Provided the CB is localized at the polyblend interphase, the CB percolation threshold can be as low as 0.4 wt %.

LOW FREQUENCY AC FREQUENCY AND PERMITTIVITY

It has been known for a long time that in systems like CB-polymer composites tunneling plays an important role in the vicinity of the percolation threshold. CB's generally do not exist as discrete individual particle. Usually a number of particles are clustered together in fibroidlike aggregates.It is not easy to define the percolation threshold in these conditions. Before close contacts between these aggregates are established the electrical conductivity appears to vary in a exponential way with concentration Such a behaviour is characteristic of hopping and tunneling processes. As discusssed in a number of recent papers the low frequency dispersion of the ac electrical conductivity and permittivity of these systems under and in the vicinity of the percolation threshold is a reflection of the complex morphology of the percolating clusters and the nature of the conduction processes.

In the present paper we present the results of measurements of the ac conductivity and dielectric constant of some of the composites discussed in [1] i.e as a function of CB concentration and molding compression time With increasing molding pressure time the morphology of the polymer composite becomes coarser decreasing the percolation threshold in the conducting phase (i.e. the polymer component in which the CB is localized) The experimental results are consistent with a recent model proposed by Brouers and Sarychev [2].

Noticing that the dispersion of the conductivity and the dielectric constant observed in many composites in the range 10^{-3} - 10^{7} Hz close to the percolation threshold in materials where the conduction is of electronic nature cannot be explained by the usual percolation theory, Brouers and Sarychev have suggested that the conductor-dielectric scaling law

$$\sigma_e(p,\omega) = \sigma_e(p)\Phi\left[\frac{-i\omega\epsilon_e(p)}{\sigma_e(p)}\right] \quad (1)$$

could be used also in the concentration range where conduction is dominated by tunnelling. In that case they have shown using heuristic arguments that that the effective macroscopic conductivity and dielectric constant are given by

$$\sigma_e(p) = \sigma_0 \left|\Delta p\right|^{-m} exp(-\lambda_0 pc \left|\Delta p\right|^{n}) \quad (2)$$

$$\epsilon_e(p) = \epsilon_0 \left|\Delta p\right|^{-s'} \quad (3)$$

$$\sigma_e(p_c) = \sigma_0 \lambda_0^{-t/n} \quad (4)$$

when the frequency ω is much larger than the crossover frequency $\omega_c \propto \sigma_e(p)\left|\Delta p\right|^{s'}$ where the intercluster tunnelling resistive and capacitive conductivity's are of the same order of magnitude, the scaling function behave as a power law :$\Phi(\omega) \propto \omega^{x'}$. This means that in that frequency range $\sigma'_e(p,\omega) \propto \omega^{x'}$ and $\epsilon'_e(p,\omega) \propto \omega^{y'}$ with x'+ y' = 1. The exponent are expressed in terms of the usual percolation exponents i.e. $n = s+\nu(d-2)$ and $m = \nu(d-2)(n-1)$ where ν is the correlation function exponent. The renormalised dielectric exponent s' and the dispersion exponent x' are different from the usual percolation exponent s and $x = \frac{t}{s+t}$ since the nature of the conduction is different. Estimations of s' and x' have been computed for 2d systems. Preliminary computations for 3d systems indicate that x' should be very close to one as this has been observed in

AC PROPERTIES OF CARBON BLACK FILLED POLYMER BLENDS

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ABSTRACT

The macroscopic electrical properties of carbon black filled polyethylene (PE)/polystyrene (PS) blends depend strongly on the selective localization of carbon black particles in one of the phases of the polyblend. The electrical and dielectric properties of these materials can be understood in the framework of the double percolation theory. It appears that in the vicinity of the carbon black percolation threshold, the electrical conduction is dominated by tunneling. The recent theory of Brouers and Sarychev which includes quantum tunneling in the percolation scaling laws provides the basis for a discussion of the observed frequency dependence of the conductivity and the dielectric constant in the range $10^{-3} - 10^{6}$ Hz and its relation to the blend morphology.

INTRODUCTION

Conducting polymer composite materials (CPCM), that consist of a random distribution of a conducting filler throughout an insulating polymer, deserve interest in several application fields. They are used as antistatic materials and low-temperature heaters, and they are very promising for electromagnetic radiation shielding. The lasting use of carbon black (CB) in CPCM makes it appear as the most universal conducting filler. One major problem in the production of CPCM is the filler content, that must be as low as possible, otherwise the mixture processing becomes difficult, the mechanical properties of the composites are poor, and the final cost is high.

The percolation theory is the most adequate for modelling conductivity of CPCM. It involves convergence of particles to distances at which the probability of transfer of current carriers between them undergoes a jump of several order of magnitudes. The so-called percolation threshold, i.e. the lowest concentration of conducting particles at which continuous conducting chains are formed, has to be determined from the experimental dependence of conductivity on the filler concentration. It is a very useful tool to probe the filler concentration within a polymer matrix.

The only way to reduce the CB content in CPCM is to favor inhomogeneities in the material. Using a two-phase polymer blend as the polymer matrix in CPCM is a posible solution which has received increasing attention. Several possibilities have actually been considered [1]. Here we will limit our investigations to the case where the CB is dispersed in the minor phase of a two cocontinuous phase polymer blend. It is essential to know what effect the CB particles can have on the phase morphology of the polyblend. Typical questions are is the originally co-continuous two-phase morphology preserved ? Is it possible to decrease the interfacial area while preserving the cocontinuity of the phases and as a result, to decrease the percolation threshold? In a previous work[1] the phase cocontinuity of polyethylene (PE)/polystyrene (PS) blends has been studied in the presence of various amounts of CB by selective extraction of one polymeric component, followed by microscopic and image analysis. Electrical conductivity has also been measured in order to establish a relationship between the morphology of the polymer composites and their electrical properties. As shown in this recent publication a double percolation is the basic requirement for electrical conductivity in these composites. One needs a structural continuity of the 3D or 2D space in which the CB particles are selectively localized and one needs a minimum amount of CB in order to have a continous percolating path.

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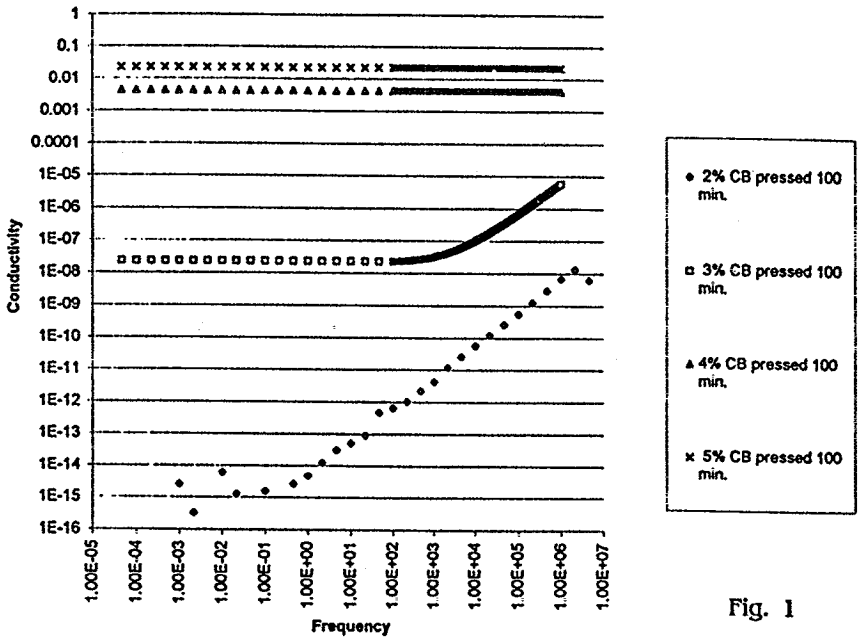

Fig. 1

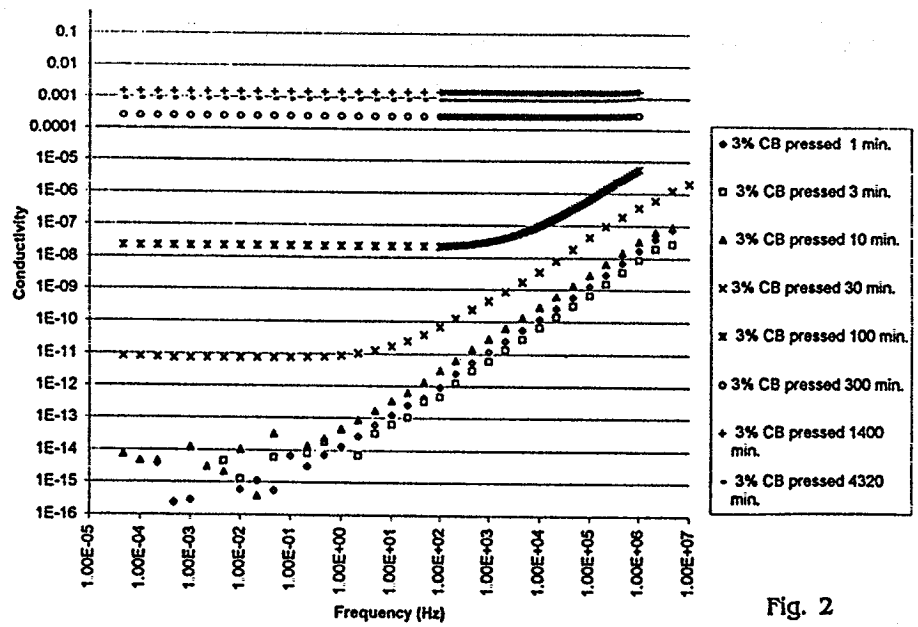

Fig. 2

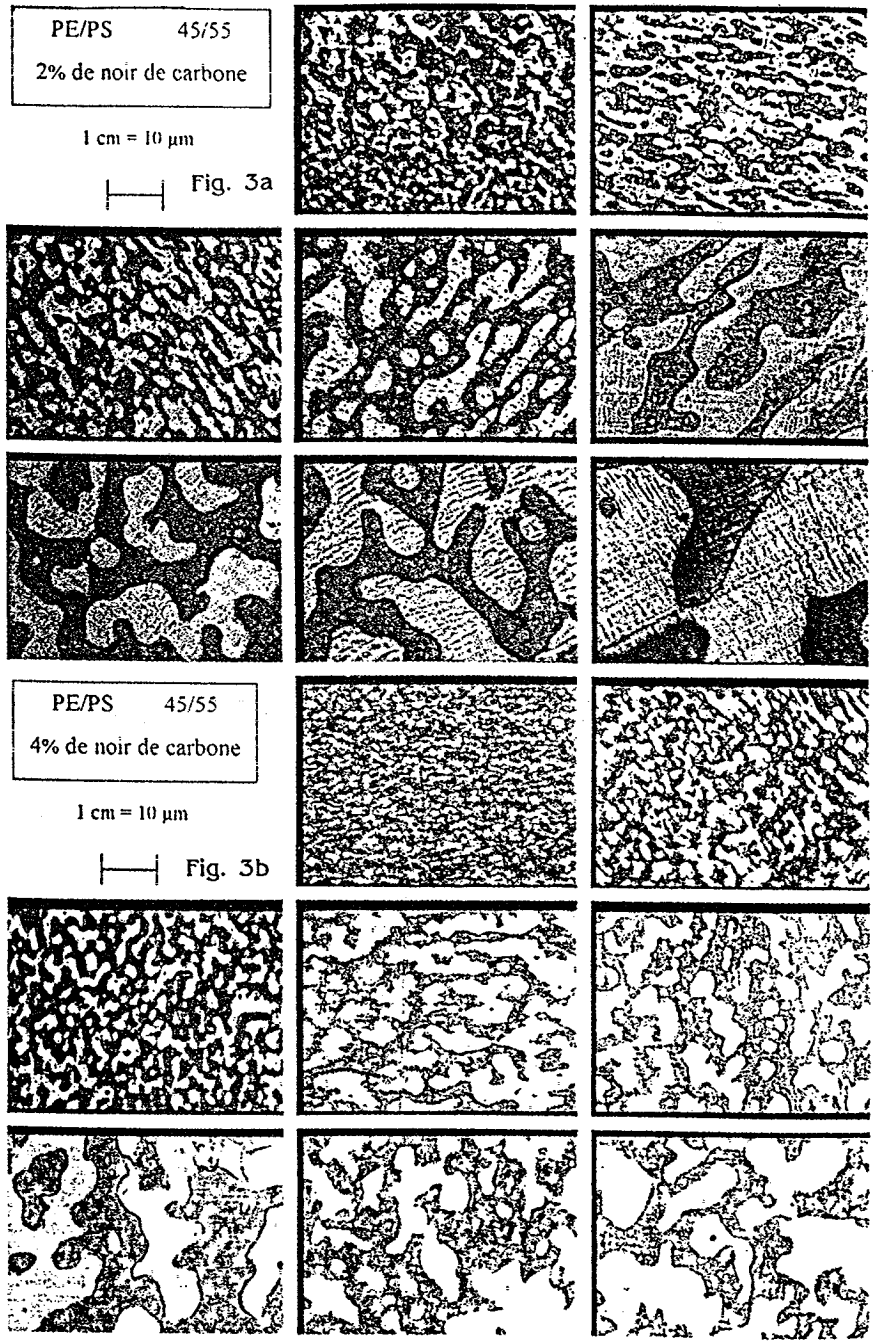

Fig. 3a

Fig. 3b

a number of physical systems, allowing the introduction of new scaling exponents in the tunneling regime under the percolation threshold.

As far as our experimental results are concerned the following conclusions are of importance

1. The dc conductivity depends exponentially on $p - p_c$
2. The conductivity and dielectric conductivity follows a power law behaviour over several decades above a cross-over frequency and the dispersion exponents are tunelling specific 1
3. The cross-over frequency is a function of $p - p_c$ and is proportional to the dc conductivity.

The compression molding time and the carbon black percentage has a decisive effect on the blend co-continous morphology and the d.c resistivity. This has been discussed in detail in Ref.[1]. Two physical parameters are modified by the change of time of compression : the tunelling constant and the percolation threshold which depends on the CB cluster morphology in the conducting phase and the polymer composite morphology.

For a.c. properties the variation of the same parameters can explain the variation of the dispersion of the conductivity and the permittivity as the concentration of carbon black is increased or for a given BC concentration for increasing moulding compression time. The decrease of the tunnelling constant λ_0 and p_c induced by the morphological change can account for the increase of the d.c. conductivity, the increase of the cross-over frequency according to Equation. (2-4).

We present in Fig. 1 the evolution of the frequency dependence of the electrical conductivity of a PE/PS-45/55 blend with 2,3,4,5 % C.B. weight and a moulding compression time of 100 minutes. It can be seen that the exponent is very close to one as in the theory of Ref [2]. Fig. 2 represents the evolution towards percolation threshold of the frequency dependence of the composite conductivity as the compression time increases (1,2,10,30,100,300,1400,4320 minutes) for a loading of 3 % carbon black weight. Fig 3a and 3b illustrate the change of morphology induced by moulding compression for the same succession of pressure time for 2% and 4% BC concentration. It is interesting to notice that the carbon black stabilizes the co-continuous two-phase blend morphology. The moulding compression increases the electrical conductivity but does not destroy the co-continuous two-phase structure in contrast with what happens in a blend without carbon black as this was also noticed in [3].

CONCLUSIONS

The preliminary results presented in this communication show the interest of coupling phase polymer blend morphology studies with a.c. electrical measurements in order to better understand the correlation between polymer morphology, carbon black localization and electrical and dielectric dispersion and to optimize the electrical and mechanical properties of these materials. A complete analysis of the a.c. conductivity and morphology of these composites is in progress.

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