Composites Science and Technology 163 (2018) 49–55

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Synergistic effect of flame retardants and carbon nanotubes on flame retarding and electromagnetic shielding properties of thermoplastic polyurethane

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ARTICLE INFO

Keywords:
Thermoplastic polyurethane
Carbon nanotubes
Intumescent flame retardants
EMI shielding property
Flame retardancy

ABSTRACT

Thermoplastic polyurethane (TPU)-based composites filled with carbon nanotubes (CNTs) and intumescent flame retardants (IFRs) were fabricated through melt compounding method. For comparison, TPU/IFR and TPU/CNT composites with different filling proportions were prepared, respectively. The results presented that the addition of 1 wt% CNTs and 10 wt% IFRs into TPU could achieve good flame retarding and electromagnetic interference (EMI) shielding properties simultaneously. With regard to flame retardancy, the compounding of CNTs and IFRs effectively suppressed the heat release rate and the UL-94 rating was upgraded to V-0 accompanied with prompt self-extinguishment and disappeared melt-dripping, which was equivalent to incorporate 20 wt% IFRs alone. However, the flame retardancy became deteriorated by loading more CNTs. It was revealed that the addition of CNTs could strengthen the carbonization effect of IFRs, but suppress their intumescent effect. Hence, a right amount of CNT loading was of critical importance to achieve synergistic effect with IFRs. Moreover, compared with the TPU/CNT system, the TPU/IFR/CNT system possessing the same CNT contents had a lower percolation threshold. When 1 wt% CNTs were introduced, the electrical conductivity was increased about two orders of magnitude and EMI shielding effectiveness was doubled in the presence of IFRs. The morphological observation and rheological analysis demonstrated that mixing with IFRs not only improved the dispersion of CNTs through particle collisions, but also benefited for establishing the continuous conductive pathways among the IFR particles. Accordingly, this work provided a promising and facile route to fabricate EMI shielding polymeric composites with excellent flame retardancy.

1. Introduction

With rapid development of electronic devices, such as laptops, cell phones and the like, electromagnetic interference (EMI) has become a serious concern in contemporary society. Among the shielding materials of choice, polymer composites are highly desirable because of their light weight, anticorrosive, flexibility, processability, etc. [1–5]. Nevertheless, the combustible polymeric matrix usually restricts some special applications requiring high fire safety. Therefore, it is of great significance to design and prepare a polymer-based material with excellent flame retarding and electromagnetic shielding performances.

The EMI shielding behaviors of polymer materials are generally realized by introducing conductive particles (e.g. carbon black (CB) [4], carbon nanotube (CNT)[2, 3], carbon fiber [5], metal nanowires [6], etc.). It is widely recognized that a high conductivity would benefit for obtaining a large EMI shielding effectiveness (SE) [2,7,8]. On the other side, by virtue of good thermal conduction and charring capacity, the conductive particles can effectively suppress the fire propagation and reduce the heat release rate (HRR) of the composite system [9]. As a consequence, it is easy to speculate that the balance between flame retarding and electromagnetic shielding performances is able to be figured out through high particle loading, but unfortunately it also correlates to low toughness, high cost and poor processability. Moreover, from the perspective of practical applications, an excellent flame regarding material not only should have a low HRR in the combustion process, but also needs to rapidly extinguish after being ignited or even be incombustible [10]. Based on previous reports, adding conductive particles may not fulfill this stringent requirement, because they were proven to be not helpful in passing the traditional flame retarding evaluation, such as the LOI and UL-94 tests [11].

Incorporating flame retarding components is one of the most effective methods to reduce the flammability of conductive polymer

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https://doi.org/10.1016/j.compscitech.2018.05.007
Received 3 December 2017; Received in revised form 26 March 2018; Accepted 3 May 2018
Available online 07 May 2018
0266-3538/

composites [12,13]. Commonly, there are two different ways. One is grafting flame retarding groups on conductive particles [12]. Most studies primarily focus on reducing the HRR, but few mention the extinguishing capacity. Besides, since the chemical graft may inevitably break the conjugate structure of conductive particles, the electrical related properties are less concerned. The other is physically mixing the flame retardants with conductive particles together, which is regarded to be more facile and effective in improving the flame retardancy (including extinguishing and heat release capacities) of polymeric materials [13]. With regard to the electrical properties, a daunting challenge needs to be faced that the addition of flame retardants may be detrimental to the connection between conductive particles, so that its influence on EMI shielding capacity is seldom reported, to the authors' best knowledge.

Recently, the EMI shielding composites with a low particle loading received increasing attention. Many investigations have demonstrated that segregating a small amount of conductive particles into confined continuous spaces constructed through phase separation [4], foaming [1,5], freeze-drying [3] or solid-phase compression [7] could promote the formation of a dense conductive and shielding network. Inspired by this strategy, the flame retardants can also be regarded as those foams or solid phases and the conductive particles are selectively located in the spare spaces. Accordingly, the continuous conductive pathways may be created by controlling the compounding proportion of these two types of particles.

In this work, thermoplastic polyurethane (TPU) was used as a polymeric matrix for its wide application in electronic devices and carbon nanotubes (CNTs) were chosen as conductive particles based on their high electrical conductivity as well as large length-to-diameter aspect ratio. Besides, halogen-free intumescent flame retardants (IFRs) were used as environment-friendly additives for improving the flame retardancy of the TPU matrix. As a representative, only one type of IFRs was introduced in present work. TPU/IFR/CNT, TPU/IFR and TPU/CNT composites were fabricated through melt compounding method and different particle proportions were chosen. The synergistic effect of CNTs and IFRs on flame retarding and EMI shielding properties of TPU was investigated and corresponding mechanism was proposed.

2. Experimental

2.1. Materials

The polyester-based TPU elastomer with a hardness of S58A and density of 1.21 g/cm^3 was purchased from BASF group (Germany). The multiwall carbon nanotube (MWCNT) was supplied by Nanocyl S.A (NC7000, Sambreville, Belgium). The commercial IFR (Doher 6487; Phosphorus ≥ 32 wt%; Nitrogen ≥ 7 wt%, purity ≥ 99%) with a mean size of about 4 μm, was purchased from Dongguan Doher Chemical Company Ltd. (China).

2.2. Specimen preparation

Prior to melt processing, TPU, IFRs and CNTs were dried separately in a vacuum oven at 80 °C for 24 h. All samples were prepared via melt blending at 185 °C in a Hapro Rheomix batch mixer (RM-200C) for 10 min with a rotor speed of 30 rpm. Ultimately, the blends were compression molded into sheets of about 1.6 mm under 10 MPa at 185 °C for 10 min and cooled to ambient temperature under the same pressure. The formulation of the prepared samples is presented in Table 1.

2.3. Characterization

The dispersion of particles in each composite system was observed through an Olympus BX51 optical microscope equipped with a camera. A thin slice of approximately 10 μm in thickness from each sample was obtained using a microtome. The microstructure of the residual chars yield after combustion was observed through scanning electron microscopy (SEM, JEOL JSM-5900LV) under an accelerating voltage of 20 kV. The surface each specimen was coated with a layer of gold in a vacuum chamber prior to visualization. The distribution of CNTs was further examined using transmission electron microscopy (TEM) (FEI Tecnai G2 F20, USA) at an accelerating voltage of 200 kV. Each specimen was cryo-microtomed (Leica EM FC6, Germany) into ultrathin slices with a diamond knife at −90 °C and dropped on a copper grid for observation.

Table 1
Formulation of the TPU-based composite samples.

Sample code	TPU, wt%	CNT, wt%	IFR, wt%
TPU	100	0	0
TF-X	100-X	0	X
TC-Y	100-Y	Y	0
TFC-X-Y	100-(X + Y)	X	Y

The limited oxygen index (LOI) values were measured according to ASTM D2863 by using an oxygen index meter (HC-2C, Jiangning Analytical Instrument Factory, China). The dimensions of each specimen are 130 × 6.5 × 1.6 mm^3. The Laboratories-94 (UL-94) vertical burning test was conducted on an HK-HVR vertical burning tester (Zhuhai Huake Testing Equipment Co., Ltd) according to ASTM D3801-10. The dimensions of each specimen are 130 × 13 × 1.6 mm^3. The cone calorimeter (FTT4100, Fire Testing Technology, UK) was also used to evaluate the flammability of the composites under an external heat flux of 35 kW/m^2 according to ISO 5660. The dimensions of each sample are 100 × 100 × 3 mm^3.

All thermogravimetric tests were performed on a thermogravimetric analyzer (TGA, TG-209F1, NETZSCH, Germany). Each sample, with a weight of 5–10 mg, was heated from 30 °C to 700 °C with an air flow rate of 60 ml/min and a heating rate of 10 °C/min.

Dynamic rheological behavior was performed using a rheometric expansion system (AR 1500/ex, TA, US New Castle). The measurements were carried out in an oscillatory shear mode using a parallel plate geometry (25 mm diameter) with gap settings of about 1 mm at 200 °C under nitrogen atmosphere. To investigate the frequency dependence of the storage modulus (G′), loss modulus (G″) and complex viscosity (η*) of the composites, a constant value of the strain amplitude was applied set at 0.5% and the frequency range is from 0.01 to 100 Hz.

The DC electrical resistivity of each specimen was measured by a Keithley 6487 picoammeter (6487, Keithley Co. Ltd., USA). The specimen was cut into 10 cm in length and 1 cm in width, two copper electrodes were clamp on each side along the length direction. The contact faces were coated with silver paste to eliminate the contact resistance between sample edges and electrodes. The constant voltage applied to the samples was fixed at 1 V. Five specimens were measured for each sample to achieve an average value.

The EMI SE of the composites was measured by using a vector network analyzer (VNA, Agilent N5230A, USA). As illustrated in Fig. S1, each specimen with thickness of 1.6 mm was placed between two waveguide parts, which were connected to the VNA. The measuring frequency range was 8.2–12.4 GHz (X band).

3. Results and discussion

3.1. Flame-retarding properties

LOI and UL-94 tests were performed to directly evaluate the combustion behavior of TPU/IFR composites. The related results are given in Table 2. For neat TPU, the LOI value is 21.5 indicating that it could be ignited in air. During the UL-94 test, the ignited sample rapidly extinguished because the fire was carried away by the molten drops,