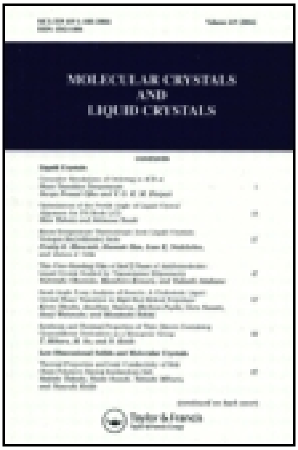

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Transport and Mechanical Properties of Polyaniline—Poly(methyl methacrylate) Blends Exhibiting Low Percolation Threshold

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Transport and Mechanical Properties of Polyaniline – Poly(methyl methacrylate) Blends Exhibiting Low Percolation Threshold

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The electronic transport and the dynamic mechanical behavior of conducting polymers blends are studied as a function of the conducting phase content. Electrical percolation is demonstrated for an ultra low threshold (0.03%), whereas a dramatic increase of the relaxed elastic modulus is observed beyond a higher threshold (0.5%). From the analysis of the thermal dependence of conductivity, and the comparison between mechanical and transport data, an image of the phase segregated morphology is proposed.

Keywords: conducting polymers; blends; electrical percolation; viscoelasticity

INTRODUCTION

Since their discovery twenty years ago, the interest for conducting polymers (CP) has been stressed many times with a particular focus on their potential ability to combine mechanical and electrical properties in a single material. It was renewed in the beginning of the 90's when the thermal or solution processibility and the stability of CP were greatly improved. One example is given by polyaniline (PANI) which was found to be soluble in its doped – i.e. conducting – state if specific doping agent (camphor sulfonic acid, CSA) and solvent (*m*-cresol, MC) were used[1]. Since then, high values of the conductivity at room temperature (RT) ($\sigma \geq 300\,\mathrm{S\,cm^{-1}}$) and at liquid helium temperature

($1 < \sigma(300\text{K})/\sigma(4\text{K}) \leq 3$) were reported. Moreover, a conductivity maximum at T_m (in the range 200 – 280 K) was the proof of a "metallic behavior".

The mechanical properties of those systems have not been studied in great details but do not reveal, even qualitatively, as remarkable as the electrical ones. Blending is a traditional method to take advantage of specific properties of multi-component systems. For the new generation of CP described above, this strategy has proved to be of great fertility. As a matter of fact, it is possible to realize conducting films with a very small amount of PANI dispersed in various insulating matrices such as poly(methyl methacrylate) (PMMA) or cellulose acetate (CA). Typical characteristics are: 1 S cm^{-1} for 1 wt. % of PANI, and an even lower concentration remains suitable for basic applications such as anti-static products. Properties of the host polymer such as flexibility or optical transparency are thus fully retained in the blends.

In addition to this practical interest, many fundamental questions arose from the physical characterizations. They deal with the general problems of geometrical and electrical percolation, transport in disordered and/or fractal systems, all of them being related to the microstructure of the multi-phase system. The pioneering works in this field dealt with PANI(CSA)/PMMA blends[2]. PANI(PPA)/CA, where PPA stands for phenyl phosphonic acid, exhibits similar properties and was also studied in details[3] from the electronic transport point of view. In both cases, the percolative behavior of the dc conductivity was clearly ascertained, leading to percolation thresholds lower than 0.1 wt. % of PANI. Hopping was recognized as the major transport mechanism, at low T at least. However, the quantitative analysis of $\sigma(T)$ data involved non canonical models – with respect to Mott's Variable Range Hopping or Sheng's Granular Metal models – because of a continuous dependence of the parameters with the concentration. This unconventional behavior was assumed to originate from a small scale (i.e. sub-micronic) segregation process between conducting and insulating phases. The microstructure was described as a fibrillar conducting network, which is corroborated, at least geometrically, by real space imaging[4][5].

In this paper we present a deeper insight in the relationship between geometrical and electrical features by joint studies of dynamic mechanical analysis (DMA) and electrical conductivity $\sigma(T)$ on the same samples. We have chosen the most celebrated combination PANI(CSA)/PMMA, but adding a new degree of freedom by plasticizing the matrix at different rate. We show in the next sections that this addition coherently affects conduction and viscoelastic properties in a way that can be sketched as follows: the more the amount of plasticizer, the stronger the influence of the minority PANI phase at a given concentration.

It is also shown for the first time that a mechanically connected network does span the macroscopic sample at least when the PANI content exceeds 0.5 wt. %. The discrepancy between mechanical and electrical threshold might be understood if tunneling between disconnected "grains" is considered, in agreement with modified percolation models.

EXPERIMENTAL

The synthesis of the samples used throughout this study has been described in details in Ref. [6]. Briefly, blends are prepared from co-solutions of PANI (doped with CSA) and PMMA with various amounts of the plasticizer dibutylphtalate (DBPh): $x = \text{mass of DBPh} / \text{mass of PMMA} = 0, 0.25 \text{ and } 0.35$. The common solvent is MC. The number molecular average weight of PMMA is $M_n = 45800$ and the polydispersity $M_w / M_n = 1.9$. The inherent viscosity of PANI in the oxidation state of emeraldine base (EB) is equal to 1.49 dl/g at 25 °C (0.1 wt. % of EB in H_2SO_4). Films of a few tens of micrometers thick are obtained after evaporation of MC at 40°C. For the 3 series defined by the value of x, PANI contents p between ca. 0.05 and 5 wt. % have been used. p is defined as the ratio of the mass of EB to the total mass (EB+CSA+PMMA+DBPh).

Conductivity measurements are performed with the standard four probe method. Gold electrodes are evaporated onto the sample to insure a good electrical contact. The ohmic behavior is checked at each temperature. The temperature is varied between 4 and 315 K inside a continuous flow liquid helium cryostat Oxford 1200D.

Dynamic mechanical tests are carried out in the glass-rubber temperature transition (T_g) range with a Rheometrics RSA2 spectrometer in the tensile mode. Test conditions are chosen in such a way that the measurements are in the linear viscoelasticity region (the maximum strain ε was around 5×10^{-4}). The specimen is a thin rectangular strip with typical dimensions of $20\times6\times0.1$ mm. The setup measures the complex tensile modulus E^*, i.e. the storage component E' and the loss component E''. In the present work, results are displayed through E' and $\tan\delta$ ($=E''/E'$). Measurements are performed in isochronal conditions at 1 Hz, and the temperature is varied by steps of 3 K.

CONDUCTIVITY RESULTS

Percolative behavior

It has been shown in Ref. [6] that the dependence of the RT dc conductivity with the concentration p can be satisfactorily described by the scaling law of percolation:

$$\sigma(p)=\sigma_0(p-p_c)^t \tag{1}$$

σ_0, the percolation threshold p_c, and the conductivity exponent t, are given in Table 1 for the 3 series. They have been determined by looking for the best linearity of $\ln\sigma$ vs. $\ln\frac{p-p_c}{p_c}$ for different trial p_c. p_c decreases and t increases as x increases. Fig. 1 shows that Eq. (1) is followed at each temperature with the same $p_c = 0.07$ wt. % but different t and σ_0. The monotonic dependence of t with T is shown in Fig. 2. At RT, $t=1.42$, it increases strongly up to $t=4.34$ at $T=9\text{K}$. Data in Fig.2 have been fitted to

$$t(T)=\alpha+\beta/T \tag{2}$$

the value of $\alpha = \lim_{T\to\infty} t = 1.39$ is close to that at 300K. Deviations from Eq. (2) are observed for $T \geq 130$ K but remain remarkably small despite the change in the conduction mechanism (see below).

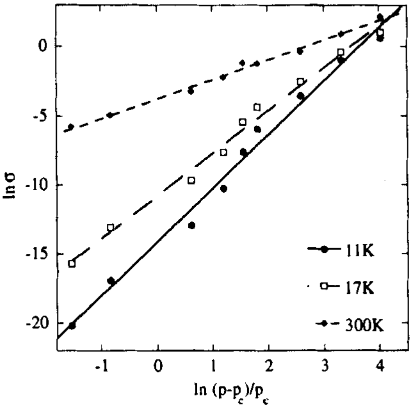

FIGURE 1. Percolation behavior of PANI(CSA)/PMMA($x = 0$) at various temperatures. Lines are fit to Eq. (1) with the same $p_c = 0.07$.

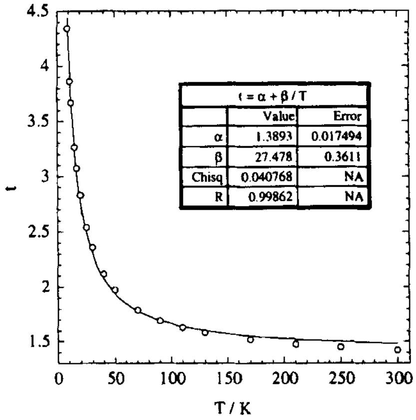

FIGURE 2. Thermal dependence of the scaling exponent t for $x = 0$ and $p_c = 0.07$.

Thermal Dependence

The most remarkable feature to be emphasized in $\sigma(T)$ measurements is the presence of a maximum at every concentration $p > p_c$ with a characteristic $T_m(p) \le 300\text{K}$. Data for $x = 0$ are plotted in reduced units $\sigma(T)/\sigma(T_m)$ vs. T/T_m in Fig.3. A similar evolution is found for each value of x. As $p \rightarrow p_c$, the decrease of σ with decreasing T becomes faster. The low temperature part of the curve is characteristic of hopping conduction in disordered systems and may be fitted to the general expression

$$\ln\sigma_h \propto -\left(\frac{T_0}{T}\right)^{\gamma} \qquad (3)$$

where T_0 and γ are both p-dependent. The high T regime is not so well defined but may be reasonably fitted to the quasi-1D metallic conductivity formula[7]

$$\sigma_m \propto \exp\left(\frac{\hbar\omega}{k_B T}\right) \qquad (4)$$

where ω is the frequency of scattering phonons at $\approx 2k_f$ $\left(\hbar\omega/k_B \approx 1200\text{K}\right)$, and k_B the Boltzmann constant.

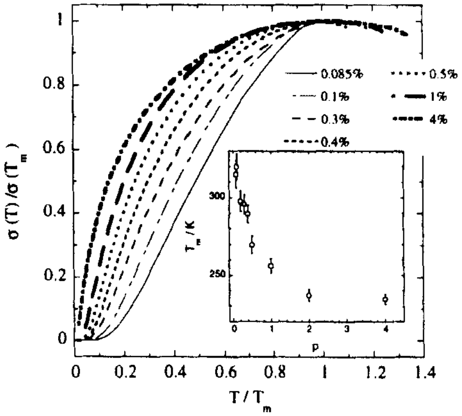

FIGURE 3. Thermal dependence of conductivity for PANI content $0.085 \le p \le 4$ and $x = 0$ in reduced units. Inset: p dependence of the temperature T_m where $\sigma(T)$ reaches its maximum.

As already suggested in heterogeneous disordered conductors[8], the global behavior is schematically understood as resistive parts in series with respective values σ_h^{-1} and σ_m^{-1} and T-dependent weights. Fig.4 shows fits to Eqs. (3) and (4).

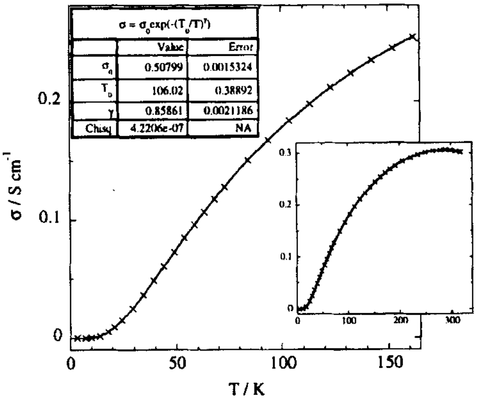

FIGURE 4. Fit of the low-T part of $\sigma(T)$ following Eq.(3) for $p = 0.4$. Inset: fit of the whole curve by serial combination of Eqs. (3) and (4)

DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical measurements have been performed on all the three series of samples. For clarity, only the results for the non-plasticized and $x = 0.35$ plasticized series are shown here.

Fig. 5 displays the logarithm of the storage tensile modulus E' vs. T measured on the non-plasticized samples. The open-circle curve, corresponding to pure PMMA, is typical of thermoplastic behavior with, however, a hardly visible rubbery state, due to its low M_w. Above 300K, E' decreases rapidly with temperature indicating the transition of PMMA from the glassy state towards the rubbery state; the transition temperature $T_g \approx 330\,\text{K}$. In the terminal zone, the relaxed elastic modulus rapidly drops, due to irreversible flow.

The curves obtained from the blends can be classed into two groups.

First, the addition of PANI essentially induces an increase of T_g without any significant change in the shape of the curves at higher temperature. This behavior holds up to concentrations as high as 0.5 wt % of PANI. For more concentrated blends, the relaxed elastic modulus remains constant over a large temperature range (typically 100K) until the sample breaks. The value of this rubbery plateau increases from log(*E*')=5.6. to log(*E*')=6.6 as p increases from 1 to 4 wt. %. Moreover, we notice an augmentation of the modulus above 500K for the sample with $p=4$, which reminds the signature of reticulation mechanisms. The inset in Fig.5 shows the loss angle tangent $\tan\delta$ vs. T for blends with PANI contents in the range [0.3 – 4 wt. %]. The maximum in $\tan\delta$ is generally associated with T_g. In our case, T_g slightly increases with p and lies between 345 and 352K.

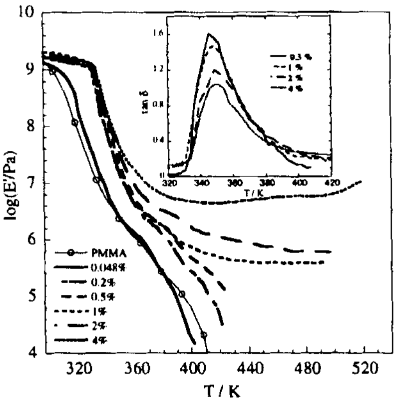

FIGURE 5. Storage tensile modulus E' and loss angle tangent tanδ (in inset) vs temperature at 1 Hz for non-plasticized samples.

The addition of plasticizer dramatically alters this behavior, especially when a large quantity is used. The plot of $\tan\delta$ vs. T for $x=0.35$ blends with $p=0.075$, 0.3, 0.5 and 1 are displayed in Fig.6. For this series, T_g lies in the range $[330-345\,\mathrm{K}]$ which corresponds to lower values than those recorded at $x=0$, as expected for a plasticizing effect. More unexpected is the dependence of T_g with p: the more the PANI content, the lower T_g. It goes as if PMMA exhibited a effective lower M_w as PANI chains are included. Moreover, the wide rubbery plateau mentioned above sets up at lower PANI concentrations: between 0.3 and 0.5 wt %.

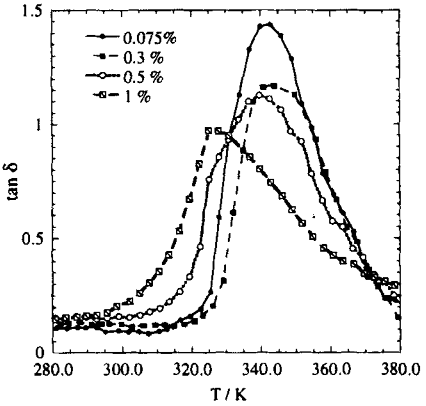

FIGURE 6 Loss angle tangent tanδ vs. temperature at 1 Hz for 35 wt. % plasticized samples.

DISCUSSION AND CONCLUSION

Transport Properties

In the ongoing debate related to the nature – heterogeneous or homogeneous? – of the disorder in CP, the appearance of a maximum in $\sigma(T)$ curves has been put forward in favor of the former[9]. Heterogeneity is depicted by the assembly of high and low conductivity areas with competing transport behaviors: metallic and hopping, for instance. Their balance is responsible for the non monotonic $\sigma(T)$ and the location of T_m. The crucial difference with respect to homogeneous models is to be found in the role of (at least) one mesoscopic characteristic lengthscale: the size of low conducting "barriers" and/or the size of high conducting "grains". This lengthscale – in the nanometer range – is a major parameter which monitors the macroscopic conductivity through T_0 in Eq. (3) for instance[10].

In the blending process, heterogeneity is not reduced. However, depending on the lengthscale, the dispersion exhibits various signatures. It has been shown[5], by probing the charge carrier motion along the chain, that transport is not affected at the smallest scale. Conversely, the percolation scheme, that seems to apply very well at the sample scale, suggests that the morphology induced by dispersion controls the macroscopic conductivity. At the "grain" scale, a more complex behavior is inferred from the continuous dependence of γ (Eq. (3)) with p. In Refs. [5] and [11], it was suggested that a change in the grain connectivity as $p \to p_c$ was related to an effective change in the local conductivity distribution, thus leading to the observed behavior.

To our knowledge, the continuous variation of exponent t (Eq. (1)) with T has never been evidenced to date. Ref. [2] gives the following result for 2 temperatures: $t_{300\,\mathrm{K}} = 1.4, t_{10\,\mathrm{K}} = 1.9$. This is the same sense of variation than ours. Many other systems leads to non–universal exponents[12], that may be greater or lower than $t_{\mathrm{un}} = 2.0$, the admitted value for 3D lattice percolation. A continuous percolation model has been derived, which essentially assumes that local conductivities $\{\sigma_{\mathrm{loc}}\}$ are widely distributed. Consequently the average conductance of a link involving $N\sigma_{\mathrm{loc}}$ depends on N. On the percolation cluster, $N \propto (p - p_c)^{-1}$, hence an additional contribution Δt to $t = t_{\mathrm{un}} + \Delta t$. Δt is related to the parameters that control $\{\sigma_{\mathrm{loc}}\}$. In Ref [13], the tunneling distance r is distributed and $\sigma_{\mathrm{loc}} \propto \exp(-r/\xi)$, leading to $\Delta t = a/\xi - 1$, where a is the average value of $\{r\}$. In the hopping mechanism, r decreases when T increases – the exact relationship depending on the model – and a does as well. This might explain, not the exact form of Eq. (2), but its qualitative behavior.

Mechanical Properties

The mechanical results must be interpreted keeping in mind the mechanical behavior of the pure PANI$(CSA)_{0.5}$ films cast from MC[14]. This polymer exhibits a T_g of approximately 450K and a high and steady value of the relaxed tensile modulus (log(E'/Pa) = 8.85) which even increases above 500K because of reticulation mechanisms.

Looking at the shape of our curves and considering the very different mechanical features in a narrow range of PANI content, we are tempted to define a "mechanical percolation threshold", p_m. Above p_m a continuous PANI-phase sets up and spans geometrically the sample communicating its intrinsic mechanical properties to the blend. The high and steady relaxed tensile modulus as well as its increase with the PANI content support this analysis. The signature of the reticulation observed in the most concentrated sample $(p = 4)$ at the same T than in pure PANI [14] emphasizes the fact. In our case, p_m lies between 0.3 and 1 wt. % of PANI depending on the rate of plasticizer in the blend. The inverse evolution of T_g vs. the PANI content taking place in plasticized and non-plasticized samples could be explained adopting the following description. In the non-plasticized sample all goes as if the additional amount of PANI above p_m was mainly used to reinforce the existing network. Conversely, the plasticizer favors the interface between PANI and the matrix. Thus more PANI means more ramifications in the network with respect to the PANI content, leading to new fixed points along the PMMA chains. Consequently free PMMA segments should become shorter in average modifying the relaxation temperature. Therefore the effect of the plasticizer should explain the lower value of p_m and the evolution of T_g with p.

Conclusion

The presence of a PANI network has been simultaneously evidenced by transport and mechanical characterizations. Even if one could expect that the same parameters would describe both of them, it is clearly not the case : $p_m >> p_c$.

This could be understood if conduction proceeds via hopping and/or tunneling between conducting grains and does not need true geometrical connectivity. This question has already been addressed in the field of carbon black/polymer blends[13]. However, inspection of the exponent t is not sufficient to discriminate between activation and tunneling within continuous percolation.

To summarize, the first dynamic mechanical studies on conducting PANI-PMMA blends has been carried out. It has proved to be an useful tool in our understanding of the phase segregated morphology, especially if one takes into account various amounts of platicizer. In this case, the formation of the PANI network can be qualitatively correlated with the increase of the DC conductivity and the evolution of the parameters describing percolation.

TABLE 1: Fitting parameters to the percolation scaling law (Eq. (1))

x	0	0.25	0.35
P_c (wt. %)	0.070 $^+$/- 0.003	0.038 $^+$/- 0.005	0.028 $^+$/- 0.005
t	1.42$^+$/- 0.05	1.65 $^+$/- 0.05	3.0 $^+$/- 0.1
σ_0 (S.cm^{-1})	2.31 10^{-2}	5.66 10^{-3}	5.31 10^{-5}

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