Structure-Dependent Conductivity and Microhardness of Metal-Filled PVC Composites

Yevgen P. Mamunya[1], *Eleonora G. Privalko*[1], *Eugene V. Lebedev*[1], *Valery P. Privalko*[1*], *Francisco J. Balta Calleja*[2], *Policarpos Pissis*[3]

[1]Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kharkiv Shausse 48, 253160, Kyiv, UKRAINE
[2]Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, SPAIN
[3]National Technical University of Athens, Zografou Campus, GR 15780 Athens, GREECE

Summary: Metal-filled composites of a commercial PVC (polyvinyl chloride) powder (mean particle size $d_p \approx 100$ microns) and a metal powder (mean particle size d_f about 100 microns for copper, Cu, and about 10 microns for nickel, Ni) prepared by mechanical mixing in a ball mill, subsequent hot-pressing at 443 K and rapid cooling to 300 K, were characterized by the room-temperature measurements of electrical conductivity σ, density ρ and microhardness H.

The sudden jumps of about 17 orders of magnitude followed by a much slower growth up to the limiting filler fraction φ^* on the $log\ \sigma$ vs. φ plots are the evidence for the onset of percolation transitions. at filler volume contents $\varphi_{c1} = 0.05$ and 0.04 for PVC/Cu and PVC/Ni, respectively For both systems, the values of H exhibited an initial steep increase up to $\varphi_{c2} = 0.07$, followed by an apparent plateau extending up to $\varphi = 0.18$. However, drastic differences in the patterns of composition dependence of H were observed at higher metal loadings, i.e., a continuous increase of H up to the leveling-off at φ^* for PVC/Cu, in contrast to a sudden drop of H at $\varphi = 0.20$ and subsequent slow increase for PVC/Ni. For both composites the apparent density ρ' of a polymer matrix remained the same as that of the neat PVC in the composition interval $\varphi < 0.20$, while at $\varphi > 0.20$ a precipitous drop of ρ_l was observed due to the formation of polymer-free voids between filler particles (crowding effect) as φ approaches φ^*.

The observed effects were analyzed in terms of a tentative model envisaging cross-overs from "dilute suspension regime" to "semi-dilute suspension regime" in the concentration range φ_{c1} to φ_{c2} , and from "semi-dilute suspension regime" to "concentrated suspension regime" above $\varphi = 0.20$. Different behavior in this latter regime was explained by intrinsic differences in the structure of conductive infinite clusters between mixtures of particles of about the same size (PVC/Cu) and of widely different sizes (PVC/Ni).

Introduction

Low-resistivity polymer/metal composites with volume content of metal, φ , slightly in excess of the so called percolation threshold, φ_c , are widely used in electronic industry[1)]. Theoretically, a sudden drop of resistivity associated with the formation of an "infinite

CCC 1022-1360/00/$ 17.50+.50/0

cluster" (InC) of conductive spherical particles within a structureless, continuous matrix of a non-conductive component, is achieved at the universal value of φ_c regardless of the intrinsic properties of components[2)]. In technological practice, however, the structure of a conductive InC (hence, the apparent values of φ_c for a composite) may be varied over a fairly broad range by appropriate changes of the shape and dimensions of particles of one or both components, by preparation method, etc[1, 3-7)].

Experimentally, the onset of percolation at φ_c in polymer composites can be detected by jump-like changes of coefficients of heat and mass transfer (i.e., thermal conductivity[2-4)], electrical conductivity[1, 7-10)], gas permeability[11)], etc.) ; however, characteristic changes in selected static, structure-sensitive properties may be also anticipated. In fact, sudden changes in both the density and the adhesive strength in the vicinity of φ_c were reported[12-13)] for carbon-black filled polymer composites.

In view of a reasonably high sensitivity of microhardness to structural features of different polymer systems[14-16)], it is the purpose of the present communication to derive information on the structure evolution in metal-filled polyvinyl chloride, PVC, from complementary measurements of electrical conductivity and microhardness in function of composition.

Experimental

Materials

Metal-filled composites were prepared by mechanical mixing at room temperature of a commercial PVC powder (mean particle size $d_p \approx 100$ microns) with a metal powder (mean particle size d_f about 100 microns for copper, Cu, and about 10 microns for nickel, Ni) in a ball mill, subsequent hot-pressing at 443 K and rapid cooling to 300 K. Disc-like specimens (diameter : 30 mm, thickness : 2 mm) prepared in this fashion, were subsequently ground and polished to remove a thin, filler-depleted surface layer.

Techniques

The electrical conductivity σ of disc-like samples at $\varphi < \varphi_c$ was measured with a teraohmmeter E6-13A using annealed aluminium foils as electrodes. Flat, plate-like samples with dimensions 50×10×2 mm were used for measurements at conductivities $\sigma > 10^{-2}$ S/m using four-electrode method[10)]. Tight pressing of electrodes to the sample surface is assumed to minimize the contact resistance at the electrode-sample interface.

A Leitz Tester equipped with a square-based diamond indenter was used for the microhardness (H) measurements. The H values were calculated from the standard equation[14-16], H [MPa] = kS, where S is the slope of the straight-line plot of the residual projected indentation area A [m^2] = h^2 vs. the contact load applied P [N], h [m] is the diagonal length of the impression, and $k = 1.854$ is the geometrical factor. In a loading cycle of 0.1 min, the loads of 1.0, 1.5 and 2.5 N were used. For each point, at least 3-5 measurements were averaged. The correlation coefficients and the standard deviations for the linear A vs. P fits obtained were within the limits of 0.96-0.98 and 1.5-2.8, respectively.

Surface morphology of polished samples was studied with the optical microscope Biolar in reflection mode.

Bulk densities of composites and densities of metal powders were determined by hydrostatic weighing and picnometry techniques, respectively. These values were used to estimate the apparent density of a polymeric component (ρ') assuming additivity. The volume fractions φ of fillers in composites were calculated assuming ρ_2 = 8.94 and 8.90 g/cm^3 as densities of Cu and Ni, respectively.

The limiting filler fractions φ^* corresponding to the dense random packing (0.30 and 0.50 for copper and nickel particles, respectively) were determined by a vibration densification method[8]. Such unusually low value of φ^* for Cu (compared to $\varphi^* \approx 0.6$ for solid spheres) can be attributed to a non-spherical, highly irregular shape of its particles[3,4].

Result and Discussion

Conductivity

The familiar sudden jumps of about 17 orders of magnitude in fairly narrow concentration intervals followed by a much slower growth up to the limiting filler fraction φ^* on the $\log \sigma$ vs. φ plots for both PVC-Cu and PVC-Ni (Fig. 1) are the typical fingerprints of percolation transitions. In terms of Aharoni's classification scheme[17], the onset of a jump-like increase of σ (at 0.04 and 0.05 for PVC/Cu and PVC/Ni, respectively) corresponds to the start of formation of an InC with one contact per conducting particle at the first percolation threshold φ_{c1}, while the formation of an InC is completed at the second percolation threshold φ_{c2} (0.07 for both types of composites) associated with two contacts per particle. These dependencies will be analyzed in terms of tentative model[3] (Fig. 2) assuming intrinsic structural differences between mechanical mixtures of particles of about the same size (PVC/Cu) and of widely different sizes (PVC/Ni).

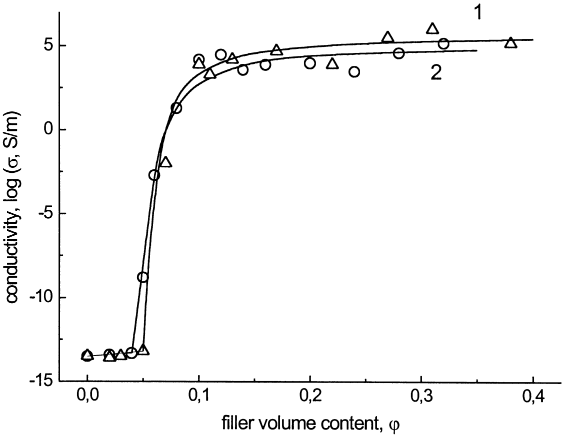

Fig. 1: Composition dependence of conductivity for PVC/Cu (1) and PVC/Ni (2).

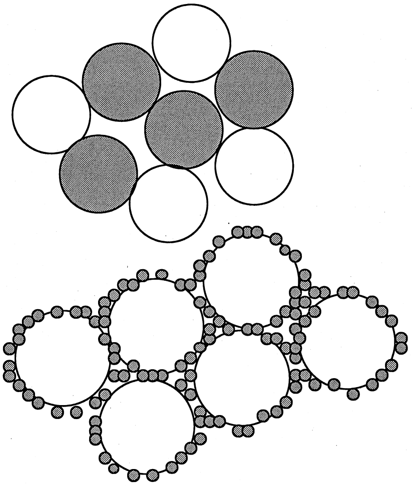

Fig. 2: Schematic of the assumed distribution of polymer and metal particles (opened and filled circles, respectively) for mechanical mixtures of PVC/Cu (a) and PVC/Ni (b).

In the former case (Fig. 2a), the initial random distribution of metal particles will remain essentially unchanged after hot-pressing. Therefore, the observed pattern of the composition dependence of σ may be associated with the formation of the first InC of Cu and merging with other infinite clusters of Cu particles at higher metal contents.

In the latter case, small Ni particles are assumed$^{3)}$ to form "shells" around randomly distributed, large PVC particles in the initial mechanical mixture (Fig. 2b). It can be readily shown that a complete coating of each PVC particle by outer shells of Ni particles would be achieved at $\varphi' \approx 0.21$. It becomes evident, however, from inspection of Fig. 2a that a lower metal content, $\varphi_{c2} = \varphi'(1 - \varphi'')$, would be sufficient for the formation of a continuous structure (i.e., an InC) of Ni shells (here φ'' is the fraction of Ni shells which would overlap in the case of a complete coating). The value $\varphi'' = 0.67$ derived assuming $\varphi_{c2} = 0.07$ and $\varphi' = 0.21$, appears quite reasonable.

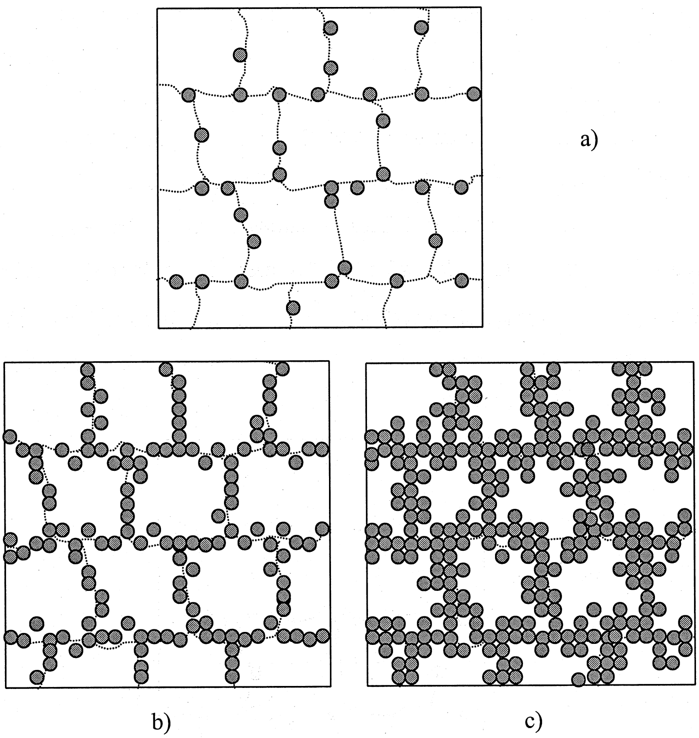

Fig. 3: Schematic of the evolution of shell-structure with filler content for PVC/Ni.

The expected evolution of the distribution pattern of Ni particles with φ is depicted schematically in Fig. 3. In the 'dilute suspension regime' at very low filler loadings (i.e., when the effective surface-to-surface interparticle distance, $L = d_f [(\varphi^* / \varphi)^{1/3} - 1]$[2], is larger than the mean polymer particle size d_p), the filler particles are randomly distributed within a continuous polymer matrix. As φ grows, more and more filler particles are localized at the boundaries between polymer grains (Fig. 3a), until the conductivity sets on concomitant to the formation of a first InC at the cross-over to a ‘semi-diluet suspension regime’ at φ_{c1} (Fig. 3b). At still higher filler loadings (i.e., in the ‘concentrated suspension regime’), the structure of an InC is completed at φ_{c2} , and the number n (i.e., the effective thickness) of densely-packed filler shells increases at the expense of the size of remaining filler-free polymer grains (Fig. 3c).

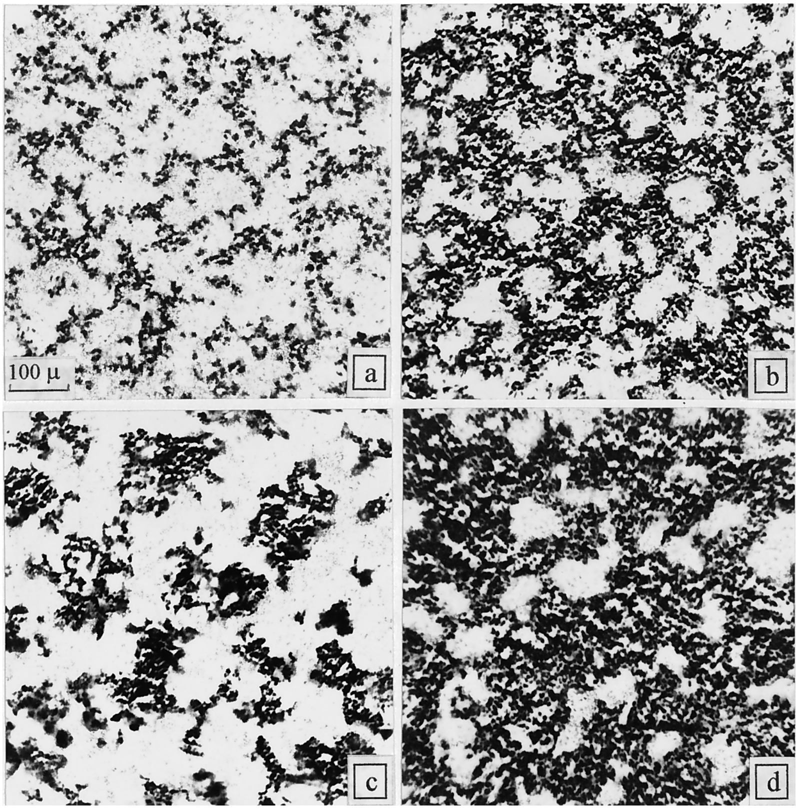

Fig. 4: Optical microphotographs of PVC/Ni (a, b) and PVC/Cu (c, d) at filler contents 0.035 (a, c) and 0,15 (b, d) and equal magnifications.

As can be seen from Fig. 4, these qualitative considerations are reasonably close to the actual morphology of studied samples below and above the apparent percolation thresholds, respectively. In fact, the structure of PVC/Ni composites in Figs. 4a and 4b, are similar to the assumed schematic models in Figs. 3b and 3c. Also expected from model considerations (Fig. 2) is the change over from random distribution of large copper particles within PVC matrix at $\varphi < \varphi_c$ (Fig. 4c) to a conductive cluster at $\varphi > \varphi_c$ (Fig. 4d).

A strong dependence of the effective percolation threshold on the ratio of sizes of conducting (d_f) and non-conducting (d_p) particles[18)] can be rationalized[2,19,20)] by differentiating between the overall filler concentration in a composite, φ , and the local filler concentration within a shell, φ^* . Moreover, the existence of a continuous structure of conducting metal-particle shells invites for consideration of the relevant packing factor, φ_s.

As shown elsewhere[19)],

$$\varphi_s = \varphi^* (1/K_s), \qquad (1)$$

where the filler segregation factor K_s is defined as

$$1/K_s = 1 - (1 - nd_f/d_p)^3 \qquad (2)$$

It is apparent from Fig. 2a that the completion of a metal-particle shell around a polymer grain in a hot-pressed sample implies $n = 2$; in this case, from eqs. (1) and (2) one obtains $\varphi_s = 0.25$ which compares favorably with our previous estimate of φ' . Moreover, assuming $X_c = 0.25$ for a critical concentration factor[21)], one derives $\varphi_{c2} = X_c\varphi_s = 0.06$ which is again very close to the experimental value of $\varphi_{c2} = 0.07$.

Microhardness and Density

As can be seen from Fig. 5, for both systems the values of H exhibited an initial steep increase from 140 MPa for a neat PVC to 200 MPa during the cross-over from the "dilute suspension regime" to the "semi-dilute suspension regime" at $\varphi_{c2} = 0.07$, followed by an apparent plateau extending up to $\varphi = 0.18$. However, drastic differences in the patterns of composition dependence of H were observed for the "concentrated suspension regime" at higher metal loadings, i.e., a continuous increase of H up to the leveling-off at $H = 310$ MPa and $\varphi = 0.32$ for PVC/Cu, in contrast to a sudden drop of H down to 175 MPa at $\varphi = 0.20$ and subsequent slow increase for PVC/Ni . For both composites the apparent density of a polymer matrix (ρ') remains the same as that of the neat PVC ($\rho = 1.400$ g/cm^3) in the composition interval $\varphi < 0.20$, while at $\varphi > 0.20$ a precipitous drop of ρ' is observed. This latter effect can be attributed to the formation of polymer-free voids between filler particles (crowding effect) as φ approaches φ^*.

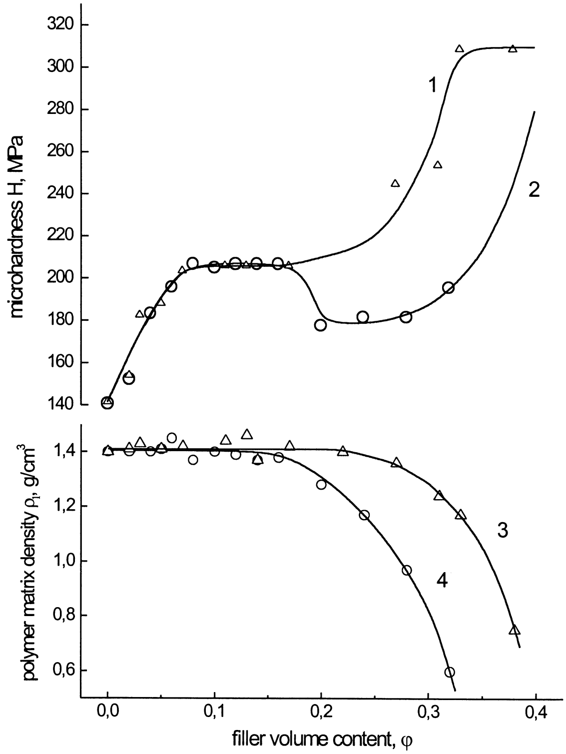

Fig. 5: Composition dependencies of microhardness (1, 2) and polymer matrix density (3, 4) for PVC/Cu (1, 3) and PVC/Ni (2, 4) composites.

In the context of model considerations discussed above (Figs. 2 and 3), the observed patterns can be explained in a following manner. The basic condition for microhardness measurements is the formation of an indentation mark at the surface of a studied solid polymer[14)]; this condition can be met if only the local compressive stress from an indenter is well in excess of the polymer yield stress σ_y . Thus, the initial steep increase of H common to both PVC/Cu and PVC/Ni composites in the concentration interval, $0 < \varphi < \varphi_{c2} = 0.07$, reflects the increased resistance of a polymer matrix to yielding due to a reinforcing effect of metal fillers during the cross-over from the "dilute suspension regime" to the "semi-dilute suspension regime" at φ_{c2} . In so far as the σ_y of a filled polymer composite usually decreases due to a polymer/filler debonding process, a subsequent leveling-off of the microhardness in the "semi-dilute suspension regime" at $0.07 < \varphi < 0.18$ (Fig. 5) may be the result of competing, opposite effects of an earlier yielding of a polymer matrix, and of its reinforcement by a filler.

It can be easily verified that the effective surface-to-surface interparticle distance L in the "concentrated suspension regime" at $\varphi > 0.18$ becomes significantly smaller than the mean filler particle size d_f ; however, the pattern of the plastic flow (yielding) is expected to depend on the structure of an InC (i.e., on the ratio d_f/d_p). In the case of PVC/Cu composites ($d_f/d_p = 1$), the further increase of φ above 0.18 would result in a gradual suppression of the plastic flow contribution from a polymer matrix due to a continuous increase of the size and/or the mechanical strength of an InC ; hence, the microhardness will smoothly increase up to its value for a neat copper ($H_{Cu} = 310$ MPa) at $\varphi \geq \varphi^* = 0.30$ (Fig. 5).

In contrast, as a result of packing limitations (crowding effect) in the case of PVC/Ni composites ($d_f/d_p = 0.1$), extra Ni particles will be forced to penetrate into the interior of the soft PVC matrix and thus to destroy a continuous InC of Ni shells ; this explains the onset of the decrease of microhardness at $\varphi = 0.18$ (Fig. 5). Subsequent increase of H observed at still higher filler loadings suggests, however, that this randomization effect leads to a gradual structural transformation of an initial InC of connected shells (Fig. 2b) into that of a highly branched InC of randomly connected Ni particles.

Conclusion

The patterns of concentration dependencies of electrical conductivity, microhardness and density of copper- and nickel-filled composites of poly(vinyl chloride) are in a qualitative agreement with a tentative model envisaging cross-overs from "dilute suspension regime" to "semi-dilute suspension regime" in the concentration range of the onset and stabilization of conductive, infinite clusters (InC) of metal particles at percolation thresholds φ_{c1} and φ_{c2} , respectively, and from "semi-dilute suspension regime" to "concentrated suspension regime" above $\varphi = 0.20$. Different behavior in this latter regime is explained by intrinsic differences in the structure of InC between mixtures of particles of about the same size (PVC/Cu) and of widely different sizes (PVC/Ni).

References

1. D.M. Bigg, in : *Metal-filled Polymers. Properties and Applications*, ed. By S.K. Bhattacharya, Marcel Dekker, Inc., New York, 1986, p. 165.
2. V.P. Privalko, V.V. Novikov, *The Science of Heterogeneous Polymers. Structure and Thermophysical Properties*, Wiley, Chichester, 1995.
3. R. Kusy, R.D. Corneliussen, *Polym. Eng. Sci.*, **15**, 107 (1975).
4. D.M. Bigg, *Adv. Polym. Sci.*, **119**, 1 (1995).
5. Y. Baziard, S. Breton, S. Toutain, A. Gourdenne, *Eur. Polym. J.*, **24**, 633 (1988).
6. In-Gann Chen, W.B. Jonson, *J. Mater. Sci.*, **26**, 1565 (1991).
7. F. Lux, *J. Mater. Sci.*, **28**, 285 (1993).
8. V.E. Gul, L.Z. Shenfill, *Conductive Polymer Composites,* Khimia, Moscow, 1984 (in Russian).
9. A. Larena, G. Pinto, *Polym Compos.*, **16**, 536 (1995).
10. E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Polym. Compos.*, **16**, 318 (1995).
11. A.E. Chalykh, *Diffusion in Polymer Systems*, Khimia, Moscow, 1987 (in Russian).
12. B. Wessling, *Synth. Metals*, **27**, A83 (1988).
13. K. Miyasaka, K. Watanabe, E. Jojima, H. Aida, M. Sumita, K. Ishikawa, *J. Mater. Sci.*, **17**, 1610 (1982).
14. F.J. Balta Calleja, *Trends Polym. Sci.,* **2**, 419 (1994).
15. W.P. Paplham, J.C. Seferis, F.J. Balta Calleja, H.-G. Zachmann, *Polymer Compos.*, **16**, 424 (1995).
16. F.J. Balta Calleja, E.G. Privalko, A.M. Fainleib, T.A. Shantalii, V.P. Privalko, *J. Macromol. Sci. Physics*, in print.
17. S.M.Aharoni, *J. Appl. Phys.*, **43**, 2463 (1972).
18. A. Malliaris, D.T. Turner, *J. Appl. Phys.*, **42**, 614 (1971).
19. E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Kolloid. Zh.*, **52**, 145 (1990).
20. E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Kompoz. Polym. Mater.,* No. 50, 37 (1991).
21. E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Dopov. AN UkSSR*, ser.B, No. 5, 127 (1991).

Acknowledgement. This work was supported by the project INTAS-97-1936 and by the DGICYT, Spain (grant PB94-0049).