EFFECT OF COMPOSITE MICROSTRUCTURE ON ELECTRICAL

AND MECHANICAL PROPERTIES OF POLY(VINYL ACETATE)

COMPOSITES WITH CARBON BLACK AND CLAY

A Thesis

by

SETHU M. MIRIYALA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2007

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,	Jaime C. Grunlan
Committee Members,	Xinghang Zhang
	Perla Balbuena
Head of Department,	Dennis L. O'Neal

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ABSTRACT

Effect of Composite Microstructure on Electrical and Mechanical Properties of

Poly(vinyl acetate) Composites with Carbon Black and Clay. (August 2007)

Sethu M. Miriyala, B.E., Andhra University, India

Chair of Advisory Committee: Dr. Jaime Grunlan

The electrical and mechanical behavior of carbon black filled poly(vinyl acetate) latex-based and solution-based polymer composites was examined. A set of experiments were performed to distinguish composites with a segregated network (emulsion-based) from those with random dispersion (solution-based) of the filler. The percolation thresholds for the emulsion-based composites were near 1.2 vol% carbon black, while the solution-based composites were around 8.2 vol% carbon black. This difference is due to the segregated network formation, which leads to excluded volume effects in emulsion-based systems. This excluded volume created by the solid polymer particles forces the carbon black particles into conductive pathways at low concentration. In the solution-based case, fully solvated polymer results in a random dispersion of carbon black. The segregated network composite also shows significant improvement in both electrical conductivity and storage modulus with low carbon black loading, while the solution-based composite achieves significant property enhancements at higher carbon black loading because of the greater percolation threshold. The effect of clay in both emulsion and solution-based composites with carbon black was also studied by preparing composites with three clay concentrations (0.2, 0.4 and 2 wt%). In emulsion-based

composites, low clay concentration reduced the percolation threshold from 1.2 vol% to 0.8 vol% carbon black, but with solution-based composites clay increased the percolation threshold from 8.2 vol% to 11.7 vol% carbon black. It is assumed that clay helps to force the carbon black particles into the conductive pathways in the emulsion-based composites. In solution-base composites, clay improves the dispersion of carbon black, thereby destroying the carbon black network and reducing conductivity and storage modulus. The storage modulus in emulsion-based composites improved with 0.2 wt% clay but greater clay concentration resulted in a drop in modulus due to porosity from excess excluded volume effects.

ACKNOWLEDGEMENTS

Firstly I would like to thank Dr. Jaime Grunlan who accepted me as his student and helped me in finishing my thesis. I can never forget him for working with me; he has been a tremendous influence on me. I learnt many minute things in life which play a very major role in completeness. Next I would like to thank my parents who have been with me throughout my life supporting and encouraging me to pursue my higher studies. I would also like to thank Dr. Bolton and Mr. Golla for supporting me financially and making my life easier. I would like to extend my gratitude to Dr. Zhang and Dr. Balbuena for serving as my committee members. Last but not the least; I thank my lab mates Yeon, Tom, Lei and Woo who were really friendly and helpful. Finally, I would also like to thank the Mechanical Engineering Department here at Texas A&M University for giving me the opportunity to further my education beyond my undergraduate degree.

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CHAPTER I

INTRODUCTION

Electrically conductive polymer composites are useful for a wide range of applications. Some examples include electromagnetic shielding [1, 2] (primarily focused on electronics packaging [3, 4]), self regulating heaters [5, 6], chemical sensors [7-10], electrostatic charge dissipation [11, 12] and super capacitors for charge storage [13, 14]. Despite their increasing utility, these composites typically suffer from a poor balance of electrical and mechanical behavior. The high levels of filler required to achieve good electrical conductivity lead to brittle films [15]. Processing also becomes difficult as the filler concentration rises and the final cost increases. Lowering the percolation threshold can be an efficient method to get sufficient conductivity and improve the mechanical properties [16], but the techniques used to accomplish this often produce mechanically weak composites [15, 17]. The primary goal of the present work is to produce carbon black filled composites that have a good balance of electrical and mechanical properties by lowering the percolation threshold and adding clay as secondary filler.

Thesis Overview

This introductory chapter provides background for the work described in subsequent chapters. Percolation theory is outlined, followed by overviews of clay and carbon black. Chapter I ends with a review of the segregated network concept. Chapter II compares emulsion and solution based composites with a poly(vinyl acetate) matrix. The materials

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The thesis follows the style of Carbon.

used, film preparation and instrumentation used for characterization are discussed in detail for both systems. Microstructure, electrical conductivity and storage modulus are evaluated. Chapter III is focused on the effect of clay in both PVAc solution and emulsion based systems. The electrical conductivity and mechanical properties of both systems are compared with each other and compared to those without clay. Chapter IV summarizes this work and provides some ideas about future work.

Percolation Theory

Carbon black has been used for years as a strengthening agent in elastomers [18-22] and a pigment in ink systems [18, 20-22]. In addition, it's electrically conductive nature has also made carbon black a widely studied filler for conductive composites [23-27]. As carbon black (or any other conductive filler) is added to a polymer matrix, a network begins to form and extend large distances. Once this conductive network reaches a critical size, on the order of the composite sample size, the two-component material makes a transition from insulator to conductor. The critical amount of filler (usually expressed as a volume fraction or percent) required to cause this insulator-to-conductor transition is known as the percolation threshold. Figure 1(a) shows how the composite microstructure changes with carbon black concentration. At the percolation threshold (Image 2 in Fig 1(a)), a conductive path stretches across the sample. Composite electrical conductivity typically obeys a power law as a function of carbon black concentration [28]:

$$\sigma = \sigma_0 \, (V - V_c)^s$$

where σ is the composite conductivity (S/cm), σ_0 is the effective intrinsic conductivity of the filler, s is the power law exponent (usually between 1.5 and 2.5), and V_c is the volume fraction of the filler at the percolation threshold. The three schematic images in Figure 1(a) correspond to locations on the loading curve shown in Figure 1(b). The step rise in electrical conductivity is the percolation threshold. Two well known techniques to reduce percolation threshold are forming a segregated network of filler [20-22, 33-36] and changing the filler geometry [21, 29-32].
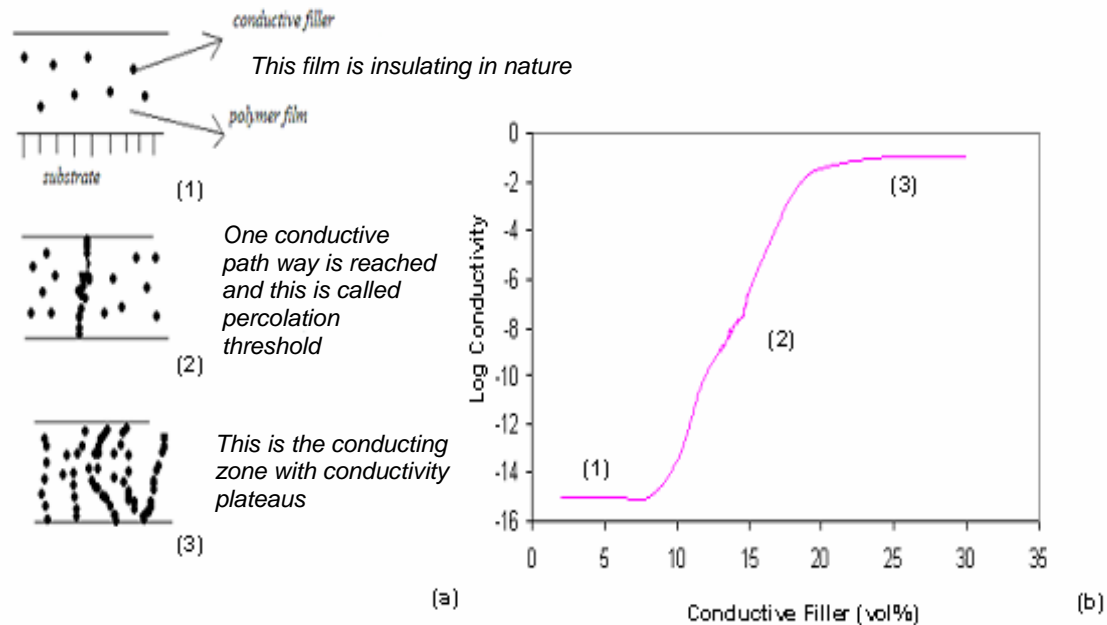
Figure 1. Schematic of electrically conductive polymer composite with changing filler loading (a), electrical conductivity as a function of filler loading (b).

Composite Conduction Mechanisms

The four primary conduction mechanisms involved in carbon black filled polymer composites are dielectric break down, electron tunneling, capacitance and graphitic

conduction [37]. The zones shown in Figure 1 have different combinations of each of these mechanisms.

Insulation Zone

When the carbon black concentration is below the percolation threshold the electrical properties of the composite are similar to those of an unfilled polymer. The carbon black particles are separated from each other and unable to form a conductive pathway. The conduction mechanism in this zone is transport by ionic impurities and space charge that results from ionic diffusion through the composite [38].

Percolation Zone

Once the carbon black concentration has reached the percolation threshold several mechanisms of electrical transport are available. At this stage the carbon black particles are close enough to create a conductive pathway. Mechanisms like capacitance, tunneling, internal field emission or dielectric breakdown may come into play depending upon temperature, frequency and electric field strength [38].

Conduction Zone

Beyond the percolation threshold, the gaps between the conductive carbon black particles become so small (0.35 – 1.5 nm) that the mechanisms of electrical conductivity become independent of frequency, temperature and field strength. The wave functions begin to overlap one another when the gap is less than 1.5 nm leading to high conductivity. If more carbon black is added such that the gap between the particles is less than 0.35 nm,

graphitic conduction becomes active. Graphitic conduction is a zero band gap situation with conductivity tending to rise with temperature as electrons are promoted to the conduction band.

Carbon Black Overview

Carbon black is a low cost, colloidal, amorphous carbon material that has a distorted graphite structure [39]. Figure 2 shows the typical carbon black size and structure. Applications for carbon black include improving stability, imparting conductive behavior, extending the shelf life of rubber with its antioxidant properties and pigmenting [39]. The three important characteristics of carbon black, used as a conducting pigment in polymer composites, are particle size, structure, and surface chemistry [40-42]. High surface area and high porosity are important characteristics of carbon black that ensure good networking [43]. As the surface area of the carbon black particles in a polymer composite increases, the gaps between the polymer and the conductive aggregates becomes less [42]. Carbon black with elongated aggregates, composed primarily of particles with extensive branching, is called high structure carbon black [41]. This type of carbon black can be prepared by the furnace process, where oil is thermally decomposed to form carbon black particles [40].
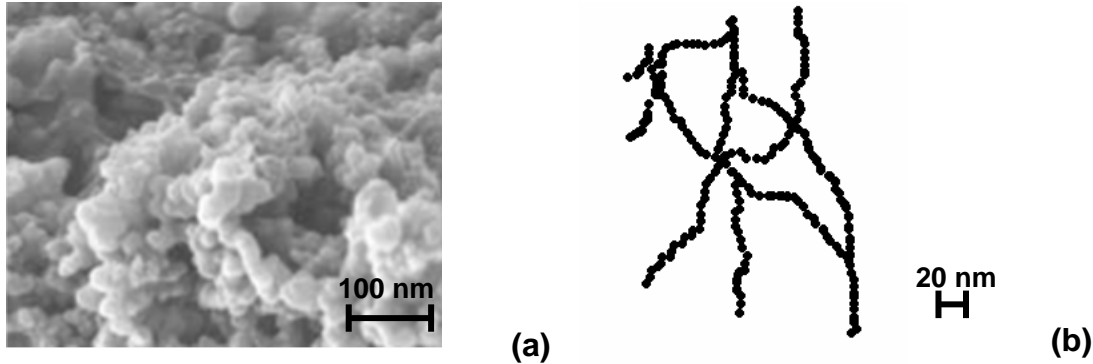
Figure 2. SEM image of carbon black with a primary particle size of 20 nm (a) and a schematic of networked high structure carbon black (b).

Clay Overview

Hydrous sodium or aluminium phyllosilicates which are typically less than 2 μm in diameter are known as clay [44, 45]. Figure 3(a) shows the structure of a typical aluminosilicate clay. When clay particles are dispersed in a polymer matrix three types of polymer composites can be formed [46], as shown in Figure 3(b). The first type is a conventional composite that has clay tactoids with layers aggregated in a face-to-face form. Here the clay tactoids are dispersed only as a segregated phase, resulting in poor mechanical properties of the composite material. The second type is intercalated polymer–clay nanocomposites, which have one or more molecular layers of polymer entering the clay layers. The third type is exfoliated polymer–clay nanocomposites. These are characterized by low clay content and a separation between clay nanolayers that depend on the polymer content of the composites. Exfoliated polymer–clay nanocomposites have improved properties because of the homogeneous dispersion of clay and large interfacial area between polymer and clay [48-52].
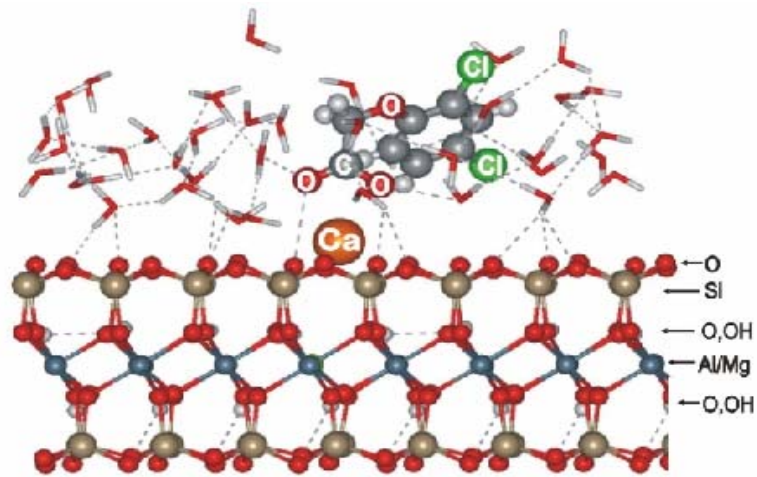
(a)
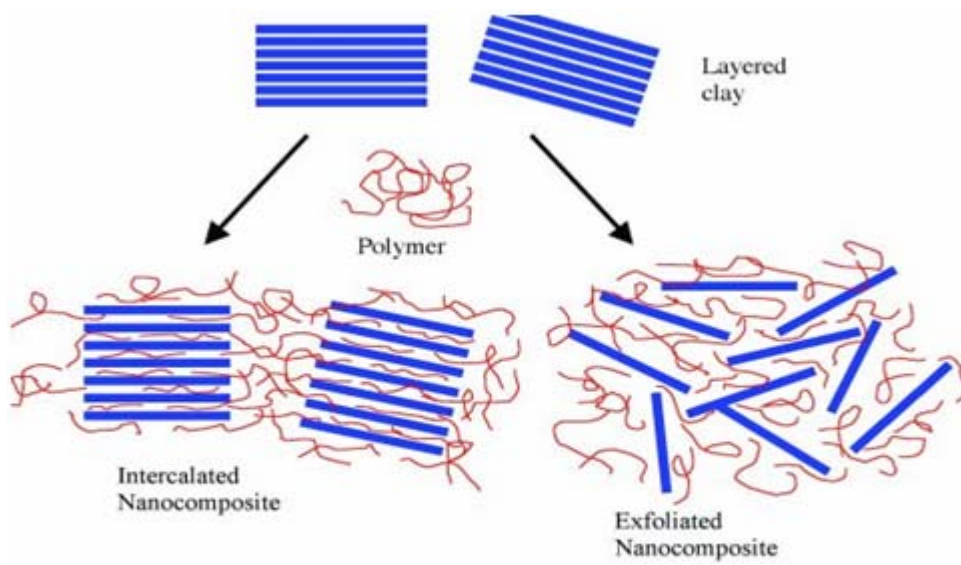
(b)

Figure 3. Schematic of structure of a typical clay (a) and common types of clay composites formed (b) [47].

Segregated Networks

Kusy, when studying electrically conductive mixtures of polymer and metal powders, initially coined the term "segregated network" [53]. Segregated networks are formed when conductive filler is mixed with a polymer matrix having a phase separated microstructure. The conductive filler is given a small volume within the matrix, which leads to the formation of a network at low concentration. There are several ways to produce segregated network composites. Segregated networks are formed in polymer blends if the conductive filler is forced to occupy one of two dissimilar polymers or the junction between the two polymers, as shown in Figures 4(a) and (b) [20, 34, 54, 55]. Low percolation thresholds are obtained when the conductive filler is dispersed into a melt of less favorable polymer, followed by adding a more favorable one later [56]. With continuous mixing, the carbon black particles move towards the more favorable polymer and the system is cooled prior to the particles passing through this second phase. These types of composites can achieve percolation thresholds as low as 1 vol% (or less) carbon black and maximum achievable conductivities range between 0.01 and 0.1 S/cm [57, 58]. Segregated networks of carbon black with three kinds of polymer blends (HDPE/PP, PP/PMMA, and HDPE/PP) were studied by Sumita and coworkers resulting in a percolation threshold as low as 0.1 vol % and maximum conductivity of 0.001 S/cm [20]. Composites synthesized using semicrystalline polymers also exhibit segregation due to the amorphous and crystalline phases acting as separate phases [57, 58]. The conductive filler can only occupy the amorphous regions within the polymer matrix, resulting in a lower percolation threshold.
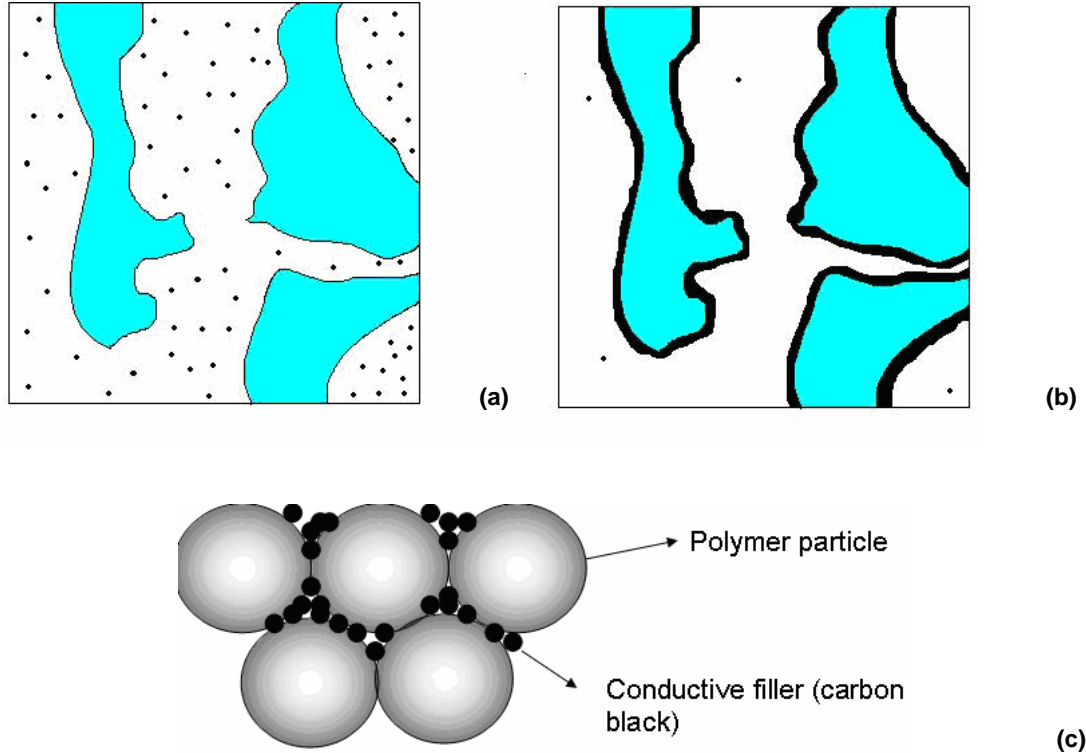
Figure 4. Filled polymer blends (black dots are carbon black filler particles immersed in two different polymers distinguished by color change with CB only one phase (a) or at the interphase between phases (b). Compressed polymer powder with carbon black is also shown (c).

Another common segregated network system is made with polymer powder and conductive filler [24, 53, and 59]. The powder and the filler material are pressed at temperatures near the melting point of the polymer. Figure 4(c) shows the structural arrangement of the particles. The percolation threshold is higher than those of polymer blends, but the conductivity is similar. Malliaris and Turner [24] used compression molding to prepare mixtures of polyethylene (PE) and nickel. Their results showed that the percolation threshold decreases as the size ratio of the polymer particles to metal powder increases. The electrical and dielectric behavior of carbon black and polyethylene systems prepared by compression molding was studied by Yacubowicz and coworkers

[59]. They found that the percolation threshold ranges between 0.3 – 0.7 vol % and the dielectric constant increases rapidly up to the percolation threshold. Some researchers used ceramic particles for segregated network composites [35]. They studied the effects of pressure, temperature and particle size ratio on percolation threshold. High temperature and pressure increased the maximum conductivity at high loadings, but percolation threshold also increased.

Polymer emulsions are a third type of segregated system that has been used to create networks with antimony tin oxide [60], carbon black [32, 61] and carbon nanotubes [62]. These composites can have very low percolation threshold (< 1 vol %) and the maximum achievable electrical conductivity is around 1 S/cm, which is better than polymer blends and dry powders. Figure 5 shows the formation of a segregated network in a polymer emulsion. In contrast to emulsion based composites solution or melt based composites have a random dispersion of filler due to the liquid-like state of polymer during processing. Figure 6 shows SEM images of emulsion and solution based composites. A polymer emulsion is a stable dispersion of microscopic polymer particles in water prior to film formation [63]. The solid particles create excluded volume and hence force the filler material into the interstitial space between them. This reduces the space for conductive filler to form a network and decreases the percolation threshold. The electrical and mechanical behaviors of carbon black-filled poly(vinyl acetate) latex-based polymer composites were examined by Grunlan and coworkers [32]. They found that the percolation threshold was an order of magnitude less for a latex based composite system compared to a water based solution. It was later found that the percolation threshold

could be reduced to 0.04 wt% by replacing carbon black with single walled carbon nanotubes [64].
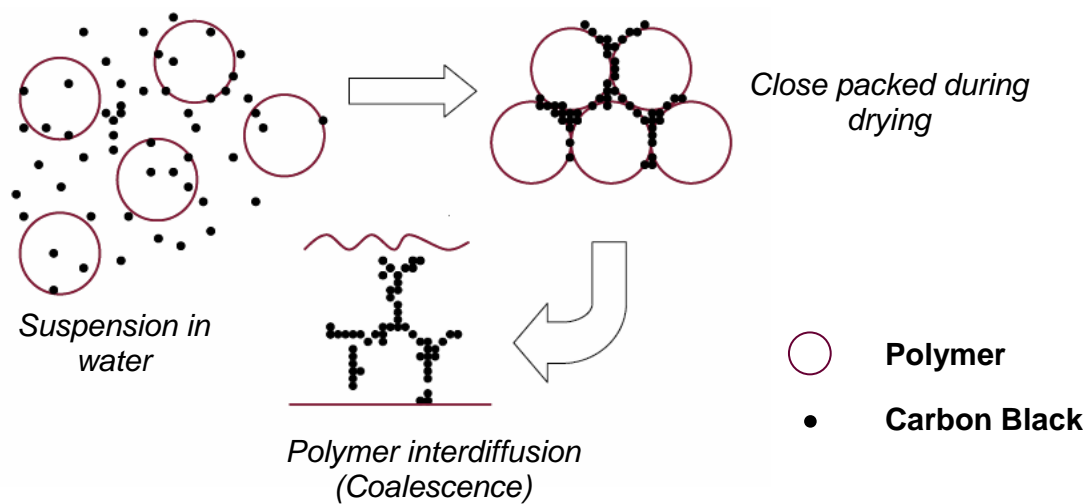
Figure 5. Process of producing a segregated network nanocomposite using a polymer emulsion.
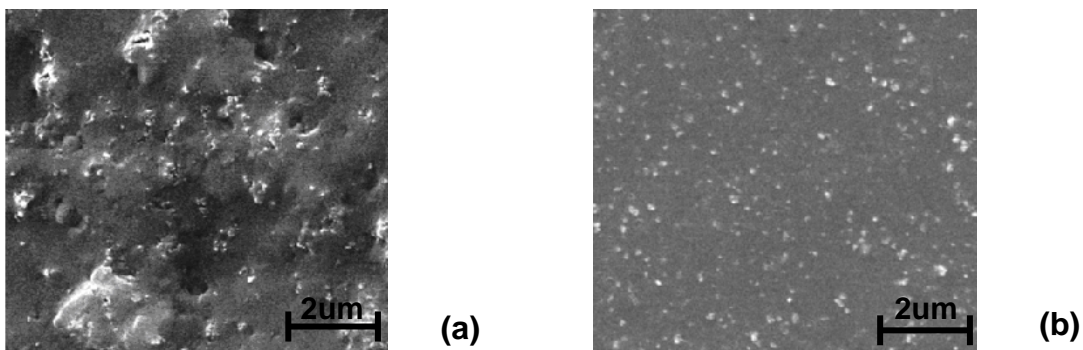
Figure 6. FEGSEM freeze-fractured cross-sections of PVAc latex-based (a) and solution-based composites (b) containing 2.5 volume% carbon black.

CHAPTER II

COMPARISON OF EMULSION AND SOLUTION-BASED

POLYMER COMPOSITES

Attaining the proper balance of mechanical properties and electrical conductivity in polymer nanocomposites by lowering the percolation threshold has been studied for years [16, 20, 23, 32, 54]. In this chapter, a polymer emulsion is used as the composite starting material to reduce the percolation threshold. This work shows that latex-based composites provide low percolation threshold in comparison to solution-based composites, but the maximum conductivity is not as high as solution-based composites. A general description of the materials and methods is provided. The characterization of the polymer composites is discussed in detail pertaining to electrical and mechanical properties. The SEM images of films are shown at various carbon black concentrations to provide a basis for structure-property comparisons. The effect of drying temperature on the formation of segregated networks is also examined.

Materials and Methods

Materials

The latex used in this study is a poly (vinyl acetate) (PVAc) emulsion (tradename Vinac XX210) supplied by Air Products (Allentown, PA). This latex is 55.5 wt% solids with an average particle size around 640 nm (with a broad distribution). PVAc pellets with a molecular weight of 101,600 g/mol were purchased from Acros Organics (Morris Plains, NJ) and used in the preparation of the solution-based composites. Dimethylformamide (DMF) purchased from Acros Organics was used to dissolve the PVAc pellets. Carbon

black (tradename Conductex 7055 Ultra) was supplied by Columbian Chemicals (Marietta, GA). This high structure carbon black has a nitrogen surface area of 55 m²/g, primary particle size of 42 nm and a density of 1.89 g/cm³.

Emulsion-Based Composite Film Preparation

The latex was diluted to 10 wt% solids by adding deionized water, which reduces the viscosity. The maximum carbon black loading was then added to the latex and mixed for 15 minutes with a high speed impeller operated at 3100 rpm. In this study, the carbon black concentration was varied from 12 wt% to 1.5 wt%. After stirring, some amount of the mixture was taken out to prepare films and an additional amount of diluted PVAc emulsion was added to reduce the carbon black concentration to the desired level. This process was repeated to create a series of composites with decreasing carbon black concentration. Composites were prepared by pouring 10 grams of mixture into 4 in² polystyrene molds. The mixtures were then dried at 80° C for two hours followed by one day in a vacuum desiccator [65]. Dried composite films were 150-200 μm thick.

Solution-Based Composite Film Preparation

DMF was chosen to dissolve PVAc pellets due to its high boiling point (150°C) and polarity. Carbon black can be dispersed in a DMF-based solution without using an added dispersing agent and solvent evaporation is minimal during processing. A 10 wt% PVAc solution was prepared by rolling for one day on a cell-production roller apparatus, made by BELCO Biotechology (Vineland, NJ), with a rotation speed of 10 rpm. Composite mixtures were prepared in the same manner as the latex-based mixtures. For solution

based composites, the mixtures were poured into aluminum molds because DMF dissolves polystyrene. The films were dried at 120°C to ensure complete evaporation of DMF. Dried composite films were 150-200 μm thick.

Composite Characterization

Electrical conductivity was measured using a home built four-point probe system [66]. Current was measured using a multimeter and voltage was recorded using a Lab View program [66]. Dynamic mechanical analysis was performed with a Q800 DMA by TA Instruments (New Castle, DE). Tests were run at 1 Hz with a strain of 0.1 % and the temperature was ramped from -20 – 80 °C at   3°C/min**.** For all samples, the glass transition temperature (T_g) was taken as the peak of the loss modulus curve. The cross sections of the composite films were imaged using a Tescan VEGA-II SEM (Cranberry Township, PA). The films were soaked in liquid nitrogen and fractured by hand, followed by sputter coating with 4 nm of platinum prior to SEM imaging.

Results and Discussion

Composite Microstructure

Figures 7 and 8 show the SEM images of PVAc/CB emulsion based films dried at 80°C and solution based PVAc/CB films dried at 120° C respectively. The emulsion-based system creates a network of carbon black particles at very low concentration compared to that of the solution-based system. The microstructural images show that segregation occurs throughout the thickness of the latex (Fig. 7), while random dispersion of carbon black is observed in the solution-based systems (Fig. 8). It can be seen that carbon black particles appear as white dots in the images due to their conductivity and small size that create sharp features that emit secondary electrons. The emulsion-based system has a network structure of carbon black at 1.2 vol% whereas the solution-based system requires 8.1 vol% carbon black for network formation. It can also be observed that some pores are present in the emulsion based system at 6.5 vol% carbon black (Fig. 7(c)), which are not present in the solution based system (Fig. 8). Pores form when the critical pigment volume concentration (CPVC) for the system has been exceeded, which is expected at 17.5 vol% carbon black for solution based systems [32]. The order of magnitude change in carbon black concentration required to bring about macroscopic electrical conductivity is due to the segregated network in the latex-based composite. A similar conductive network can be seen at very high carbon black concentrations in the solution-based systems (Fig. 8). The exponential growth of electrical conductivity for these composite systems (described in the next sections) is due to the formation and growth of conductive filler pathways. Carbon black segregation in the composites with a latex matrix is expected to have a much lower percolation threshold than the solution-based system.
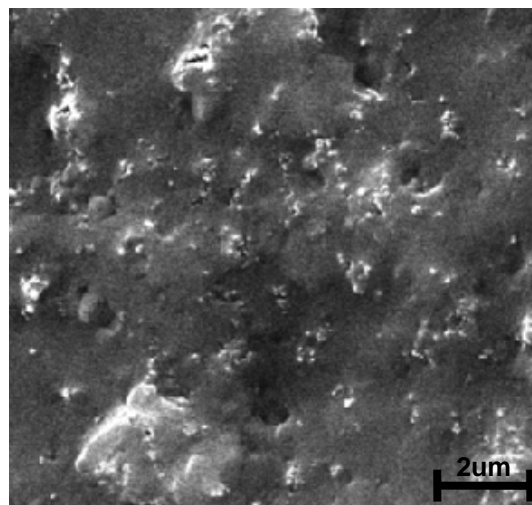
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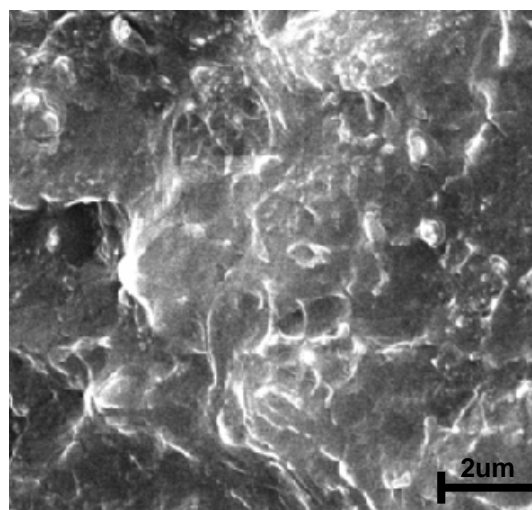
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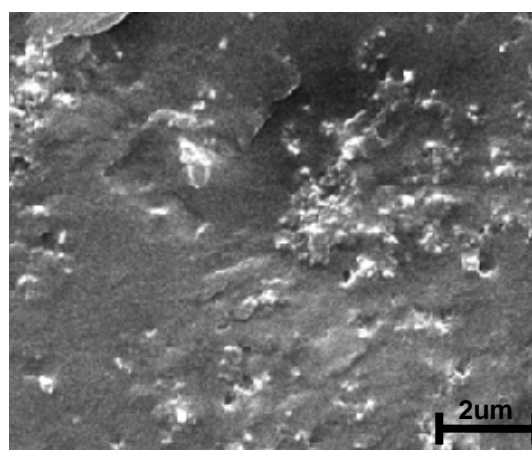
(c)

Figure 7. Freeze-fractured cross-sections of PVAc/CB latex-based composites containing 2.5 (a), 5.2 (b) and 6.5 vol% (c) carbon black.
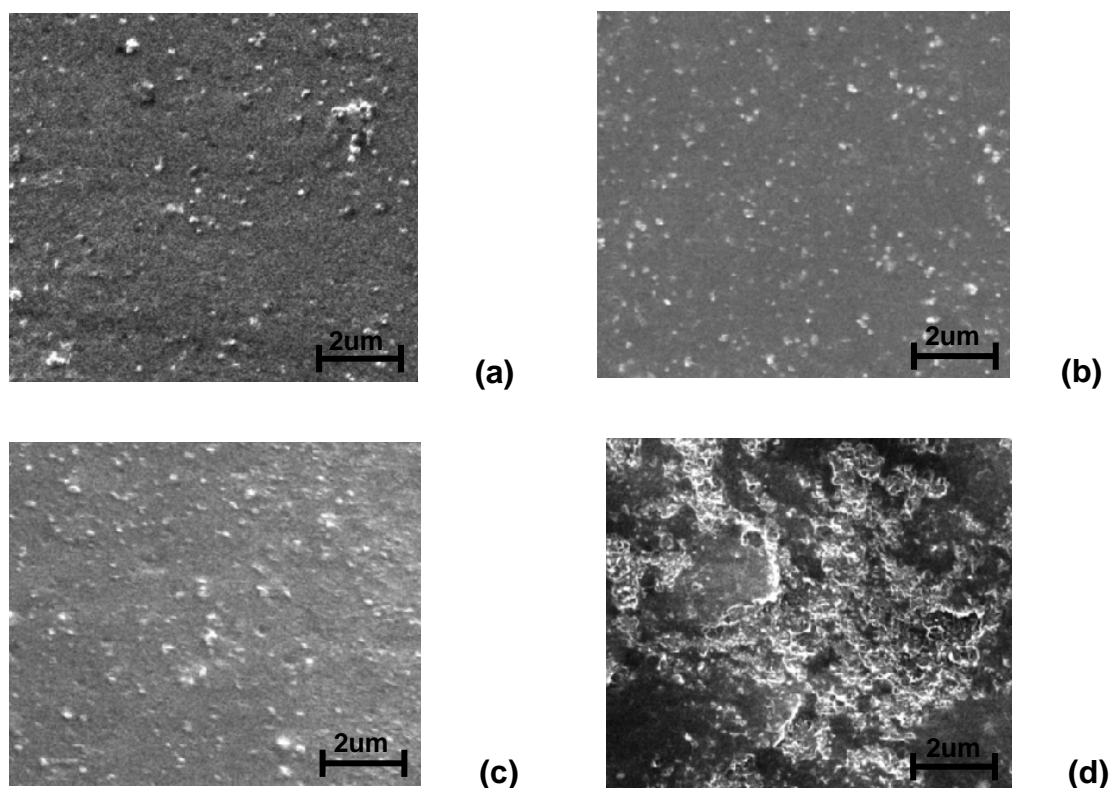
Figure 8. Freeze-fractured cross-sections of PVAc/CB solution-based composites containing 2.5 (a), 5.2 (b), 6.5 (c) and 15 vol% (d) carbon black.

Figure 9 shows the effect of temperature on the microstructure of the latex-based films. During coalescence, the latex particles deform and individual polymer molecules gradually diffuse between them [32]. At higher temperature the latex coalescence is improved because latex particles deform more readily and polymer molecules diffuse at faster rates. When coalescence is reduced, by lowering drying temperature, the porosity in these films increases (Fig. 9(a) and (c)). Boundaries between the latex particles seen in films dried at room temperature are completely eliminated at 80°C. This higher drying temperature typically improves mechanical properties and maximum electrical conductivity, but also raises the percolation threshold [32].
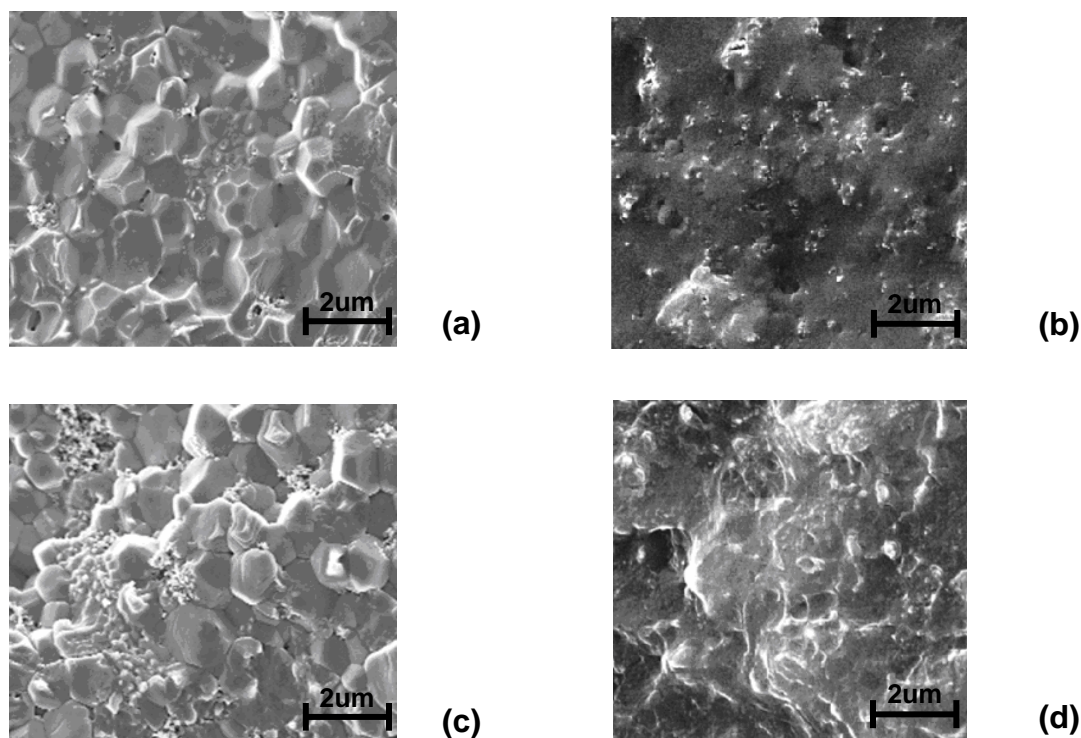
Figure 9. Freeze-fractured cross-sections of PVAc/CB latex-based films dried at room temperature ((a) and (c)) and at 80°C ((b) and (d)). Images (a) and (b) have 2.5 vol% carbon black, while images (c) and (d) have 5 vol% carbon black.

Comparison of Emulsion and Solution-Based Composite Conductivity

Tables 1 and 2 show composition, hickness and conductive behavior of the PVAc emulsion-based and solution-based composites, respectively. Figure 10 shows the electrical conductivity as a function of carbon black loading for these two systems. The weight % carbon black was converted to volume % carbon black by assuming a density of 1.19 g/cm³ for PVAc and 1.89 g/cm³ for carbon black. The percolation power law (Eq. 1) was fit to this data to obtain values for V_c, s and σ_o that are shown in Figure 10. The percolation threshold is 1.2 vol% carbon black for the emulsion-based system and 8.1 vol% for the solution-based system. This large difference in the percolation threshold can be clearly seen in Figure 10, where the solid curves represent the percolation power law

fit to the experimental data. In the case of the solution-based composites, the PVAc is dissolved in DMF and may adsorb on the filler particles during film formation. Once the film is dried, the thin polymer layer stabilizes the filler suspension and prevents aggregation, which reduces particle-to-particle contact. Furthermore, there is no excluded volume in these films during drying because the polymer matrix is fully solvated. In the suspension-based composites, the polymer matrix is suspended particles that force the smaller carbon black particles to occupy their interstices. As the carbon black is forced into the interstitial sites during drying, the filler particles form a network at very low concentration. Figure 10 also reveals that the maximum possible conductivity achieved by the emulsion-based system is lower than that achieved by the solution-based system. This limitation for the latex-based composites is due to the excluded volume that creates porosity at higher filler concentration and degrades the electrical and mechanical properties.

Table 1. Electrical properties of the emulsion-based films dried at 80°C.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
2	1.27	0.0168	9329518	156363	0.0000006
3	1.91	0.0165	43143.1	713.587	0.0014
4	2.55	0.0174	14763.3	257.177	0.0039
6	3.86	0.0166	2892.97	47.9075	0.0209
8	5.19	0.0161	1196.61	19.2415	0.052
10	6.53	0.0156	734.923	11.4648	0.0872

Table 2. Electrical properties of solution-based films dried at 120°C.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
25	17.34	0.0212	89.6976	1.898	0.5269
22.5	15.45	0.018	157.363	2.82624	0.3538
20	13.6	0.0147	371.879	5.47406	0.1827
17.5	11.78	0.0173	844.396	14.6418	0.0683
15	10	0.0148	12613.4	187.183	0.0053
12.5	8.25	0.0086	1.60000000	1406015	0.00000007
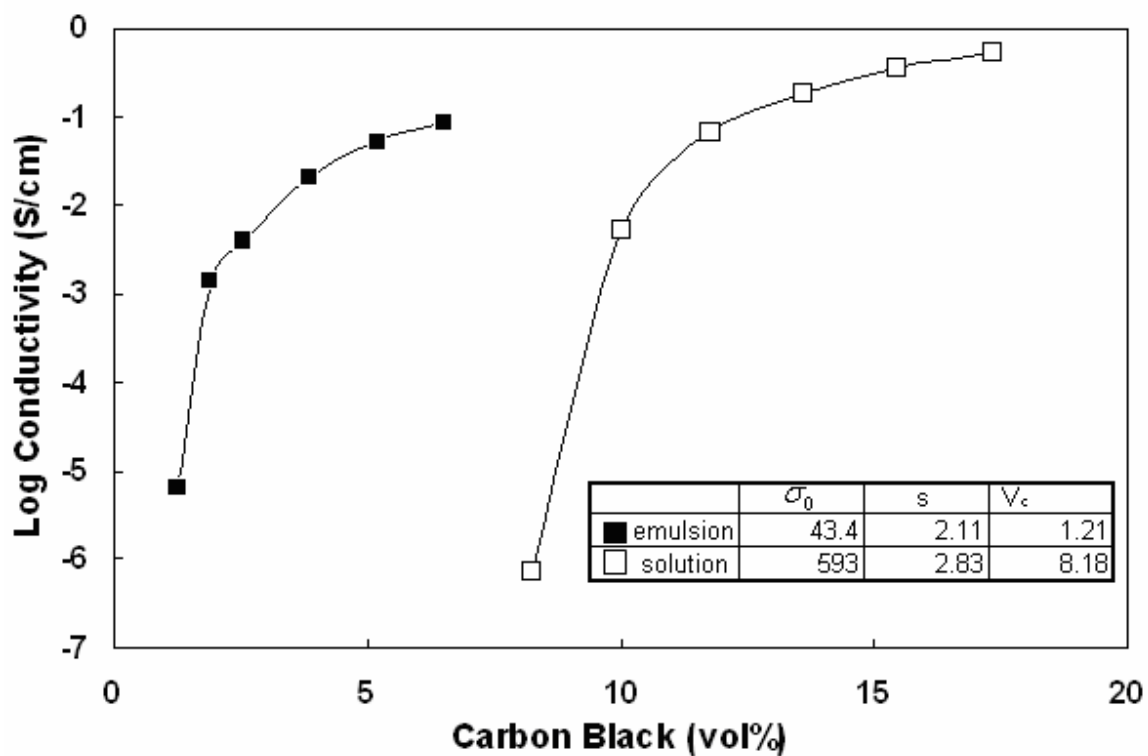
Figure 10. Electrical conductivity as a function of carbon black concentration for PVAc emulsion and solution-based composite systems.

Comparison of Emulsion and Solution-Based Composite Modulus

Storage modulus is similar to elastic modulus at room temperature [80]. Storage modulus as a function of temperature for latex based films dried at 80°C is shown in Figure 11. From this plot it can be seen that storage modulus increases with carbon black concentration. Figure 12 shows storage modulus at 20°C as a function of carbon black concentration in latex-based and solution-based films. From this graph it is evident that the storage modulus increases sharply for the latex-based composites, but eventually drops at higher carbon black concentration. This modulus peak is known as the critical pigment volume concentration [32]. At the CPVC the polymer matrix can no longer hold all of the filler particles, which results in the formation of voids. The voids behave as null modulus filler and the storage modulus decreases beyond this filler level. The CPVC is around 5 vol% carbon black.
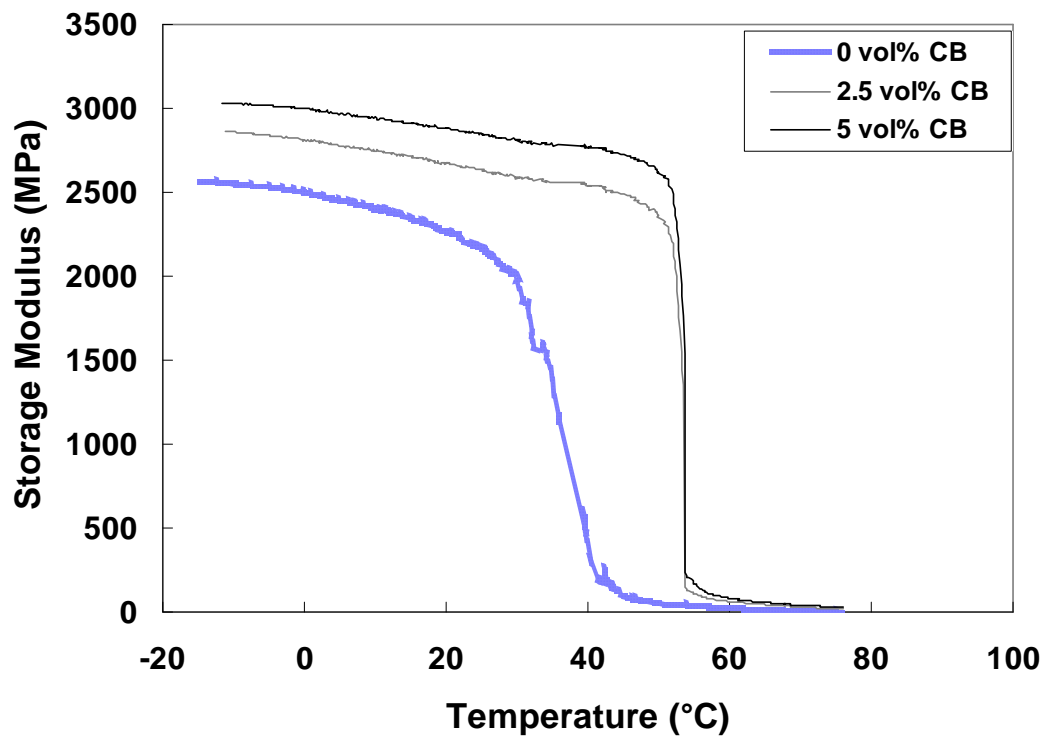
Figure 11. Storage modulus as a function of temperature for PVAc latex-based films with varying carbon black concentration.
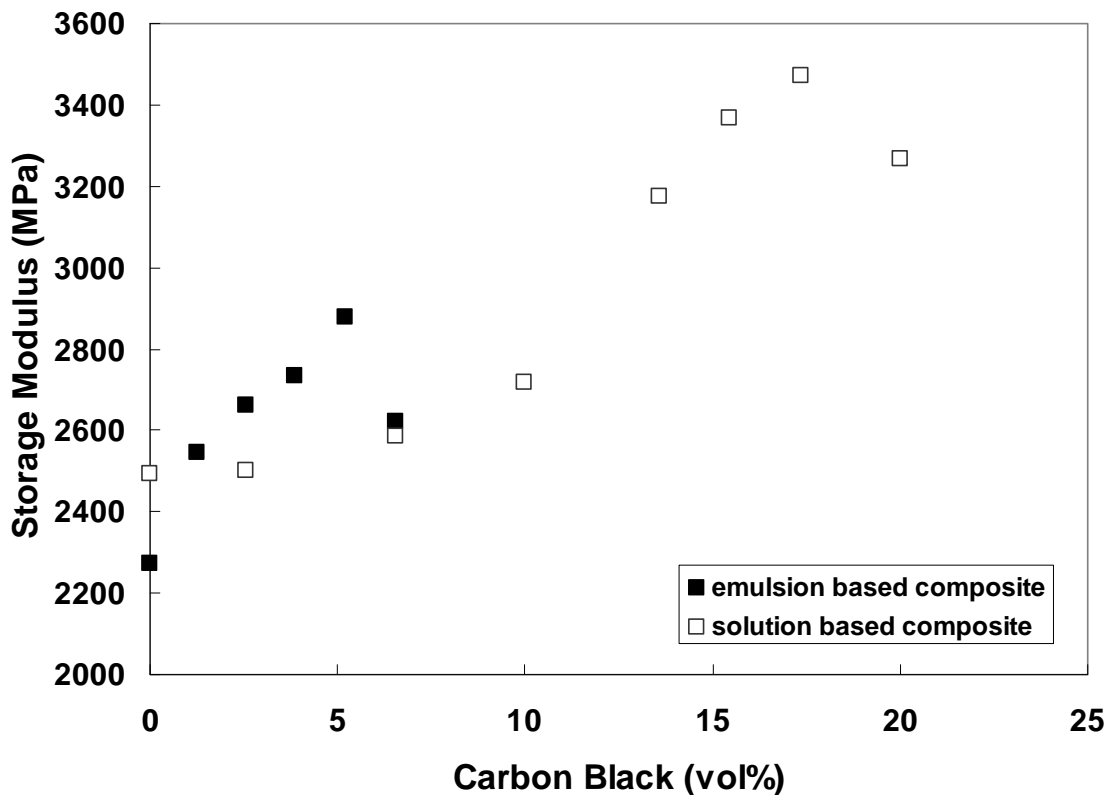
Figure 12. Room temperature storage modulus as a function of carbon black concentration for PVAc solution and emulsion-based composites.

For the solution-based composites, Figure 12 shows a more gradual increase in storage modulus up to 10 vol%, followed by a sharp increase beyond this concentration. This suggests that networking may be influencing the composite modulus. Beyond the percolation threshold, which is around 8 vol% for solution-based system, carbon black particles become more interconnected. It is believed that the networking between the carbon particles enhances the storage modulus. Beyond 18 vol% carbon black there is a drop in modulus due to the CPVC being reached. The solution-based CPVC is much greater than for the emulsion-based system, which is due to the inability of the polymer particles to effectively envelop the filler during film formation. In Figure 12 it can be seen that once the percolation threshold is reached the storage modulus in the solution-

based composites is higher than that of emulsion-based composites. In this case the solution based-composites have a high carbon black concentration, but no pore formation and hence a strong network exists. Storage modulus as a function of temperature for the solution-based composites is shown in Figure 13.
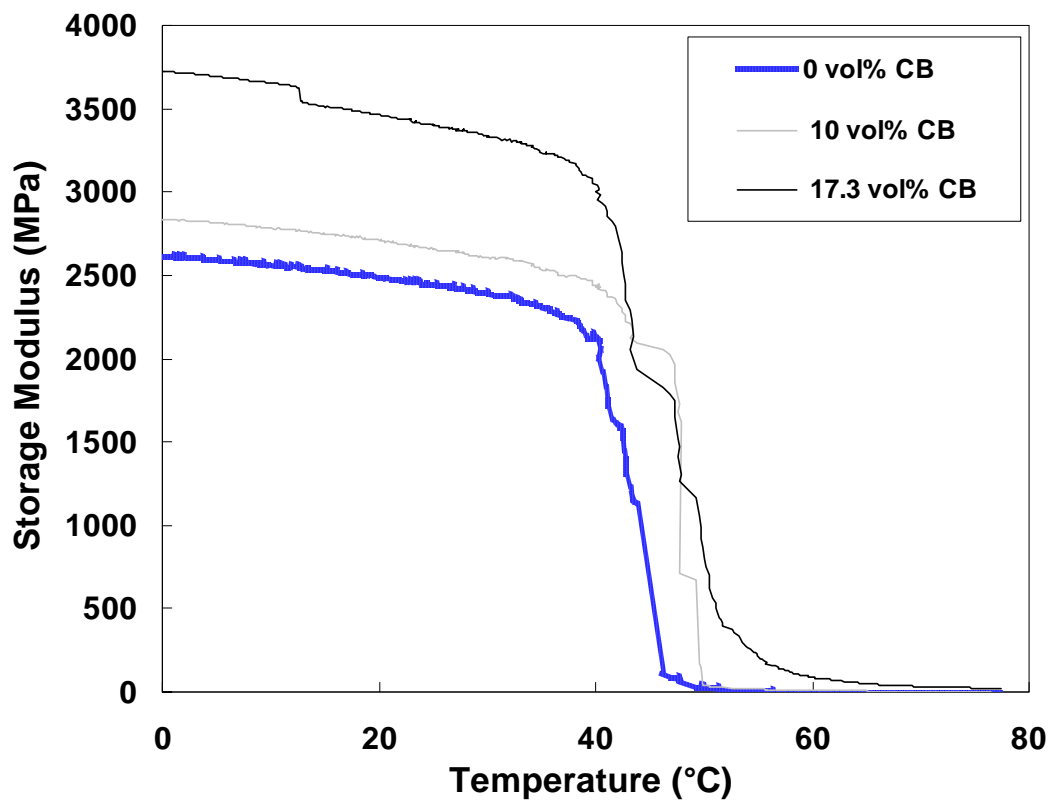
Figure 13. Storage modulus as a function of temperature for PVAc solution-based films with varying carbon black concentration.

Effect of pH on the Electrical Conductivity of Emulsion-Based Films

The intrinsic pH of the PVAc emulsion and carbon black mixture is 4.64. This pH was adjusted to 6.94 and 9.1 to determine the influence of pH on composite properties.

Figure 14 shows that the percolation threshold (V_c in Equation 1) is approximately 0.012 for all the three pH levels.
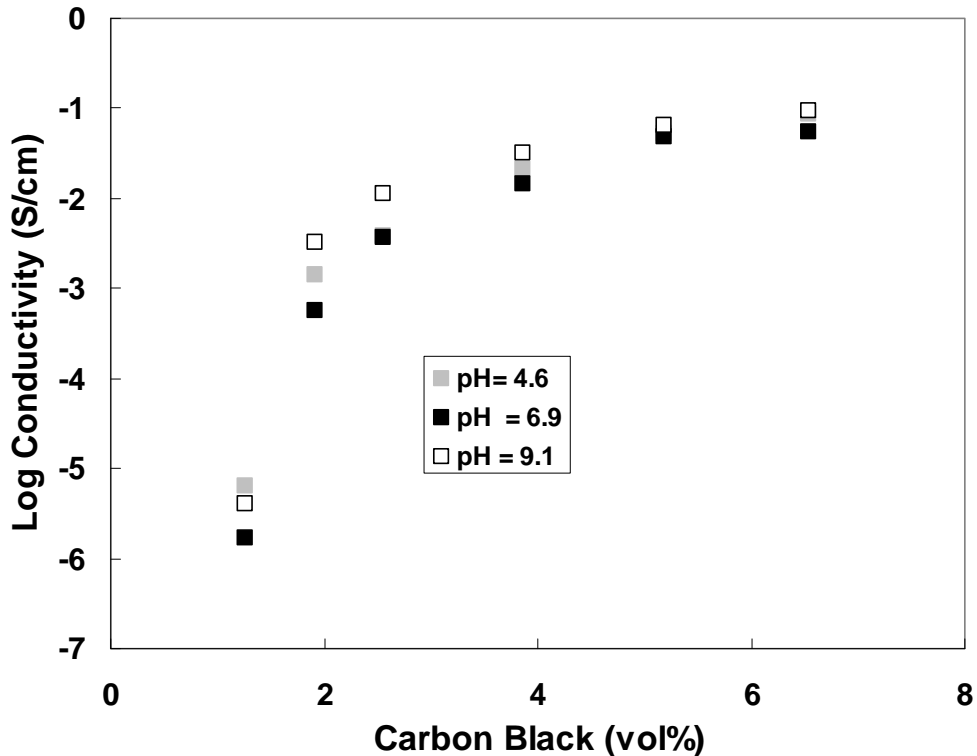
Figure 14. Electrical conductivity as a function of carbon black concentration for emulsion-based composite systems made at varying pH.

Conclusions

The effect of microstructure on the electrical and thermo-mechanical properties of carbon black-filled poly(vinyl acetate) nanocomposites has been studied. SEM images show characteristic differences between the microstructure of emulsion and solution based films. The difference between the microstructure of emulsion based films dried at room temperature and 80°C is also shown. The emulsion-based films have a percolation threshold nearly an order of magnitude less than the solution based films. This disparity is due to carbon black particles segregating around the emulsion particles during drying,

resulting in a network at low concentration. The percolation threshold of the emulsion based system is 1.21 vol% carbon black, while that of solution based system is 8.2 vol%. Despite having a greater percolation threshold, the solution-based system has greater maximum conductivity than the emulsion-based one due to unrestricted network growth. The storage modulus of emulsion-based composites increases by 25% with 5 vol% carbon black and then decreases beyond 6.5 vol% carbon black due to the formation of pores in the composite. In the solution-based system, the storage modulus is less than the emulsion based system until 5 vol% carbon black is reached. Once the percolation threshold is reached (at 8.2 vol% carbon black), there is a much sharper increase due to the formation of a network structure. A drop in the storage modulus beyond 17.3 vol% carbon black is observed as the CPVC is exceeded. From the above discussion, it is clear that solution-based films can have higher maximum achievable conductivity and storage modulus, but this requires higher filler concentration (>15vol%) to achieve. The emulsion-based systems are better overall at low filler concentration (< 5 vol%).

CHAPTER III

EFFECT OF CLAY ON THE MICROSTRUCTURE AND PROPERTIES OF EMULSION AND SOLUTION-BASED POLYMER COMPOSITES

The influence of carbon black on the electrical conductivity and mechanical properties of poly (vinyl acetate) emulsion and solution-based systems was examined in Chapter II. In Chapter III, clay is added as secondary filler in an effort to reduce the percolation threshold and improve mechanical properties. It has already been shown that carbon black has a low percolation threshold in a PVAc emulsion-based composite due to segregated network formation. In the present study, insulating clay (sodium montmorillonite) is added to increase the exclusionary volume for carbon black. Clay has been successfully used in composites to improve thermal stability [67-70], mechanical properties [71-74], and barrier properties [80-82]. These composites have been prepared using in situ intercalative polymerization [51, 52, 75-79], exfoliation of the clay in a polymer solution [48, 76] and melt-intercalation [48]. Exfoliated nanocomposites have higher phase homogeneity compared to intercalated nanocomposites, which is more effective for improving composite properties.

Feller and coworkers studied the influence of melt dispersion of intercelated montmorillonite on electrical properties of three conductive composites PE/CB, PP/CB and poly (ethylene-co-ethyl acrylate)/CB. They found that even a low concentration of clay (1.25 vol%) has a significant effect on the electrical conductivity of the composites

[48]. Liu and Grunlan demonstrated that clay could be used to reduce the percolation threshold and increase the maximum conductivity in a carbon nanotube-filled epoxy [65]. In this chapter, the electrical and mechanical properties of PVAc solution and emulsion-based composites, containing carbon black and clay, are evaluated. The addition of clay to the solution-based composites, studied in Chapter II, seems to degrade electrical conductivity and modulus due to destruction of the carbon black network. In emulsion-based composites, a small amount of clay reduces the percolation threshold and increases modulus, but these properties are diminished with increasing clay concentration. The characterization of these composites is discussed in detail in the sections following the description of materials and methods.

Materials and Methods

Materials

Carbon black, PVAc latex and PVAc pellets used in this study are described in Chapter II. Unmodified natural montmorillonite clay (Cloisite Na$^+$, CEC=92.6 meq/100g) was provided by Southern Clay Products (Gonzales, TX). When fully exfoliated, this clay has a platelet shape that is 1 nm thick and 200 nm in diameter on average.

Composite Preparation

Film preparation with clay has one difference from the film preparation discussed in Chapter II. In the case of latex-based films, the clay was sonicated for 10 minutes in deionized water at 50 W using a VirTis Virsonic 100 Ultrasonic Cell Disrupter (Gerdiner, NY). The sonicated clay solution was then added to the aqueous mixture containing

carbon black and polymer. Clay was sonicated in DMF instead of water for solution-based films. The remaining procedure for film preparation is the same as described in Chapter II. In this study, three different series of samples were made with varying clay concentration of 0.2, 0.4 and 2 wt% clay. In each of the series, the clay concentration was fixed and the carbon black concentration was varied from 1.26 to 5.5 vol%, in the case of emulsion-based, and 2.5 to 17.3 vol %, in the case of solution-based composites.

Composite Characterization

Most of the characterization done, in this study is identical to that described in Chapter II. Optical microscopy, performed with a OLYMPUS BX60 (Princeton, NJ) was used to visualize the dispersion of clay in the composite.

Results and Discussion

Emulsion-Based Composites with Clay and Carbon Black

Composite Microstructure

Figures 15 shows cross-sectional images of PVAc/CB emulsion-based films with varying clay concentration. All of the composites have 1.26 vol% carbon black to allow the influence of clay on microstructure to be evaluated. Similarly, Figure 16 has 3.86 vol% carbon black and varying clay concentration. These composites show segregation throughout their thickness. In Figure 15(a), no clay is present and carbon black has only a weak network structure. With the addition of 0.2 wt% clay (Fig. 15(b)), a strong segregated network of carbon black is observed. There is no significant change in microstructure when the clay concentration is increased to 0.4 wt% (Fig. 15(c)). With 2

wt% clay (Fig. 15(d)), the carbon black particles are no longer able to form a network. Figure 16 shows even greater microstructural variation when the carbon black concentration is increased to 3.8 vol%. In Figures 16(a) and (b), with no clay and with 0.2 wt% clay the carbon black exhibits a strong segregated network. With 0.4 wt% clay (Fig. 16 (c)), carbon black aggregation appears weakened relative to the composites with 0 and 0.2 wt% clay. With the addition of 2 wt% clay (Fig. 16 (d)), the carbon black particles appear phase-separated. Therefore, relatively high clay concentration hinders the formation of a segregated network in composites with low (Fig.15) and high (Fig 16) carbon black concentration.
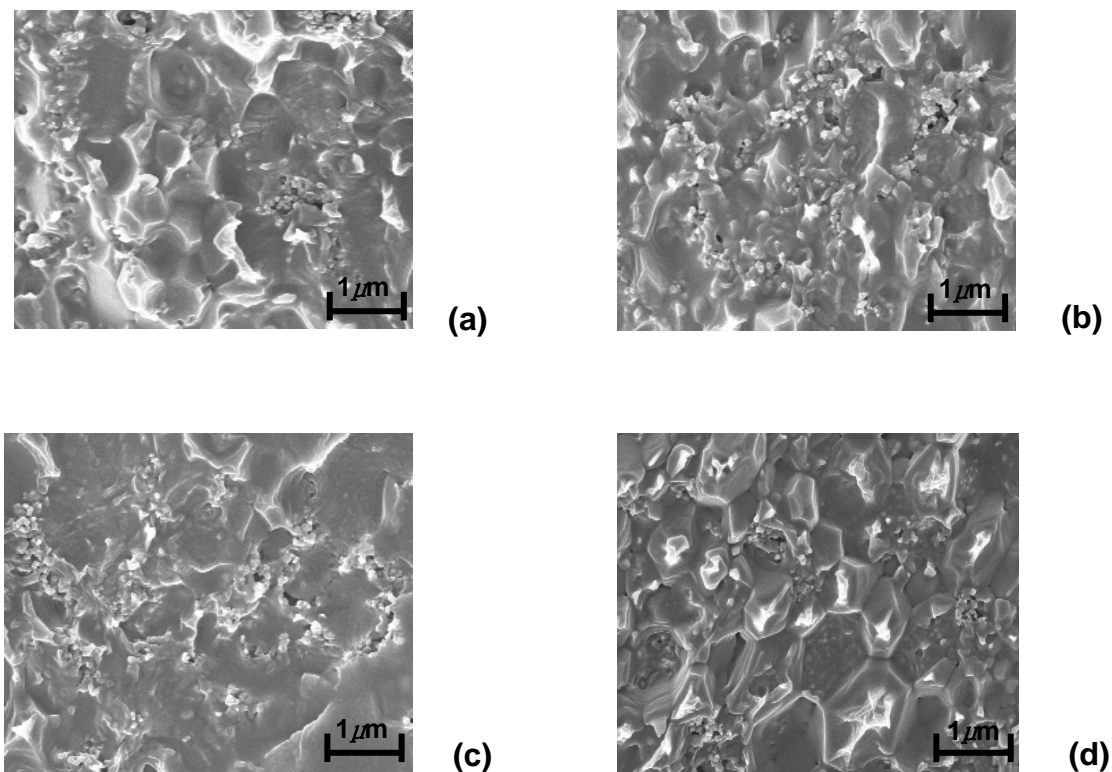
Figure 15. Freeze-fractured cross-sections of PVAc latex-based composites having 1.26 vol% carbon black and 0 (a), 0.2 (b), 0.4 (c) and 2 wt% clay (d).
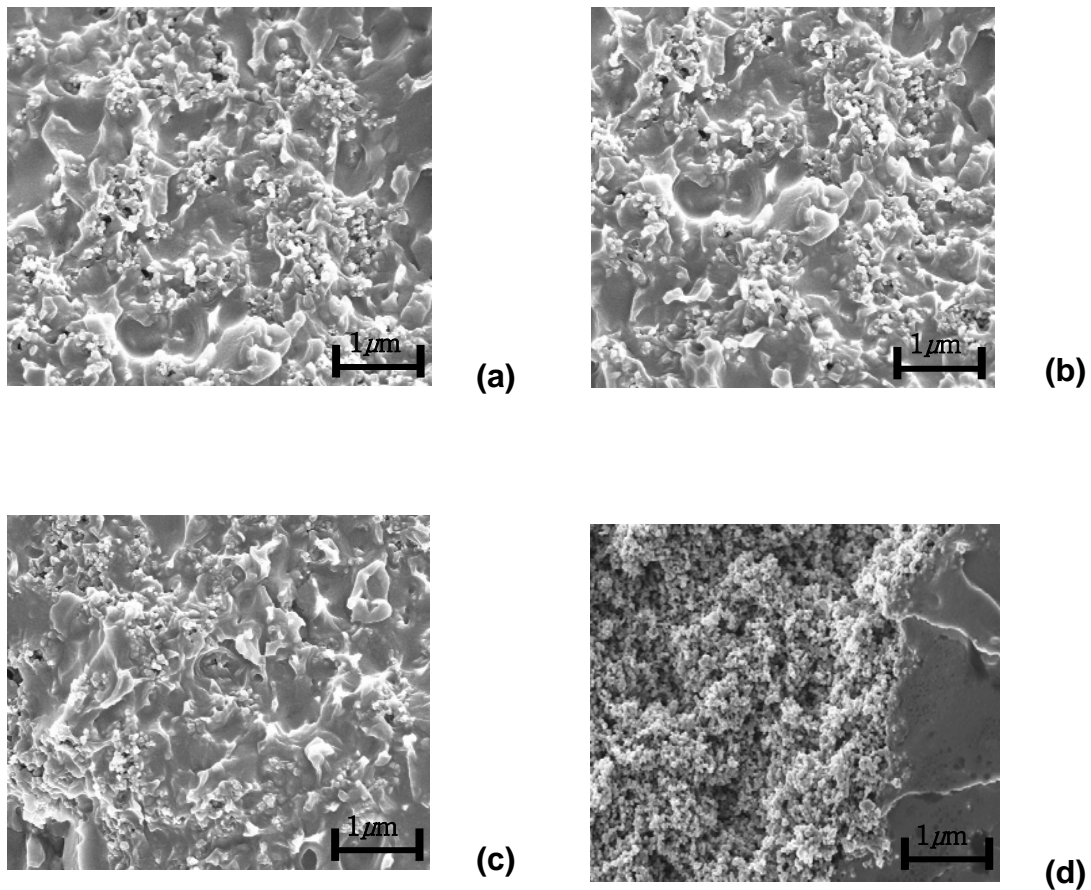
Figure 16. Freeze-fractured cross-sections of PVAc latex-based composites having 3.8 vol% carbon black with 0 (a), 0.2 (b), 0.4 (c) and 2 wt% clay (d).

The electron microscope images shown in Figures 15 and 16 do not show clay dispersion in the matrix, so optical microscope images are shown (Fig. 17) for samples with 0.95 vol% carbon black at two different clay concentrations, 0.2 and 0.4 wt%. Figures 17(a) and (c) show the cross-polarized images, whereas Figures 17(b) and (d) show the bright field images. With cross-polarized light, clay appears as white dots dispersed in a black matrix. Figure 17(c) is much whiter than Figure 17(a) because more clay is dispersed in the matrix. It can also be seen that the clay is well dispersed, which is the reason for a better network structure than a sample with no clay at low carbon black concentration. In

the bright-field condition (Fig. 17(b) and (d)), both images look identical because only carbon black particles are seen as white dots dispersed in a black matrix and both composites have the same carbon black concentration. As the clay content is increased to 2 wt%, the clay particles serve to disrupt carbon black networking, which is evident in Figure 15(d).
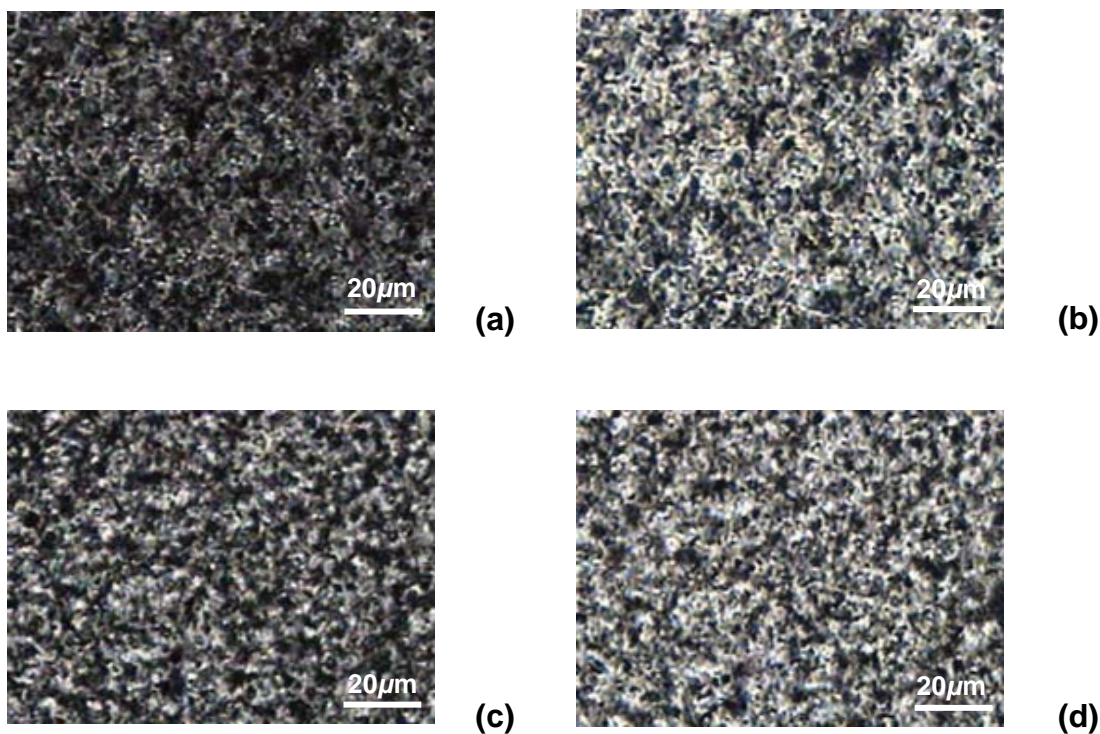
Figure 17. Optical microscope images of emulsion-based composites having 0.95 vol% carbon black and 0.2 wt% clay ((a) and (b)), 0.95 vol% carbon black and 2 wt% clay ((c) and (d)). Images (a) and (b) are taken under the cross-polarized light condition, while images (c) and (d) are taken in the bright-field condition.

Composite Conductivity

Tables 3 and 4 summarize composition, thickness and conductive behavior of PVAc emulsion-based composites with varying clay and carbon black concentration. Figure 18

shows electrical conductivity as a function of carbon black loading for the composites with 0, 0.2 and 2 wt% clay. The percolation power law (Eq. 1) was fit to these three series to obtain the percolation threshold (V_c). The curves show that with 0.2 wt% clay there is a decrease in the percolation threshold from 1.21 to 0.88 vol% carbon black. With a clay concentration of 2 wt%, the percolation threshold is nearly the same as the series with no clay. These results match expectations based upon the microstructural images shown in Figure 15.

Table 3. Electrical properties of emulsion based films with 0.2 wt% clay and varying carbon black concentration.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
1.5	0.94	0.0166	30000000	503363	0.0000002
2	1.26	0.0161	322707	5202	0.0002
3	1.90	0.0162	27312.4	441.3	0.0023
4	2.5	0.0155	9647.5	151	0.0066
5	3.20	0.0157	5119.25	79	0.0126
6	3.86	0.0153	4265.03	65	0.0153

Table 4. Electrical properties of emulsion-based films with 2 wt% clay and varying carbon black concentration.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
2	1.26	0.0166	20000000	380957	0.0000003
2.5	1.58	0.027	395115	10668	0.000009
3	1.90	0.0188	195652	3541	0.0003
4	2.5	0.0155	43942	659	0.0015
6	3.86	0.0165	7012	115	0.0086
8	5.19	0.0171	6962	118	0.0084
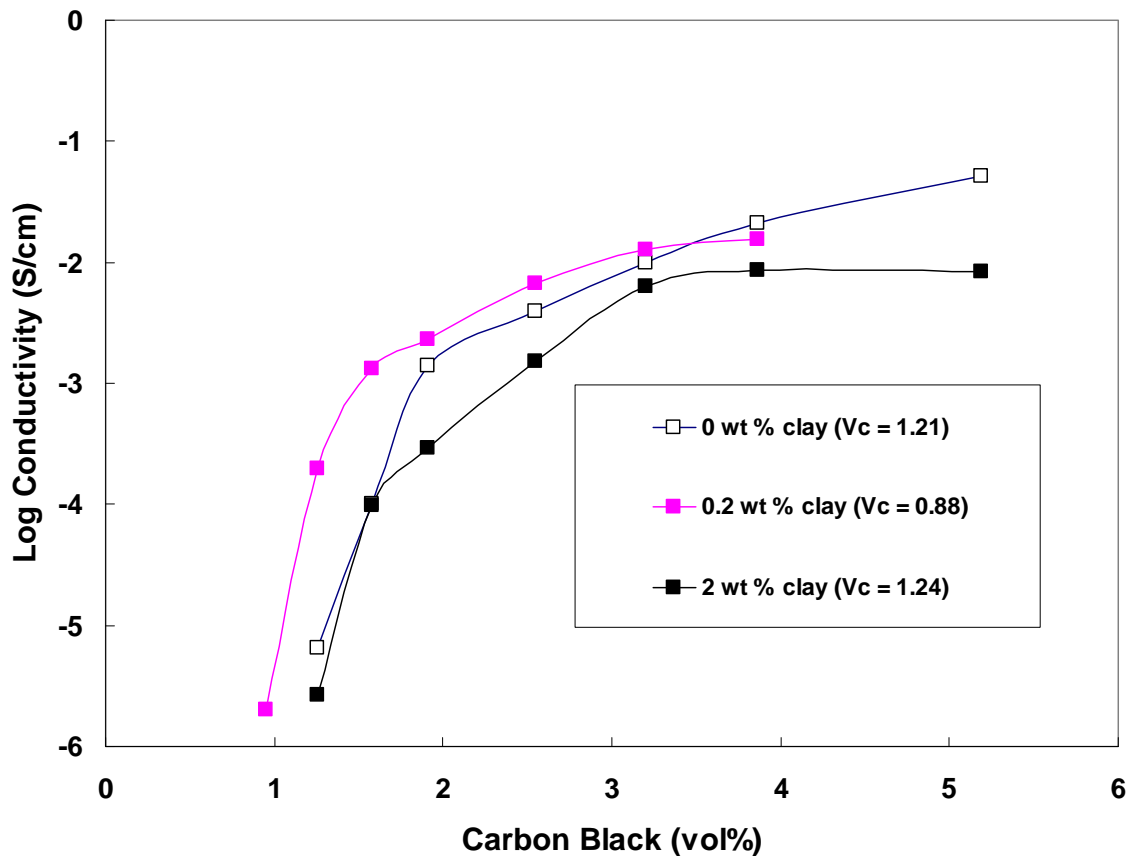
Figure 18. Electrical conductivity as a function of carbon black concentration for emulsion-based composite systems with varying clay concentration. Percolation tresholds are shown as vol% for each series.

Two phenomena may be occurring when clay is added to these carbon black-filled composites. First, there may be interactions between clay and carbon black that alter its distribution due to exclusionary effects. Figure 19 shows electrical conductivity as a function of clay concentration for composites with 1.26 and 3.86 vol% carbon black to compare the influence of clay at low and high carbon black concentration. With 1.26 vol% carbon black there is an increase in conductivity at low clay concentration, which later decreases with 2 wt% clay. This behavior can be attributed to decreased interaction between the carbon black and the polymer matrix and the association of clay with carbon black. Assuming that carbon black particles are attracted to the clay, a better network is

formed at low clay content. With an increase in clay content, the carbon black aggregates can no longer network as easily. Here the dispersive effect is not balanced by the aggregation effect, so the carbon black connectivity decreases with high clay content. In the case of high carbon black concentration, conductivity is essentially constant regardless of the clay concentration. There is a slight drop with 2 wt% clay, which is due to destabilization of carbon black that generates porosity. This is the second phenomena associated with the addition of clay.
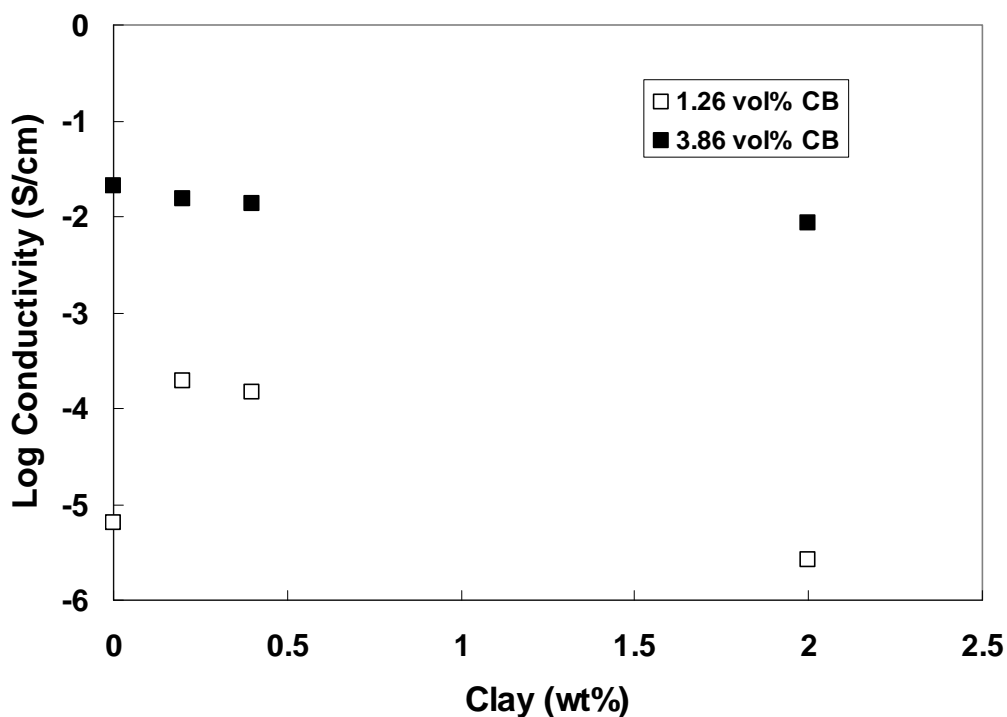
Figure 19. Electrical conductivity as a function of clay concentration for CB-filled, emulsion-based composites.

Composite Modulus

Storage modulus as a function of temperature, for latex based films with 0.2 wt% clay and varying carbon black concentration, is shown in Figure 20. The storage modulus

increases with carbon black concentration, which was also shown in Chapter II. In addition to greater concentration, the carbon black network grows stronger and enhances the modulus. It can also be seen that the glass transition temperature (T_g) increases with carbon black concentration, as indicated by the modulus drop occurring at higher temperature. Figure 20(b) shows the corresponding loss modulus curve, the peak of which marks T_g. The T_g with 1.2 vol% carbon black is 35°C and increases to a value of 45°C with 3.8 vol%. This enhanced thermal stability is further evidence that the addition of a small amount of clay strengthens the carbon black network.

(a)
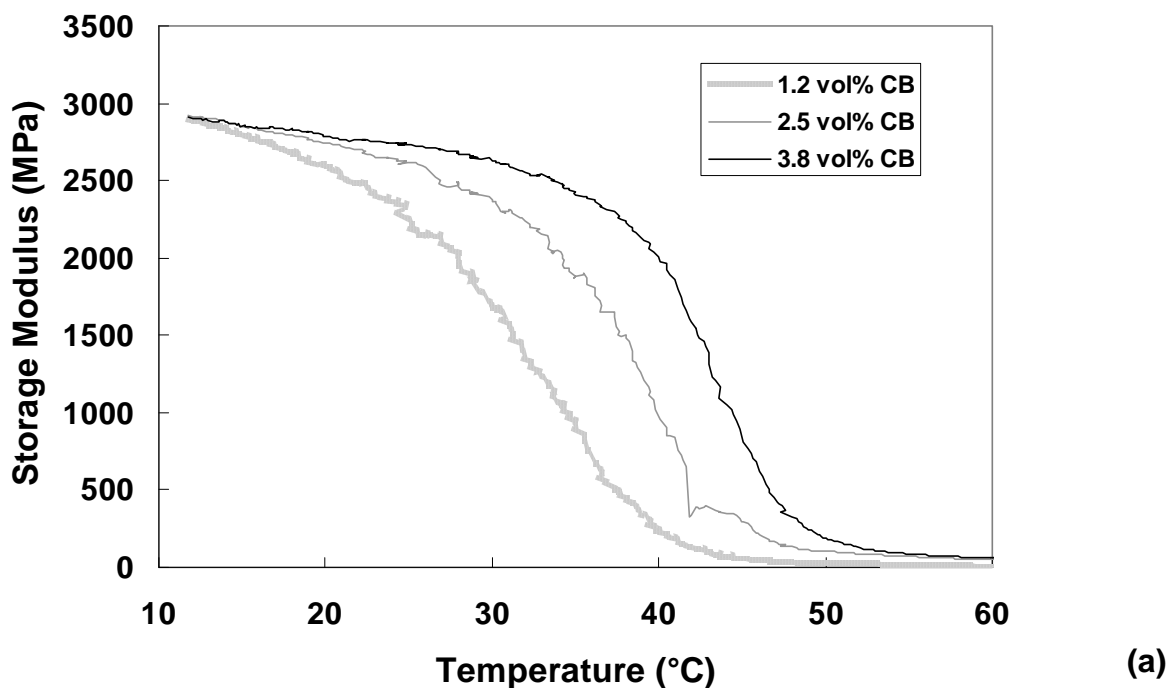
Figure 20. Storage modulus (a) and loss modulus (b) as a function of temperature for PVAc latex-based films with varying carbon black concentration and 0.2 wt% clay.
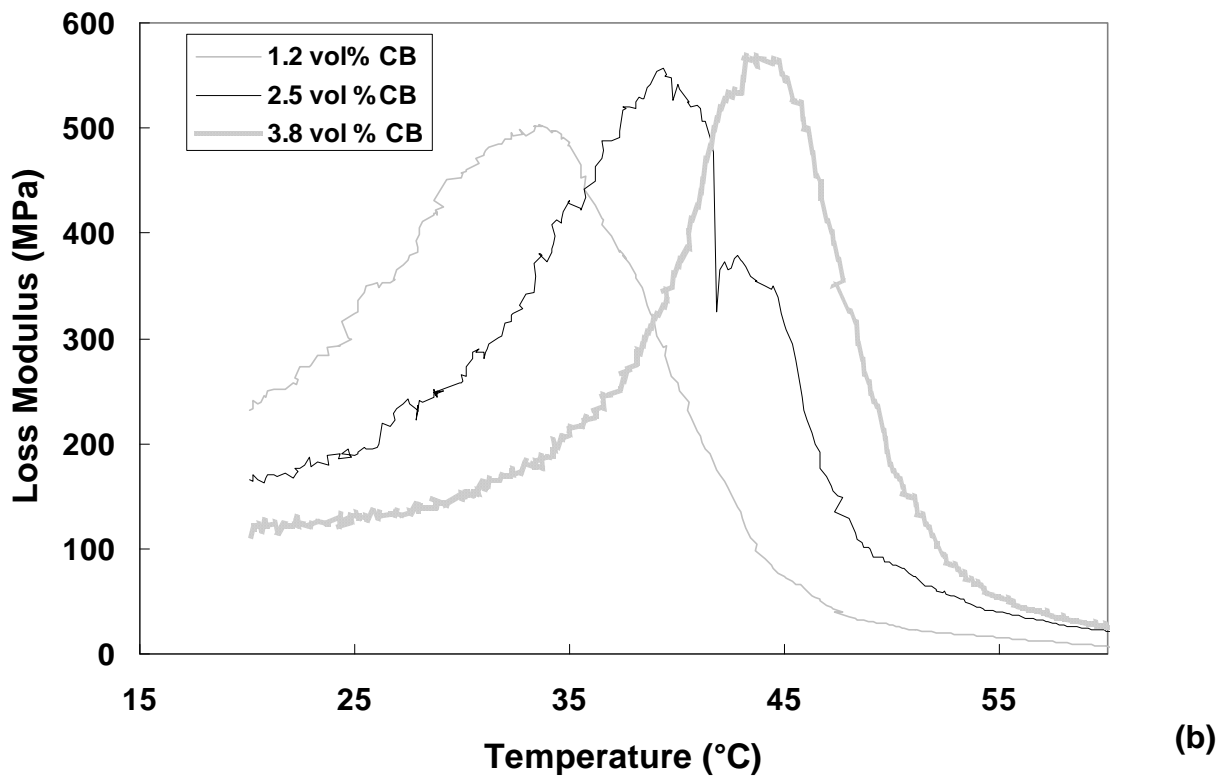
Figure 20. Continued.

Figure 21 compares carbon black-filled composites with and without added clay. With 2.5 vol % carbon black, the storage modulus at room temperature is greater with the addition of 0.2 wt% clay. It was shown in Figure 15 that 0.2 wt% clay improves the network structure relative to the same system without clay, for low carbon black concentration. A stronger network is expected to exhibit a greater room temperature modulus and better modulus retention as temperature is increased, as shown in Figure 21.
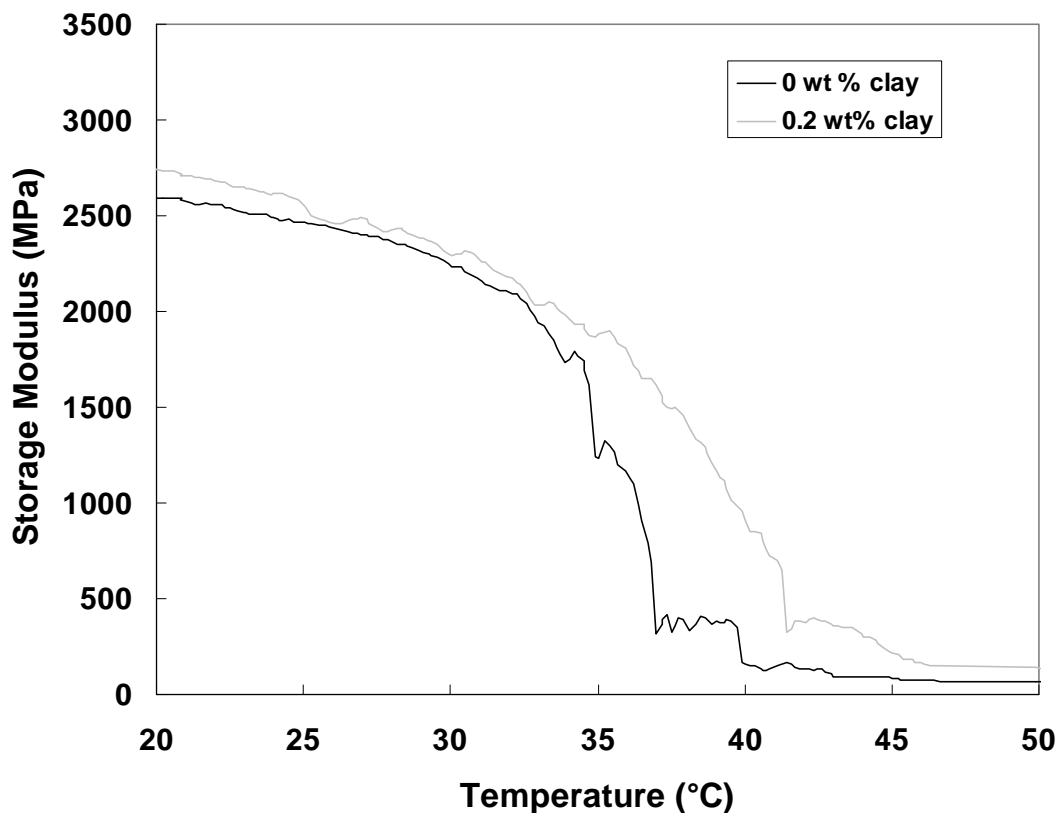
Figure 21. Storage modulus as a function of temperature for latex-based films with 2.5 vol % carbon black.

Figure 22 shows the influence of clay concentration on the storage modulus of the latex-based composites containing carbon black. It can be seen that at low carbon black concentration, 0.2 wt% clay significantly increases modulus. With 2 wt% clay, composite modulus is reduced when any carbon black is added. At low clay concentration, the carbon black is more effectively forced into a network, making modulus greater. This is primarily an excluded volume effect whose efficacy decreases with increasing carbon black concentration. With a larger concentration of clay (2 wt%), the storage modulus is reduced, irrespective of carbon black concentration, due to excessive excluded volume that causes significant carbon black aggregation and associated porosity (see Fig. 16(d)).

This also appears to happen at higher carbon black content, for composites containing 0.2 wt% clay, as evidenced by the leveling off in storage modulus.
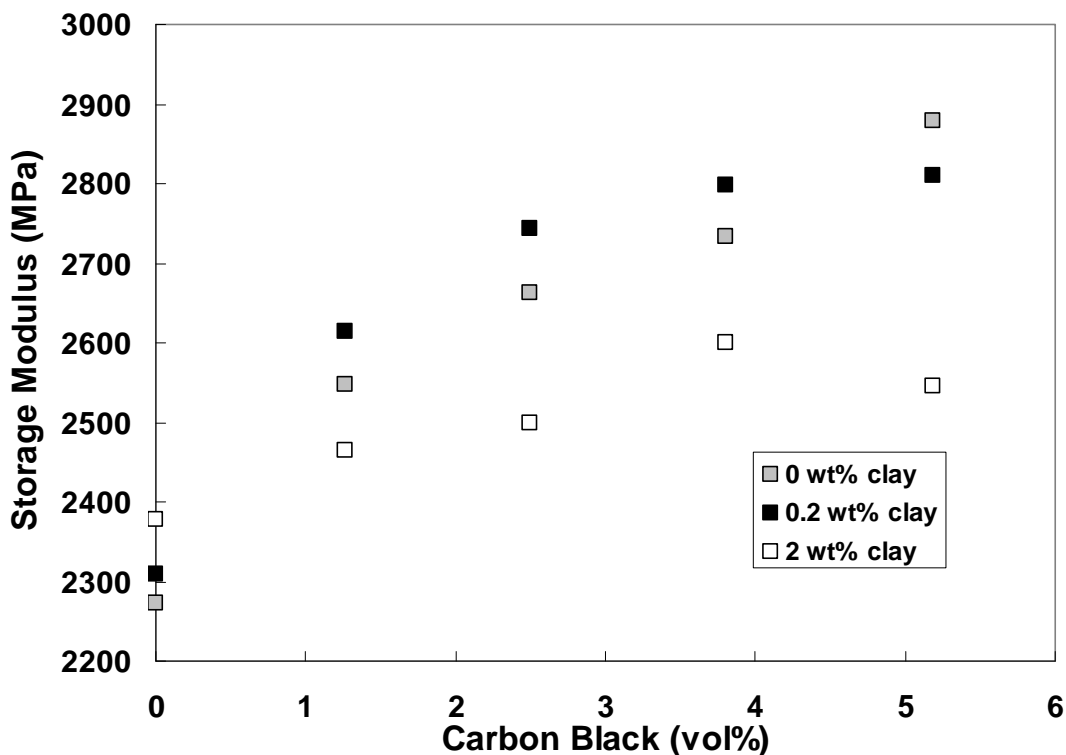
Figure 22. Storage modulus as a function of carbon black concentration with 0, 0.2 and 2 wt% clay.

To further explore the complementary influence of carbon black and clay, storage modulus as a function of clay concentration is shown in Figure 23 for series with low and high carbon black concentration. This graph demonstrates that high clay content (>1 wt%) produces a reduced storage modulus due to aggregation and pore formation. Low clay content increases storage modulus at low carbon black concentration and decreases modulus at higher carbon black concentration. The fact that emulsion-based composites produce a highly networked microstructure in the absence of clay makes them sensitive to relatively small additions of this co-filler.
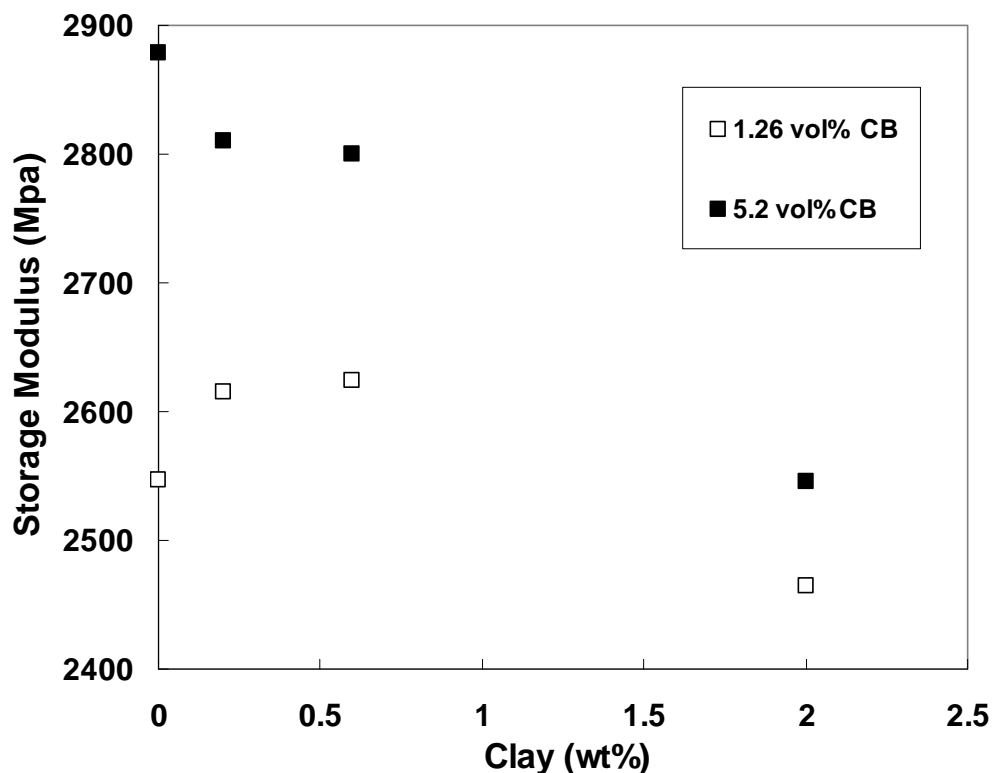
Figure 23. Storage modulus as a function of clay concentration in emulsion-based composites with a constant carbon black concentration.

Solution-Based Composites with Clay and Carbon Black

Composite Microstructure

Figure 24 shows the microstructure of PVAc solution-based composites with 10 vol% carbon black and varying clay concentration. These composites have a random dispersion of carbon black particles in the polymer matrix. The addition of clay does not appear to alter the random microstructure. With 0.2 wt% clay (Fig. 24(a)), the carbon black just begins to form a network (i.e, the carbon black concentration is near the percolation threshold at 10 vol%) and this structure looks similar as the clay concentration is increased. If anything, the composite is below the percolation threshold

at this carbon black concentration with 0.6 and 2 wt% clay. At these higher concentrations, the dispersion of the carbon black appears to improve. Unlike the emulsion-based systems, the clay is mixed with DMF for solution processing, which produces larger tactoids that may enhance carbon black dispersion during mixing. Figure 25 shows the microstructure of solution-based composites with 17.3 vol% carbon black and varying clay concentration. In the absence of clay (Fig. 25(a)), heavy aggregation of carbon black is observed, which indicates that the CPVC has been exceeded. This gradually changes as the clay is added. Figure 25(b) shows reduced aggregation with the addition of 0.2 wt% clay. Further reductions in the porosity and better carbon black dispersion are seen with 0.6 (Fig. 25(c)) and 2 wt% clay (Fig. 25(d)). Although there appears to be a diminishing benefit to adding more clay, it is interesting to see reduced carbon black aggregation with increasing clay content (the opposite effect is seen in emulsion-based composites). Improved carbon black dispersion is expected to increase the percolation threshold and improve mechanical behavior at higher filler concentration.
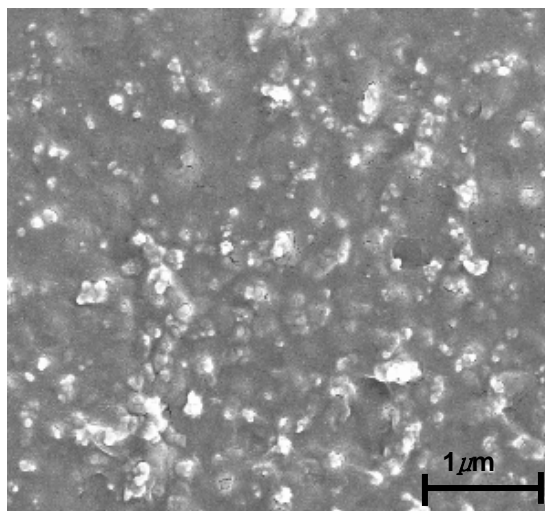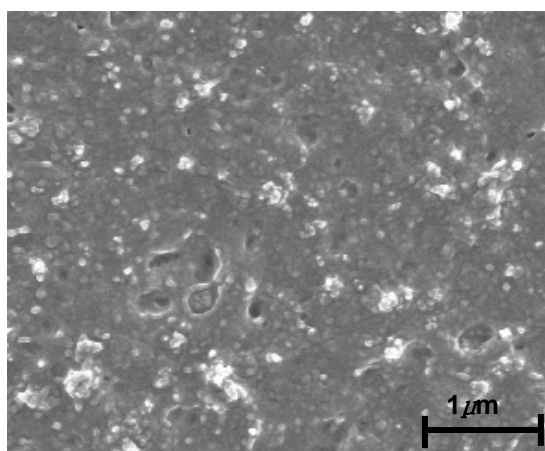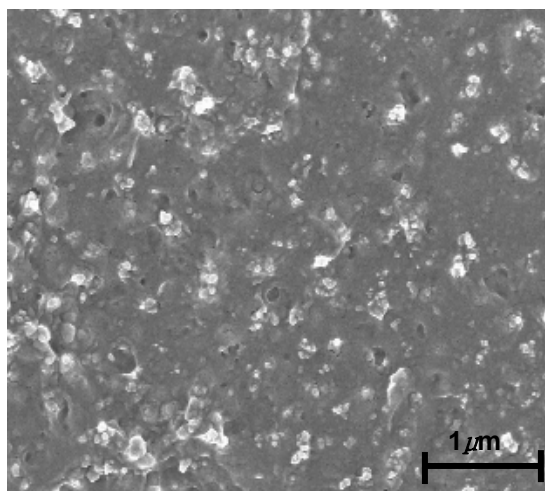
Figure 24. Freeze-fractured cross-sections of PVAc solution-based films with 10 vol% carbon black and 0.2 (a), 0.6 (b) and 2 wt% clay (c).
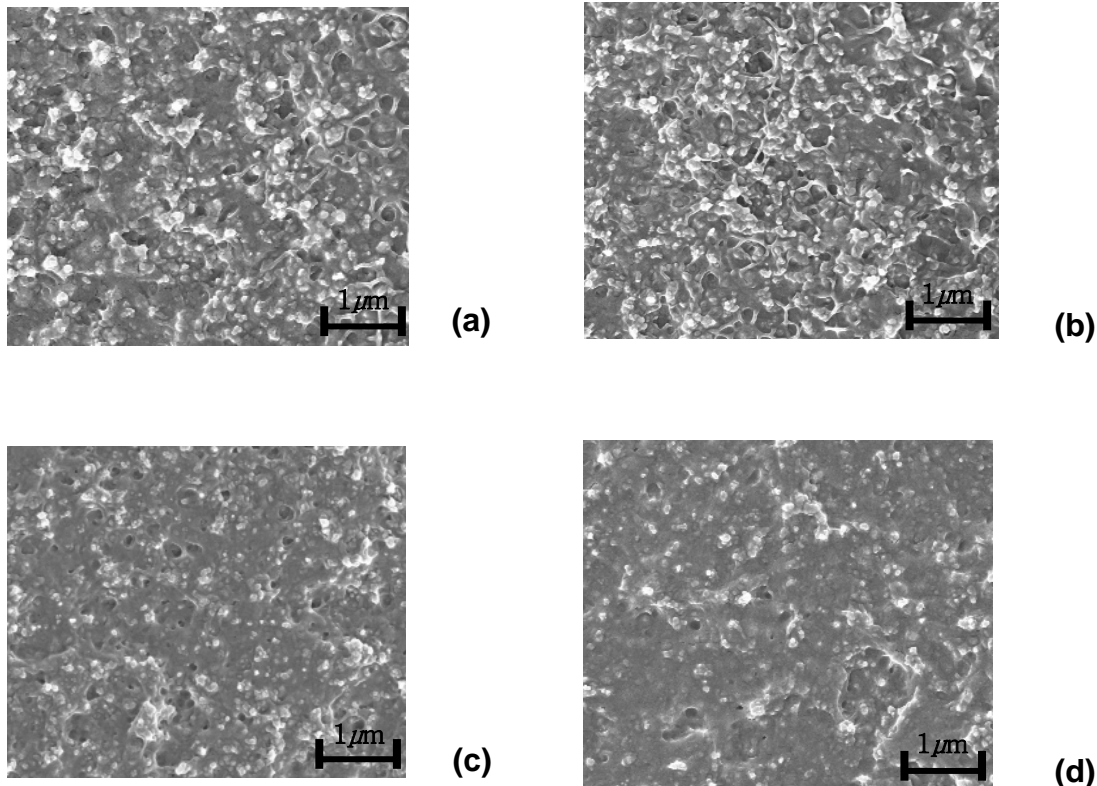
Figure 25. Freeze-fractured cross-sections of PVAc/CB solution-based films with 17.3 vol% carbon black and 0 (a), 0.2 (b), 0.6 (c) and 2 wt% clay (d).

Composite Conductivity

Figure 26 shows the electrical conductivity of the solution-based composites as a function of carbon black concentration with different clay content. Unlike the emulsion-based composites, there is no decrease in the percolation threshold with the addition of 0.2 wt% clay. With increasing clay, the percolation threshold shifts to higher values, as expected from the microstructural images (see Fig. 24 and 25). Carbon black may associate with the clay during processing due to the incompatibility of clay with DMF solvent. This effectively makes the carbon black behave as larger particles (i.e, DMF-friendly carbon

black covers relatively large clay tactoids) that are more easily dispersed and less prone to networking. Tables 5 and 6 summarize thickness and conductivity data for the series shown in Figure 26.

Table 5. Electrical properties of solution-based films with 0.2 wt% clay and carbon black concentration.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
25	17.3	0.0176	166.421	2.92236	0.3422
22.5	15.5	0.0156	196.588	3.06677	0.3261
20	13.6	0.0144	460.015	6.62421	0.151
17.5	11.8	0.0143	3186.11	45.6888	0.0219
15	10	0.0133	432345	5758.84	0.0002
12.5	8.2	0.0148	1.5000000	2182803	0.00000005

Table 6. Electrical properties of solution-based films with 0.6 wt% clay and carbon black concentration.

Carbon black (wt%)	Carbon black (vol%)	Thickness (cm)	Sheet resistance (Ohm)	Resistivity (Ohm·cm)	Conductivity (S/cm)
25	17.3	0.0164	841.49294	13.76682	0.0726
22.5	15.5	0.0161	1573.887	25.37106	0.0394
20	13.6	0.0147	6485.2374	95.46269	0.0105
17.5	11.8	0.0173	21499.986	372.8098	0.0027
15	10	0.0148	73737328	1094262	0.000000009
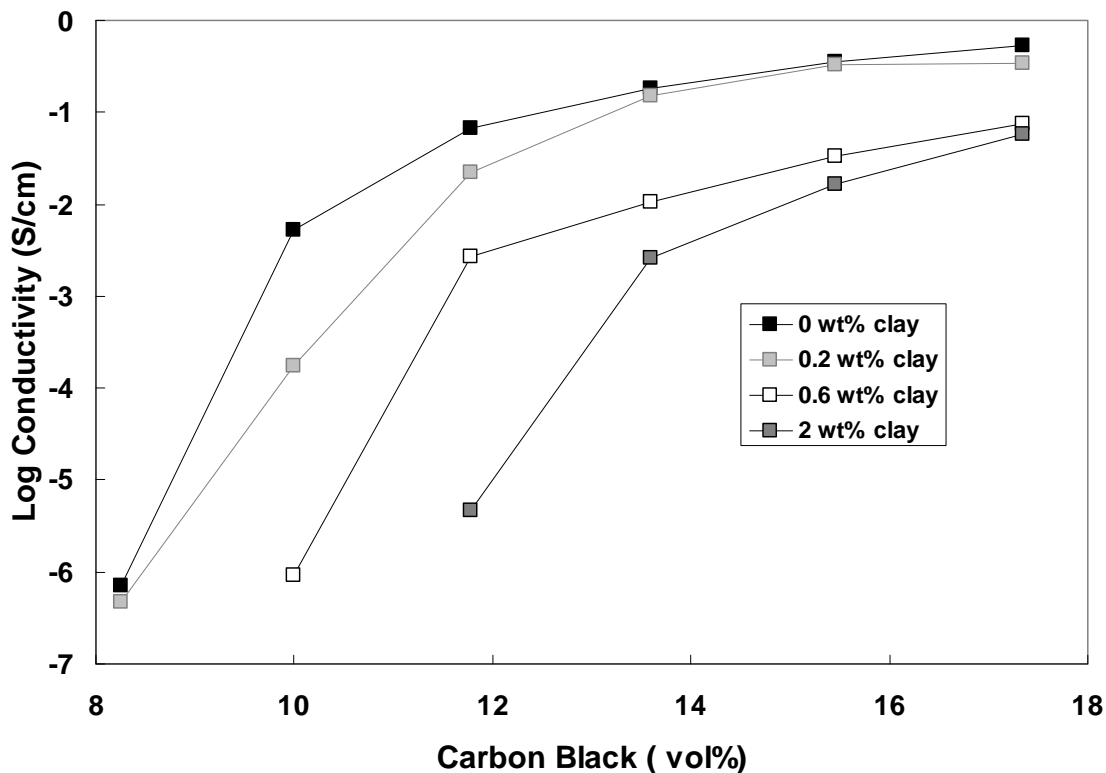
Figure 26. Electrical conductivity as a function of carbon black concentration for PVAc solution-based composites with varying clay concentration.

Figure 27 shows the effect of clay on conductivity for a composite near the percolation threshold (10 vol% carbon black) and one with high carbon black concentration (17.3 vol%). Near the percolation threshold there is a rapid drop in conductivity with increasing clay concentration, but this effect is diminished at high carbon black content. As shown in Figure 26, the percolation threshold is shifted by 1.5 vol% with the addition of 0.6 wt% clay and further shifted by 1.8 vol% with the addition of 2 wt% clay. At high carbon black concentration the conductivity drop is more gradual because the carbon black content is well beyond percolation.
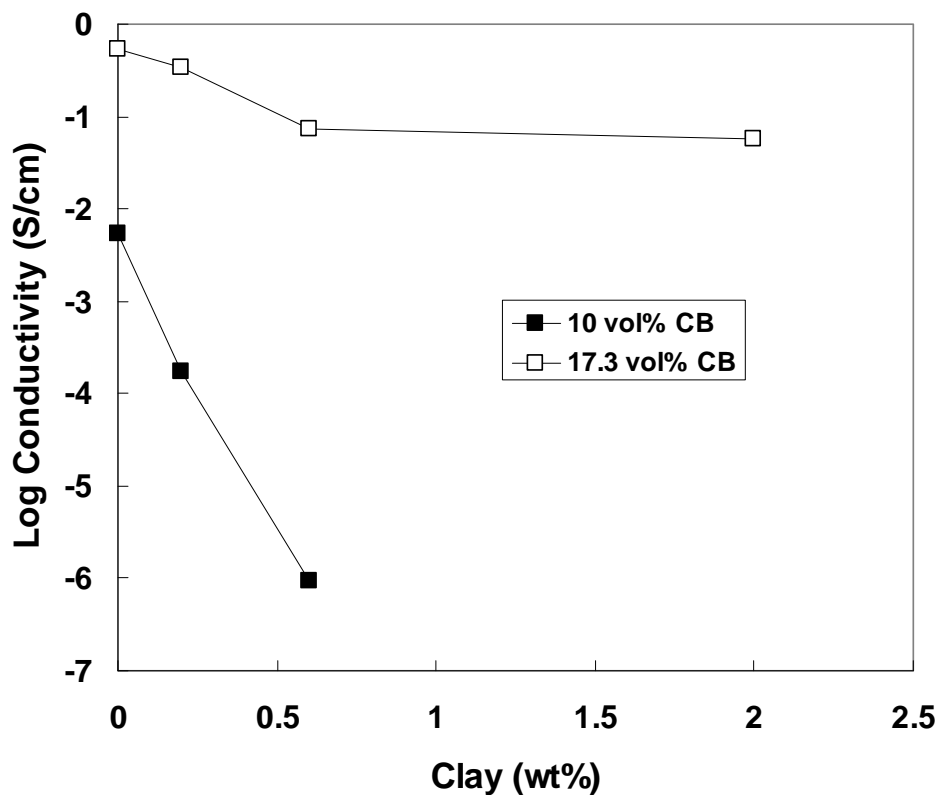
Figure 27. Electrical conductivity as a function of clay concentration for PVAc solution-based composites with varying carbon black concentration.

Composite Modulus

Figure 28 shows storage modulus as a function of temperature for PVAc solution-based films with varying carbon black concentration and 0.2 wt% clay. Composite modulus at 20°C increases as the carbon black concentration increases. The increase in storage modulus from the addition of 10 vol% carbon black matches the increase when the carbon black concentration is raised from 10 to 13.6 vol%. This is due to the fact that the percolation threshold of this system is around 10 vol% carbon black, so beyond this concentration a growing carbon black network enhances modulus more than disconnected filler. The same behavior is observed with all of the clay concentrations.
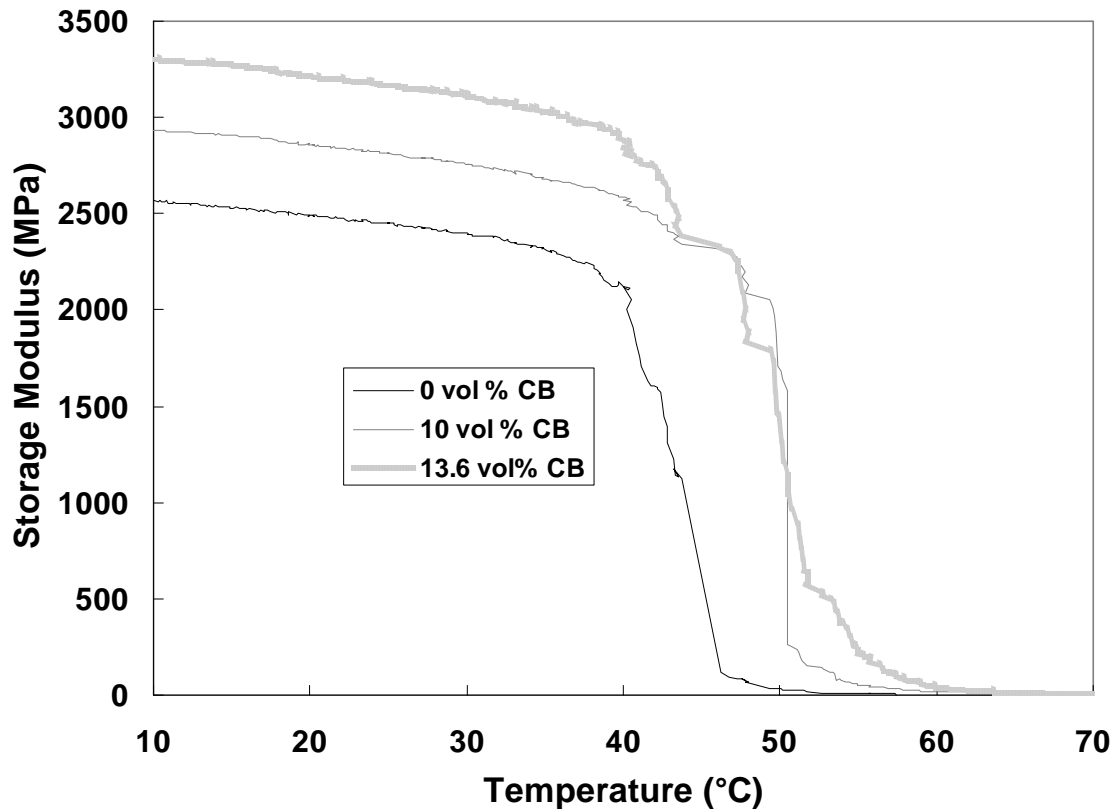
Figure 28. Storage modulus as a function of temperature for PVAc solution-based composites with 0.2 wt% clay and varying carbon black content.

Figure 29 shows storage modulus as a function of carbon black concentration for PVAc solution-based composites with varying clay content. Up to the percolation threshold of carbon black alone (~ 10 vol%), all of the composites have nearly the same modulus. At 8.2 vol%, the pure carbon black series reaches the percolation threshold (based upon conductivity measurements) and there is a steeper rise in modulus beyond this concentration. In these series the addition of clay reduces the composite modulus due to its destruction of the carbon black network. Despite having lower modulus for a given carbon black concentration, the modulus rises rapidly for each of the clay series when its percolation threshold is reached. From the microstructural images (Fig. 16), it is clear that

carbon black is better dispersed (i.e., less networked) with 2 wt% clay compared to 0.2 wt% clay.
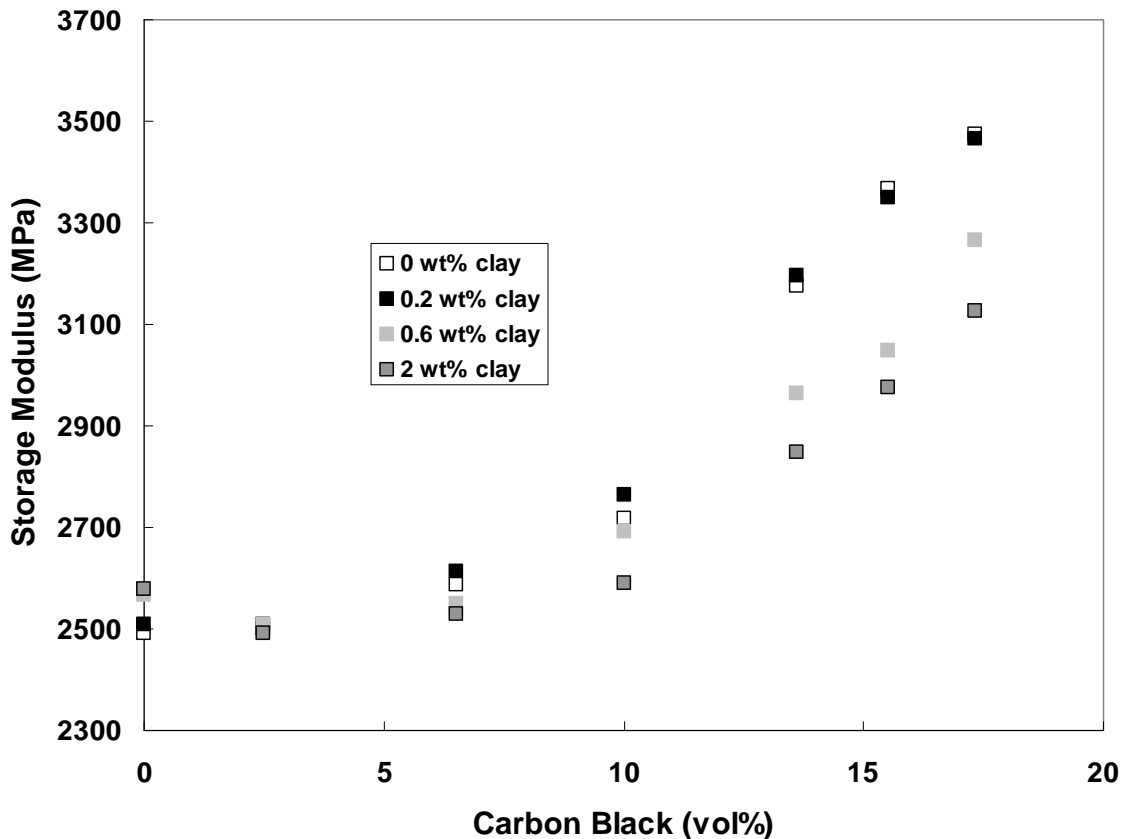
Figure 29. Storage modulus as a function of carbon black concentration for PVAc solution-based films with 0, 0.2, 0.6 and 2 wt% clay.

Figure 30 shows storage modulus as a function of clay concentration with low and high concentration of carbon black. With low carbon black content, the clay has little effect on the storage modulus, but at high carbon black content there is a drop in modulus with increasing clay concentration. There is no network formation in any of the series at low carbon black concentration, which produces little change in modulus due to poor clay compatibility with the polymer matrix. The clay exists as large tactoids that are poorly

bonded to PVAc. At high carbon black and clay content, the filler has exceeded the CPVC, which results in porosity and reduced modulus.
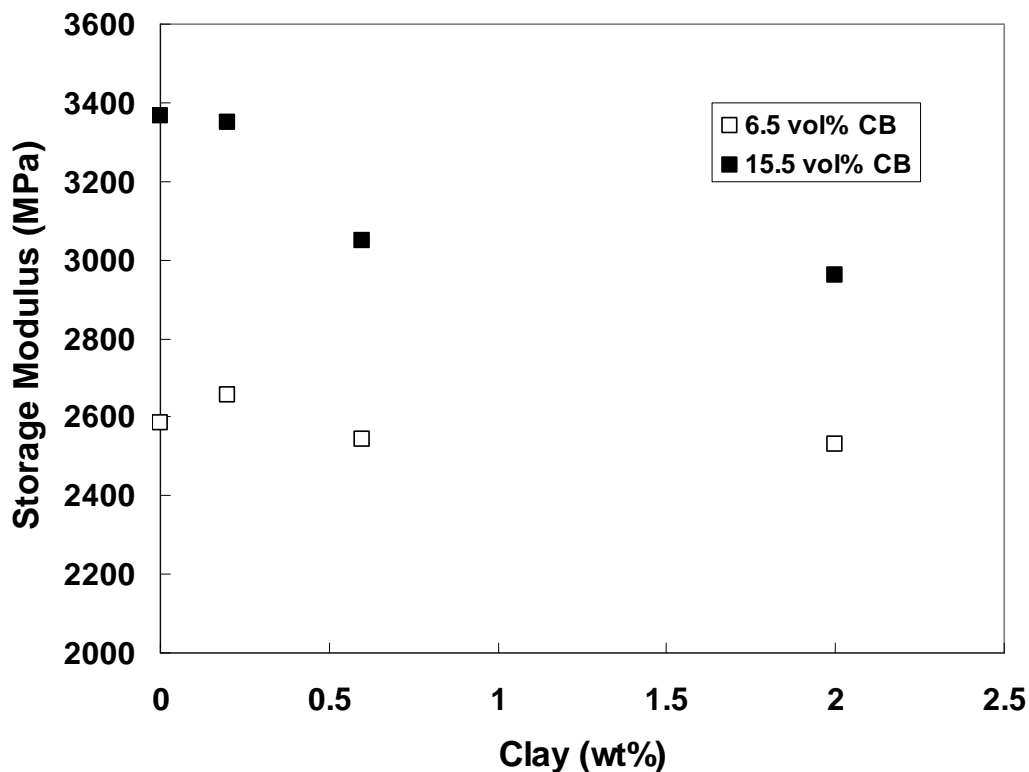
Figure 30. Storage modulus as a function of clay concentration for PVAc solution-based composites with low (6.5 vol%) and high (15.5 vol%) carbon black content.

Comparison of Emulsion-Based and Solution-Based Composites with Clay

Composite Microstructure

Figure 31 compares the microstructure of solution-based and emulsion based composites containing 5 vol% carbon black and 0.2 wt% clay. At 5 vol% carbon black, the emulsion-based composite is above percolation and contains a strong carbon black network. The solution-based composite has a random dispersion of carbon black particles due to the

lack of excluded volume. Little particle aggregation is observed in this composite because the carbon black and clay have enough room to accommodate themselves.
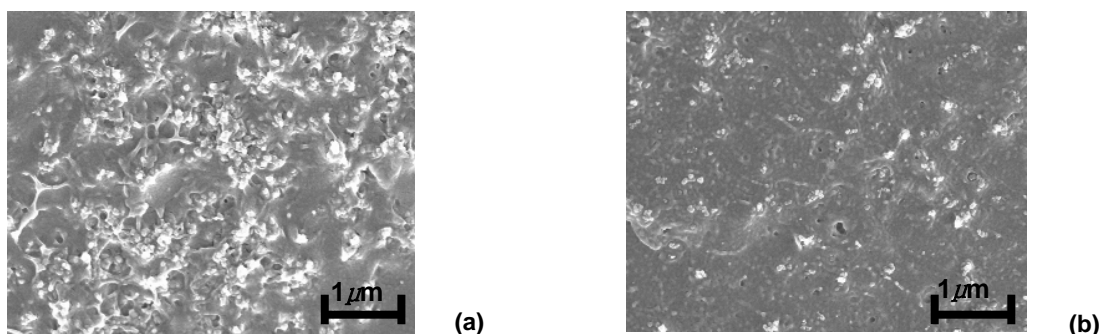
Figure 31. Freeze-fractured cross-sections of PVAc with 5 vol% carbon black and 0.2 wt% clay in an emulsion-based (a) and solution-based (b) composite.

Composite Conductivity

Figure 32 shows electrical conductivity as a function of carbon black concentration for these solution and emulsion-based composites with 0.2 wt% clay. There is an order magnitude difference in the percolation threshold for these systems. The percolation threshold for the emulsion-based system is 0.88 vol% carbon black and 8.1 vol% carbon black for the solution-based system. Similar differences between the solution and emulsion-based composites were shown in Chapter II (Fig.10) in the absence of clay.
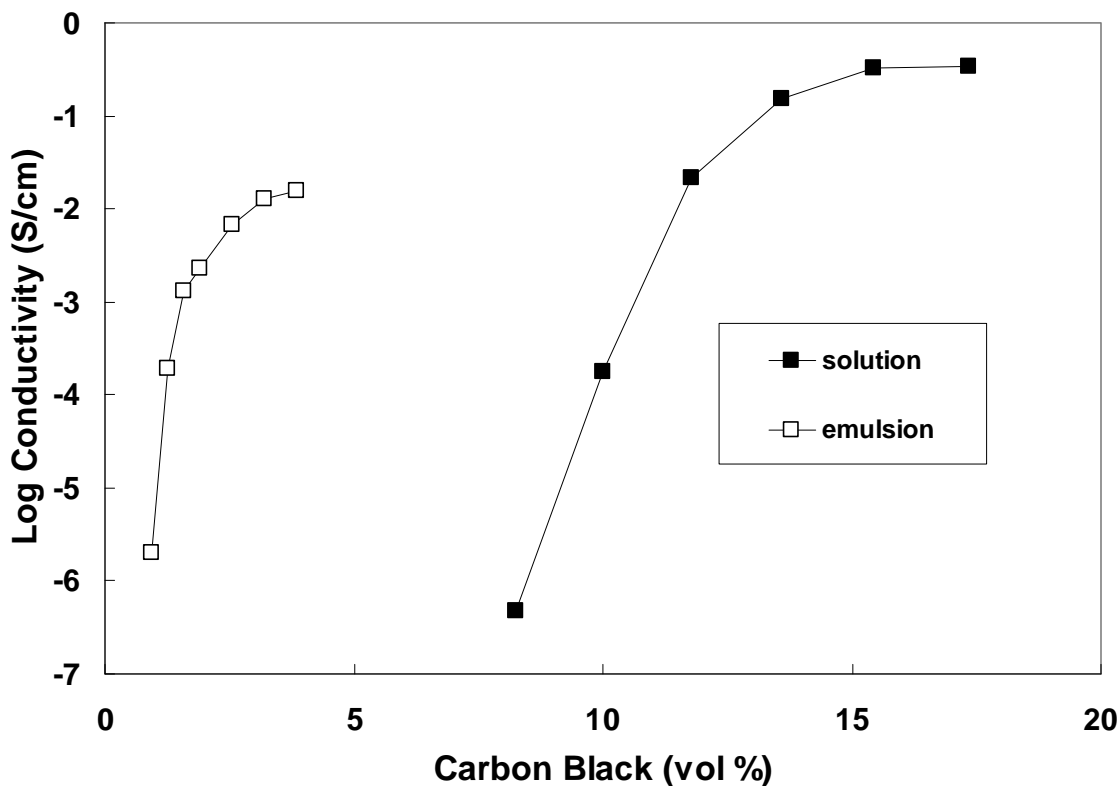
Figure 32. Electrical conductivity as a function of carbon black concentration for PVAc emulsion and solution-based composites with 0.2 wt% clay.

Composite Modulus

Figure 33 shows storage modulus as a function of carbon black concentration for the emulsion and solution-based composite systems with 0.2 wt% clay. The solution-based system achieves a much higher modulus at carbon black concentrations above 10 vol%, but the latex-based films show higher modulus at low carbon black concentration because they contain a strong carbon black network. Solution-based composites form a network near 10 vol%, after which the modulus increases sharply with additional carbon black. Emulsion-based films reach the CPVC at 5.5 vol% carbon black due to excluded volume effects, which causes the films to become porous and lose modulus. For solution-based systems, the CPVC is around 17.5 vol% carbon black.
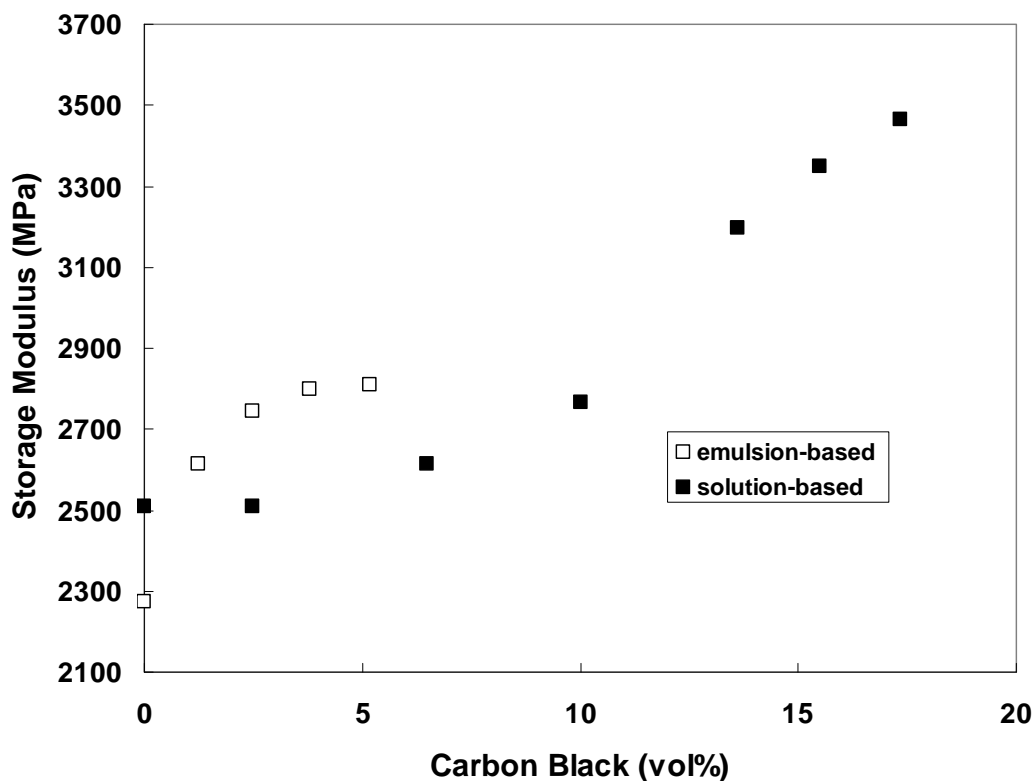
Figure 33. Storage modulus as a function of carbon black concentration for emulsion and solution-based composites with 0.2 wt% clay.

Conclusions

The effect of clay as a co-filler in combination with carbon black, in both solution and emulsion-based composites, was explored. Changes in microstructure were shown to influence the electrical and mechanical properties of carbon black-filled poly(vinyl acetate) with a constant clay concentration. Microstructural images show characteristic differences between the emulsion-based films without clay and with increasing clay concentration. With 0.2 wt% clay the percolation threshold of the emulsion-based system decreased from 1.21 vol% carbon black to 0.88 vol% carbon black. Higher clay concentration led to reduced conductivity and the percolation threshold increased to 1.25

vol% carbon black. Solution-based films show improved dispersion with increasing clay concentration. In most cases, the storage modulus of all the composites was reduced by the presence of clay due to destruction of the carbon black network. The modulus of the emulsion-based films with low clay concentration has higher modulus than the samples with 2 wt% clay. The percolation threshold was progressively raised from 8.19 vol% carbon black, with no clay, to 11.7 vol% carbon black with 2 wt% clay. In these films the storage modulus did not change much with 0.2 wt% clay, but with higher clay concentration there was a drop in the modulus due to loss of the carbon black network. Direct comparison of solution and emulsion-based composites show that clay has a good effect on the emulsion-based films and generally adverse effects on the solution-based films.

CHAPTER IV

SUMMARY AND FUTURE WORK

The primary goal of the present work was to produce carbon black filled composites with a good balance of electrical and mechanical properties by lowering the percolation threshold and adding clay as secondary filler. Emulsion-based poly(vinyl acetate) composites were compared to solution-based systems. A series of experiments were performed to better understand the formation of segregated networks and the electrical and mechanical properties of the resulting composites. The influence of clay on these composites was analyzed in a second set of experiments.

Summary

Segregated Network vs. Random Dispersion

The emulsion and solution-based poly(vinyl acetate) composites have similar chemical composition and are produced from liquid mixtures. The resulting composites have different microstructure and properties. Segregated network composites, made with a poly(vinyl acetate) emulsion, show dramatic changes in modulus and conductivity at low carbon black loading, while randomly dispersed composites exhibited more gradual changes. SEM images of composite cross sections show that carbon black creates a network with low concentration due to the excluded volume from the emulsion particles. The CB in the solution-processed composites is more uniformly (randomly) dispersed. The percolation threshold of the emulsion-based system is 1.21 vol%, which is seven times less than the solution-based system. The storage modulus of emulsion-based

composites increases by 25% with 5 vol% carbon black and then decreases due to the formation of pores in the composite. In the solution-based system, the storage modulus is less than the emulsion based system until 5 vol% carbon black is reached. Once the percolation threshold is reached (at 8.2 vol% carbon black) there is a much sharper increase due to the formation of a network structure. A drop in the storage modulus beyond 17.3 vol% carbon black is observed as the CPVC is exceeded.

Influence of Clay on Composite Behavior

The effect of clay as secondary filler with carbon black in both emulsion and solution-based composites was analyzed. SEM images show changes in microstructure that alter the electrical and mechanical properties of these composites with a constant clay concentration. The addition of 0.2 wt% clay to the emulsion-based composites reduced the percolation threshold from 1.21 to 0.88 vol% CB, but 2 wt% clay reduced the conductivity and increased the percolation threshold to 1.25 vol% CB. The storage modulus of the composites was reduced by the presence of clay due to the disruption of the carbon black network. The samples with 0.2 wt% clay have higher modulus than the samples with 2 wt% clay. The percolation threshold for the solution-based composites was progressively raised from 8.2 vol% (with no clay) to 11.7 vol% carbon black with 2 wt% clay. The storage modulus in these films did not change much with 0.2 wt% clay, but there was a drop in the modulus with 2 wt% clay due to a lack of network formation. Overall, clay has a relatively positive influence on emulsion-based composites and an adverse effect on solution-based composites.

Future Work

The segregated network concept has been studied for years [20, 53-58] and is one of the most effective ways to reduce the percolation threshold of polymer composites. Despite its benefits, complexity of processing and lack of mechanical robustness hinders the use of segregated network composites for many useful applications. Beginning with an emulsion polymer can resolve these problems because the processing is relatively simple, requires little energy, and the final composites are mechanically robust. Further research is still needed to improve the behavior of these emulsion-based composites. The influence of clay on these segregated networks can also be extended. Two ideas for future research are suggested:

- It was observed that emulsion-based systems form segregated networks due to the polymer particles, which are not present in the solution-based matrix. The size and distribution of these polymer particles is expected to play a very important role in the percolation threshold of these composite systems. Changes in maximum electrical conductivity and mechanical properties are also expected.

- Segregated networks made with a polymer emulsion and carbon nanotubes have achieved a percolation threshold below 0.05 vol% and maximum conductivity much greater than with a carbon black network [63]. These composites were produced using chemical stabilizers to disperse the nanotubes in water, but better properties may be achieved if they can be dispersed with clay or another rigid co-filler. Clay has already been shown to reduce the percolation threshold and increase the maximum conductivity in carbon nanotube-filled epoxy [65].

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