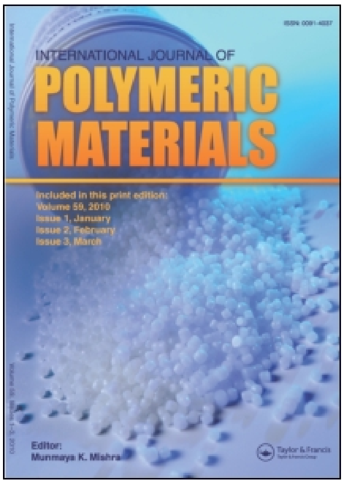

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effect of mixing on dynamic mechanical properties of ternary blends of carbon black, polypropylene, and ethylene-vinyl acetate copolymers

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To cite this Article Huang, Jan-Chan , Wu, Chin-Long and Burke, Dennis M.(2002) 'Effect of mixing on dynamic mechanical properties of ternary blends of carbon black, polypropylene, and ethylene-vinyl acetate copolymers', International Journal of Polymeric Materials, 51: 12, 1095 — 1105

To link to this Article: DOI: 10.1080/714975697

URL: http://dx.doi.org/10.1080/714975697

International Journal of Polymeric Materials, 51:1095–1105, 2002

0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290109886

EFFECT OF MIXING ON DYNAMIC MECHANICAL PROPERTIES OF TERNARY BLENDS OF CARBON BLACK, POLYPROPYLENE, AND ETHYLENE-VINYL ACETATE COPOLYMERS

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The objective of this study was to investigate the effect of mixing on dynamic mechanical properties of ternary blends of carbon black (CB), ethylene-vinyl acetate copolymer (EVA) and polypropylene (PP). PP/EVA/CB blends were made by compounding a 70/30 wt% EVA/CB blend with PP to maintain a constant ratio between EVA and CB, using a Brabender twin screw extruder. Three blends with CB concentration 3, 5 and 7.5 wt% were studied in a dynamic rheometer. Both dynamic moduli and dynamic viscosity increased when the concentration of EVA/CB increased. The storage modulus and loss modulus of 5 and 7.5 wt% CB blends increased with the increasing number of passes in extrusion. The ratio of increase diminished when the frequency of the dynamic test increased. Multiple passes in the extruder decreased the phase size of the blends and accounted for the change of modulus. Frequency dependency was explained as the result of the slippage between the interface of EVA/CB and PP phases.

Keywords: carbon black, dynamic mechanical properties, EVA, polypropylene, polymer blends

INTRODUCTION

Plastics are usually considered as insulating materials. Carbon black (CB) is a common filler used in plastics to achieve conductivity [1]. Adding conductive fillers such as CB into plastics can increase the conductivity as well as the stiffness. The applications of conducting polymers depend on the level of electrical conductivity. They range from antistatics ($10^9 - 10^{14}$ ohm-cm), electrostatic dissipation ($10^5 - 10^9$ ohm-cm), to electromagnetic interference shielding ($< 10^2$ ohm-cm) [2]. The first two applications can be achieved by using CB as an additive. There are also other applications, such as

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Received 20 August 2000; in final form 27 August 2000.

The authors would like to express their special thanks to Professor S. B. Driscoll for the measurement of dynamic mechanical properties and Dr. R. D. Deanin for his invaluable help and discussion.

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self-regulating heaters [3–5] and semiconducting layers in high voltage power cables to prevent partial discharge [6]. Both applications were also achieved by using CB as the additive.

In the preparation of filled conductive plastics, conductive particles are dispersed into the polymer matrix in a melt blending process, and a high level of electrical conductivity is obtained when a continuous conducting path is formed at a critical concentration of conductive fillers. This concentration is called the percolation threshold. In general, the percolation concentration of CB filled plastics is determined by crystallinity, interaction between the polymer and CB, and the melt viscosity of the polymer [7–10]. The percolation threshold is determined by a balance between filler–filler and filler–polymer attraction. If the filler–filler interaction is good the fillers tend to stick together and are difficult to disperse. If the interaction between the polymer and filler prevails, the filler is dispersed separately and without contact, and the formation of a conductive path is retarded until a higher concentration of filler is provided.

For amorphous polymers, conductive particles are dispersed uniformly in the matrix, and high electrical conductivity is achieved when the percolation threshold is reached. For crystalline polymers, the conductive filler particles would be rejected from the crystalline regions during crystallization and concentrated in the amorphous region. In this case the percolation threshold would decrease accordingly. In a previous study in our laboratory, the mechanical properties and electrical conductivity of a carbon black-filled ethylene-octene copolymer were reported [11]. This copolymer is a nonpolar polymer with about 10–15 wt% crystallinity. The percolation threshold was observed around 8 wt% CB. In another study [12], the processability, mechanical properties and electrical conductivity of several carbon black-filled EVAs were reported. It was found that the EVA with higher melt flow index (MFI) and higher crystallinity provided a lower percolation concentration. A percolation concentration of 4 wt% was observed.

Using CB as an additive usually results in an increase in viscosity and a decrease in tensile elongation. A low CB content provides better processability and avoids poor mechanical properties caused by high CB loading. One method to reduce the amount of CB required in conductive polymers is to use multiphase polymer blends [13–21]. When CB is added into an immiscible polymer blend it will distribute itself at different proportions depending upon its affinity to the polymer components. When CB preferentially locates in one phase the phase becomes conductive if the CB reaches a percolation level in that phase. When this CB rich phase is mixed with another polymer without CB, the phase morphology of the CB rich phase varies depending upon its weight fraction in the final blend. As the concentration of CB rich phase increases the phase starts from a dropwise domain to become a honeycomb-like structure, and the mixture of the two polymers becomes conductive. This is called double percolation [17, 18]. The applications of multiphase systems can be illustrated by a study of Gubbels and coworkers [18] on a PE/PS system. When a PE/CB blend is prepared the percolation was observed at 5 wt% CB. Since CB was selectively located in PE, the dilution by PS in a 45/55 PE/PS blend decreased the percolation threshold to about 2 wt% CB, which was consistent with the reduction of the volume fraction of the PE phase.

In thermal annealing processes the domain size of a double percolative system gradually increased and resistivity decreased, indicating that the morphology was not at equilibrium [20]. In industrial practice, mixing is usually conducted through an extruder in a continuous process. This could create a variation of experimental results because of different shearing history and a non-equilibrium state between phases. In a previous report we studied the electrical resistivity of ternary blends of CB, PP and EVA [22]. EVA and CB were blended separately before mixing with PP to maintain a constant EVA/CB ratio in the PP/EVA/CB blends. It was found that the electrical conductivity depended on the processing history. Both volume and surface resistivity of the samples extruded once showed only a small decrease from 3 to 7.5 wt% CB. After three extrusions the resistivity of 3 wt% CB increased substantially and the resistivity of 7.5 wt% CB decreased slightly. The samples extruded three times had a lower standard deviation in the resistivity measurement. In the present study we attempt to study the dynamic mechanical properties of this double percolative system.

MATERIALS AND METHODS

Polymers used in this study included EVA and PP. UE 639-35 is a product of Quantum Chemical with VA content 28% and MFI 150. Profax 6323 PP is a product of Himont with MFI 12. The carbon black used in this study was Black Pearls 2000 from Cabot Corporation. It is a product of an oil furnace process with a nitrogen surface area 1475 m^2/g, dibutyl phthalate absorption 330 cc/100 g, and volatile content 2.0%.

A microprocessor controlled Haake Torque Rheometer with Roller style mixer was used to prepare EVA/CB blends. The chamber temperature was set at 150°C, the rotor speed was 80 rpm, and the processing time was 15 minutes. The PP/EVA/CB blends were prepared using a Brabender twin screw extruder by mixing PP and EVA/CB. Three overall CB concentrations were prepared: 3, 5 and 7.5 wt%. The zone temperatures in the extruder were set at 180, 190 and 200°C from feeder forward. Screw speed was set at 30 rpm. Samples extruded with one pass and three passes were collected and compression molded into uniform flat sheets of 1/8 inch thickness at 300°F (149°C) for 3 minutes. The flat sheets were cut into circular discs with 25 mm diameter for dynamic mechanical measurement.

Dynamic mechanical properties were measured in a rheometer, model Rheometrics System Four, manufactured by Rheometrics. The initial gap between the parallel plates was 3 mm as the specimen was loaded. After the specimen was preheated for 4 minutes, the gap was reduced to 2.0 mm. Before starting the test, the excess material was cut from the edges of the plates. The temperature of the melt was maintained at 190°C while the strain was set at 20%. The frequency sweep was carried out from 0.1 rad/sec to 100 rad/sec. The storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were measured.

RESULTS AND DISCUSSION

In our previous study [22] it was concluded that in the system prepared by mixing an EVA/CB blend with PP, the CB will stay in EVA phase and the system can be considered as a mixture of two components. One is EVA with 30 wt% CB and the other is PP. Our discussion is based on this argument. Figure 1 shows the storage modulus of three blends after three extrusion passes. The value of storage modulus increased when the loading of EVA/CB increased. This indicated that the EVA/CB blend had a higher modulus and was more viscous than PP at the temperature of measurement. In our previous study, a 25 wt% EVA/CB blend had an equilibrium torque of 430 m-gm at 210°C, measured by a Haake Rheometer, which was higher than the equilibrium torque of 126 m-gm at 210°C for PP used in this study [23]. The EVA/CB, therefore, acted as a minor phase with a higher viscosity.

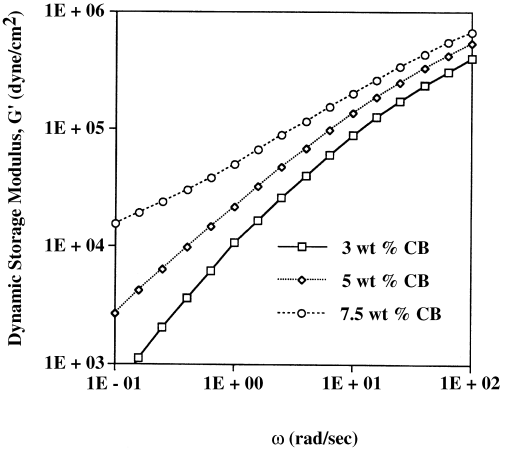

FIGURE 1 Storage modulus at 190°C for EVA/CB/PP blends extruded three times. The weight fraction of CB is calculated on total weight. Weight ratio of EVA: CB is 70 : 30.

It also had a higher surface tension than PP [22]. Shearing energy would be required to disperse it into small particles.

The same increase was also observed in loss modulus, which is shown in Figure 2. At low frequency the storage modulus was smaller than the loss modulus. This was because at low frequency the melt behaved as liquid-like and the effect of the storage component was not as significant as the loss component. At low frequency the distances separating the curves in Figure 1 were wider than those in Figure 2. This indicated that EVA/CB has more impact on elastic properties than on viscous properties at low frequency. As the frequency increased, the storage modulus increased more quickly than the loss modulus. A crossover frequency occurred when both moduli were the same. The crossover frequency was about 50 rad/sec for the three blends. This was higher than the crossover frequency for neat PP, which is usually less than 10 rad/sec [24]. This indicated that at high frequency the EVA/CB phase had more effect on raising loss modulus than storage modulus and retarded the crossover frequency.

Figure 3 shows the complex viscosity of three samples after three extrusion passes. The frequency, ω, was similar to the shear rate in the steady shear viscosity measurement. Complex viscosity can be considered to be equivalent to the apparent shear viscosity. At low frequency the complex viscosity of the 3 wt% sample gradually approached a constant plateau. In this region, the material can be considered as a Newtonian fluid, because dynamic viscosity is not a function of ω. However, in the high frequency region, dynamic viscosity decreased and melt behavior became non-Newtonian. With the CB loading at 5 wt% and 7.5 wt%, the melt flow behaved as a non-Newtonian fluid either in the low or the high frequency

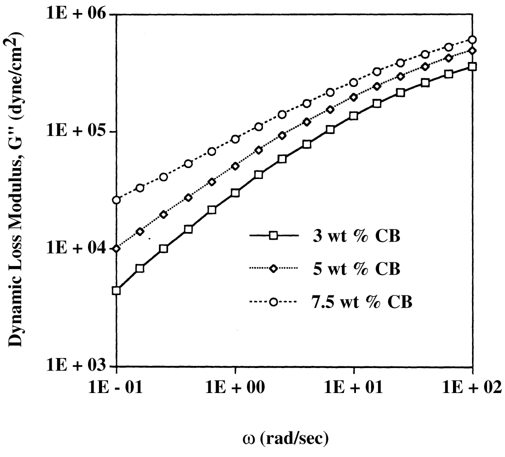

FIGURE 2 Loss modulus at 190°C for EVA/CB/PP blends extruded three times.

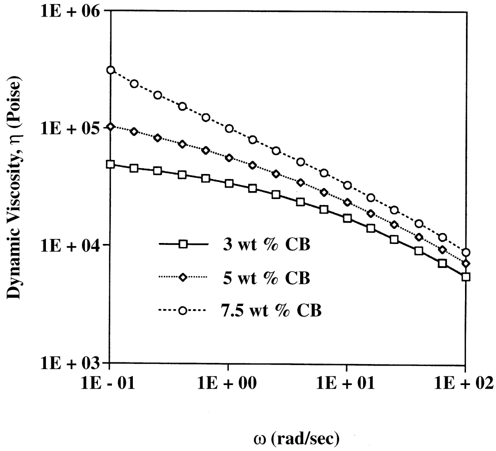

FIGURE 3 Dynamic viscosity at 190°C for EVA/CB/PP blends extruded three times.

region. For the curve of 7.5 wt% CB it can be seen that the dynamic viscosity was still in a trend of increasing as frequency decreased. This is a situation similar to a solid filled polymer melt. It indicates that the blend possessed some characteristics of a reinforced solid system.

The effect of mixing is shown in Figure 4 for dynamic modulus at frequency of 0.1 rad/sec. The moduli of three blends extruded three times were compared with the samples extruded once. It can be seen that for the

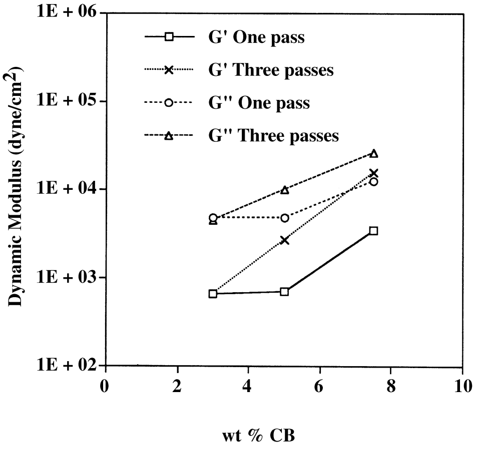

FIGURE 4 Storage and loss modulus at 190°C and $\omega = 0.1$ rad/sec for EVA/CB/PP blends extruded once and three times.

3 wt% CB sample the modulus decreased slightly after three extrusions. For 5 and 7.5 wt% CB samples the moduli increased significantly after three extrusions. A crossover as concentration of EVA/CB increased was observed for both storage and loss moduli. It was similar to the crossover of resistivity reported in our previous study [22]. In that study it was found that after three extrusions the resistivity of 3 wt% CB increased and the resistivity of 5 and 7.5 wt% CB decreased, and the crossover occurred between 3 and 5 wt% CB. An increase in modulus of samples extruded three times was similar to the change of the conductivity. It is noted that this is near the percolation concentration for resistivity. The transition from a Newtonian fluid to a non-Newtonian fluid was also apparent as this crossover occurred. Better mixing dispersed EVA/CB into the PP matrix, allowing chaining or branching of the EVA/CB phase in the PP matrix, and increasing the modulus and viscosity of the melt. This resulted in an increase of electrical conductivity reported in the previous study and the increase of modulus in this study.

Another way to compare the effect of multiple extrusion is to calculate the ratio of the modulus of samples with three extrusion passes and the modulus of the sample extruded once. Figures 5 and 6 showed the storage and loss modulus, respectively, for three samples as functions of frequency. It can be seen that both figures have the same features. For the 3 wt% sample, the modulus after three passes was slightly lower than the sample extruded once, and the ratio was less than unity. For both 5 and 7.5 wt% blends, samples with three passes had a higher values than samples extruded

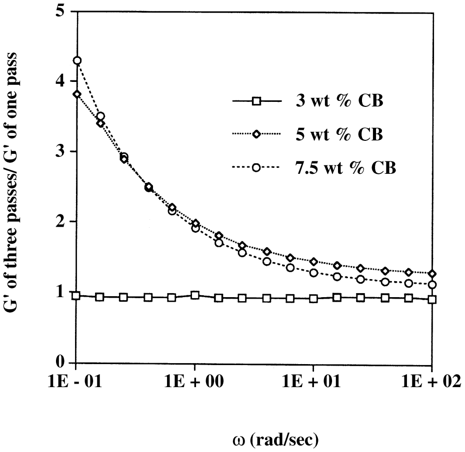

FIGURE 5 Ratio of storage modulus of EVA/CB/PP blends extruded three times to storage modulus of the blends extruded once.

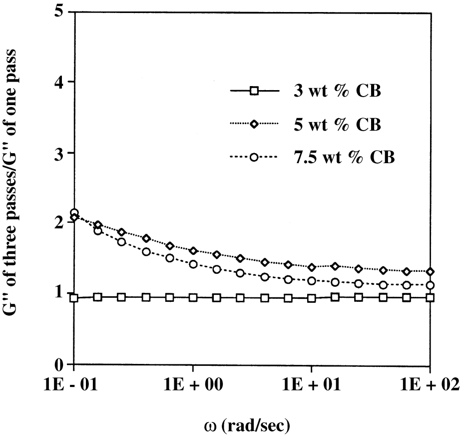

FIGURE 6 Ratio of loss modulus of EVA/CB/PP blends extruded three times to loss modulus of the blends extruded once.

once, particularly at low frequency, which was shown as a deviation of curves from linearity at low frequency in Figures 5 and 6. At higher frequency the ratio decreased towards a number slightly higher than unity, indicating a near proportional relation between the samples, and the effect of multiple extrusion was less easy to observe. It is noted that the rheological response to high frequency is equivalent to a high shear rate. The effect of mixing would be small and not easy to observe in a steady shear viscosity measurement because the test is usually done at a high shear rate. In contrast, measurement of dynamic mechanical properties at low frequency clearly showed a difference between samples with different extrusion history.

In Figures 5 and 6, the 3 wt% CB sample showed a completely different behavior compared to the 5 and 7.5 wt% samples. This was due to different phase morphology as mentioned previously. Since CB was added together with EVA at a constant ratio into PP/EVA/CB blends, a 3 wt% CB represented about 10 vol% minor phase in PP, and a 5 wt% CB sample will have near 25 vol% of minor phase. The morphology of 3 wt% CB was predominately a dropwise morphology. A double percolation can be considered to exist between 3 and 5 wt% CB in the PP/EVA/CB system. Since a twin screw extruder provides good mixing, after three passes the phase of EVA was well dispersed and the contact between EVA/CB domains decreased. This effect was particular significant at low EVA/CB concentration. In this system, a good dispersion of the minor conductive phase decreased the conductivity because of increases in tortuousity or loss of continuity. This was similar to the mechanism that increases the percolation concentration when CB is well dispersed in a single polymer.

In contrast to the 3 wt% sample, cocontinuous phases existed in the 5 and 7.5 wt% samples. After three extrusion passes, more surface area was generated, which accounted for the increase of electrical conductivity [22]. It also explains why the modulus ratio was higher at low frequency. In the dynamic test the sample is oscillating around its equilibrium position. At high frequency the interface may be slipping and less able to transmit the stress. This could happen if the interface between the two polymer phases belongs to a system with negative deviation type in their melt viscosity and the shear stress is high enough [25, 26]. In this case the modulus reading would measure only the continuous phase with little contribution from the minor phase [27, 28]. However, under low frequency oscillation the surface between EVA/CB and PP phases bonds well and the overall modulus reading is higher. In this case a well-dispersed EVA/CB can act as a filler and increase the modulus value. The same mechanism works in both storage and loss modulus and results in similar curves. Since EVA/CB is a solid-filled phase, in the low frequency region it increased the storage component more than the loss component. At high frequency, slippage created an additional loss mechanism, and accounted for the higher crossover frequency between storage and loss modulus as mentioned previously.

A crossover was seen between curves of 5 and 7.5 wt% CB samples in Figures 5 and 6. For the 7.5 wt% sample the curve started with a value higher than the 5 wt% sample. But at high frequency the curves moved below that of the 5 wt% sample. For storage modulus in Figure 5 the crossover was clearly seen to occur at about 0.3 rad/sec. But for loss modulus the crossover occurred at a smaller frequency of about 0.1 rad/sec. At low frequency the increase of storage modulus after three extrusions was about twice the value of the loss modulus. But at high frequency both ratios approached constant values. It can be seen that at the high frequency region of both Figures 5 and 6, the value of the 7.5 wt% sample was higher than the 5 wt% sample. It is not clear why the ratio of the 7.5 wt% sample was less than the 5 wt% sample. It is noted that the surface area and domain size in a near equal volume blend are not well defined [29]. Perhaps in the cocontinuous state of the 7.5 wt% sample, both phases could contribute to the dynamic modulus despite of the weak interface between them, leading to less dependency on extrusion history compared to the 5 wt% sample.

CONCLUSIONS

Three ternary blends of CB, EVA and PP were prepared by mixing a CB/EVA blend and PP. The overall concentrations of 3, 5 and 7.5 wt% CB were prepared while the CB/EVA ratio was maintained constant. The dynamic moduli of 5 and 7.5 wt% CB blends showed a dependency on extrusion history similar to their electrical conductivity. The increase of modulus after three extrusions showed a decreasing trend as frequency increased. The dependency on extrusion history was explained as an effect of mixing, while the frequency dependency was the effect of slippage between interfaces of blends at high frequency and stress.

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