod impact strength was measured at 23°C on a Ceast impact tester, using ASTM D 256 standard procedure.

Sample morphology was studied by a JEOL LSM-35 scanning electron microscope. Degree of crystallinity was measured using a Philips wide angle x-ray diffractometer with monochromatic radiation. Volume resistivity was measured according to Cabot Carbon test method No. d-7. The method measured the resistivity of a 25 × 15 × 3-mm specimen. Use of an ohmmeter having an internal source of voltage allows measurements at low resistivities, from 1 ohm-cm up to 1 Mohm-cm, which is not possible with the standard test for measuring resistivity of plastics such as IEC 502/83.

RESULTS AND DISCUSSION

The effect of a filler on the structure of the semi-crystalline polymer matrix depends on the interaction between the two. When there is no interaction the structure of the polymer is not affected by the presence of the filler. The active surface of the filler may induce a particular type of crystallization or alter its mechanism. In the case of strong absorption of polymer chains onto the surface of the filler, a boundary layer of the polymer is formed. Its properties are different from those of the bulk polymer. The density of the boundary layer would be affected by the limited mobility of the polymer chains and thus their packing ability. The thickness of the boundary layer should increase with the increase of the strength of the interaction. By increasing the concentration of filler, the relative amount of the boundary layer increases and thus its effect on macroscopic properties increases. Generally, the density of the compound follows the rule of mixtures. Figure 1 displays the effect of volume concentration of the carbon black on the density of the mixture. Good linear correlation is observed, that when extrapolated to pure carbon black, indicates its density of about 1.8 g/cm^3. The density of the carbon black is in fact reported[11] to be in the range of 1.8–1.9 g/cm^3 and depends on the particular structure of the clusters of the particles and the mixing conditions. Lowering of density may result if air is trapped because of high viscosity and poor wetting of filler by the polymer. In this case there was no indication of the presence of air in the sample. If the density of the matrix was lowered by the presence of carbon black caused by lowering of crystallinity or formation of an adsorbed layer, the extrapolated value for carbon black would be lower than that reported in literature. Such changes however are very small because difference in densities between PP and carbon black are much larger than that between the crystalline and amorphous phase. Density measurements however, indicated that samples were homogeneously mixed. Furthermore, density continued to increase smoothly at percolation level (about 10 vol %).

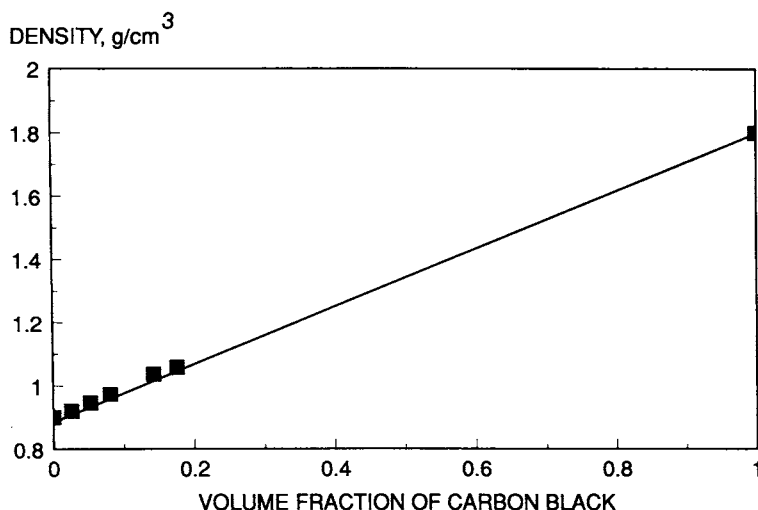MFR was strongly dependent on filler concentration. The ability to flow was lost above 15% car-

DENSITY, g/cm^3

Figure 1 Dependence of density on the carbon black volume fraction.

bon black. Figure 2 demonstrates effect of carbon black concentration on MFR of carbon black filled PP. Rapid decrease of fluidity in carbon black and PP mixtures is caused by their strong interaction. In the absence of interactions, viscosity (the inverse of fluidity) at low filler concentrations increases according to Einstein's equation [$\eta/\eta_o = (1 + 2.5\phi)$], and it is independent of particle size. MFR in our case decreased much faster than in calcium carbonate filled PP. The morphology of the composites as a function of carbon black concentration is illustrated in Figures 3(a–d) and 4(a–d), using magnification of $10^3\times$ and $10^4\times$, respectively. The figures show features of the broken surfaces. At low con-

MFR, g/10 min

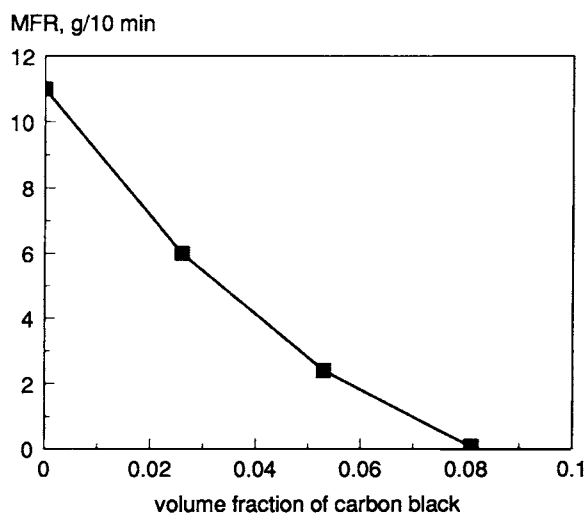volume fraction of carbon black

Figure 2 Dependence of MFR on carbon black concentration.

centrations (5 wt %) of carbon black, mainly evenly distributed individual particles of the filler are observed [Fig. 4(a)]. The estimated size of the particles is about 50 μm. At 10 wt % of carbon black some agglomeration of filler particles is observed [Figs. 3(b), 4(b)]. Large domains of carbon black are formed at 20 wt % of filler, while at 30 wt %, an interpenetrating structure of polymer matrix and carbon black domains is developed. An interaction between polymer and filler can be assessed from the appearance of carbon black particles at the broken surfaces. In the case of a strong polymer–filler interaction, a cohesive break occurs: that is, the surface of the particle is covered by the polymer or the crack is propagated through the polymer matrix and carbon black cluster not involving carbon black–polymer interface. Figures 4(c,d) show both fibers drawn at the interface and carbon black particles covered by matrix polymer or its remains on the carbon black clusters. No voids or debonding of the matrix and particles are observed, which illustrates a strong interfacial interaction.

Thermomechanical curves were used to measure the linear coefficient of expansion, α, at room temperature (midpoint of the range from 0°C to 40°C). The results presented in Table II demonstrate the decrease of α with the increase in carbon black concentration. As shown in Figure 5, this decrease is linear with volume concentration of the filler. Kerner proposed a relationship[12] between volume thermal expansion coefficient of the mixture, β, and filler concentration, ϕ_f:
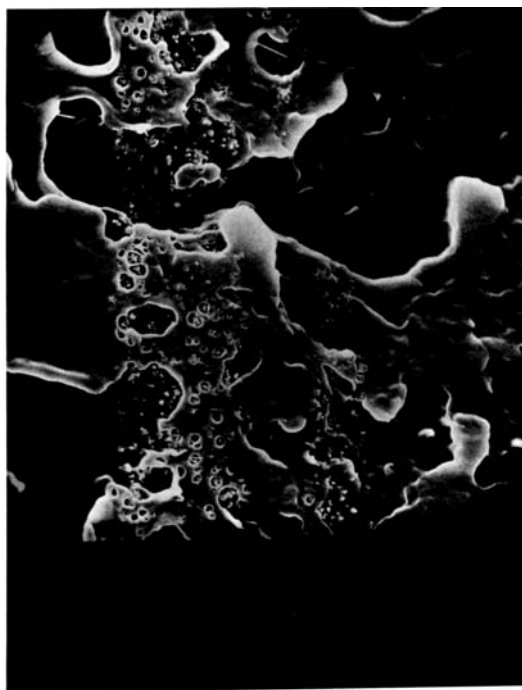
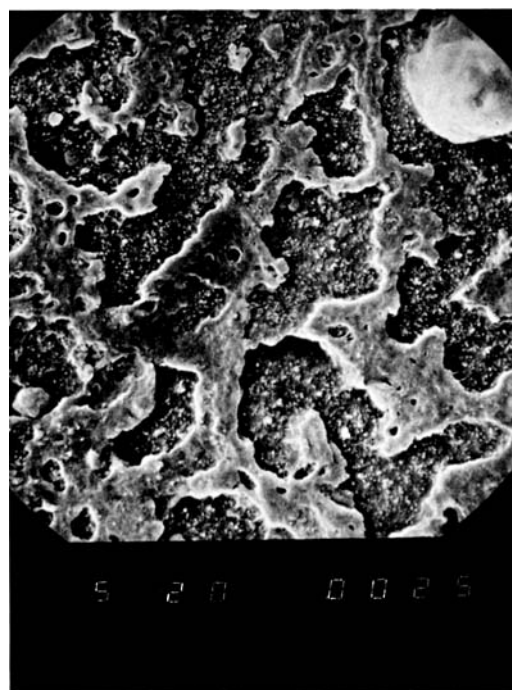$$\beta = \phi_m\beta_m + \phi_f\beta_f - (\beta_m - \beta_f)\phi_m\phi_f\theta \qquad (2)$$
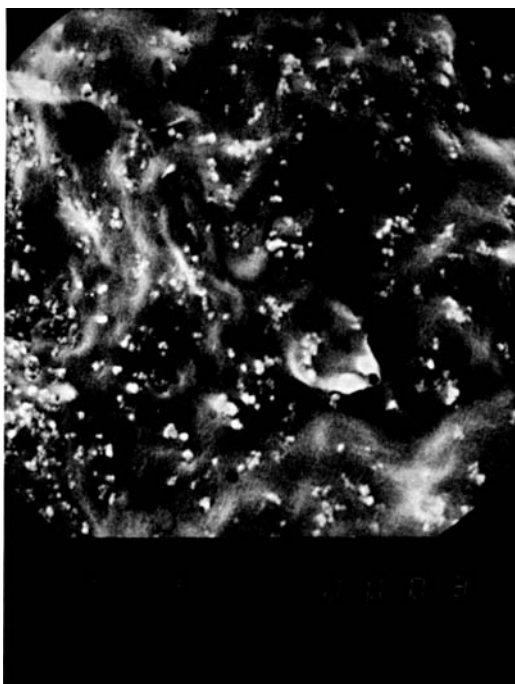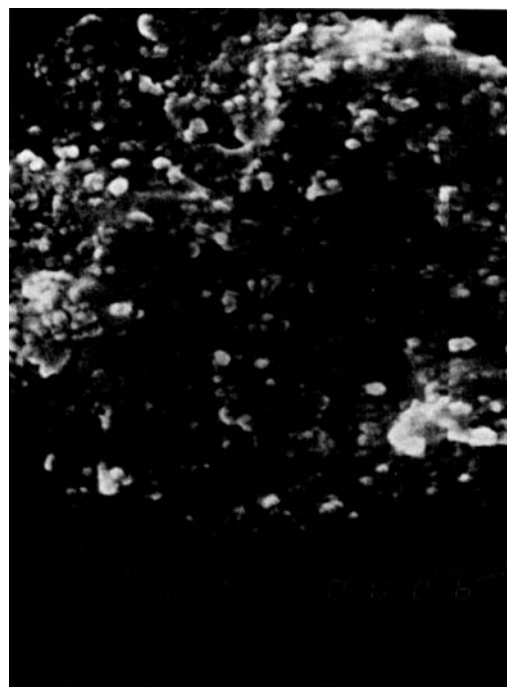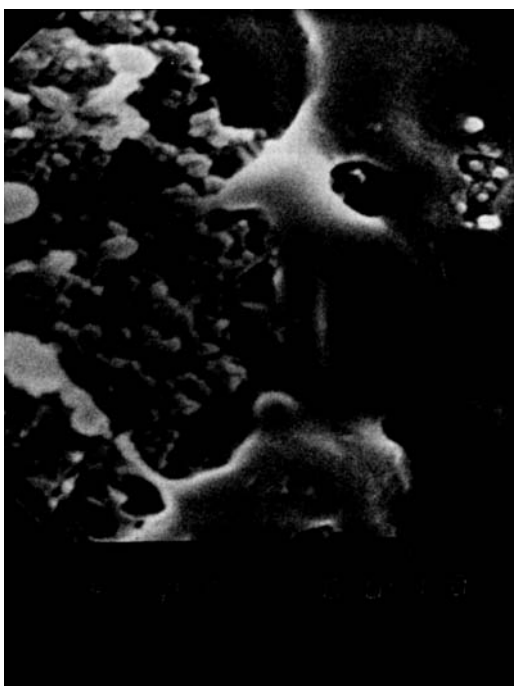
a) 5%
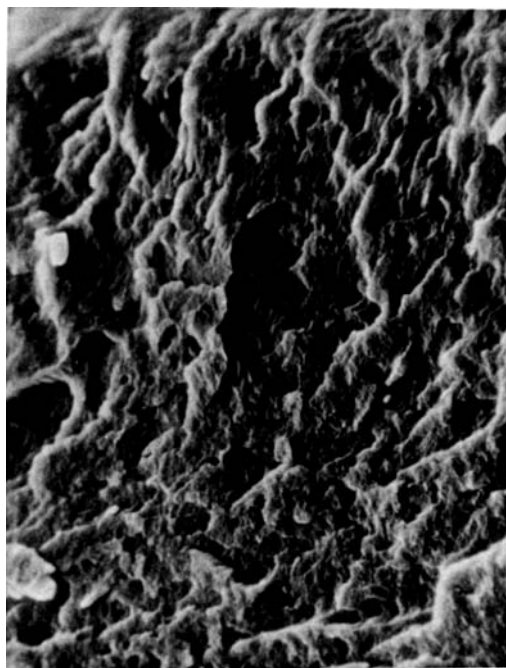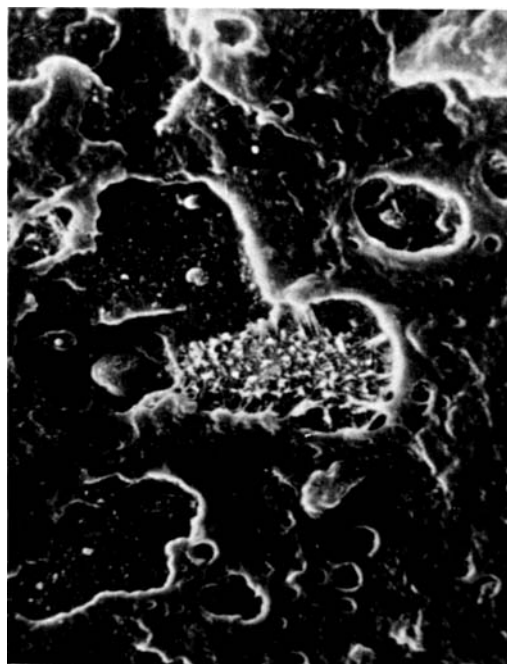
b) 10%

c) 20%

d) 30%

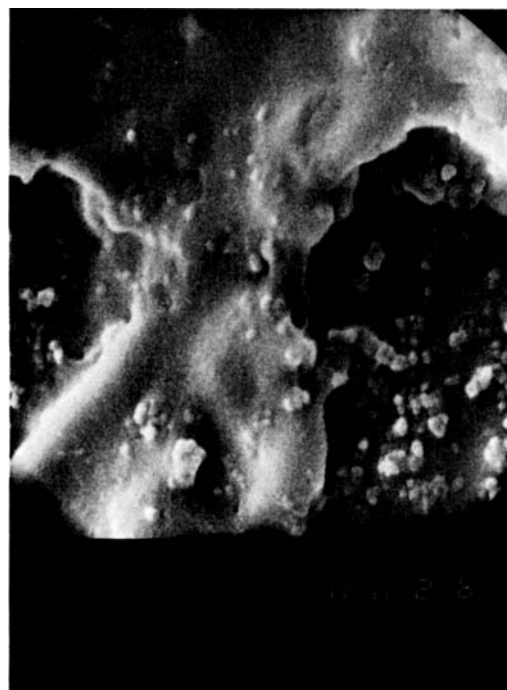**Figure 3**   Morphology of the PP/carbon black samples as observed by electron microscope.

a) 5%

b) 10%

c) 20%

d) 30%

Figure 4 Electron micrographs of the broken surfaces of PP/carbon black mixtures.

Table II   Dependence of Linear Coefficient of Expansion, α, Standard Deviation (SD), and Coefficient of Variation (CV) on Carbon Black Concentration

| Samples	$\alpha \times 10^6$ [1/K]	SD $\times 10^6$	CV
I	95	3.88	0.04
I	84	1.06	0.01
III	71	6.15	0.08
IV	71	2.76	0.04
V	56	2.04	0.04
VI	63	12	0.19

where

$$\theta = \frac{(1/K_m) - (1/K_f)}{(\phi_f/K_m) + (\phi_m/K_f) + (3G_m/4)} \tag{3}$$

K_m, K_f being bulk moduli of the matrix and filler, and G_m shear modulus of the matrix. In the case of no adhesion between the matrix and the filler, the thermal coefficient of expansion is independent of filler concentration, but if the Kerner model is valid it should decrease nonlinearly with the increase of volume fraction of the filler. Experimental results seem to suggest that this is not the case and that an LME type of interaction between the phases exists. This could be explained by the relatively narrow range of volume fractions where nonlinearity can be approximated by linear relationships. It should be considered that the morphology of the matrix itself is very complex, consisting of the amorphous and crystalline regions with complex supermolecular organization such as spherulites, whose size is not discernible here. Each of the phases is characterized by its own coefficient of expansion. Measurement temperature and degree of crystallinity, which is affected by the cooling regime, also play an important role. Thus, this system behaves as a multicomponent mixture and the proposed modeling is only an indication of the practical situation.

A strong interaction between the filler and PP affects crystallinity and glass transition (T_g) of the compound. The wide angle X-ray diffraction pattern of the sample IV, which has 20 wt % of carbon black, displays a small peak of the β-form. This suggests that the mechanism of crystallization is affected by the presence of the carbon black because this peak is absent in the pure PP. Additional tests under the same testing conditions showed that carbon black was almost transparent; that is, it did not contribute either to the crystalline or the amorphous area of the diffractogram. Measuring crystallinity, using the Weidinger and Hermans method,[13] has shown a decrease in degree of crystallinity with an increase of carbon black concentration from 60% for pure PP to about 50% for the sample VI (Fig. 6). This phenomenon may possibly be explained by lower crys-
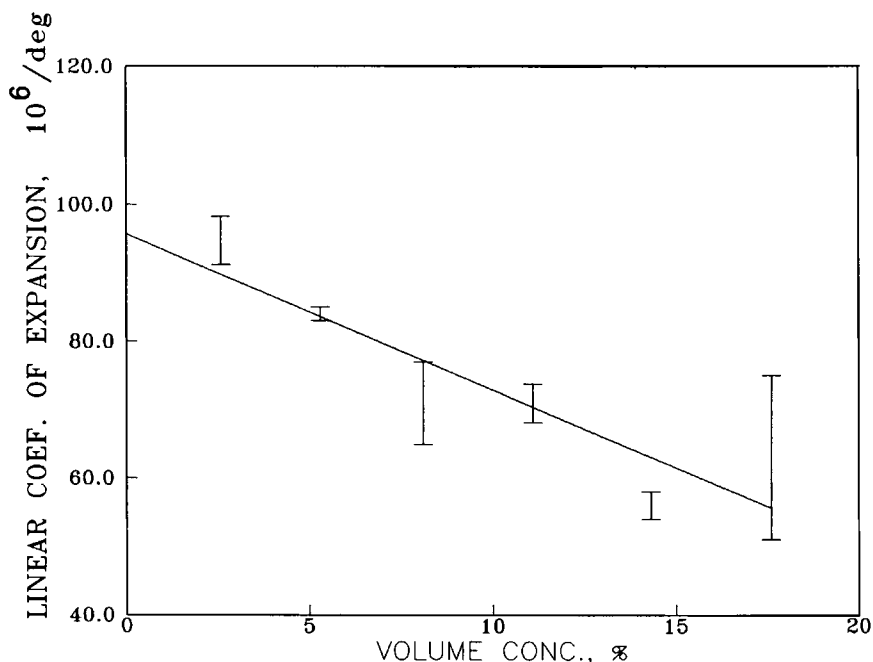
Figure 5   Variation of linear coefficient of expansion with composition of PP/carbon black mixtures.

degree of crystallinity, %
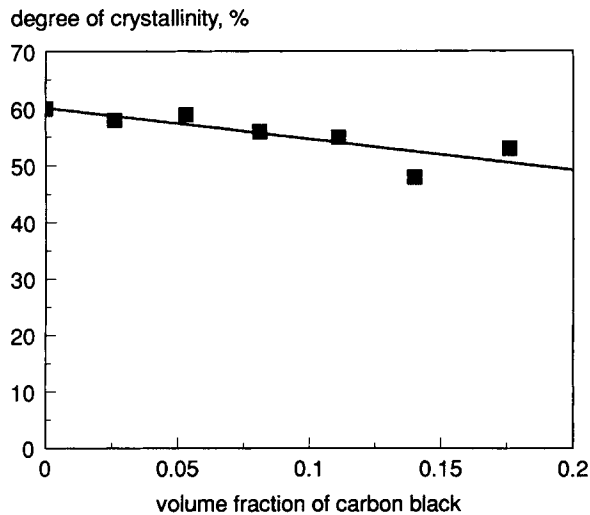
Figure 6 Dependence of the degree of crystallinity of PP with the increase of concentration of carbon black.

tallization in the boundary layer. Because carbon black is microcrystalline, it may act at low concentrations as a nucleating agent, thus affecting the size of the spherulites.

The (T_g) of the amorphous part of PP was studied by thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). Unfortunately TMA was not sensitive enough to produce reliable information. Figures 7 and 8 show the dependence of storage moduli and tan δ with temperature for samples with various carbon black concentrations. In-

teraction of carbon black and PP strongly affects modulus particularly near the melting point. The network of secondary carbon black–PP bonds helps maintain high modulus near the melting point, while modulus of the neat PP drops precipitously by several orders of magnitude in the same temperature region. T_g of PP as measured by the maximum on the tan δ curve, was found to be about 15°C and was dependent on frequency. The values of T_g, estimated from Figure 8, were about 14°C for the first five samples and about 16°C for the sample VI, at 1 Hz. At 10 Hz, T_g was about 18°C for the first five samples and about 22°C for the sixth. Thus the interaction between the matrix and the filler was most visible at the highest concentration of the filler content. Shift of T_g with change of frequency corresponds to an activation energy of about 70 kJ/mol for PP and the first five samples, and 52 kJ/mol for the sample VI. It appears that at low concentrations of carbon black a portion of amorphous polymer segments may be adsorbed at the filler surface, while a considerable portion is not bound, each phase having its own T_g, superimposed into a single broader peak. Only at higher filler concentration does the bound phase exhibit a dominating, higher temperature peak. The scatter of results does not allow quantitative assessment of interactions between polymer and the filler. A strong interaction should be reflected on the magnitude of the modulus of elasticity. According to Nielsen,[14] the modulus of elasticity of the composite, M_c, depends on the moduli of the matrix,
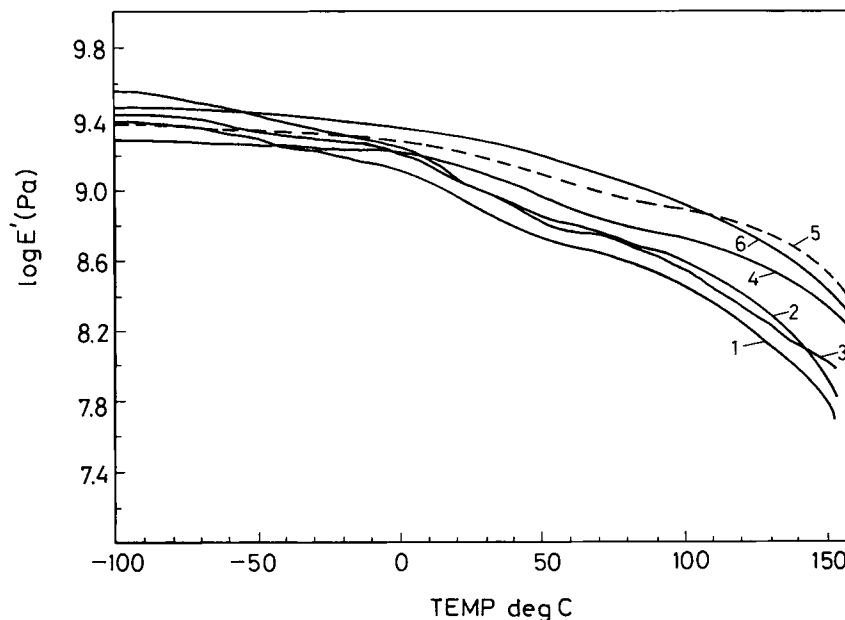
Figure 7 Dynamic mechanical curves of PP/carbon black composites. Change of storage moduli with temperature and concentration of carbon black.
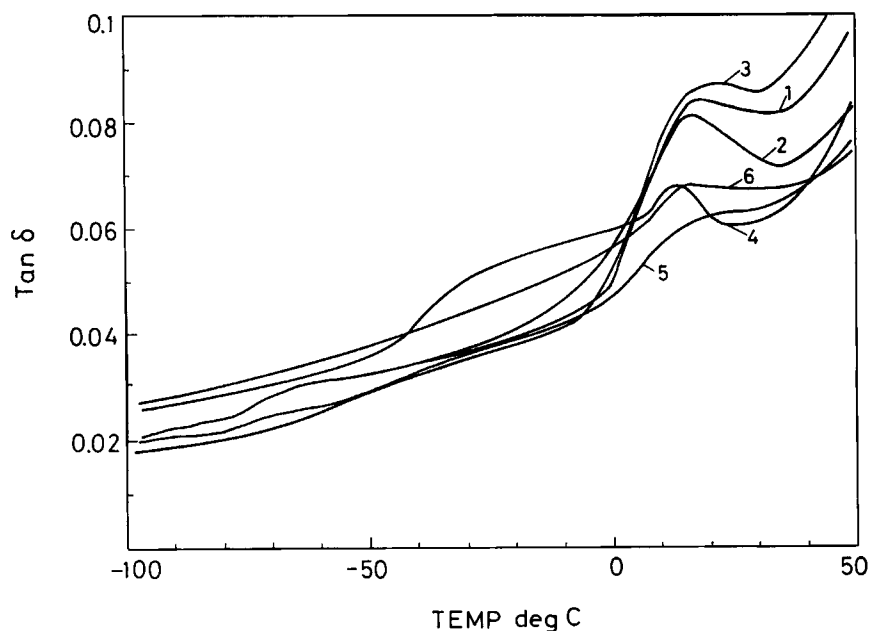
Figure 8 Dynamic mechanical curves of PP/carbon black composites. Change of tan δ with temperature and concentration of carbon black.

M_m, and that of filler, M_f, according to the following relationship:

$$\frac{M_c}{M_m} = \frac{1 + A^*B^*\phi_2}{1 - B^*\Psi^*\phi_2} \qquad (4)$$

where

$$B = \frac{M_f/M_m - 1}{M_f/M_m + A} \qquad (5)$$

where $A = k_E - 1$; the Ψ parameter is dependent on the maximal degree of packing; and k_E is Einstein's coefficient, being 2.5 for spherical particles. The Young's modulus of the composites was calculated taking values for Young's modulus for the filler from tables, and assuming spherical particles as a first approximation. Figure 9 shows the calculated values from the Nielsen model were considerably lower than the actual values obtained from the bending measurements. Apparently even 5 wt % of carbon black increases the modulus of the composite by almost 50%. These results imply a powerful reinforcing effect of the carbon black. Tensile strength however, was found to decrease linearly with volume fraction of carbon black, as shown in Figure 10. Because this property is strongly dependent on the defects in the material, it can be assumed that introduction of carbon black clusters means inclusion of potential weak spots whose effect may prevail over

reinforcement by the filler. Also, any immobilization of the rubbery, amorphous part of the polymer, whose role can be linked to slowing down crack propagation, may have some influence on tensile strength. In any event, the decrease in tensile strength is relatively small.

Impact strength changes with carbon black concentration in a complex manner. Notched Izod impact strength of the pure PP is 10.2 J/m. Addition of filler increases impact strength, but the maximum is obtained at 10 wt %, although the overall effect is relatively small (Fig. 11). At the very least, carbon black has a strengthening effect. Literature suggests a decrease in impact strength with increase in carbon black concentration.[15] As the broken surfaces in Figure 4 show, the crack propagates through both the filler particles and the filler/polymer interfaces indicating similar adhesive and cohesive forces between PP and carbon black and within the carbon black agglomerate.

Figure 12 illustrates the effect of carbon black content on volume resistivity of the PP/carbon black compound. The percolation level could be placed in the region of 5–10 vol % of carbon black. Volume resistivity is dependent not only on the conductive filler concentration but also on the particular morphology of the filler particles and their distribution. Generally, it is accepted that at a certain filler concentration, called the percolation level, a continuous path of conductive particles is formed.
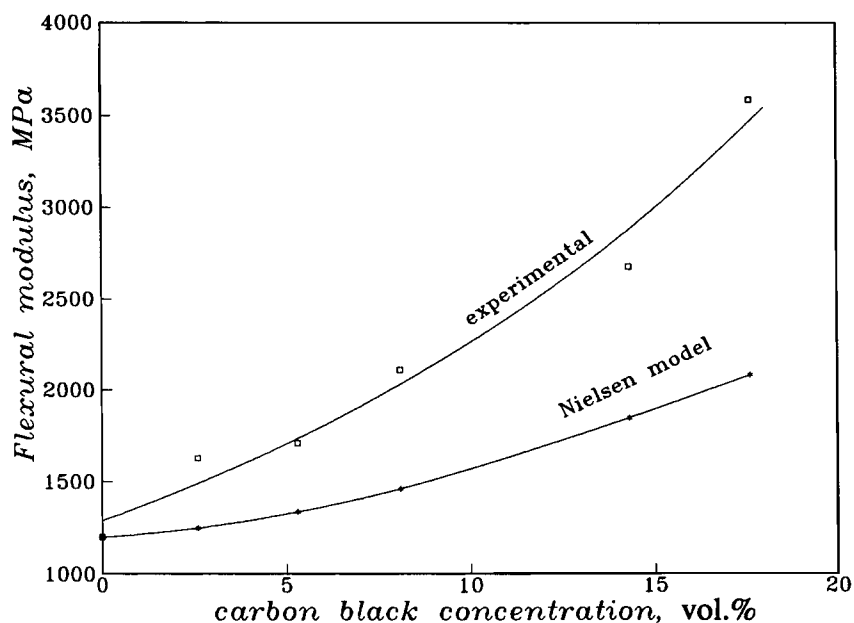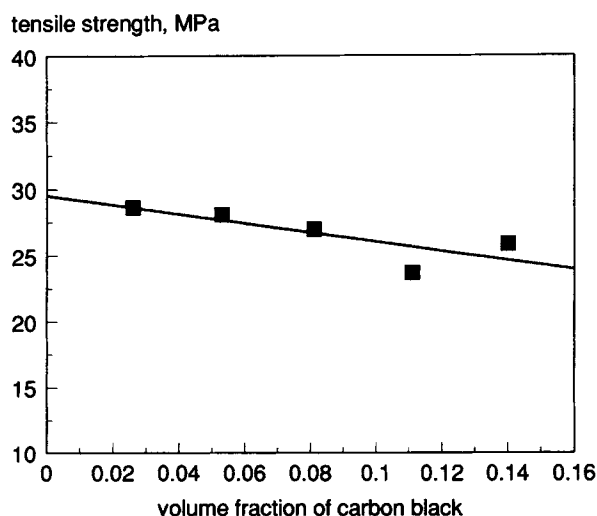
Figure 9   The effect of carbon black concentration on modulus of PP/carbon black composite.

Percolation is characterized by a sudden drop in resistivity and its relative independence of further filler addition. There are many theories of the effect of conductive filler concentration on the conductivity of a composite.[4,5,6,9,15] Odelevsky[16] has proposed several generalized relationships for the calculation of electrical and heat conductivity and dielectric permittivity of both matrix and statistical mixtures. In the percolation concept, conductivity is interpreted purely on geometrical considerations. If a

Figure 10   The effect of carbon black volume fraction on tensile strength.

symmetrical distribution of spherical particles of the conductive filler in the matrix is assumed, the volume fraction of the filler necessary to reach percolation conductivity would depend on the number of contacts that each particle form with its neighbours. If six contacts are assumed, 52% of the volume should be filled with filler, irrespective of its particle size.[17] If however, the number of contacts is reduced to between two and four, the percolation level would only be about 27 vol % of the filler. Lower percolation levels require special arrangements of particles that are not obtainable in actual mixing conditions. A model, according to which 30-nm large primary particles are arranged linearly into a secondary agglomerate or aggregate and whose structure is retained at least partially even during compounding, has been proposed.[18] None of the models take into account polymer/particle interaction. Wessling[4,15,17] challenged percolation models that could not explain percolation at extremely low concentrations of carbon black. He has acknowledged the importance of the interfacial phenomena, and proposed a model where at low carbon black concentration, particles are completely dispersed, with their structure disintegrated. At higher concentrations,[17] the carbon black associates into a "predominantly linearly structured network." The structure thus formed is kinetically controlled. The essential role is played by the polymer/carbon and carbon/ carbon interaction. In the case of poor wetting of
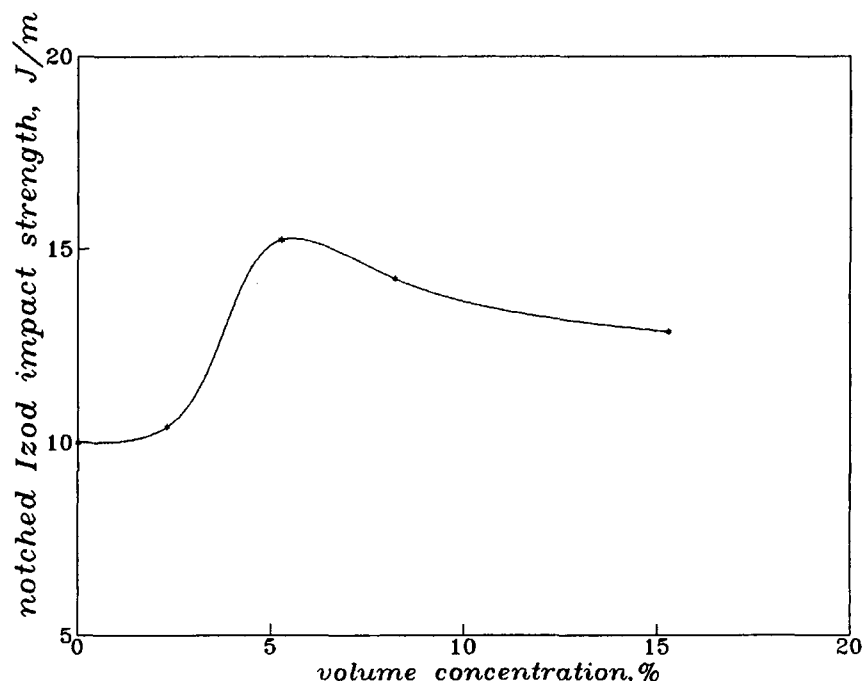
Figure 11 The effect of carbon black concentration on Izod impact strength.

the carbon black surface by polymer (high surface tension), carbon/carbon bonds are preferred and thus a lower percolation level is obtained. Polypropylene displays lower wetting properties than polar polymers. In order to explain the low percolation level of carbon black, Wessling proposed the formation of layers of conductive particles ("seams"). The percolation threshold was related not only to filler concentration but also to interfacial energy, the molecular weight of the matrix polymer, the crystallinity of the matrix, and specific surface.[19] The important role of thermodynamic effects, and interfacial energy in particular, on conductivity was recognized earlier by Miyazawa et al.[8] They have demonstrated that the concentration of carbon black at the threshold conductivity decreases with decreasing surface tension of the matrix and decreasing particle size. Some attempts to describe relationships between the percolation level of carbon black and other variables are purely empirical and have only limited applicability. Assessment of some of the parameters is often impossible.

In this case, the relatively good interaction between carbon black and PP cannot be represented quantitatively. Percolation level was reached between 5 and 10 vol % of carbon black, which agrees with some commercial literature.[20] Obviously, the

geometrical considerations in explaining conductivity are not sufficient and thermodynamic properties have to be taken into account.

CONCLUSIONS

Highly disperse carbon black, Ketjen black EC, forms relatively strong interfacial bonds with PP, that is, it has a reinforcing effect. This effect is manifested as a strong increase of viscosity (lowering of MFR) with increase in filler concentration, a large increase of modulus in the solid state and melt, and a significant decrease of thermal expansion coefficient. Also, direct observation of the polymer/filler interface by electron microscopy suggests good wetting of the filler particle. The effect of concentration of carbon black on T_g was observed only at relatively high carbon black concentration. Degree of crystallinity seems to decrease with an increase in carbon black concentration. Tensile strength and elongation were found to decrease but impact strength to increase with the increase of filler concentration. Percolation level for insulator–conductor transition was found to be between 5 vol % and 10 vol % of carbon black.
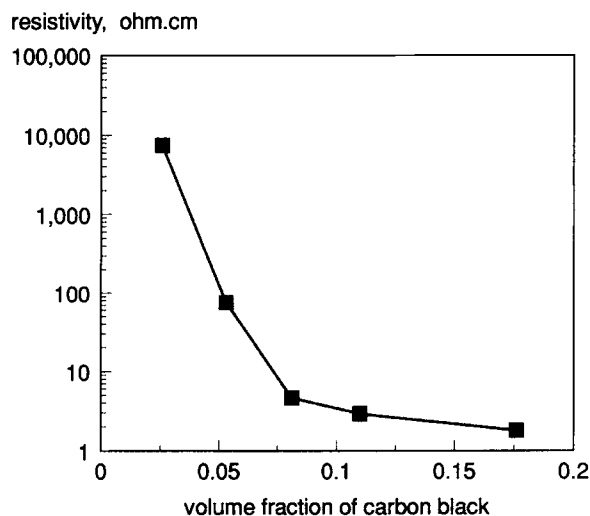
resistivity, ohm.cm

Figure 12 The effect of carbon black concentration on volume resistivity of the compound with PP.

REFERENCES

1. Yu. S. Lipatov, *Fizicheskaya Himiya Napolnenih Polimerov*, Himiya, Moskva, 1977.
2. J. K. Acosta, M. Rodriguez, A. Linares, and J. R. Jurardo, *Polym. Bull.*, **24**, 87 (1990).
3. J. R. Jurado, C. Moure, P. Duran, M. Rodriguez, A. Linares, and J. L. Acosta, *J. Mater. Sci.*, **26**, 4022 (991).
4. B. Wessling, *Polym. Eng. Sci.*, **31**, 1200 (1991).
5. A. P. Losoto, V. M. Usichenko, Yu. M. Budnitskii, M. S. Akutin, A. T. Ponomarenko, and A. A. Ovchinikov, *Dokl. Akad. Nauk SSSR, Phys. Chem.*, **274**, 1410 (1984).
6. A. I. Medalia, *Rubb. Chem. Technol.*, **59**, 432 (1986).
7. W. Y. Hsu, W. G. Holtje, and J. R. Barkley, *J. Mater. Sci. Lett.*, **7**, 459 (1988).
8. K. Miyazawa, K. Watanabe, E. Jojima, H. Aida, M. Sumita, and K. Ishikawa, *J. Mater. Sci.*, **17**, 1610 (1982).
9. E. K. Sichel, Ed., *Carbon Black-Polymer Composites*, Marcel Dekker, New York, 1982.
10. H. S. Katz and J. V. Milewsky, Eds., *Handbook of Fillers and Reinforcements for Plastics*, Van Nostrand Reinhold Co., New York, 1978.
11. *Enciklopediya Polimerov*, Vol. 2, Sovyetskaya enciklopediya, Moskva, 1974, p. 356.
12. E. H. Kerner, *Proc. Phys. Soc. (B)*, **69**, 808 (1956).
13. A. Weidinger and P. Hermans, *Makromol. Chem.*, **50**, 98 (1961).
14. L. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker Inc., New York, 1974.
15. B. Wessling, *Processing of Electrically Conductive Polymers and Compounds—Tools for Exploring and Using Structure and Properties*, Internal material of Zipperling Kessler & Co., Germany.
16. B. I. Sazhin, *Elektricheskie Svoystva Polimerov*, Himiya, Moskva, 1977, p. 52.
17. B. Wessling, *Kunststoffe*, **76**, 930 (1986).
18. G. H. Kleinheins, in *Elektrisch leitende Kunststoffe*, H. J. Mair and S. Roth, Eds., Carl Hanser Verlag, Munchen 1986, pp. 77, 91.
19. B. Wessling, *Synthetic Metals 27* (1988) A83-A88.
20. Denka black, Technical literature of Denki Kagaku Kogyo Kabushiki Kaisha Co.