



Measurement of heat capacity and thermal conductivity of HDPE/expanded graphite nanocomposites by differential scanning calorimetry

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Received 19.04.2011; published in revised form 01.07.2011

ABSTRACT

Purpose: In this study, heat capacity and thermal conductivity of nanocomposites formed by high density polyethylene (HDPE) matrix and expanded graphite (EG) conductive filling material were investigated.

Design/methodology/approach: Nanocomposites containing up to 20 weight percent of expanded graphite filler material were prepared by mixing them in a Brabender Plasticorder. Two grades of expanded graphite fillers were used namely expanded graphite with 5 μm (EG5) and 50 μm (EG50) in diameter. Heat capacity and thermal conductivity of pure HDPE and the nanocomposites were measured using differential scanning calorimetry (DSC).

Findings: A substantial increase in thermal conductivity was observed with the addition of expanded graphite to HDPE. Thermal conductivity increased from 0.442 W/m.K for pure HDPE to 0.938 W/m.K for nanocomposites containing 7% by weight of expanded graphite. Heat capacity increases with the increase in temperature for both pure HDPE and the nanocomposites filled with expanded graphite and no appreciable difference in the values of heat capacity were detected due to particle size. Heat capacity decreased with increasing graphite particle content for both particle size, following the law of mixtures.

Practical implications: Layers of expanded graphite have become of intense interest as fillers in polymeric nanocomposites. Upon mixing the expanded graphite intercalates and exfoliates into nanometer thickness sheets due to their sheet-like structure and weak bonds normal to the graphite sheets. That way they have very big surface area and high aspect ratio (200–1500) what results in a formation of percolating network at very low filler content. The nanoparticles usage results in significant improvement in thermal, mechanical, and electrical properties of polymers even with very low loading levels compared with microparticles.

Originality/value: To see the effect of conducting fillers on thermal conductivity and heat capacity two different sizes of expanded graphite were used.

Keywords: Conductive nanocomposites; Expanded graphite; HDPE; Heat capacity; Thermal conductivity

Reference to this paper should be given in the following way:

I. Tavman, Y. Aydogdu, M. Kök, A. Turgut, A. Ezan, Measurement of heat capacity and thermal conductivity of HDPE/expanded graphite nanocomposites by differential scanning calorimetry, Archives of Materials Science and Engineering 50/1 (2011) 56-60.

TECHNICAL PAPER

1. Introduction

Over the last years, conducting polymer composites filled with carbon materials such as carbon black, carbon fiber, graphite and carbon nanotube have been widely studied [1-8]. From these studies, it was noticed that the electrical, mechanical, and thermal properties have been strongly influenced by the filler's type, size, shape, content, distribution and also the processing methods of these composites [9-16]. Mostly, the conventional method is used for preparing electrically conductive polymer nanocomposites by adding and mixing conductive solid fillers such as graphite or carbon nanotubes into the common polymer in molten state.

More recently, polymer based nanocomposites reinforced with expanded graphite [17-23] have shown great improvements in mechanical, electrical conductivity and other thermophysical properties over the unmodified polymer. The reason for this is the sheet-like structure of natural graphite where the atoms are strongly bonded on a hexagonal plane but weakly bonded normal to that plane. If these sheets layers could be separated down to a nanometer thickness, they would form high aspect ratio (200-1500) and high modulus graphite nanosheets. Furthermore, the graphite nanosheets could have a very big surface area (up to 2630 m²/g) considering both sides of the sheets are accessible. Therefore, the dispersion of such nanosheets in a matrix will play a key role in the improvement of both physical and mechanical properties of the resultant nanocomposite.

Pötschke et al. [17], investigated the comparison of carbon black (CB) as spherical particles multiwalled carbon nanotubes (MWNT) as fiber-like filler, and expanded graphite (EG) as platelet-like filler into polycarbonate matrix. Their results indicate that EG is a good candidate for cost-effective conductive filler materials for antistatic applications and its percolation concentration is significantly lower than that of CB.

Zhao et al. [18], prepared nanocomposites based on poly(phenylene sulfide) (PPS) and expanded graphite (EG) or ultrasonicated EG (S-EG) by melt blending. They concluded that the PPS/S-EG nanocomposites exhibited higher conductivity, mechanical strength and thermal stability than the PPS/S-EG nanocomposites due to the small particle size of S-EG.

Royal et al. [19] fabricated EG-filled poly(phenylene sulfide) (PPS) matrix composites by hot pressing and discussed their electrical conductivity properties. They obtained a percolation threshold at 1 wt.% (0.6 vol.%) EG and the electrical conductivity was improved to 14 orders of magnitude higher than the pure PPS. They concluded that PPS/EG nanocomposites may prove to be the futuristic high performance materials for antistatic/EMI shielding applications.

Chen et al. [20] prepared polyurethane (PU)/expanded graphite powder (EGp) composite foams by filling mold curing reaction. They investigated the electrical properties of the prepared PU/EGp composite foams. They found the percolation threshold of PU/EGp composite foams about 5 wt.%, which is much lower than that of graphite nanosheets (GN) composite and carbon black (CB) composite. From the results they deduced that PU/EGp composite foams can be widely used for packing materials for the electron components.

Mirzazadeh et al. [21], investigated the effect of interface and degree of interfacial interaction upon electrical conductivity threshold in polypropylene/expanded graphite (PP/EG)

nanocomposites, and dispersion state of graphite nanosheets. They used maleic anhydride grafted polypropylene (PPgMA) and maleic anhydride grafted EPDM (EPDMgMA) as compatibilizer. Nanocomposite samples containing 1-5ϕ vol.% of EG were prepared by melt mixing method using laboratory scale internal mixer. They obtained that the PPgMA is more effective and suitable as compatibilizer for reducing the electrical resistivity of PP/EG nanocomposites.

As it is mentioned above, EG is a good candidate for cost effective filler and polymer nanocomposites reinforced with EG have shown great improvements in physical properties over the unmodified polymer. In this study, heat capacity and thermal conductivity of nanocomposites formed by high density polyethylene (HDPE) matrix and expanded graphite (EG) conductive filling material were investigated.

2. Material and method

2.1. Preparation of composite materials

HDPE (BP 5740 3 VA) supplied by British Petroleum UK, was used as matrix material with two types of expanded graphite fillers having nominal particle sizes of 50 μm (EG50) and 5 μm (EG5) in diameter. The respective trade name is Ecophit G (GFG50 and GFG5), supplied by SGL Technologies GmbH.

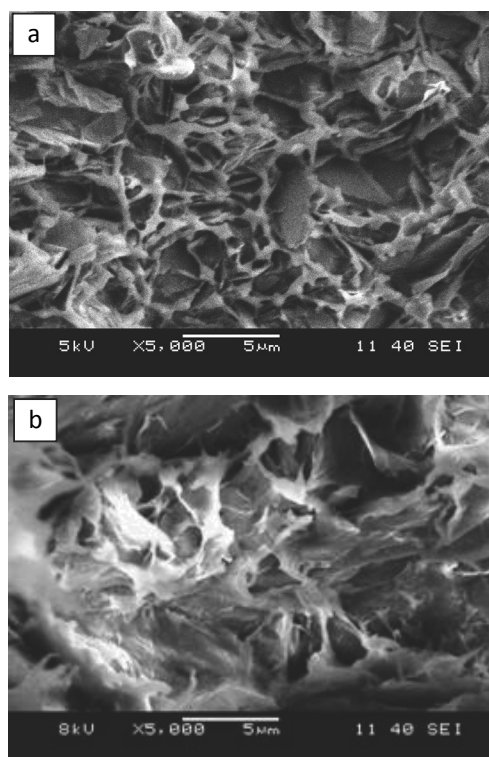


Fig. 1. SEM images of (a)HDPE-EG5 (75/25 weight%) and (b) HDPE-EG50 (75/25 weight%) samples

For specific heat measurements, specimens with 1mm thick were prepared by compression molding at temperature of 180°C and under pressure of 45 kPa for 1 min using a laboratory press Fontijne 200 (The Netherlands). In this way samples of 2, 5, 7, 10, 13, 15, 20, 25, 30, 40 weight percent by weight were obtained for both filler materials. The SEM images of HDPE-EG composites are given in Fig. 1.

2.2. Thermal conductivity measurements

The thermal conductivity of nanocomposite materials were measured at a heating rate of 10°C/min with nitrogen flow rate of 100 mL/min. 6 sensor material which gives clear different melting peaks between 48°C and 157°C were used. The sensor materials are given in Table 1. At the first step of DSC measurements, sensor materials pellet (5 mm diameter) prepared under 500 MPa pressure were placed into 5 mm alumina container and then the melting curves were determined. At the second step, the sensor material was placed on the polymer nanocomposite material which is cut in 6.5 mm. diameters and in a specific height illustrated in Fig. 2. Subsequently the DSC measurements were carried out again until the sensor material melted.

Table 1.
List of sensor materials and their melting point

Sensor materials	Melting point (°C)
Benzophenone	48.0
Stearic acid	66.0
Phenantren	99.0
Fluorene	112.0
Benzamid	127.0
Indium	156.6

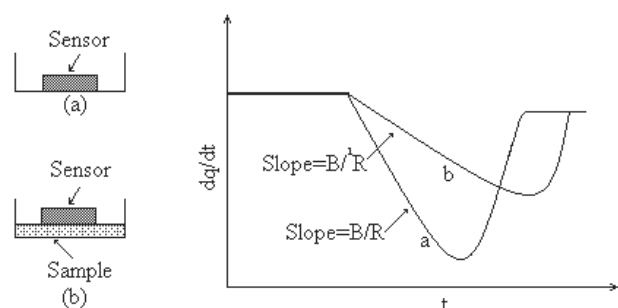


Fig. 2. a) Sensor b) sensor + sample and DSC curves sensor and sensor + sample

The purpose of this measurement is to determine the thermal conductivity values by the method of Flynn and Levin [24]. By taking up the slopes of the DSC curves at melting stage of the sensor material, the thermal resistance of sample is determined by Eq. 1.

$$R_s = R^i - R \quad (1)$$

where, R is the thermal resistance between calorimeter and sensor material, R^i is the thermal resistance between calorimeter and sensor material with sample, and the B in the Fig. 2 is the heating rate. The thermal conductivity is determined by Equation 2.

$$k = \frac{L}{A(R^i - R)} = \frac{L}{AR_s} \quad (2)$$

where, L is the sample height, A is the contact area between sample and sensor material.

2.3. Heat capacity measurements

The heat capacity measurement of the samples was carried out at a heating rate of 10°C/min between -10°C and 200°C temperature range. For these measurements Perkin Elmer Diamond DSC (Differential Scanning Calorimeter) was used. The heat flow curves of the empty container, standard material (sapphire) and samples were obtained at the following temperature levels for determining the heat capacity (C_p):

- 1) 2 min. isothermal at 0°C,
- 2) Increasing temperatures by a heating rate of 10°C/min from -10°C to 200°C,
- 3) 2 min. isothermal at 200°C.

Taking into account these three levels, at first the measurements were carried out by placing the two aluminum empty container and cover into sample and reference parts of the DSC furnace to determine the heat flow curve (baseline) of empty container. Secondly the standard material curve was obtained by placing the standard material (sapphire) in empty container taken place sample part. Finally the sample heat flow curve was obtained by placing sample in sample part. The temperature dependence of heat capacity was determined from these curves by Pyris 8.0 standard analysis program.

3. Results and discussion

3.1. Thermal conductivity results

First of all thermal conductivity of pure HDPE was measured at three different temperatures using the method explained in section 2.2. The results shown in Fig. 3 are in good agreement with literature values; thermal conductivity decreases with increasing temperature. Then, thermal conductivity of HDPE nanocomposites containing 7 weight of EG5 and EG50 were measured using the same method. The measurements were done at 46°C and the results were given in Table 2. It may be noticed that thermal conductivity value for nanocomposite filled with larger particle size graphite was much higher than the smaller particle size filled nanocomposite. The higher aspect ratio filler is the principal cause for higher thermal conductivity values.

Table 2.
Thermal conductivity of HDPE / EG5, HDPE / EG50 samples and pure HDPE

Particle weight concentration (%)	Particle volumetric concentration (%)	HDPE-EG5 Sample	HDPE-EG50 Sample
		Thermal conductivity (Wm ⁻¹ K ⁻¹)	
0	0	0.442	0.442
7.0	3.1	0.468	0.938

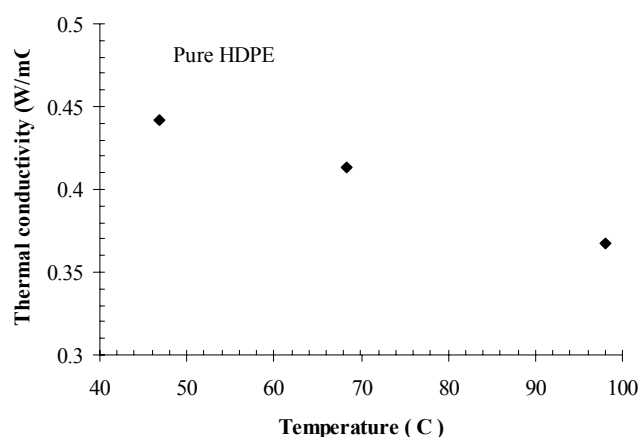


Fig. 3. The variation on thermal conductivity of pure HDPE versus temperature

3.2. Heat capacity results

The measured specific heat capacity values of pure HDPE and of HDPE/EG5 as well as HDPE/EG50 nanocomposites are given in Table 3 and Fig. 4. The theoretical specific heat (C_p) values of the nanocomposite were calculated according to the rule of mixture (Eq. 3) considering a two-phase system and using C_p values of HDPE (C_{pHDPE}) and expanded graphite (C_{pEG}) and ϕ_{wt} is the mass fraction of the filler:

$$c_p = \phi_{wt} c_{pEG} + (1 - \phi_{wt}) c_{pHDPE} \quad (3)$$

As expected, a linear dependence of specific heat upon the weight filler fraction is observed for these nanocomposites, and the experimental values measured for specific heat of both HDPE/EG5 as well as HDPE/EG50 nanocomposites follow quite well the calculated values from Eq. 3, see Fig. 4. It is evident that for the same expanded graphite weight content of composites, specific is not dependent on the size of the graphite particle which is also justified by the experimental results.

Table 3.
Specific heat capacity results (J/kgK)

Particle weight concent.	Particle vol. concent.	Cp model Eq (3)	HDPE EG5	HDPE EG50
0	0.000	1821	1821	1821
0.02	0.009	1797	1728	1739
0.05	0.022	1764	1762	1639
0.07	0.031	1742	1715	1722
0.1	0.045	1708	1626	1719
0.13	0.059	1676	1668	1685
0.15	0.069	1654	1621	1629
0.2	0.095	1598	1544	1529
0.25	0.123	1542	1516	1510
0.3	0.153	1486	1438	1480
0.4	0.220	1374	1354	1349

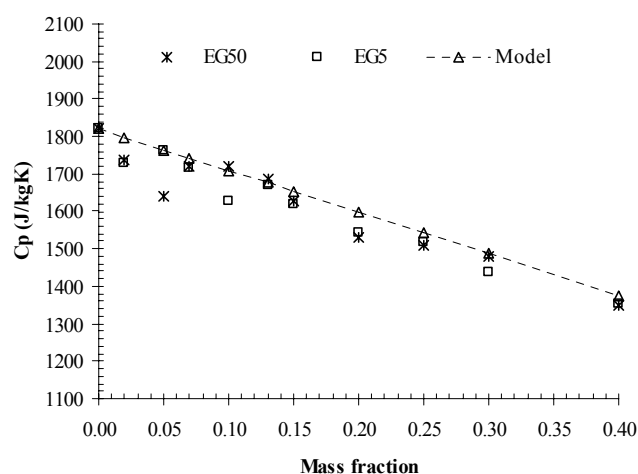


Fig. 4. Specific heat capacity versus filler weight fraction for HDPE-EG5 and HDPE-EG50 samples

4. Conclusions

Two grades of expanded graphite fillers were used namely expanded graphite with 5 μ m (EG5) and 50 μ m (EG50) in diameter. Heat capacity and thermal conductivity of pure HDPE and the nanocomposites were measured using differential scanning calorimetry (DSC). A substantial increase in thermal conductivity was observed with the addition of expanded graphite to HDPE. Thermal conductivity increased from 0.442 W/m.K for pure HDPE to 0.938 W/m.K for nanocomposites containing 7% by weight of expanded graphite. Heat capacity increases with the increase in temperature for both pure HDPE and the nanocomposites filled with expanded graphite and no appreciable difference in the values of heat capacity were detected due to particle size. Heat capacity decreased with increasing graphite particle content for both particle size, following the low of mixtures.

Acknowledgements

This research was supported by the Scientific Support of the bilateral Project No. 107M227 of TUBITAK and SAS (Slovak Academy of Sciences).

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