

Composites of multifunctional benzylaminofullerene with low-density polyethylene

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Abstract

Benzylaminofullerene (BAF, $[C_{60}H_{4.7}(NHCH_2C_6H_5)_{4.7}]$)/low-density polyethylene (LDPE) composites containing up to 10 wt.% BAF have been prepared from solution. BAF is evenly distributed as small articles of 1–5 μm in polyethylene (PE). The BAF particles do not aggregate even when PE was heated to melt. The dielectric permittivity and loss factor have been studied as a function of BAF loading and frequency. The composites have almost same small dielectric loss as LDPE partly due to the volume increase after mixing. The composite materials have been characterized by optical microscopy, X-ray diffraction, dynamic mechanical and thermal mechanical techniques. The introduction of BAF does not affect the crystal structure and the crystallinity of PE, indicating that BAF is distributed in the amorphous region of PE. The composites show higher storage modulus and loss modulus than LDPE; but higher BAF loading has adverse effect on the modulus. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymeric composites are an important class of functional and/or structural polymeric materials formed by incorporating active materials into host matrices of polymers. These materials can combine successfully electronic, optical and magnetic properties of inorganic or organic materials with attractive mechanical properties, especially the processability of conventional polymers. Recently, fullerene-containing polymer composites have found more and more uses in preparation of electronic and optical materials that have attractive photoinduced electron transfer or photoexcitation properties [1–9]. Conventional polymers such as polyethylene (PE) and polystyrene have been used as matrices in the composites. It has been shown that the structure and properties of these composites are strongly dependent on the properties and concentrations of the active component [10]. Higher compatibility of the active component and polymer matrix results in higher quality of the composite. Previous investigation has shown that PE and C_{60} have a very low compatibility [11]. As a result, C_{60} forms big particles (30–50 μm) in PE from solution and is concentrated on the surface of PE composite.

In an attempt to improve the compatibility of C_{60} with PE, efforts have been made to modify the structure of the fullerene. For example, (phenyl)- C_{61} -butoxy(methoxy) and [5,6]-phenyl- C_{61} -butyric acid cholesteryl have been reported in conjugated polymer — polystyrene or PE systems [10]. These modified fullerenes are mono-substituted C_{60} derivatives.

In this work we report on the synthesis of a multi-substituted C_{60} derivative, benzylaminofullerene (BAF) and the preparation of a composite system using the multi-substituted C_{60} derivative and low-density polyethylene (LDPE). The thermal property of the composites will be studied using differential scanning calorimetry (DSC), dielectric analysis (DEA) and dynamic mechanical analysis (DMA). The morphology of the composites will be investigated using optical microscopy and X-ray scattering.

2. Experimental

2.1. Materials

Fullerene (C_{60} , 99.9%) was obtained from Peking University. Benzylamine was purchased from Merck, Darmstadt, Germany. LDPE was provided by Nova Chemicals. All materials were used as received.

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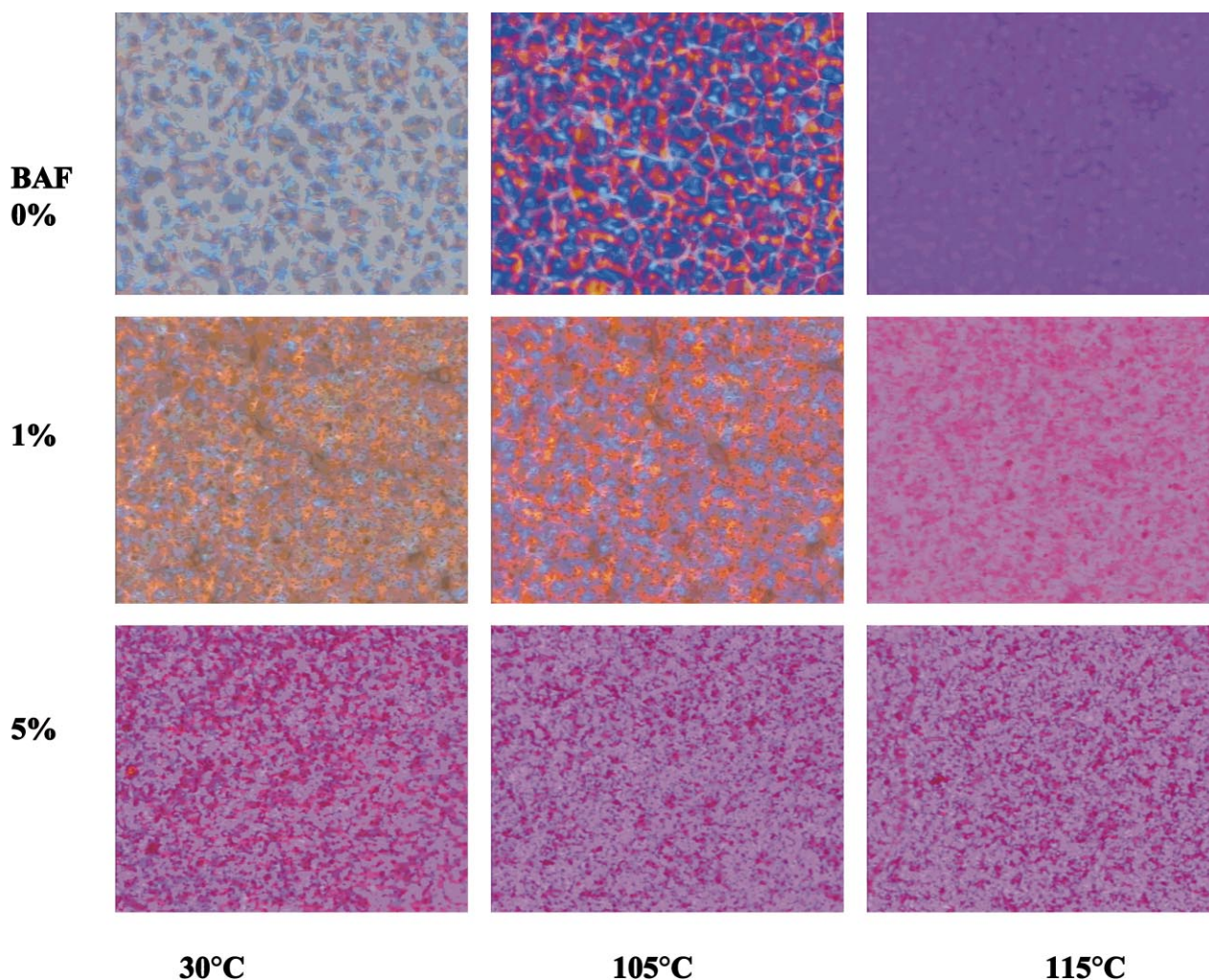


Fig. 1. Micrographs of various LDPE samples with different BAF ($315 \times 235 \mu\text{m}$).

2.2. Characterization

FTIR measurement was performed on a Perkin–Elmer 1725X FTIR spectrophotometer. Sixteen scans were signal-averaged at a resolution of 2 cm^{-1} . The sample was prepared by dispersing the samples in KBr and compressing the mixture to form a disc.

UV–Vis spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer with a Hewlett–Packard Vectra QS/165 computer system. The 90 MHz ^1H NMR spectrum was obtained using a Jeol FX90Q in CDCl_3 with TMS as an internal standard.

DSC was performed using a TA Instruments 2920 Modulated DSC. Samples of 5–10 mg were heated and cooled at a rate of $20^\circ\text{C}/\text{min}$ under nitrogen. Each sample was scanned several times to check the repeatability of the results.

Micrographs were recorded using a microscope (Olympus BX50) equipped with a heating stage (Linkam THMS-600) and a Nikon digital camera. The polymer

sample was put on a glass slide and heated in a range of $30\text{--}130^\circ\text{C}$ on the heating stage. The images were then recorded and analyzed. The magnification used was normally 200.

Wide angle X-ray diffraction was carried out using a Philips X'Pert X-ray diffractometer, Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The diffractometer was operated at 45 kV and 40 mA. The diffraction pattern of the sheet was obtained by scanning the sample in a range of $2\theta = 10\text{--}50^\circ$ at a sampling step of $0.05^\circ (2\theta)$.

Polymer samples for DEA were prepared using a compress molding machine. The polymer materials were melt compressed at 130°C to a diameter of 2.5 cm with a thickness of 0.6 mm under a force of 1 t. Dielectric property was tested using a DEA2970 dielectric analyzer with a frequency range of 1–100 kHz.

Dynamical mechanical test was performed using a TA instrument DMA 2980 analyzer. Film samples with a thickness of about 0.3 mm were heated at a frequency of 1 Hz and a heating rate of $3^\circ\text{C}/\text{min}$ in a range of $30\text{--}80^\circ\text{C}$.

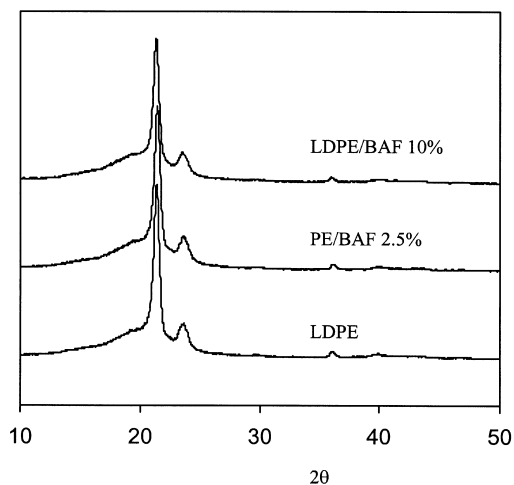


Fig. 2. X-ray diffraction patterns of LDPE and LDPE/BAF composites.

Thermal mechanical test was performed using a TA instrument TMA 2940 thermomechanical analyzer. Film samples with a thickness of about 0.25 mm were heated with a heating rate of 5°C/min in a range of 30–100°C.

2.3. Synthesis of BAF

Similar to our previous reported method [12], benzylamine (1.0 g, 9.3 mmol) was added to a magnetically stirred mixture of C₆₀ (500 mg, 0.69 mmol) in 100 ml of DMF. The mixture turned to green and then brown rapidly. Stirring was continued at room temperature for 40 h to allow C₆₀ to react completely, and a deep brown clear solution was obtained. Most solvent was removed by rotary evaporation under reduced pressure. It was then poured into methanol to precipitate the product that was further purified by precipitation from THF into methanol and washed with methanol twice. The product was dried in vacuo at room temperature for 48 h, to give 820 mg of red brown powder BAF [C₆₀H_{4.7}(NHCH₂C₆H₅)_{4.7}]. The average composition was obtained from elemental analysis: C 88.87, H 2.91, N 5.40. IR (KBr, cm⁻¹): 3420 (–NH–), 1644, 1425 (C=C), 1182, 734, 689, 575, 525. ¹H NMR (CDCl₃, δ, ppm): 7.4 (m, –C₆H₅), 4.4 (m, –NH–), 2.2 (m, –CH₂–, C₆₀H). UV (in chloroform): λ_{max} = 270 nm.

2.4. Preparation of BAF/PE composites

BAF-containing PE was prepared by solution blending. In a typical procedure, after LDPE was dissolved in chlorobenzene at a concentration of 0.1 mg/ml at 90°C BAF was added and dissolved in the solution. The solution was cast on glass at 90°C in oven and dried for 6 h. The resulting film was further dried in vacuo at 90°C for 3 h.

3. Results and discussion

3.1. C₆₀ modification

C₆₀ is grafted readily with primary and secondary amine in polar solvents such as DMF and DMSO at room temperature, but the grafting is not quantitative. The final product can have up to 12 amine groups per C₆₀ if an extensive excess of amine is used in the reaction. By lowering the molar ratio of amine and C₆₀, C₆₀/amine adduct with different composition can be prepared. In our previous report [12], it was shown that 3:1 (mol/mol) benzylamine/C₆₀ gave an adduct with an average composition [C₆₀H_{1.9}(NHCH₂C₆H₅)_{1.9}]. This indicates that 67% of benzylamine has added with C₆₀. In this study, 13:1 (mol/mol) benzylamine/C₆₀ produces an adduct with an average composition [C₆₀H_{4.7}(NHCH₂C₆H₅)_{4.7}]. The percentage of benzylamine addition is about 36%, showing that the addition percentage of benzylamine decreases significantly with increasing ratio of benzylamine and C₆₀. The solubility of the C₆₀/benzylamine adduct however improves with increasing the content of benzylamine groups on the C₆₀ backbone. The adduct [C₆₀H_{4.7}(NHCH₂C₆H₅)_{4.7}] is soluble in common organic solvents such as THF, chloroform, benzene and chlorobenzene.

3.2. Morphology

LDPE is insoluble in common organic solvents at room temperature and polar organic solvents even at elevated temperature. Both LDPE and BAF dissolve in hot chlorobenzene (90°C). The resulting clear solution is orange to brown depending on the concentration of BAF. After removing chlorobenzene, each sheet sample is opaque due to the crystallization of LDPE and the aggregation of BAF. Fig. 1 shows the microscopic structure of LDPE and various LDPE samples with different BAF loading. Most of BAF is in finely small particles and distributes evenly in the polymer matrix. The particle size is in a range of 1–5 μm for most of the BAF, which is much smaller than the reported C₆₀ particles in PE (30–50 μm) [11]. With an increase in BAF concentration, the population of BAF in polymer matrix increases but the size of aggregate hardly changes. This result demonstrates that modified C₆₀ have better compatibility with LDPE than the unmodified C₆₀, mainly due to the better miscibility between LDPE and functional groups. LDPE crystal melts at about 110°C. It is interesting to see that the particle size and distribution of BAF in LDPE do not change significantly despite the LDPE/BAF composite being heated to above 110°C as shown in Fig. 1. This suggests that BAF particles are in the amorphous region of PE and that the melting of crystalline region hardly affects the dispersion of BAF.

X-ray diffraction patterns of the pure PE and PE/BAF composite are shown in Fig. 2. The diffraction signature and intensity of PE are not affected by incorporation of

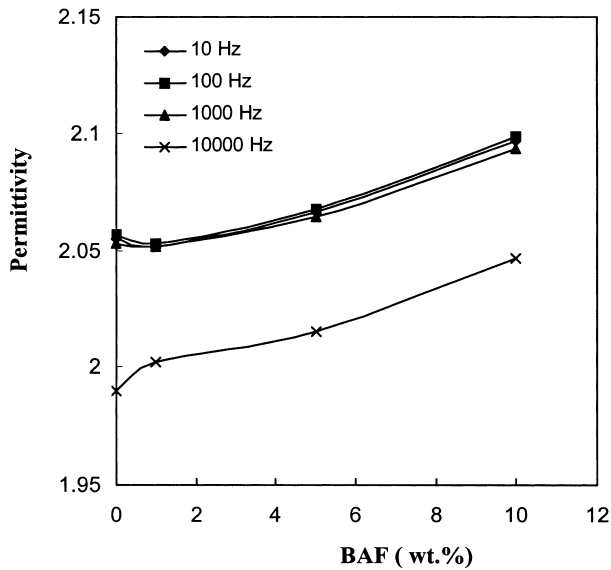


Fig. 3. Dielectric permittivity versus BAF loading for various LDPE samples at 30°C.

BAF, indicating that the crystal structure and the crystallinity of PE/BAF composite is also similar to that of pure PE. This provides a further indication that BAF is dispersed in the amorphous region of the PE.

3.3. Dielectric property

It may be thought that the introduction of BAF into the polymer matrix could lead to a low dielectric constant of the resulting polymer composites, since the bulky balls of C_{60} provide many nano-scale voids, the situation here is different. Fig. 3 shows the permittivity of the LDPE samples with BAF loading up to 10 wt.% at 30°C for different frequencies. It is seen that the permittivity increases slightly with an increase of BAF content.

The effect of BAF on the dielectric property of the resulting polymer composites can be twofold: first, BAF increases the interfacial, dipole, atomic and electronic polarization

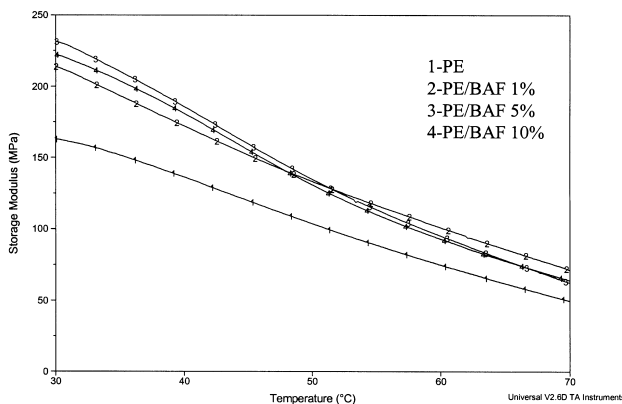


Fig. 4. Storage modulus versus temperature for LDPE and LDPE/BAF composites.

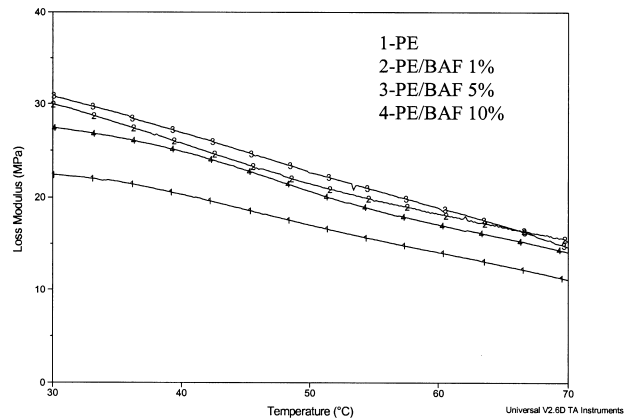


Fig. 5. Loss modulus versus temperature for LDPE and LDPE/BAF composites.

because each BAF molecule contains an average of 4.7 amine groups. This would lead to an increase of dielectric constant. Secondly, an increase of free volume due to the incorporation of BAF also plays a role in influencing the dielectric property of the polymer since air has much lower dielectric permittivity. The increase of free volume can be explained by considering the loose packing of BAF particle and the PE chain.

3.4. Thermal mechanical property

The storage modulus and loss modulus of PE and composites decrease with temperature, as shown in Figs. 4 and 5, respectively. Composites have a higher modulus than PE probably, in part, due to the rigid BAF. However, the modulus does not increase linearly with density or the content of BAF. High content of BAF, up to 10%, in the composite results in lower storage modulus and loss modulus, suggesting that a higher BAF loading has an adverse effect on the mechanical properties of the composites. This is because as the particle concentration increase, the local stress state will be affected. Yield stress and hence

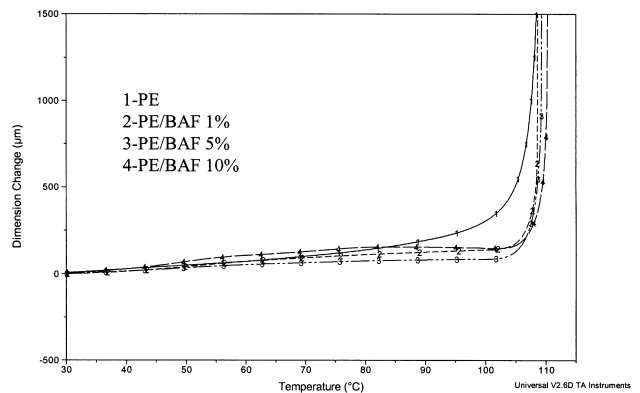


Fig. 6. Thermal mechanical analysis curves of LDPE and LDPE/BAF composites.

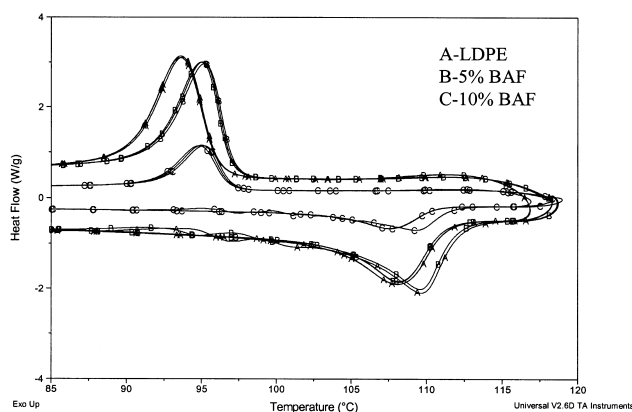


Fig. 7. DSC curves of: (A) LDPE; and (B) LDPE/BAF composites with 5% BAF and (C) 10% BAF.

the modulus of the composite strongly depend on particle concentration. High concentration of BAF in composite would facilitate the shear yield and hence reduce modulus of the material. It has been found [13] that in a polymer composite with 30 wt.% of particles, the polymer exhibit shear yielding. Assuming the crystallinity of PE is about 70% and all the BFA is distributed in amorphous region as indicted in this study, the concentration of BFA in amorphous region is about 30 wt.% which reaches a critical concentration for shear yielding.

The thermal mechanical curves of PE and BAF/PE composites are shown in Fig. 6. The dimension change increases with increasing temperature. All composites melt around 108°C, similar to that of LDPE (105°C). DSC measurements show that the composites and LDPE have almost same melting points (peak value 108°C, Fig. 7), which is consistent with the thermal mechanical analysis. It further demonstrates that the crystalline structure of PE is not affected by the BAF. The PE crystals and BAF are phase separated and BAF particles are in the amorphous part of PE.

4. Conclusions

BAF/LDPE composites containing up to 10 wt.% BAF have been prepared from solution. BAF evenly distributes as small particles of 1–5 μm in the amorphous region of PE. BAF does not affect the crystal structure and crystallinity of PE in the loading range of this study. The dielectric constant of PE increases slightly with the context of BAF. Both storage modulus and loss modulus increase with BAF loading, while a higher BAF loading has an adverse effect on the modulus.

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