Effect of Acrylic Copolymer Dispersants Bearing Epoxy Groups on Rheological and Dielectric Properties of Carbon Black-Filled Epoxy System

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ABSTRACT: In this article, the use of copolymeric dispersants with an acrylic backbone and epoxy side groups for formulating carbon black (CB)-epoxy composites are described. Six epoxy-containing acrylic copolymer dispersants were prepared from hexyl methacrylate (HMA), poly (ethylene glycol) ethyl ether methacrylate (PEGMA), and glycidyl methacrylate via a group transfer polymerization technique. The epoxy-containing acrylic copolymer of the highest concentration of PEGMA showed a desirable passivation effect on CB, and was found to lower the viscosity of the CB-epoxy paste, leading to the well-cured composite af-ter heat treatment. The thick composite film prepared by employing the [CB/acrylic dispersant/epoxy] paste was built up on a Cu plate by a screen printing process followed by thermal curing. The dielectric properties of the 3.1 vol % CB-filled epoxy film showed us high dielectric constant (Dk 4900) and rather low dissipation factor (*Df* 29%) at 1 MHz. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3440–3449, 2012

Key words: high-k polymer composite; epoxy; carbon black; dielectric constant; dielectric loss; acrylic copolymer dispersant; group transfer polymerization
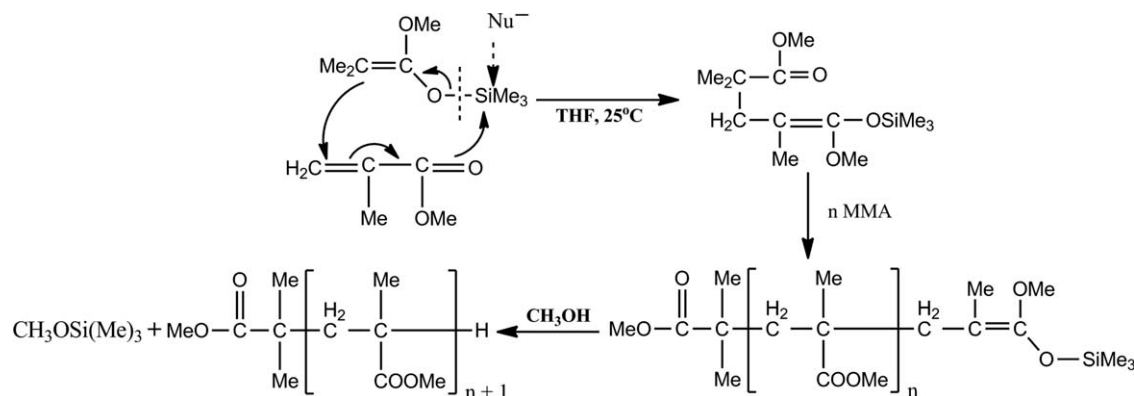
INTRODUCTION

Capacitors are passive electronic components that store electrical energy in the order of microfarads and assist in filtering. Capacitors have two main applications; one of which is a function to charge or discharge electricity, while the other is a function to block the flow of direct current. Driven by ever growing demands of miniaturization, embedded capacitors are one of the key emerging technologies for realizing the system integration that will enhance the performance and functionality of future electronic devices.[1] Material requirement for the commercial applications of embedded capacitor dielectrics includes high dielectric constant (K) and low dielectric loss (or dissipation factor, Df).[2] Furthermore, thermo-mechanical reliability, low processing temperature, low-cost, and good adhesion are additional challenges, which should be overcome to realize embedded capacitors. Many studies have been done to achieve high-k and low-loss at low tempera-tures by thin film deposition,[3] anodization,[4] sol-gel process,[5] and polymer thick film composites.[6,7]

For the polymer thick-film methods, a lot of work have been done on ceramic-polymer composites that employ traditional ceramics as fillers, such as BaTiO$_3$ or lead magnesium niobate-lead titanate (PMN/PT).[6,7] However, in most cases those ceramic-polymer composites have relatively low dielectric constants (usually <100), although ceramic-polymer thick-film approaches have many advantages such as insensitivity to substrate roughness, inexpensive processing, and good thermo-mechanical stability on organic substrates. On the other hand, many attempts have been tried to increase the dielectric constant of polymers (especially epoxy) by employing conductive fillers such as carbon black (CB) for percolative high-k polymer composites.[7,8] These percolative systems can exhibit very high dielectric constants at filler loadings very close to the critical point. However, high dielectric loss (usually >100%) of CB-polymer composites was obtained due to the imperfect passivation (i.e., insulating coating) of CB leading to the current leakage through CB particles near the percolation threshold. Additionally, good dispersion (and passivation) of CB particles in the polymer matrix is considered as a very effective way to lower dielectric loss. In addition, the homogeneity of CB-based dielectric layers is also required when a

Scheme 1 GTP of acrylic monomers.

large-area printing process is considered for a mass production. Those requirements could be achieved by controlling CB paste formulations. When the paste is formulated, the CB content in paste, the paste viscosity, the packing density after drying and printability should be controlled to obtain high performance of CB-polymer dielectric layers. In our group, various types of sophisticated dispersants (e.g., Triton derivatives) are often employed as a viscosity modifying agent.[9,10]

Synthesized acrylic dispersants with well-defined compositions have captivated both academic and industrial polymer engineers. Recent works have been done to improve the modification of classical syntheses toward more precisely controlled acrylic backbones, which are required in the design of advanced dispersants.[11,12] Commercially, acrylic copolymers are prepared by classical radical polymerization processes, which do not provide precise control over molecular properties, although recent developments in the field of "controlled" radical polymerization process offer great promises (e.g., atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer (RAFT) polymerization).[11–13] However, two problems need to be overcome in ATRP: residual halides and metals in the product would be a problem for electronic device uses. The rate of polymerization may be too slow increasing the cost of the polymerization process. In case of RAFT method for the controlled polymerization of acrylic monomers, the product is often smelly and colored. On the other hand, the alternative technique, developed by DuPont, group transfer polymerization (GTP) meets most of the required criteria such as nearly colorless product, low sensitivity to impurities, minimal metallic or halide impurities in the final product, nontoxic ingredients, low odor product, and low overall cost of resin.[14] In addition, GTP has the major advantage of operating at (and above) ambient temperatures, and is applicable to most of acrylic monomers. (Meth)acrylic dispersants have been commercially synthesized by GTP, a well-known "living"

method, which secures a narrow size distribution of the dispersants and their structures.[11,14]

This study relates to a synthetic process for novel acrylic copolymer dispersants bearing epoxy groups via GTP using various acrylic monomers[14] (Scheme 1). Their synthesis and characterization were determined by ^{1}H-NMR spectroscopy and GPC analysis. We also attempted to use the acrylic copolymer dispersants for the formulation of CB-epoxy pastes. To evaluate the effect of these dispersants on the dispersion of CB particles in epoxy resin, a rheological characterization of the pastes was performed. The dense-structured polymer thick films of CB were prepared by the screen printing process of the CB-epoxy pastes followed by the heat treatment for curing.[15] The optimum concentration of the dispersant and the CB powder loading in the paste (and the thick film) were determined by rheological tests. Finally, we experimentally compared the thermal behaviors and the dielectric properties of the CB-epoxy film made from the paste using the acrylic copolymer dispersant with the ones of the control sample employing no dispersant.
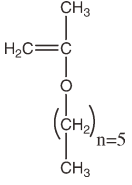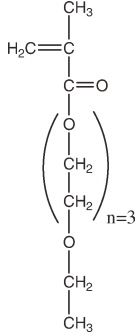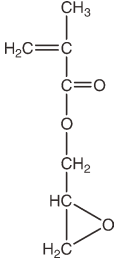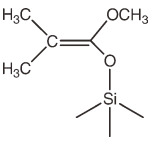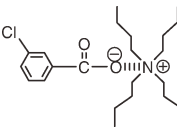
EXPERIMENTAL

Materials

Three kinds of acrylic monomers used in this study were hexyl methacrylate (HMA), poly(ethylene glycol) ethyl ether methacrylate (PEGMA), and glycidyl methacrylate (GMA), and they were purchased from Aldrich (Table I). 1-Methoxy-1-trimethylsiloxy-2-methyl propene (MTS), tetrabutylammonium hydroxide (TBAH), 3-chorobenzoic acid and tetrahydrofuran (THF) were purchased from Aldrich. Acetonitrile was received from Samchun. The GTP catalyst, tetrabutylammonium *m*-chlorobenzoate, was prepared by the reaction of TBAH with 3-chlorobenzoic acid according to Dicker et al.[16]

3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate from Aldrich was used as an epoxy

	HMA	PEGMA	GMA
Formular weight Monomer	170.25	246	142.15
Initiator	Methyl trimethylsilyl dimethylketene acetal		
Catalyst	Tetrabutylammonium m-chlorobenzoate		
Solvent	Anhydrous THF		

resin, and hexahydro-4-methylphthalic anhydride from Aldrich was used as a curing agent. 1-Methyl imidazole from Aldrich was used as a curing catalyst (Fig. 1). Ethyl acetate from Aldrich was used as a temporary solvent which was completely evaporated after dispersion of CB. The conductive CB powder, type Ketjen Black EC300J (KB300) provided by Mitsubishi chemical company, was selected as conducting filler for high dielectric constant percolative epoxy composites because of its small particle size and large surface area. The primary particle size was 30 nm with a median secondary aggregation size of 150 nm. The surface area and the amount of dibutyl phthalate (DBP) adsorption were 960 m^2/g and 360 mL/100 g, respectively. In addition, the dielectric constant value of CB ranges from 2.5 to 3.0. To remove any physically adsorbed water and volatile organics on the powder surface, the powder was vacuum dried at 100°C for 24 h before use.

Characterizations

^{1}H-NMR (500-MHz) spectra were recorded on a Varian® Unity Inova Spectrometer in CDCl$_3$ with tetramethylsilane (TMS) as an internal standard except when reported. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of the synthesized copolymer dispersants

were determined by gel permeation chromatography (GPC) on a Waters Model 410, equipped with 4 mm styragel columns from 500 to 10 Å in series, at a flow rate of 1.0 mL/min (eluent: THF, 36°C, polystyrene as a standard). The curing profiles of CB pastes were monitored by a differential scanning calorimeter (DSC, TA Instruments 2920) at a heating rate of 5°C/min under a nitrogen atmosphere. Thermogravimetric analyses (TGAs) were carried out both in nitrogen and air at a heating rate of 10°C/min using a TGA 2050 (TA instruments). The flow rates for both cases were maintained at 10 and 90 ml/min for the balance part and for the furnace area, respectively. In each case, samples weighed ∼ 10 mg. The rheological behaviors of the CB pastes were monitored using a stress- and strain-controlled rheometer (AR2000, TA Instruments). The experiments were carried out with a cone and plate geometry (diameter: 60 mm, angle: 2°, and truncation: 54 μm). The CB particles were also examined by transmission electron microscope (FEI Titan 80-300 S-Twin).
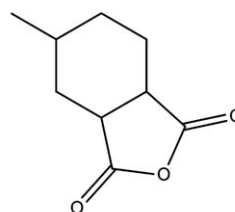
Synthesis of acrylic copolymer dispersants

The synthetic routes to various acrylic copolymer dispersants with different monomeric units are shown in Scheme 2, and only a representative example (i.e., HMA/PEGMA/GMA 1/1/1) is given here.

The GTP was carried out at room temperature in a 100 mL round-bottomed flask equipped with a dropper, a rubber septum, and a magnetic stirrer. The reaction flask was evacuated and dried by flame while filling the flask with nitrogen. Two milliliter of THF and 1.52 mL of MTS initiator were charged in the flask,
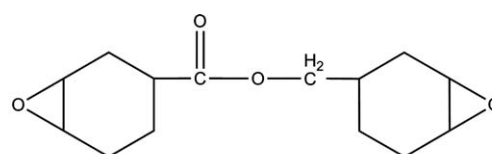
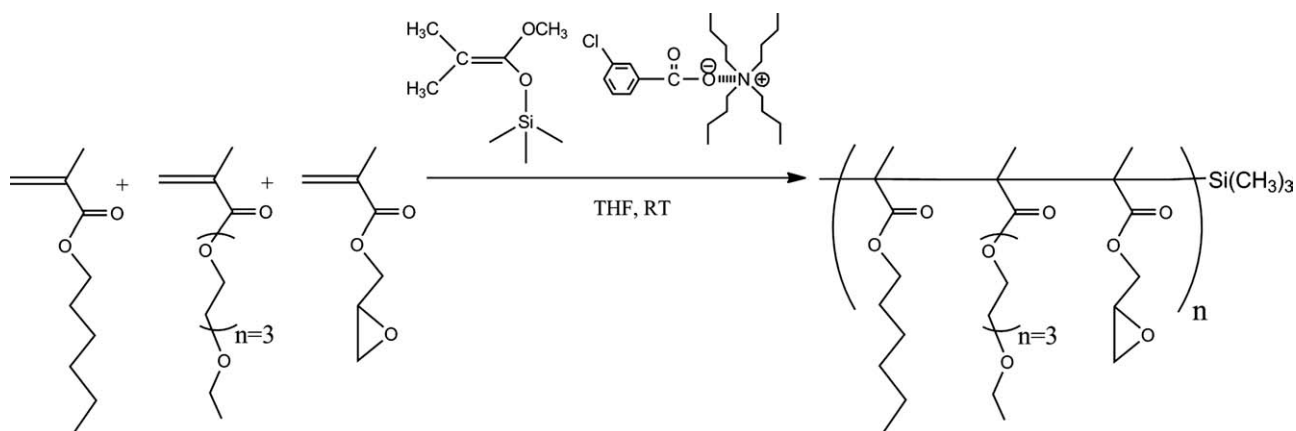Epoxy resin: 3,4-Epoxycyclohexylmethyl-3,4-epoxycylohexanecarboxylate

Anhydride Hardener: Hexahydro-4-methylphthalic anhydride
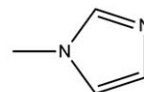
Curing Catalyst: 1-Methylimidazole

Figure 1 Epoxy resin, curing agent, and curing catalyst employed in this study.

Scheme 2 Synthesis of acrylic copolymer dispersants by GTP method.

and a feed containing tetrabutylammonium *m*-cholor-obenzoate (0.06 g) in acetonitrile (1 mL) was added. The initiation of MTS was activated over 2 min. Then, a mixture of monomers containing HMA (5.30 mL), PEGMA (6.50 mL), and GMA (3.55 mL) was added slowly using the dropper over 5 min. The mixture was stirred for 2.5 h at room temperature under a nitrogen atmosphere. The reaction was monitored by thin-layer chromatography and gas chromatography. After the complete consumption of the monomers, the reaction mixture was poured into methanol to quench the polymerization. The precipitated acrylic copolymer was dissolved in methylene chloride and reprecipitated using large amounts of hexane, followed by filtering and drying overnight in vacuum oven yielding yellowish viscous oil: yield = 90%.

Preparation of [CB/acrylic dispersant/epoxy] composites

A representative example of [CB/acrylic dispersant/epoxy] composites was prepared by mixing CB (0.159 g), acrylic dispersant (0.111 g), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (1.577 g), hexahydro-4-methylphthalic anhydride (1.051 g), and 1-methylimidazole (0.005 g) in the presence of ethyl acetate solvent (90 g). The whole mixture was stirred using a high-speed homogenizer (3 min) and ultrasonicated (3 min), respectively. The process was repeated three times. The solvent was removed at 30°C using a rotary evaporator under a reduced pressure. The resulting CB-epoxy paste was used to form a dielectric that was coated onto a copper clad substrate with a single edge blade. Then the sample was cured at 160–190°C for 2 h in the furnace.

Fabrication of parallel plate capacitors

The capacitance and the dielectric loss of CB-epoxy composites were measured with impedance analyzers (HP4194A and HP4291B). The frequency range of dielectric analysis was from 10 Hz to 10 MHz at room temperature. The CB-epoxy paste was printed on the Cu-clad laminate substrate with a thickness of 25 μm and an area of 32 cm^2 for a standard sample, which was necessary to obtain sufficient platinum coverage. Then, the coated sample was cured at 160–190°C for 2 h under nitrogen. The cured CB-epoxy composite was sputtered with a Pt-target. The obtained top Pt-electrode has a radius of 500 μm and a thickness of 100 nm.

RESULTS AND DISCUSSION

Synthesis of acrylic copolymer dispersants bearing epoxy groups

Dispersion mechanisms of (nano)particles can be divided into three ways in the manner of applying the repulsive forces on the particle surfaces depending on the medium polarities: (1) Steric forces in nonpolar media, (2) Electrostatic forces in aqueous systems. (3) Electrosteric forces in slightly polar organic media.[17] Therefore, two important strategies were considered for achieving high-k, low-loss CB-epoxy composites as follows: (1) Applying (slightly polar) nonionic dispersants having different polarities (i.e., hydrophilic and hydrophobic moieties) on CB particles leading to the formation of passivation layers on the CB surfaces. (2) Modifying CB surfaces by introducing epoxy groups to provide anchoring sites for epoxy curing agents leading to the enhanced compatibility between the CB powder and the polymer matrix. The more effective passivation of epoxy-modified CB particles by the epoxy polymer matrix is considered as an effective way to prevent the current leakage increasing the dielectric loss. As a result, the isolated conductive CB particles are expected to increase the capacitance when AC-current is applied without much increasing the dielectric losses. Therefore, we designed comb-type copolymeric dispersants with an acrylic backbone and epoxy side groups for formulating CB-epoxy composites (Fig. 2).
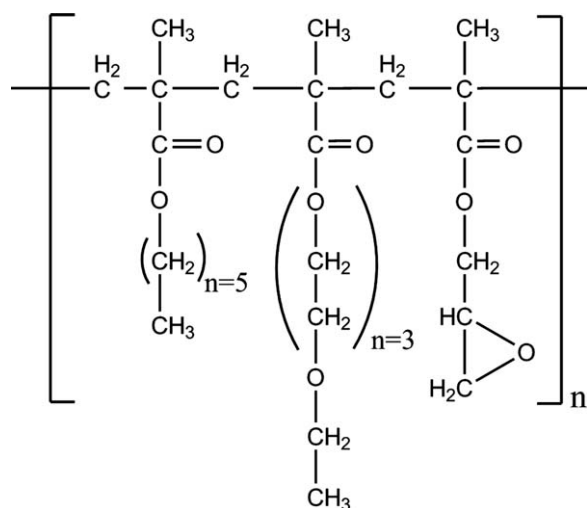
Figure 2 The typical structure of acrylic copolymer dispersants bearing epoxy groups.

Six epoxy-containing acrylic copolymer dispersants were prepared from HMA, PEGMA, and GMA via the GTP technique (Scheme 2). As shown in Figure 2, the hydrophobic *n*-hexyl chains of HMA moieties (as well as the acrylic backbone) are expected to anchor CB particles to keep away from agglomeration, and epoxy group-containing GMA moieties are also expected to be introduced on CB surfaces. On the other hand, the hydrophilic oxyethylene units of PEGMA moieties are expected to be in polar dispersed media.

Since, the GTP technique we employed in this study gave us almost quantitative yields (close to 100%), good molecular weight (MW) controls with a narrow MWD, a wide spectrum of MWs and compositions of acrylic dispersants can be obtained by changing the molar ratio of the components (Table II). Figure 3 shows the GPC chromatogram of dispersant 1 (HMA/PEGMA/GMA 1/1/1, random copolymer, target MW 2000 g mol^{-1}, GPC MW 1774 g mol^{-1}) indicating a unimodal peak with a narrow MWD. The target MW in most dispersant syntheses was 2000 g mol^{-1} except the case of Dispersant 4 (i.e., 4000 g mol^{-1}). The GPC MWs were reasonably close to the target MWs, and the polydispersities were relatively

TABLE II
Various Acrylic Copolymer Dispersants Synthesized in This Study

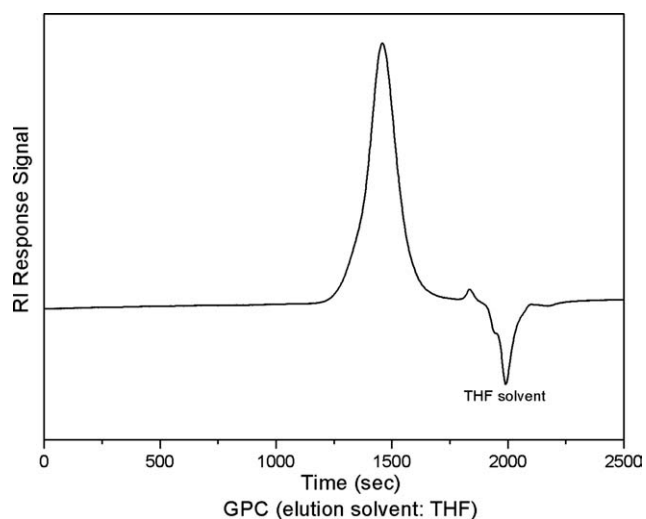| Dispersant	[HMA:PEGMA:GMA] monomer ratio	M_n	M_w/M_n
1	1 : 1 : 1	1774	1.175
2	5 : 1 : 1	1812	1.246
3	2 : 0 : 1	1820	1.217
4	2 : 0 : 1	3389	1.334
5	6 : 0 : 1	1753	1.219
6	0 : 2 : 1	1627	1.296

Figure 3 GPC chromatogram of dispersant <u>1</u> (HMA/PEGMA/GMA 1/1/1).

low (<1.3) as expected because of employing the GTP "living" technique.[14]

Figure 4 shows the ^{1}H NMR spectrum of dispersant 1. The specific proton peaks from HMA, PEGMA, and GMA moieties of the copolymer dispersant were observed and characterized.

CB-epoxy pastes prepared by using acrylic copolymer dispersants

The TEM image of KB300 (Fig. 5) shows that the CB consists of aggregated particles which fuse together
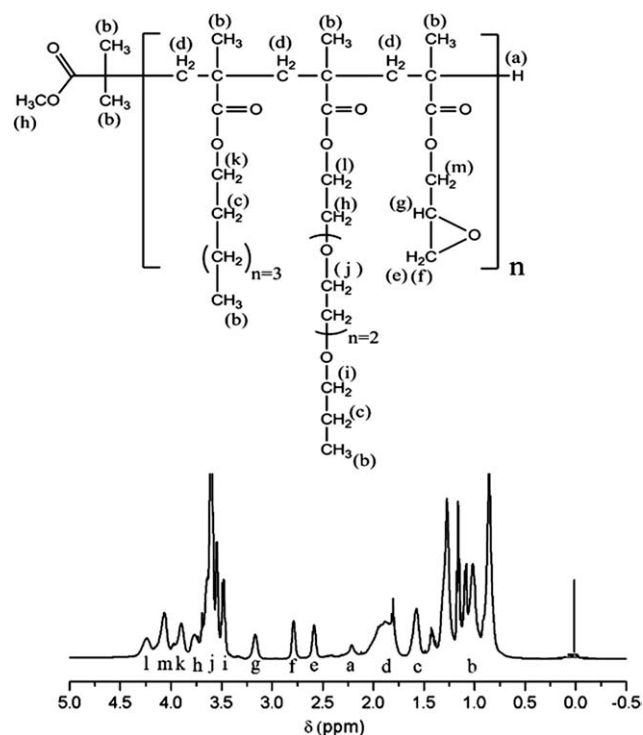

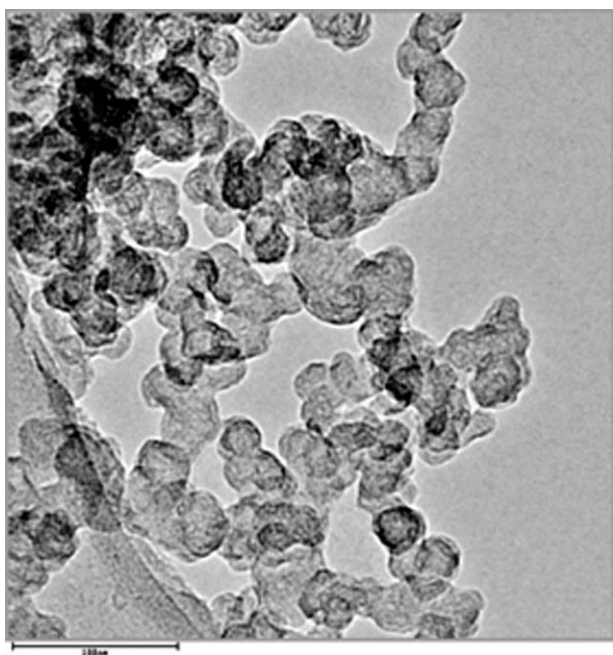**Figure 4** ^{1}HNMR spectrum of dispersant 1.

Figure 5 TEM micrograph of KB300 carbon black.

to form branching and long chaining. This kind of structure makes it highly conductive, and the CB particles easily form a conductive network uniformly in the matrix.[18] In percolative polymer composites, the percolation threshold is the concentration at which an infinite network appears in an infinite lattice. For the most polymers the critical volume fraction of filler is determined between 5 and 20 vol %.[19–21] which is in good agreement with the geometrical models; however, a lower percolation threshold has been observed for CB filled polymer systems not obeying the predictions of the standard percolation model, which is suitable for randomly dispersed noninteracting fillers.[22–24] The conductive CB employed in our study, KB300, has a very high structure which provides a large surface area for electron conduction compared to a low-structure CB. Thus the CB loading in the epoxy matrix needed to reach a high dielectric constant is expected to be relatively low.

In the initial stage of our paste formulations, we tried to determine the optimum amount of CB in the epoxy matrix (without dispersant) by monitoring the viscosity of the pastes with CB loading up to four volume fractions. Figure 6 shows that the paste viscosity increases with the increase in the CB loading level. At low concentrations (0–2.5 vol %) the viscosity is almost linearly proportional to the CB loading. It then increases very sharply beyond 3.0 vol %. This behavior indicates that the particles are severely agglomerated in the CB paste of 3.0 vol % solid loading, which is roughly close to the percolation threshold.

The viscosity of a CB paste, whose volume fraction was 3.0 vol %, was measured as a function of dispersant concentration to determine the optimum amount of dispersant in CB pastes. Figure 7 shows the effect of the amount of dispersant 1 (HMA/PEGMA/GMA 1/1/1, acrylic random copolymer) as a dispersant on the viscosity of the CB paste at the constant shear rate of 20 s^{-1}. As shown in Figure 7, the viscosity decreased sharply until the dispersant was added up to about 70 wt % based on CB. It is thought that the viscosity drop might be caused by the increase in the rate of dispersant adsorption on the particle surface, as the amount of dispersant 1 in the paste increases. Beyond 70 wt % of dispersant addition, the viscosity of the paste increased slightly, which might be due to the attraction between the excessive dispersants that were not adsorbed on particles (Upon adding a profile of the dispersant at various concentrations without CB into the matrix, we also observed a slight concentration effect in viscosity measurements).
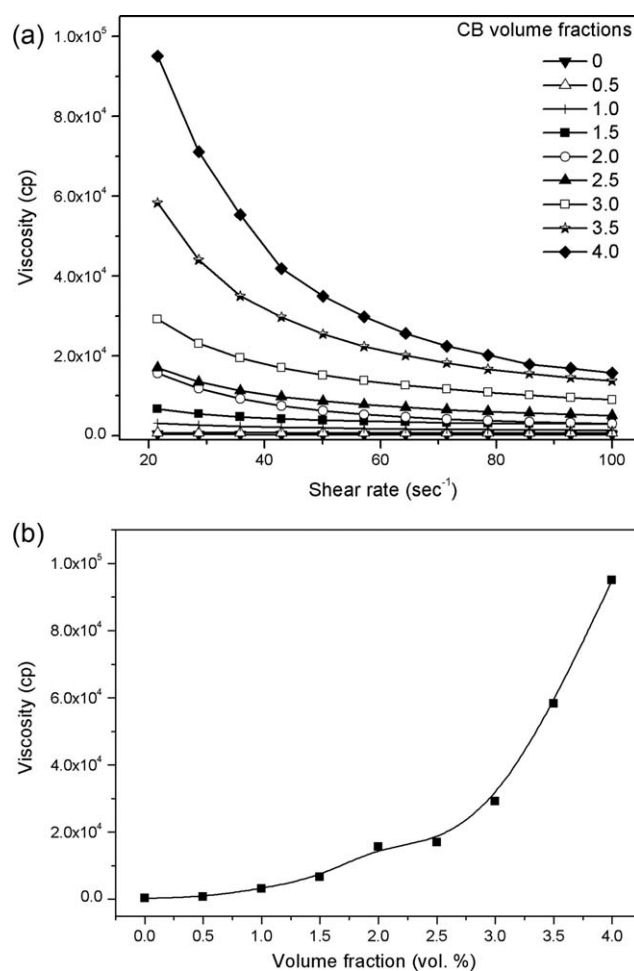

Figure 6 (a) Apparent viscosity of [CB/epoxy] pastes as a function of shear rate (CB 0 ∼ 4 vol %). (b) Apparent viscosity of [CB/epoxy] pastes as a function of CB volume fraction (shear rate 20 s^{-1}).
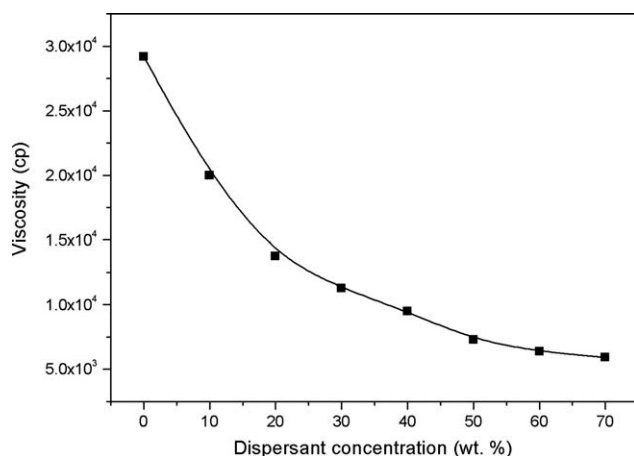
Figure 7 Apparent viscosity of CB (3.0 vol %)-filled epoxy pastes as a function of Dispersant 1 amount (based on CB) at shear rate of 20 s^{-1}.

To study the CB dispersion (and passivation) effect by various acrylic copolymer dispersants, dispersants 1–6 (70 wt % based on CB) were introduced into the 3.0 vol % CB paste, respectively. Figure 8 shows that in the presence of the acrylic copolymer dispersants, much lower viscosity was observed compared to the paste without dispersant in the matrix. It is obvious that all the acrylic copolymer dispersants anchor on the CB surfaces and prohibits the particle agglomeration, resulting in a reduced viscosity. From Figure 8 it can be clearly seen that dispersant 1 (HMA/PEGMA/GMA 1/1/1) with proper amounts of hydrophilic and hydrophobic moieties gives the best CB passivation effect with the lowest viscosity.

It is observed that dispersant 2 having more hydrophobic hexyl groups (i.e., less hydrophilic oxyethylene units) results in higher viscosity. With dispersants 3–5 having no oxyethylene unit, higher viscosities of the corresponding pastes are also found
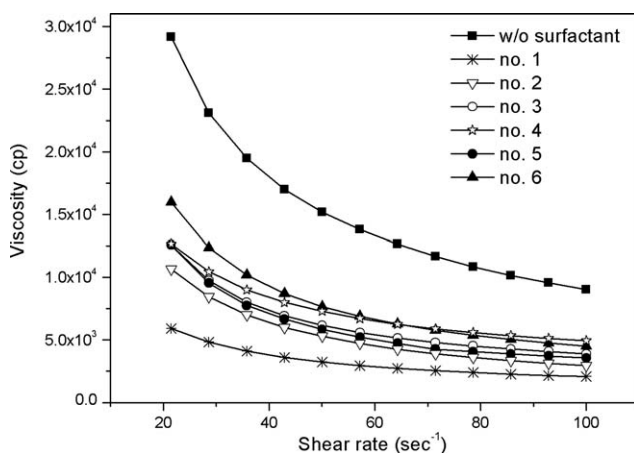

Figure 8 Apparent viscosity of [CB (3.0 vol %)/epoxy] pastes in the presence of various acrylic copolymer dispersants as a function of shear rate.
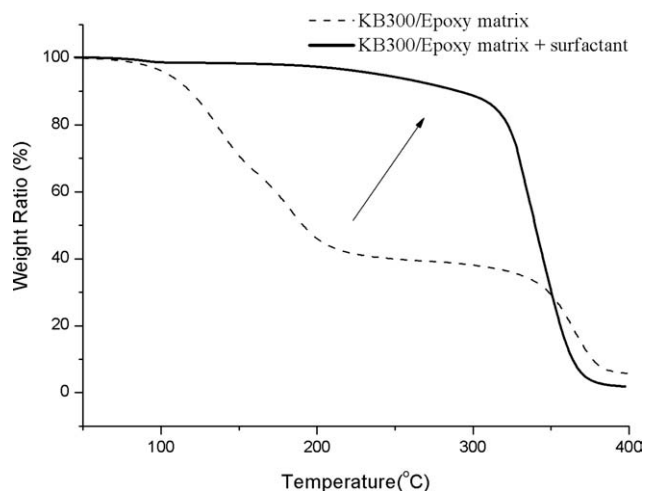

Figure 9 TGA plots of [CB (3.0 vol %)/epoxy] pastes with and without dispersant 1.

regardless of their compositions and MWs (i.e., the more the oxyethylene unit, the better the dispersion effect). However, the paste with dispersant 6 having no hexyl group shows the highest viscosity implying the most agglomerates and the least stable dispersion state. It is likely that the anchoring effect of acrylic dispersants towards CB particles can be significantly enhanced by introducing the hydrophobic hexyl groups in the acrylic backbone. The polymeric dispersant 1 of a given composition (i.e., HMA/PEGMA/GMA 1/1/1) provides the best dispersion properties.

TGA plots of the CB (3.0 vol %)-epoxy pastes with and without dispersant 1 show the significant passivation effect of the acrylic copolymer dispersant on the CB surfaces (Fig. 9). From the TGA of the paste with no dispersant it can be clearly seen that large amounts of starting materials (especially anhydride hardener and 1-methylimidiazole) were evaporated (up to 50 wt %) in the temperature range of 100–200°C. Basic 1-methylimidiazole catalyst is understood to be adsorbed onto CB surfaces, which makes the catalyst lose its accelerating role in the epoxy curing process[25] and causes the uncured part of the paste (especially volatile anhydride) to evaporate in the course of the heating up to 200°C. On the other hand, by introducing the dispersant into the paste, the almost complete epoxy curing and no evaporation of starting materials were observed because the dispersant effectively passivated the CB surfaces resulting in no 1-methylimidiazole adsorption on CB surfaces.

Representative DSC thermograms of the CB (3.0 vol %)-epoxy pastes with and without dispersant 1 are shown in Figure 10. The curing exotherm of the paste without the dispersant shows a maximum at 150.1°C. Upon the addition of dispersant 1 into the paste, the exothermic peak temperature shifts from
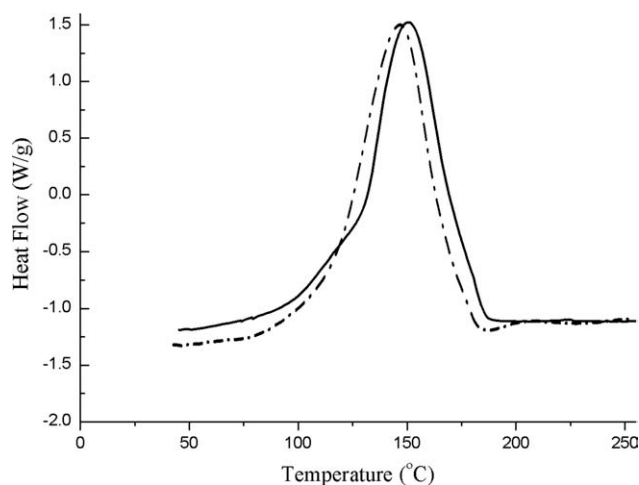
Figure 10 DSC thermograms of [CB(3.0 vol %)/epoxy] pastes with (--) and without dispersant 1(—).

150.1 to 142.9°C, and the enthalpy of the epoxy curing reaction increases from 64 cal/g (for the paste with no dispersant) to 88 cal/g (for the paste with dispersant 1). It is thought that the epoxy functional groups of the dispersant introduced onto CB surfaces enhance the epoxy curing efficiency in the matrix.

Dielectric properties of [CB/acrylic dispersant/ epoxy] composite films

In a percolative system, it is generally thought that each conducting CB particle plays a role as an electrode in the polymer matrix, while the epoxy resin between CB particles is the dielectric component. Therefore, as the amount of CB increases, the distance between CB particles is extremely narrowed, leading to a high dielectric constant. To prove this concept and confirm the experimental limit of dielectric constant from the percolative system, we studied
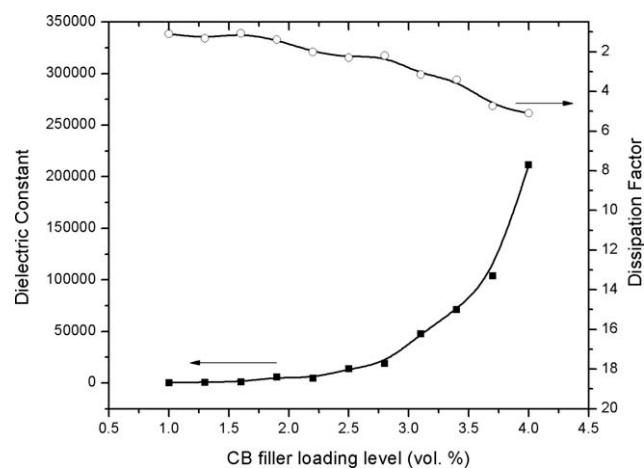

Figure 11 Dielectric properties of CB-filled epoxy composite as a function of filler loading.
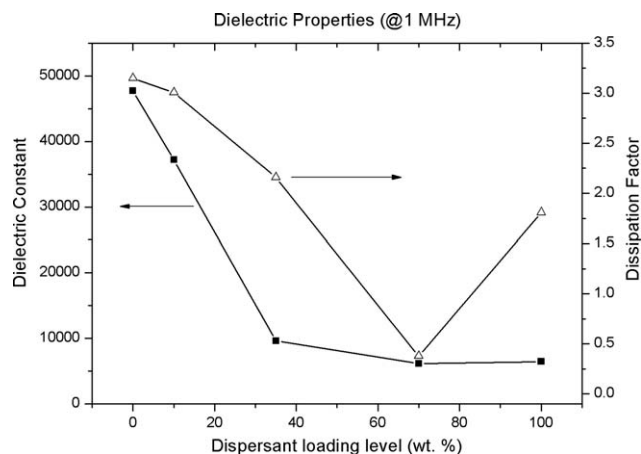

Figure 12 Dielectric properties of CB (3.1 vol %)-filled epoxy composite as a function of dispersant loading.

the effect of the amount of CB on the dielectric properties of CB-epoxy system. Figure 11 shows dielectric properties of CB-filled epoxy composites at 1 MHz as a function of CB loading. The addition of CB (up to 2.8 vol %) into the epoxy matrix leads to the gradual increase both in dielectric constant (K) and dissipation factor (Df). When the amount of CB in epoxy is about 3.0 vol % (presumably close to the percolation threshold), the remarkable increase in K is observed because of the piling of charges at the extended interface. This indicates that the capacitor network can be formed in an epoxy matrix due to the distribution of CB particles. However, when the amount of CB reaches the percolation threshold of about 3.0 vol %, the conduction path through CB particles might form, leading to a high dielectric loss ($Df > 300\%$).

Since, the passivation of conductive CB particles was essential for our percolative composite system, we tried to encapsulate CB by dispersant 1 to accomplish the passivation of each CB particle. Figure 12 shows dielectric properties of CB (3.1 vol %)-filled epoxy composites at 1 MHz as a function of the amount of dispersant 1. The remarkable reductions both in K and Df were observed upon the incorporation of the dispersant. The epoxy composite with a dispersant content of 70 wt % based on the amount of CB gives the lowest dissipation factor of about 0.35, which is much lower than the one of the epoxy composite with no dispersant (Df 3.15). Meanwhile, the dielectric constant K still maintains over 1000 (K 2090). The significant reduction of dielectric loss is likely to be attributed to the dispersant layer coated on CB surfaces, since it could serve as a barrier layer to prevent the formation of a conduction path in the matrix. Lower K than expected might be partly attributed to the porosity possibly caused by the absorbed dispersant layer, which was also reported by Qi et al.[26] Excess amounts of the

dispersant, however, increase both K and Df of the epoxy composite (see Fig. 12, dispersant content of 100 wt %).

Considering the curing conditions, when a sample was heat-treated at 190°C for 2 h, the unreacted chemicals (see Fig. 13 for supporting evidences), presumably anhydride, were evaporated at 190°C and trapped in the epoxy matrix leading to the formation of bubbles and pin-holes which decreased the dielectric constant (and also increased the dielectric loss over 100%). As the curing temperature increased slowly (160–190°C for 2 h), dielectric constant values were increased dramatically because of the completion of epoxy curing and lower dielectric loss was observed (K 2090 $\geq$ 4900, Df 0.35 $\geq$ 0.29). It is also likely that the epoxy functional groups of the dispersant introduced onto CB surfaces enhance the epoxy curing efficiency in the matrix (*vide supra*).

The best dielectric property results of CB-epoxy composites we produced employing the various types of acrylic copolymer dispersants containing epoxy groups were summarized in Table III. As shown in Table III, among various dispersants, dispersant 1 (HMA/PEGMA/GMA 1/1/1) with proper amounts of hydrophilic and hydrophobic moieties gives the best CB passivation effect with high K in epoxy (similar to the rheological test results, *vide supra*). Although, the dielectric loss at high frequency is somewhat high, as far as we know, this result is the first report showing remarkably high dielectric constant of 4900 and low dielectric loss of 29.0% at 1 MHz.

From our results, we concluded that in a percolative system with no dispersant, as increasing the CB volume in the epoxy matrix, the dielectric constant of CB-epoxy composites increases rapidly at the near the percolation threshold due to the decrease in the
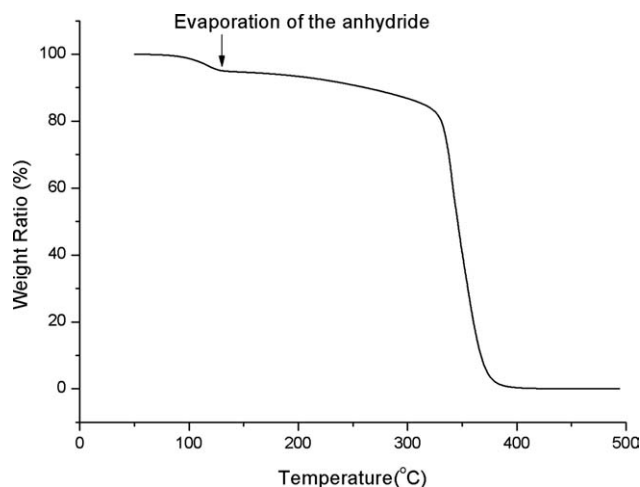
TABLE III
Dielectric Properties at 1 MHz of CB (3.1 vol %)-Filled Epoxy Composites with Various Kinds of Acrylic Copolymer Dispersants (70 wt % Based on the Amount of Filler Employed)

Dispersant employed	Dielectric constant (K)	Dissipation factor (Df)
Dispersant 1	4894	0.29
Dispersant 2	1235	0.33
Dispersant 3	1381	0.30
Dispersant 4	1573	0.49
Dispersant 5	2090	0.35

gap between CB electrodes. However, the dielectric loss also greatly increases because of the percolation of CB particles resulting in high current leakage. On the other hand, the CB-epoxy system modified with acrylic copolymer dispersants bearing epoxy groups which provide the enhanced passivation layer showed that the dielectric constant increases as the CB volume increases, while the dielectric loss maintains at the nearly constant value (Table III).

CONCLUSIONS

Generally, percolative polymer-conducting filler composites for embedded capacitor applications show high-k and high loss characteristics at the same time. As the volume of the conducting filler increases up to the percolation threshold, the distance between conducting particles dramatically decreases leading to the high dielectric constant. Because of the current leakage through the narrow gap between filler particles, however, the loss also increases dramatically.

In this study, the passivation of conducting CB particles by acrylic copolymer dispersants bearing epoxy groups was employed in order to make it possible to maintain the low dielectric loss (Df) which is normally increased by the current leakage through conducting CB particles. Well-defined acrylic copolymer dispersants synthesized by the GTP method were incorporated into the epoxy matrix for controlling CB dispersion/ passivation. Among various dispersants we employed, dispersant 1 (HMA/PEGMA/GMA 1/1/1) with proper amounts of hydrophilic- and hydrophobic-moieties gives the best CB passivation effect with low viscosity in the epoxy paste and high K/low-loss in the CB-epoxy composite film.

Figure 13 A TGA plot of [epoxy/anhydride/curing catalyst] showing the evaporation of unreacted volatile anhydride.

References

1. Coombs, C. P. Printed Circuits Handbook, 6th ed; McGraw-Hill:, 2007.
2. Xu, J.; Wong, C. P. Appl Phys Lett 2005, 87, 082907/1–082907/3.
3. Nami, Z.; Misman, O.; Erbil, A.; May, G. S. J Cryst Growth 1997, 179, 522.

4. Dimos, D.; Lockwood, S. J.; Schwartz, R. W.; Rodgers, M. S. IEEE Trans Compon Packag Manuf Technol A 1995, 18, 174.

5. Zhang, J.; Luo, S.; Gui, L. J Mater Sci 1997, 32, 1469.

6. Xu, J.; Moon, K. S.; Tison, C.; Wong, C. P. IEEE Trans Adv Packag 2006, 29, 295.

7. Lu, J.; Wong, C. P. IEEE Trans Dielectr Electr Insul 2008, 15, 1322.

8. Raj, P. M.; Balaraman, D.; Abothu, I. R.; Yoon, C.; Kang, N. K.; Tummala, R. IEEE Trans Compon Packag Technol 2007, 30, 569.

9. Lee, D. I.; Choi, J. Y.; Lee, E. S.; Ha, C. S.; Bae, J. Y. J Appl Polym Sci 2007, 104, 162.

10. Lee, D. I.; Choi, J. Y.; Lee, S. M.; Lee, E. S.; Bae, J. Y. J Appl Polym Sci 2007, 105, 2012.

11. Simms, J. A. Prog Org Coat 1999, 35, 205.

12. Baskaran, D. Prog Polym Sci 2003, 28, 521.

13. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921.

14. Webster, O. W. Adv Polym Sci 2004, 167, 1.

15. Cho, S.-D.; Jang, K.-W.; Hyun, J.-G.; Lee, S.; Paik, K.-W.; Kim, H.; Kim, J.-H. IEEE Trans Electron Packag Manuf 2005, 28, 297.

16. Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. Macromolecules 1990, 23, 4043.

17. Hiemenz, P. C. Principles of Colloid and Surface Chemistry, 3rd ed.; Dekker: New York, 1997, Chapter 4.

18. Donnet, J. B.; Bansai, R. C.; Wang, M. J. Carbon Black: Science and Technology, 2nd edn; Dekker: New York, 1993.

19. Schueler, R.; Petermann, J.; Schulte, K.; Wentzel, H.-P. J Appl Polym Sci 1997, 63, 1741.

20. Liang, J.; Yang, Q. J Appl Phys 2007, 102, 083508/1.

21. Arshak, K.; Cunniffe, C.; Moore, E.; Vaseashta, A. Functionalized Nanoscale Materials, Devices and Systems, NATO Science for Peace and Security Series B: Physics and Biophysics, Volume ISBN 978-1-4020-8902-2; Springer: Netherlands, 2008; p 321.

22. Flandin, L.; Prasse, T.; Schueler, R.; Schulte, K.; Bauhofer, W.; Cavaille, J.-Y. Phys Rev B: Condens Matter Mater Phys 1999, 59, 14349.

23. Rwei, S.-P.; Ku, F.-H.; Cheng, K.-C. Colloid Polym Sci 2002, 280, 1110.

24. Ranjbar, Z.; Rastegar, S. Colloids Surf A: Physicochem Eng Aspects 2006, 290, 186.

25. Lubin, G. Handbook of Composites; Van Nostrand Reinhold: New York, 1982; Chapter 1.

26. Qi, L.; Lee, B. I.; Chen, S.; Samuels, W. D.; Exarhos, G. J. Adv Mater 2005, 17, 1777.