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Carbon black-loading induced phase fluctuations in PVDF/PMMA miscible blends: dynamic percolation measurements

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Abstract

In this work, we investigated the effect of carbon black (CB)-loading on the miscibility of poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) blends using the CB particle as a self-diagnosing probe. The mobility of the CB particles both in homogeneous and PVDF/PMMA blend matrices was real-time monitored through in situ recording the variation of electrical resistivity with time during annealing treatments. It was found that the dynamic percolation curves in a homogeneous matrix behave with self-similarity to different annealing temperatures and CB concentrations, and the activation energy of the percolation time is near to that of the zero-shear-rate viscosity of polymer matrix regardless of the filler concentrations. However, in the CB-filled PVDF/PMMA system, both the shape of the dynamic percolation curves and the activation energy of the CB mobility were found to change with the annealing temperature. These facts implicate that the PVDF/PMMA blend matrices filled with CB are not homogeneous. SEM and AFM observations as well as DSC and DMA studies confirmed that the incorporation of CB induces the phase fluctuations in PVDF/PMMA miscible blends due to a preferential adsorption of PVDF molecules on the CB surface. As a result, the CB particles are heterogeneously distributed in the miscible blends and thus greatly reduce the percolation threshold of the PVDF/PMMA/CB composites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon black; Poly(vinylidene fluoride); Poly(methyl methacrylate)

1. Introduction

Recently, it was shown that an introduction of a mineral filler into a binary polymer mixture might promote the compatibility between two polymers [1–5]. A thermodynamic analysis based on the framework of the Flory–Huggins theory suggested that the filler has compatibilizing effect both for immiscible and miscible polymer blends, due to an decrease in the thermodynamic interaction parameter χ to a negative value [1,6]. It should be pointed out that if a mineral filler can serve as a compatibilizer in such a general way, it would constitute a major technical achievement [7,8].

Carbon black (CB) is the most important reinforcing filler in the rubber industry, and as conductive filler, it is also widely used for fabricating the conductive polymer composites. The mechanical and electrical properties of the CB-filled polymer blends are known to be influenced essentially by the morphology of the matrix [9–14]. However, few have been reported concerning the effect of CB on the compatibility of the polymer blends. This may be due to the small amount of the chemical group such as hydroxyl etc. on the CB surface resulting in a weak CB–polymer interaction and thus less influence on the compatibility of the polymer blends. Another reason might be that the CB-filled mixture is black in its color, and it is not possible to determine the state of miscibility by the conventional procedure such as the cloud-point method [3] and light scattering analysis [15] etc. In most cases, one has to use the information obtained from differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) measurements [5,7].

In the previous work [16], we developed a new technique to real-time monitor the mobility of the CB particles in the polymer matrix by means of in situ recording the variation of electrical resistivity with time during isothermal treatments at molten temperatures. This is based on the fact that the CB particles dispersed in the polymer matrix are easy to agglomerate together in a way of the Brownian movement, and finally form the three-dimensional (3D) inter-particle networks. The percolation time is characterized at a certain annealing time where the resistivity starts to decrease drastically. We call this phenomenon as dynamic percolation. Theoretical analysis as well as experimental results [16] revealed that the percolation time is directly

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correlated to the zero-shear-rate viscosity of polymer matrix, regardless of the filler concentrations. Accordingly, it seems that each pair of the CB particles in the polymer matrix might be regarded as a sensitive probe like a micro-rheometer during the dynamic process of forming the CB networks. This characteristic may provide an incisive methodology to detect the state of miscibility in CB-filled miscible polymer blends. Since any phase fluctuations and/or phase separation in the miscible blend matrix will inevitably change the constituent component and the bulk mobility of the polymer layer surrounding the CB particles and thus disturb the dynamic process of CB mobility, the dynamic percolation behavior should respond to these changes sensitively.

Poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) are known to be molecularly miscible in the melting state, and exhibit a lower critical solution temperature (LCST) around 330°C [17]. They are used as matrices in this work to investigate the influence of CB-loading on the miscibility of PVDF/PMMA blends by means of the dynamic percolation measurements. Our preliminary interest using various miscible blends as matrices had been on the effect of blend ratio on the electrical properties of CB-filled composites, and furthermore, on monitoring the fluctuation of electrical conductivity during the phase separation (both spinodal and binodal decomposition) in order to design the structure-controlled conductive device. The results of the dynamic percolation measurements let us notice that the introduction of CB might cause a phase fluctuation even within a miscible temperature range of PVDF/PMMA.

2. Experimental

2.1. Materials

Raw materials used in this study were commercial products. PMMA (HA) was supplied by Mitsubishi Rayon Co., PVDF (Foraflon F1000HD) was by Showa Denko Co., and CB (Seast 300) was by Tokai Carbon Co., with a diameter of 28 nm and a N_2 surface area of about 86 m^2/g.

2.2. Preparation of blends

Polymers and CB were dried at 105°C for 24 h under vacuum before using. The mixing of PVDF/PMMA, PVDF/CB and PMMA/CB was carried out at 200°C for 10 min using a two-roll mill. For the composites of PVDF/PMMA/CB, the PVDF was first mixed with PMMA at 200°C for 10 min followed by the addition of CB and then mixed for 15 min. The mixing temperature was selected at which both PVDF and PMMA have a close viscosity. The composites were compression molded at 190°C for 5 min under a pressure of 20 MPa, and finally quenched in water.

2.3. Techniques

The time dependence of electrical resistivity (dynamic percolation) was measured by a Keithley 487 picoammeter equipped with a direct current voltage source at a given annealing temperature. The specimens with dimensions of $18 \times 18\ mm^2$ size were cut from the center area of the molded film and fixed on a glass slide using a polyimide tape. A silver paste was used to ensure good contact of the sample surface with the copper electrodes. The prepared sample was then placed in a temperature-controlled chamber. Nitrogen gas was used during measurements in order to prevent the samples from oxidation. The applied voltage for measurements was 1 V.

Dynamic rheological measurements were carried out with a universal dynamic spectrometer (Physica UDS200, Physica Messtechnik). A cone and plate fixture, with a cone angle of 4° and a diameter of 25 mm was used at angular frequencies from 0.001 to 100 rad/s. The strain amplitude was maintained at 0.5%. Dry nitrogen was used for preventing the degradation of the sample.

Differential scanning calorimetry (DSC) was measured with a thermal analyzer (TA-50WS, Shimadzu) at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was carried out on a dynamic mechanical analyzer (IT-DVA200s, Air Tech. Japan) at a heating rate of 5°C/min with a strain amplitude of 0.1% and a frequency of 50 Hz.

Scanning electron microscopy (SEM) observation was carried out by means of a field emission type scanning electron microscopy (FE S800, Hitachi). Specimens were fractured in liquid nitrogen. The surface of prepared specimens was etched by the Ar ion for 15 min using an Eiko IB-3 equipment and coated with Pt–Pd.

The surface morphology of the PVDF/PMMA blends filled with or without CB was observed by using atomic force microscopy (AFM) (SPA 300, Seiko Instruments). The cantilever (Olympus) used for AFM observation was micro-fabricated from SiN_4 with a spring constant $0.09\ N\ m^{-1}$. The surface of the samples was prepared by silica wafer and scanned at a rate of 1 Hz.

3. Results and discussion

3.1. Dynamic percolation in homogeneous matrix

Fig. 1a shows the time dependence of the electrical resistivity for PMMA/CB mixtures annealed at 185°C with different CB concentrations while Fig. 1b shows the dynamic percolation curves for 15 phr CB-filled PMMA composites at various annealing temperatures. It is observed that: (1) The electrical resistivity of the composites reduces as the annealing time increases slightly at first and then abruptly when the percolation time is reached, i.e. an insulator to conductor transition takes place. (2) The shape of the dynamic percolation curves for the PMMA/CB composites

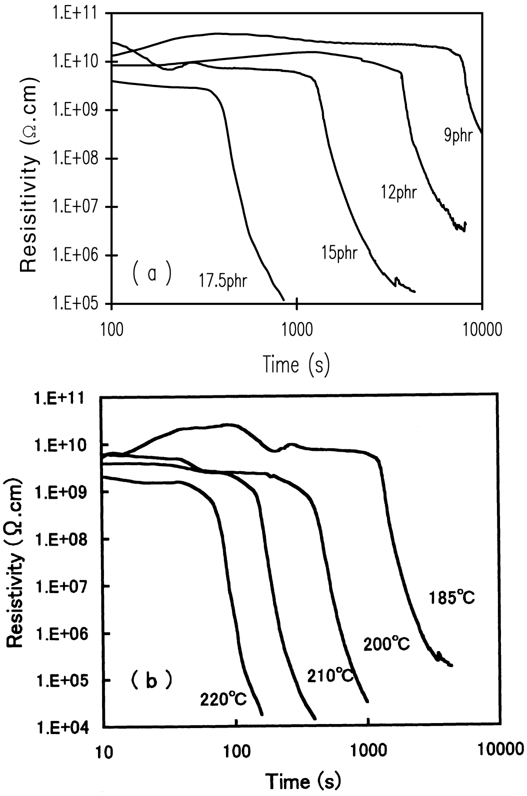


Fig. 1. Dynamic percolation curves for PMMA/CB composites: (a) various CB concentrations annealed at 185°C; (b) annealed at various temperatures with a constant CB concentration of 15 phr.

does not change with the change in the CB concentrations and annealing temperatures. They remain self-similar to each other. (3) The dynamic percolation curves shift to a lower percolation time with the increase of the CB concentration and the annealing temperature.

The reduction of the resistivity with the annealing time should be correlated to the contact number of the CB particles in the matrix [16]. When the contact number increase to a certain value, the CB particles coagulate to form the 3D networks, leading to the drastic reduction of the resistivity. The self-similarity of the dynamic percolation curves strongly suggests that the primary characteristic of the conductive network structure in the homogeneous matrix does not change with the change in the annealing temperature and the CB concentration. This feature also indicates that the family of the dynamic percolation curves may shift to form a master curve. Fig. 2 shows the Arrhenius plots of the percolation time against the annealing temperature for PMMA/CB mixtures containing various concentrations of CB from 6 to 17.5 phr. Here, the percolation time was determined at an onset time when the resistivity starts to drastically decrease. A family of parallel linear relationship for various concentrations is observed in Fig. 2. Their activation energies are calculated to be about 168 kJ/mol regardless of the CB concentration used.

Similar characteristic was observed for PVDF/CB system. As shown in Fig. 3a, the shape of the dynamic percolation curves remains self-similarity to each other and the percolation time decreases with an increase in the annealing temperature. Comparing to that for PMMA/CB, the reduction of the resistivity at the percolation range for PVDF/CB is found to be much gradually. Furthermore, the Arrhenius plot of the percolation time against temperature

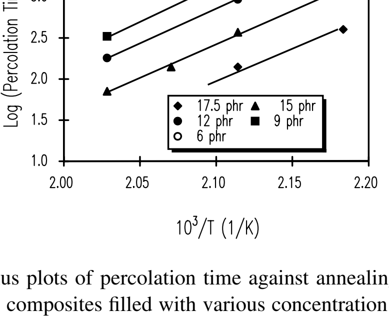


Fig. 2. Arrhenius plots of percolation time against annealing temperature for PMMA/CB composites filled with various concentration of CB.

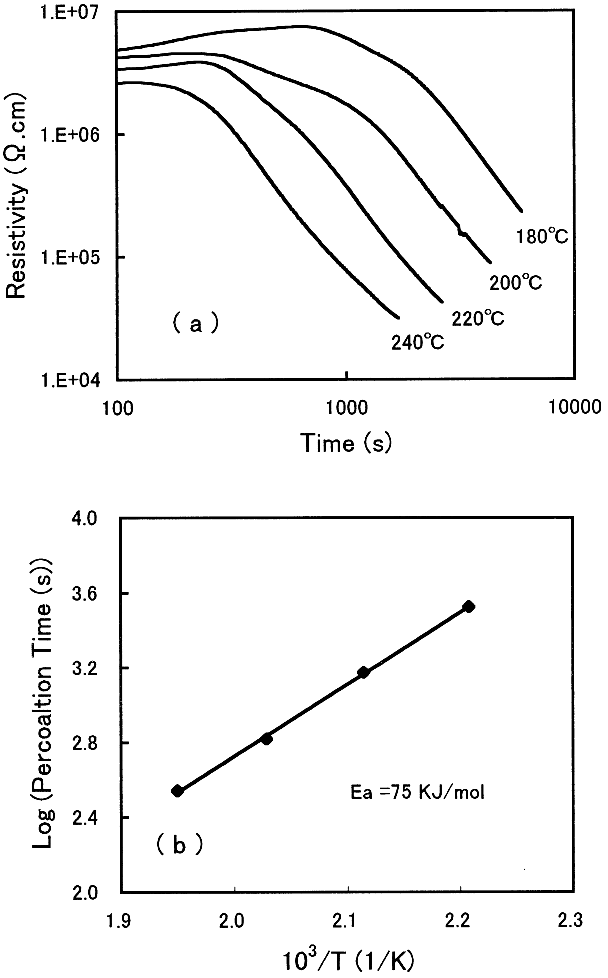


Fig. 3. Dynamic percolation behavior of PVDF/CB composites annealed at various temperatures with a CB concentration of 12 phr: (a) dynamic percolation curves; (b) Arrhenius plot.

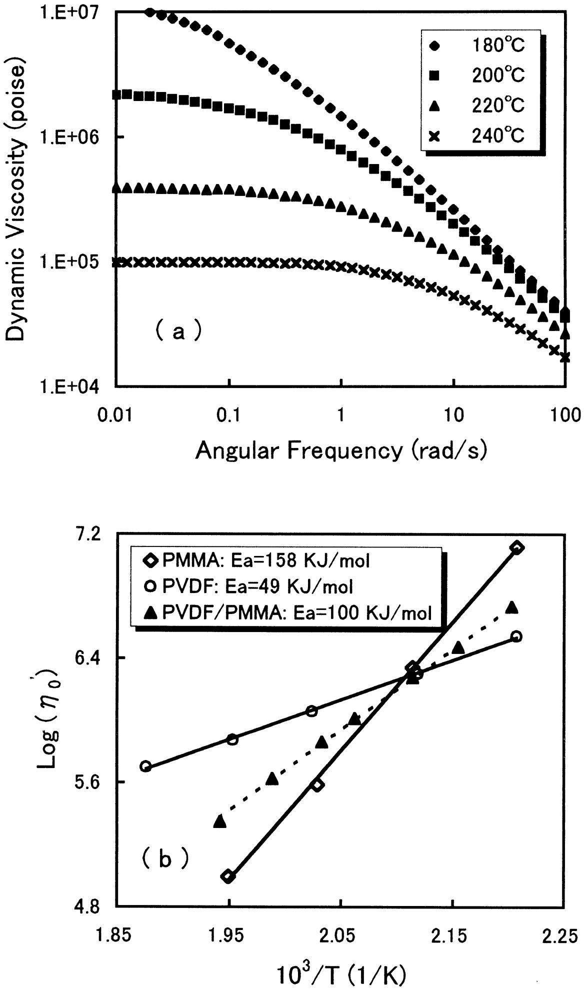


Fig. 4. (a) Angular frequency dependency of the dynamic viscosity for PMMA measured at various temperatures; (b) the Arrhenius plots of the zero-shear-rate viscosity (η'_0) and the activation energy for PVDF, PMMA and PVDF/PMMA (50/50) blend.

for 12 phr CB-filled PVDF/CB shows that the activation energy is about 75 kJ/mol as seen in Fig. 3b, which is much lower than that for PMMA/CB. Our previous study [16] has confirmed that higher interaction of CB with matrix would strongly delay the process of coagulation, therefore, the gradual reduction of resistivity in PVDF/CB system might correspond to the higher interactions between PVDF and CB particles.

The dynamic percolation behavior was found to correlate with the dynamic rheology of the polymer matrix. Fig. 4a shows the angular frequency dependence of the dynamic viscosity for pure PMMA at various temperatures. It is observed that the viscosity increases with the decrease of frequency until it reaches a constant value called zero-shear-rate viscosity, η'_0 [18]. The increase in the measuring temperature accelerates the relaxation process of PMMA macromolecules resulting in a decrease in η'_0. Similar measurements were carried out for PVDF. An Arrhenius plot of η'_0 for PVDF and PMMA polymer is shown in Fig. 4b and the activation energy was calculated to be about 49 and 158 kJ/mol, respectively. These values are comparatively close to the activation energy of the percolation time obtained from PVDF/CB and PMMA/CB systems, suggesting that the decrease in the percolation time with increasing the annealing temperature should correspond to the reduction of η'_0 of the polymer matrix.

Generally, the contact process of two carbon particles can be equivalent to the excluding process of the polymer molecules between two CB particles, and thus, the mobility of the CB particles in the matrix actually reflects the bulk mobility of polymer layer surrounding CB. Since the particle–particle interaction force is very weak, the shear stress and shear rate in the polymer melts is so small that the movement of the polymer layer between CB particles might be regarded as in a state of zero-shear-rate. This may be the reason why the percolation time is correlated to the zero-shear-rate viscosity. A slight increase of the activation energy for PMMA/CB composites (from 158 to 168 kJ/mol) might just reflect the restricted mobility of PMMA molecules due to the interactions with the CB surface. For the PVDF/CB composites, this increase is higher (from 49 to 75 kJ/mol), indicating again the stronger interactions between PVDF and the CB surface [16,19].

3.2. Dynamic percolation for PVDF/PMMA/CB

Before the discussion about the dynamic percolation, we checked the miscibility of pure PVDF/PMMA blends. It was observed that: (1) the pure PVDF/PMMA blends (with composition ratio of 75/25, 50/50 and 25/75 wt%, respectively) are optically transparent; (2) results of rheological measurements showed that the dynamic viscosity of the PVDF/PMMA blends obtained at various temperatures can be superposed to make a master curve; (3) the plot of the storage modulus (G') against the loss modulus (G'') on a double logarithmic scale for various blend compositions was found to lie between those of the constituent components, i.e. PVDF and PMMA, and are independent of temperature. These features are the same as those reported for PVDF/PMMA blends prepared from the solvent cast and two-screw compounding [20–22], indicating that our samples prepared from two-roll mill are in the miscible state.

The Arrhenius plot of η'_0 for PVDF/PMMA (50/50) against temperature is shown in Fig. 4b. It is observed that the η'_0 of the PVDF/PMMA blend lies between that of PVDF and PMMA. A straight line with the activation energy of η'_0 about 100 kJ/mol is obtained, which is close to the value reported by Yang and Han [21].

Dynamic percolation curves measured at different annealing temperatures for PVDF/PMMA (50/50) composites filled with 8 phr CB are shown in Fig. 5a. As usual, we observe a decrease in the percolation time with increasing the annealing temperature. However, it is found that the shape of the dynamic percolation curves changes with

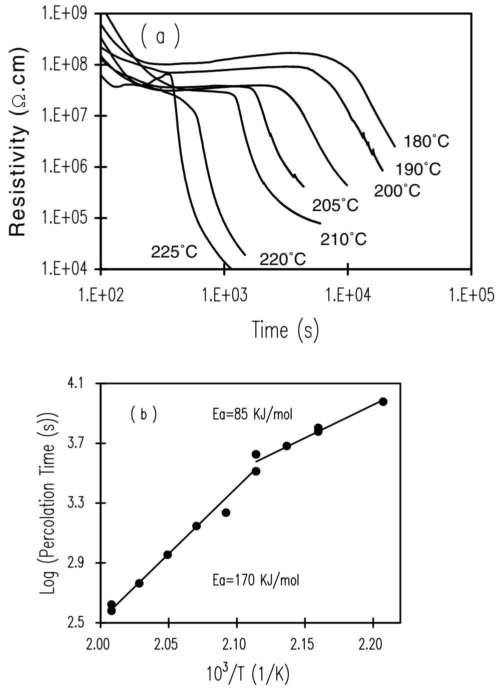


Fig. 5. Dynamic percolation behavior of PVDF/PMMA(50/50) composites filled with 8 phr CB: (a) dynamic percolation curves; (b) Arrhenius plot.

annealing temperatures. The reduction of resistivity is found to be much rapid for samples annealed at a temperature higher than 200°C compared with those annealed at lower temperatures. This is greatly different from the behavior in homogeneous matrix including PVDF/CB and PMMA/CB systems. Furthermore, an Arrhenius plot of the percolation time against the annealing temperature for the PVDF/PMMA/CB composites results in a non-linear relationship. As shown in Fig. 5b, the apparent activation energy of the percolation time calculated from the samples annealed at temperatures lower than 200°C is found to be about 85 kJ/mol, while it increases to about 170 kJ/mol for those annealed at higher temperatures (the activation energy is apparent because these data may be not really in a linear relation). Both values are largely deviated from the activation energy of the dynamic viscosity for PVDF/PMMA blend (about 100 kJ/mol, see Fig. 4b). It should be pointed out that the fluctuation of the dynamic percolation curves and its activation energy with the annealing temperature was also observed in other composition ratio systems.

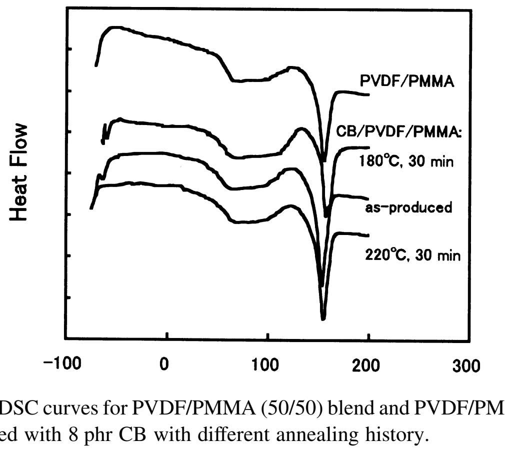


Fig. 6. DSC curves for PVDF/PMMA (50/50) blend and PVDF/PMMA (50/50) filled with 8 phr CB with different annealing history.

We have learned in the previous section that if the matrix is homogeneous, the shape of dynamic percolation curves is self-similarity to the different annealing temperatures and CB concentrations, and their percolation time is well correlated to the zero-shear-rate viscosity of the matrix. The great change in the dynamic percolation behavior of PVDF/PMMA/CB composites with the annealing temperature should be ascribed to the fluctuation of constituent component surrounding the CB surface, resulting in the disturbance of CB agglomeration to form the networks. In other words, the PVDF/PMMA blend matrix filled with CB particles is not in a homogeneous state.

Further evidences are needed to confirm whether a phase separation takes place in the PVDF/PMMA blend matrix or not. Meanwhile, it is also interesting to inspect the distribution of CB during the annealing treatments at different temperatures.

3.3. DSC and DMA analysis

DSC and DMA are commonly used to determine the miscibility of polymer blends [5,7]. Fig. 6 shows the DSC curves for PVDF/PMMA (50/50) and PVDF/PMMA (50/50) filled with 8 phr CB. It can be seen that all the curves exhibit a glass transition process in a similar temperature range about 50°C, no matter whether the sample is filled with CB or not. Fig. 7 shows the DMA results (tan δ versus temperature) for PVDF, PMMA, and PVDF/PMA (50/50) blends. Only one relaxation peak around 90°C is observed for the PVDF/PMMA blend, which is located between the

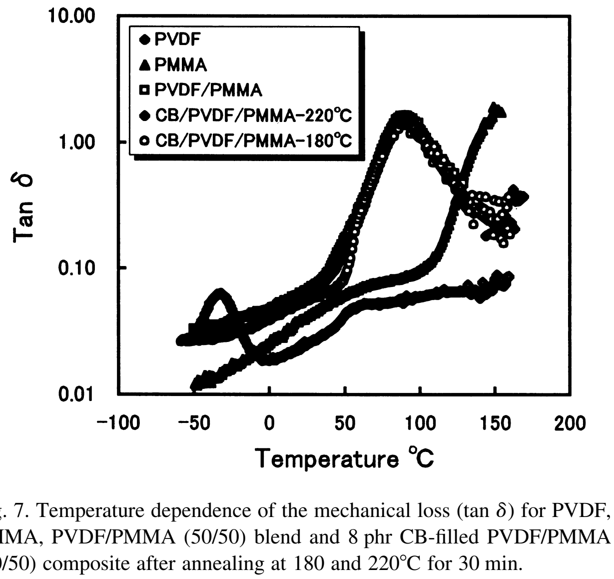


Fig. 7. Temperature dependence of the mechanical loss (tan δ) for PVDF, PMMA, PVDF/PMMA (50/50) blend and 8 phr CB-filled PVDF/PMMA (50/50) composite after annealing at 180 and 220°C for 30 min.

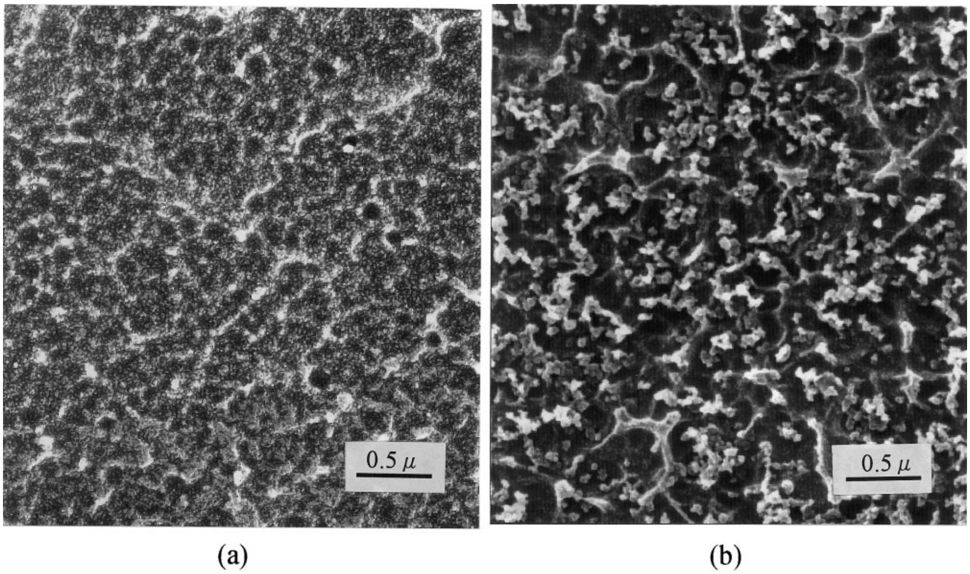


Fig. 8. SEM pictures for: (a) PVDF/PMMA (50/50) blend; (b) PVDF/PMMA/CB (8:50/50) (as-produced sample).

glass transition temperature of PVDF (−34°C) and PMMA (150°C), indicating the miscibility of the pure PVDF/PMMA blend. Fig. 7 also shows the DMA curves for the PVDF/PMMA blend filled with 8 phr CB. It is found that the incorporation of CB and further isothermal treatments at different temperatures do not shift the peak temperature. These results demonstrate that the phase separation does not occur in the CB-filled PVDF/PMMA blend matrix [23,24].

However, no phase separation determined by DSC and DMA measurements does not mean the homogeneity of the PVDF/PMMA blend matrix. For example, in the concentration or temperature range between the binodal and spinodal points, miscible blends are metastable towards composition fluctuations [18]. This process is difficult to be detected by DSC and DMA. Even at the early stage of the spinodol decomposition, what we can observe in the DSC curve is a slight broad range of the glass transition temperature. Actually, the addition of CB to the polymer blends broadening the glass transition temperature range is observed in Fig. 6. Moreover, the annealing treatment of PVDF/PMMA/CB at 180°C for 30 min results in the splitting of the melting peak and a slight increase in the melting temperature from 155 to 159°C (see Fig. 6). These evidences might be correspondent to the phase fluctuation in PVDF/PMMA/CB mixture as further verified by SEM and AFM observations.

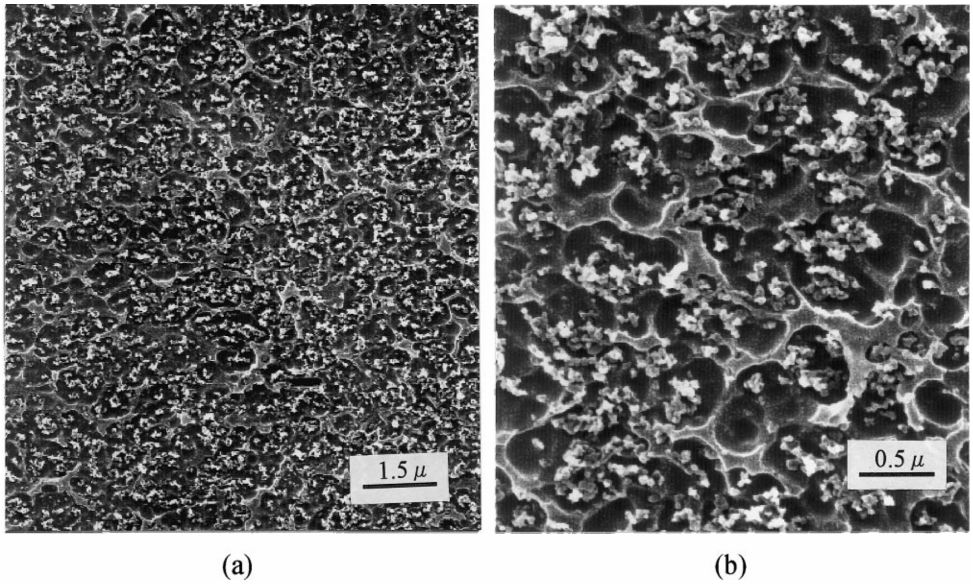
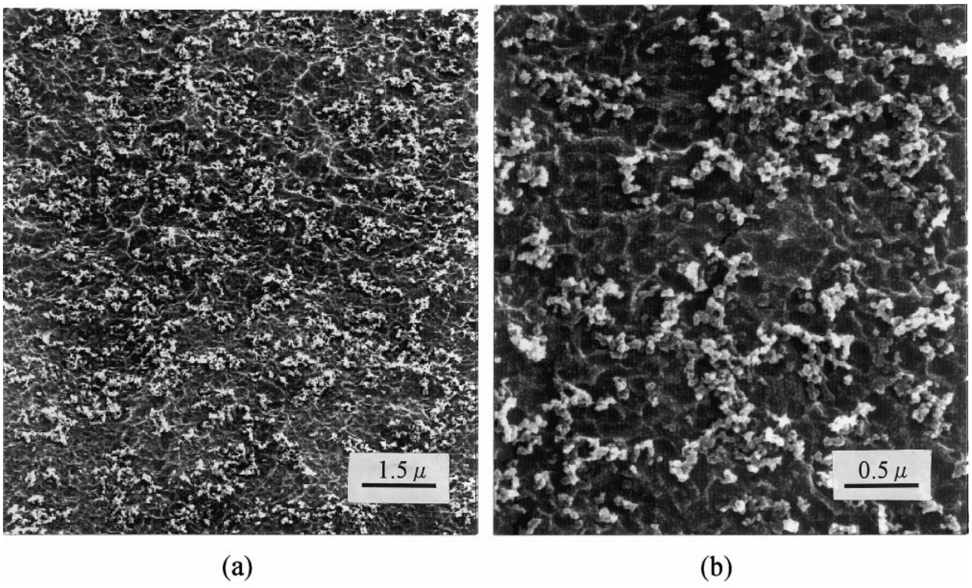


Fig. 9. SEM pictures for PVDF/PMMA/CB (50/50/8) composites annealed at 180°C for 30 min with magnification: (a) 10k; (b) 30k.



(a) (b)

Fig. 10. SEM pictures for PVDF/PMMA/CB (50/50/8) composites annealed at 220°C for 30 min with magnification: (a) 10k; (b) 30k.

3.4. SEM and AFM observations

Fig. 8a and b shows the SEM morphology for PVDF/PMMA (50/50) and PVDF/PMMA (50/50) filled with 8 phr CB (as-produced sample), respectively. Figs. 9 and 10 show, respectively, the morphology for the PVDF/PMMA/CB after annealing at 180 and 220°C for 30 min with different magnifications. Remember that all the samples were fractured in liquid nitrogen under same procedure and then ion etching at the same time. As shown in Fig. 8a, the fracture surface of the pure PVDF/PMMA blend is rather flat and uniform as characterized by small "net eyes" with a size of about 0.1 μm. The incorporation of the CB particles greatly alters the size and flatness of the "net eyes", especially for the sample after annealing at 180°C for 30 min. It is found in Fig. 9b that the "net eyes" developed to a size bigger than 0.5 μm and most of the CB particles are segregated to locate in the holes of the "net eyes". For the sample annealed at 220°C for 30 min, the fracture surface returns to the flat pattern and the "net eyes" is relatively small with a size of about 0.2 μm (see Fig. 10b). It should be mentioned that the morphology of the matrix in Fig. 9 is recoverable from the pattern shown in Fig. 10 if the sample is once again annealed 180°C for a given time.

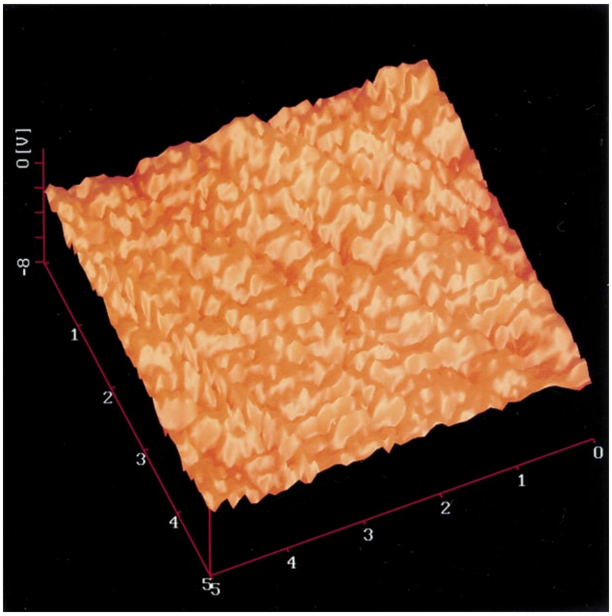


Fig. 11. AFM imaging for PVDF/PMMA/CB (59/50/8) composites annealed at 180°C for 30 min.

The great change in fracture surface with annealing temperature clearly indicates the occurrence of the phase fluctuations in the PVDF/PMMA/CB mixtures. Since PVDF is easy to be erased by the ion etching, the large hole in Fig. 9, where the CB particles are preferentially located, might be the PVDF-rich domains. This is consistent with our previous results that PVDF has a high interaction with CB compared with PMMA.

The phase fluctuations for CB-filled samples annealed at different temperature was also detected by the AFM image under friction mode. Fig. 11 shows the surface morphology of PVDF/PMMA/CB (50/50/8) after annealed at 180°C for 30 min. It can be observed that for 180°C annealed sample, there exists two co-continuous but distinguishable domains [25]. However, for the 220°C annealed samples, the domain was found to vanish (not show here).

3.5. Room-temperature resistivity

As conductive polymer composite materials, the electrical resistivity at room temperature is one of the most important properties. Fig. 12 shows the room-temperature resistivity as a function of CB concentration for PVDF, PMMA and PVDF/PMMA (50/50) based systems. All of

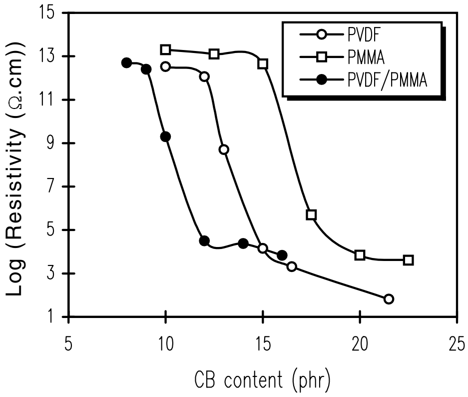


Fig. 12. CB concentration dependency of the room-temperature resistivity for PVDF/CB, PMMA/CB and PVDF/PMMA/CB (50/50/8) composites compression-molded at 180°C for 30 min.

the samples were pressed at 180°C for 30 min under a pressure of 20 MPa. It is found that the percolation threshold, a critical concentration of CB where the resistivity starts to reduce abruptly, for CB-filled PVDF/PMMA composites is about 9 phr, which is much lower than that for PVDF/CB (12 phr) and PMMA/CB (15 phr). Fig. 13 shows the effect of the blend ratio on the percolation threshold of the PVDF/PMMA/CB composites molded at 180 and 220°C for 30 min, respectively. A negative deviation of the percolation threshold from the additive law is observed. It seems that the deviation for the samples annealed at 180°C is larger than those annealed at 220°C.

Generally, the percolation threshold of the conductive polymer composites filled with a given type of CB is mainly affected by the viscosity of matrix [26], the interfacial free energy between CB and matrix [27] and dispersion of CB [28]. Since both the viscosity and the surface tension of PVDF/PMMA blends are between those of PVDF and PMMA [21,29], the large reduction of the percolation threshold for the PVDF/PMMA/CB composites should be ascribed to the heterogeneous distribution of CB in PMMA/PVDF matrix. This is in agreement with the SEM observations. In fact, the heterogeneous distribution of CB is very common in CB-filled immiscible polymer blend composites. Many experimental results have showed that the CB particles always selectively located in one phase or at interfaces in immiscible polymer blends resulting in a great reduction of the percolation threshold [12–14,30–32].

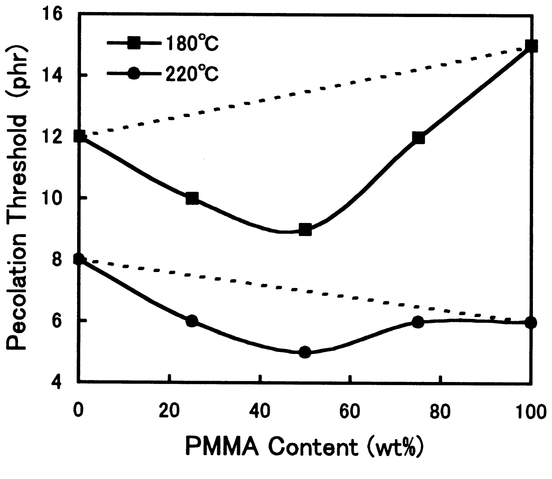


Fig. 13. The effect of PMMA amount on the percolation threshold of PVDF/PMMA/CB composites compression-molded at 180 and 220°C, respectively, for 30 min.

Now, we return to further discuss the result of dynamic percolation shown in Fig. 5. When PVDF/PMMA/CB is annealed at a temperature lower than 200°C, it is reasonable that the activation energy of the percolation time is very near to that of PVDF/composites since the PVDF molecules selectively adsorbed by the CB surface and the CB particles are surrounded in the PVDF-rich domains. However, it is not clear why the activation energy of the percolation time at high temperature range becomes so large, even larger than that in PMMA/CB composites. There are two possible reasons. One is the change in the composition of polymer nearby the CB surface, from the PVDF-rich domain to the PMMA-rich domain, with increasing the annealing temperature. The other is the acceleration in the phase fluctuation with increasing the annealing temperature, resulting in the acceleration in the formation of the CB networks. Detailed study is needed to further understand the dynamic percolation behavior in CB-filled miscible polymer blend composites.

4. Conclusions

1. Phase fluctuations occur in PVDF/PMMA polymer blends due to the incorporation of CB.
2. Dynamic percolation measurement is a sensitive technique for the in situ detection of the bulk mobility of polymer layer surrounding CB particles.
3. The phase fluctuations in the PVDF/PMMA blend matrix cause a large decrease in the percolation threshold due to the heterogeneous distribution of CB in PVDF-rich domains. This phenomenon reminds us that both the structure of polymer blend matrix and the electrical conductivity of the CB-filled composites might be well controlled during the phase fluctuations or phase separation of miscible polymer blend matrices, which is a novel way potential for designing the structure-controlled conductive polymer composites.

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