MESOSTRUCTURE AND CONDUCTIVITY OF CARBON BLACK FILLED POLYMERS

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INTRODUCTION

Polymers filled with electrically conductive carbon particles have been largely studied. It is well known that their dc and low frequency ac conductivities depend strongly on the particle concentration, particularly in the neighborhood of a critical concentration called conductivity threshold, the occurence of which being related by the percolation theory to the formation of an infinite cluster of connected particles. However this theory is largely unable to predict the exact location of the transition in real materials like filled polymers. It has long been known that the value of the critical concentration is largely dependent on the kind of particles and of polymer which are used, and on material processing in a way which is not fully understood [1]. In this communication, we address to the problem of the actual mesostructure of the filled polymers and to its relationship to their conductivity. We present a systematic numerical analysis of micrographs of the materials and we show that valuable information can be obtained on the location of the conductivity threshold.

MATERIALS AND EXPERIMENTALS

Two classes of materials have been produced with either the carbon black Raven 700 by Columbian International, with elementary particle size is 20 nm and fractal dimension [2] of the primary aggregates about 1.75 (Raven series), or the carbon black Y50A by SN2A company with elementary particle size 50 nm, have been used as the filler (Y50A series). An epoxy Araldite F by Ciba Geigy is used as the unique polymer matrix. The carbon black (CB) is introduced and dispersed in the viscous resin at constant temperature 30 °C, the suspension is mixed with controlled speed, and the mixture is allowed to polymerize at 100 °C during 2 hours. Two different Raven series have been made with variable CB concentration with either 200 (Raven 200 series) or 1200 (Raven 1200 series) rpm mixing speed respectively. One Y50A series has been produced with 1200 rpm speed.

The dc electrical conductivity measured as a function of CB volume concentration exhibits the expected conductivity threshold at 6.5%, 3.5% and 0.7% in the Raven 200, Raven 1200 and Y50A series respectively, showing that the critical concentration depends on the CB and on mixing conditions.

Thin slices of materials, about 70 nm thick, have been observed under transmission electron microscope. Micrographs evidence uniform CB dispersion in the Y50A samples, and, in the Raven samples, a complex mesostructure composed with well dispersed aggregates coexisting with micron size agglomerates.

We have performed numerical image analysis on sets of micrographs with a Pericolor equipment [3]. Histograms of the sizes of the observed objects show a single distribution in the Y50A samples, a bimodal distribution in the Raven samples, whatever the respective concentration is. This leads us, in this last case, to define two classes of clusters smaller and larger than approximately 500nm, in agreement with visual analysis of the micrographs.

RESULTS AND DISCUSSION

It has been first verified that the integrated apparent surface concentration of the CB particles varies linearly with the volume concentration. However, it is overestimated by a factor of approximately four in every series. This has been attributed mainly to the slice thickness which is several times the carbon particle size. We conclude that the error in the determining the surface concentration is mostly systematic and that the numerical results are well representative of the composition and mixing mode of the samples.

We have next determined the apparent surface occupied by the agglomerates in the Raven series. We find that it remains close to the total surface, that it depends linearly on the CB volume concentration, that it does not depend on the mixing conditions. We conclude that most of the CB particles form the agglomerates and, recalling the dc conductivity threshold dependence on mixing condition, that the micron size agglomerates do not contribute to the dc conductivity.

The behavior of the apparent surface occupied by the particles in small aggregates and clusters is just the opposite. Its concentration dependence is not linear and does depend on mixing condition and kind of CB. Figure 1 is a plot of the local apparent density of small aggregates in Raven series in the regions not occupied by agglomerates and of the apparent density (no agglomerates) for the Y50A series. We find that in all three series this suface density is close to 4 % at the respective critical volume concentration, as indicated on the figure.

CONCLUSIONS

We have shown that the mesostructure of a CB filled polymer may be complex, that most of the black may form micron size agglomerates which do not contribute to the dc conductivity (they do not percolate in this concentration range), that a variable proportion of the black is in well dispersed small aggregates and that, at least in the investigated series, there seems to exist some kind of a universal local critical concentration of particles in well dispersed aggregates of order 1 %, insensitive to the mixing conditions and to the nature of the CB. It would be most interesting to study how such a figure depends on the polymer matrix and if it can be generalized to other kinds of CB.

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REFERENCES

1. F. Carmona, Ann. Chim. Fr. 13, 395 (1988)
2. L. Salome and F. Carmona, Carbon 29, 599 (1991)
3. T. Meraoumia, Thèse de doctorat, Bordeaux University, France, 1994.

FIGURE 1 - CB volume concentration dependence of the apparent surface density (Y50A series) and of the local apparent surface density of small aggregates (Raven series). Arrows show the respective critical CB concentration values at dc conductivity threshold in each series.