Comparing the effect of carbon-based nanofillers on the physical properties of flexible polyurethane foams

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Abstract

Flexible polyurethane (PU) foams filled with a fixed amount of carbon-based nanofillers, in particular multiwall nanotubes and graphenes, have been studied to clarify the influence of the morphology and functional groups on the physical properties of these polymeric foams. The effect of the carbon nanoparticles on the microphase separation has been analyzed by FT-IR spectroscopy revealing a decrease in the degree of phase separation of the segments. Variations of the glass transition temperature and an improved thermal stability were observed due to the presence of the nanoparticles. The EMI shielding effectiveness of flexible PU foams has also been enhanced, in particular for FGS nanocomposite foams.

Keywords

Polyurethane foams, multiwalled carbon nanotubes, functionalized graphene sheets, phase separation, EMI shielding.

Introduction

The rapid increase of electronic devices in our daily life has resulted in electromagnetic interference (EMI) problems that disrupt the device signals and reduce their performances. Thus, there is a real need to design and develop EMI shields that suppress or minimize undesired signals. Furthermore, the requirements imposed by the continuous design of ultraportable electronic devices and transport sectors have pushed the development of lightweight shielding materials. Polymer foams have shown a potential due to their lightweight characteristics but they require the inclusion of conductive particles to render them effective EMI shields. Therefore, carbon black, metal flakes, or metal fibers have been used as fillers in foams at loading fractions of up to 50 wt% [1]. The use of high aspect ratio conductive fillers, such as carbon nanotubes, can therefore be an attractive alternative. The introduction of carbon nanoparticles in polymer foams has received increasing attention because they can enhance not only the electrical conductivity [2] but also the mechanical strength, thermal stability, and surface quality [3-6]. In general, nanofillers can be easily incorporated in the cellular structure of foams reinforcing these polymeric materials with a minor effect on their structural characteristics (open-cell content, cell-size distribution, rupture of cell walls, ...) [4,7-11].

Polyurethane (PU) foams are one of the most versatile polymer foams with the largest market due to their wide range of applications [12-14]. Flexible PU foams are formed during the simultaneous reactions between an isocyanate with a polyol and water. The result of these exothermic reactions is a block copoly(urethane-urea) which forms the cellular structure due to the cogeneration of carbon dioxide [15,16]. Hence, the properties of PU foams depend not only on their final cellular structure but also on the phase-separated microstructure [15,17]. Recently, carbon nanofillers have been incorporated in PU foams showing that they did not only improve the physical properties [2,7,10,14,18] but also affected the kinetics of foaming polymerization [10,14,19].

In this study, we have introduced multiwalled carbon nanotubes (MWCNTs), functionalized MWCNTs and functionalized graphene sheets (FGS) at a fixed loading fraction in flexible PU foam. The inclusion of these carbon nanofillers has shown an enhancement of the thermal and electromagnetic shielding properties of these polymer

foams. To the best of our knowledge this is the first study in which the effect of FGS on flexible PU nanocomposite foams has been reported.

Experimental Part

Materials

The polyol used for the synthesis of flexible polyurethane foams was a polyether based triol, Voranol 6150 (OH value: 27 mg KOH/g) and the isocyanate was a methylene diphenyl diisocyanate (MDI), Voranate M2940 (NCO content: 31.4 wt.-%), both materials from Dow Plastics. The polyol based triol Voranol CP1421 (OH value: 31 mg KOH/g) was used as a cell-opener in the reaction. The next additives were employed: FASCAT 4202 (dibutyltin dilaurate, Arkema Inc.) which is a tin catalyst for the gelling reaction, TEDA-L33B (33% triethylendiamine in 1,4-butanediol) and NIAX catalyst E-A-1 (23% bis(2-dimethylaminoethyl)ether in dipropylene glycol) are tertiary amine catalysts required for the blowing reaction, DEOA (85 wt.-% diethanolamine in water) is a cross-link chain extender, SH 209 is a silicon surfactant and distilled water is used as the blowing agent. Formulation details are listed in Table 1.

Table 1 Flexible Polyurethane Foam Formulations.

Material	Description	phpp ^a
Voranol 6150	polyether polyol	100
Voranol CP1421	polyether polyol	4
Voranate 2940	isocyanate	43.4
DEOA	cross-link	0.8
TEDA-L33B	amine catalyst	0.25
NIAX E-A-1	amine catalyst	0.1
FASCAT	tin catalyst	0.05
SH 209	silicone surfactant	0.4
Water	blowing agent	2.2

^a parts by weight per 100 parts of polyol

Aligned multiwalled carbon nanotubes (MWCNTs) were synthesized using the chemical vapor deposition (CVD) injection method based on the decomposition of a ferrocene toluene vapor (3 wt.-% ferrocene in toluene) as reported elsewhere [10,19,20]. The diameters of the MWCNTs vary around 40 to 60 nm with a length of around 160 μm . These nanotubes were oxidized with a 3:1 concentrated sulfuric-nitric acid mixture and refluxed at 120°C for 30 min, then filtered and washed with distilled water until neutral pH. The functionalized multiwalled carbon nanotubes (f-MWCNTs) were dried at 120°C and stored under vacuum prior to use in order to avoid chemisorbed water on their surface.

Functionalized graphene sheets (FGS) were produced from the adiabatical expansion [4] of graphite oxide at 1000 °C under an inert atmosphere. The graphite oxide was first synthesized oxidizing the natural graphite according to the Brödie method [21].

Preparation of the Nanocomposite Foams

Flexible PU foams were synthesized in a two-step procedure. First, a fixed amount (0.5 phpp, approximately 0.3 wt.-% in the final foam) of the different carbon nanofillers was added in the polyol (Voranol 6150). In order to achieve a good dispersion, the mixtures were initially sonicated for 20 min using an ultrasonication probe in a water/ice bath to avoid temperature rising and then were stirred using an overhead stirrer equipped with a dispersion disc for 6 hours at 2400 rpm. Then, the surfactant, catalysts and distilled water were added to this mixture and stirred at 2400 rpm for 3 min. Finally, the required amount of isocyanate was added and mixed again for 20 sec. The foaming process occurred in an open cylindrical mould.

Sample Characterization

Infrared spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer fitted with an attenuated total reflectance (ATR) accessory. The cellular structure of the foams was qualitatively examined using a Philips XL30 environmental scanning electron microscope (ESEM) at 15kV. Cross-sections of the samples were cryo-fractured perpendicular to the foaming direction and the fracture surface was sputter-coated with gold/palladium. Dynamic mechanical analyses (DMA) were carried out on a DMA/SDTA 861e, Mettler Toledo, in the compression mode. The samples were

measured at a frequency of 1 Hz and heated at a rate of 3 °C/min. Thermogravimetric analysis (TGA) was performed on a TGA Q500, TA Analysis, under air environment at a heating rate of 20 °C/min over a temperature range of 25-700 °C. The EMI shielding effectiveness was measured with a Wiltron 360B vector network analyzer (VNA) in a frequency range from 8 to 12 GHz. The density was calculated from the mass and geometric volume of the DMA and EMI samples used for testing.

Results

The phase separation in PU, due to the thermodynamic incompatibility of hard and soft segments, has an important effect on the physical properties of these materials. Hence, FT-IR spectroscopy was used to study the degree of phase separation (*DPS*) in PU nanocomposite foams. Two bands in the carbonyl region corresponding to free urethane carbonyl (1728 cm⁻¹) and H-bonded urethane carbonyl (1702 cm⁻¹) were used to estimate the *DPS* (Fig. 1). H-bonds are essentially produced between the carbonyl (C=O) groups, which act as proton acceptors, and hydrogen atoms of the NH groups, acting as proton donors [22-24]. It is well-known that the urethane C=O groups located at the interfacial zone between hard and soft segments can be either free or H-bonded while the C=O groups in the hard domains are generally H-bonded only [22,25,26]. As a result, the H-bonding index (*R*) was calculated using equation 1:

$$R = \frac{C_{bC=O}\varepsilon_b}{C_{fC=O}\varepsilon_f} = \frac{A_{1702}}{A_{1728}} \quad (1)$$

where *C* and ε are the concentration and extinction coefficient of hydrogen-bonded urethane (*b*) and free urethane (*f*), while *A* is the absorbance of the corresponding bands. The value of $\varepsilon_b/\varepsilon_f$ is generally taken as 1 and the degree of phase separation (*DPS*) or degree of hard segment linking hard segment is expressed in equation 2 [22,24,27]:

$$DPS = \frac{C_{bC=O}}{C_{fC=O} + C_{bC=O}} = \frac{R}{R+1} \quad (2)$$

The values of R and DPS are summarized in Table 2. No apparent differences can be seen between the DPS and R for neat PU and pristine MWCNT sample. Hence, as-produced MWCNTs do not appear to affect the phase separated morphology of PU foams. However, R values decrease for f-MWCNT and FGS samples, suggesting that the oxygen groups on the surface of the nanofillers are hindering the hydrogen bonding between the hard segments of polyurethane. The lower value of DPS of f-MWCNT sample compared to the FGS sample can be ascribed to the different oxygen content on the f-MWCNT (O/C ratio of 17.9 at.% by XPS) compared to that on FGS (O/C of 9.2 at.%). This result can be understood as a further evidence of hydrogen bonding restrictions by the oxygen groups. Similar reductions of hydrogen bonding index and degree of phase separation have been observed in non-foamed nanoclay/PU [23] and cellulose nanocrystal/PU nanocomposites [28].

Fig. 1 FT-IR spectra of flexible PU nanocomposite foams.

Table 2 H-bonding index (R) and degree of phase separation (DPS) for PU nanocomposite foams.

Sample	R	DPS
Neat	1.32	0.57
MWCNTs	1.35	0.57
f-MWCNTs	0.86	0.46
FGS	1.24	0.55

SEM images (Fig. 2) confirm the effect of carbon nanofillers on the cellular structure of PU foams. The cell size of nanocomposite foams appears to have increase compared to the neat PU foam. This increase of the cell size has previously been observed on systems produced by reactive foaming, in particular in PU foams and has been ascribed to an increase of the polyol viscosity [10]. In the case of PU foams filled with FGS (Fig. 2 d), the frozen matrix became too fragile and resulted in a large number of broken cells.

Fig. 2 Representative SEM images of the foam samples: a) Neat; b) MWCNTs; c) f-MWCNTs and d) FGS.

Foam density is one of the most important physical properties which have a significant effect on the thermal, electrical and mechanical properties of polyurethane foams. The densities of flexible PU nanocomposite foams are summarized in Table 3. The density value increased due to the inclusion of the carbon nanofillers [10]. The presence of f-MWCNTs and FGS on the foam density is greater and it could be ascribed to the slow

down on the foaming evolution of these nanocomposite foams as has been described previously by the authors [19].

Table 3 Density (kg/m^3) of PU nanocomposite foams.

Sample	Density (kg/m^3)
Neat	53 ± 6
MWCNTs	63 ± 6
f-MWCNTs	71 ± 5
FGS	90 ± 9

The observed change in the degree of phase separation will have a profound effect on the physical and thermal degradation properties of the PU foams. The influence of carbon nanofillers on the phase separation was also observed in the glass transition temperature of the soft segment (T_g) of the PU nanocomposite foams (Fig. 3). The T_g values of the PU foams were -55.6 , -53.3 , -57.7 and -59.8 °C for Neat, MWCNTs, f-MWCNTs and FGS, respectively. In PU systems, the addition of carbon nanofillers can affect the T_g in two opposite ways [24]: by restricting the molecular motion due to the presence of well-dispersed carbon nanofillers, hence, increasing the T_g , or by modifying the degree of phase separation, thus, reducing the T_g . The decrease of the T_g values of both f-MWCNT and FGS samples could be attributed to the interactions between the functional nanoparticles and the hard segments resulting in an enhancement of the soft segment mobility and thus a decrease of the T_g [28]. In contrast, the T_g value of the sample filled with raw MWCNTs showed a modest increase suggesting a reduction of the molecular chain mobility of the soft segments. The specific storage moduli measured by DMA at 25 °C were 0.8, 2.3, 3.9, 10.5 kPa/kgm^{-3} for Neat, MWCNT, f-MWCNT and FGS samples, respectively. The observed increase in the modulus is consistent with the known reinforcing effects of the CNTs. The greater improvements of the functionalized nanofillers are attributed to the favorable interactions between functional nanoparticles and the hard segments. The best reinforcing behavior was obtained with the FGS due to their characteristic wrinkle morphology FGS which could result an enhanced mechanical interlocking and adhesion with the polymer chains [32].

Fig. 3 Damping factor ($\tan \delta$) of flexible PU nanocomposite foams as a function of temperature.

Polyurethanes degrade following a two-step process: the first step is associated with the degradation of the hard segments, which depolymerize into the main monomers, and the second step with the decomposition of the soft segments [8,29,30]. The first degradation step occurs in a temperature range between 250-450°C while the second step takes place between 500-650°C. The effect of the carbon nanofillers on the degradation temperatures of flexible PU foams is shown on Fig. 4. These two steps appear to be influenced not only by the functional groups present on the surface of the nanofillers but also by the nanoparticle morphology. While MWCNTs increase both temperatures by 20°C, f-MWCNTs only improve the first degradation temperature due to the interaction of the functional groups with the hard segments already mentioned [19]. f-MWCNT ought to have improved heat dissipation and thermal stability compared to raw MWCNT/PU sample, due to the direct covalent bonding with the matrix; but that was not the case. One hypothesis is that the hydroxyl and carboxyl groups of the modified nanoparticles disrupt the formation of large urea hard segments decreasing the thermal stability in relation to the pristine MWCNTs. Further investigations are required to corroborate this hypothesis. The inclusion of FGS shows a significant improvement of the thermal decomposition of the system, even considering the existence of the same functional groups as on f-MWCNT. Therefore, this effect should be related to both the

lower functionalization degree of FGS and to their wrinkled morphology which could result in a nanoscale surface roughness likely producing an enhanced adhesion with the polymer chains [31,32]; though, it could also account for providing more surface for chemical bonding. This morphology probably hindered the diffusion of volatile compounds and hence an enhancement of the thermal stability is observed. [33]

Fig. 4 Thermogravimetric analysis of flexible PU nanocomposite foams.

Table 4 Degradation temperatures of flexible PU nanocomposite foams.

Sample	T _{1st max} (°C)	T _{2nd max} (°C)
Neat	355	552
MWCNTs	374	577
f-MWCNTs	364	553
FGS	395	585

The EMI shielding effectiveness of PU nanocomposite foams were measured in the X-band frequency region (8-12 GHz). The measured shielding effectiveness is defined as

$$SE = 10 \log \frac{P_{in}}{P_{out}} \quad (3)$$

where P_{in} is the incident power and P_{out} is the power transmitted through a shielding material, and it is directly related with its conductivity. In order to compare the different systems, we plotted the specific EMI shielding effectiveness, i.e. the EMI SE normalized by the density of the material, as a function of frequency (Fig. 5). It is observed that, in this high frequency range, the shielding effectiveness of the PU nanocomposite foams is independent of the frequency. The inclusion of the carbon nanofillers clearly enhances the EMI shielding effectiveness compared to the neat PU foam. However, it can be observed that there is not a significant difference between MWCNTs and f-MWCNTs while for FGS samples there is an improvement of the specific EMI SE, from 7.6 of neat PU to 15.15 dB·cm³/g of FGS/PU. These results confirm that graphene sheets form a better conductive network in flexible PU foams than carbon nanotubes due to larger aspect ratio. Similar EMI SE values were achieved in a closed cell polystyrene nanocomposite foam with a loading fraction ten times higher than the loading fraction used here [11]. Furthermore, the electrical conductivity of the samples followed the same trend as the EMI SE (Fig. 6), due to the direct relationship between these two properties [34]. Similar conductivity values were obtained by Xu *et al.* [2] using a close cell f-MWCNT/PU foam at 2 wt.-% loading fraction. The characteristic open cellular structure of the developed flexible PU foams limits the formation of the continuous network to the cell edges. Hence, it could be expected that a closed cell, rigid PU foam would result in a larger increase in both conductivity and EMI shielding effectiveness.

Fig. 5 Specific EMI shielding effectiveness of flexible PU nanocomposite foams as a function of frequency.

Fig. 6 Electrical conductivity as a function of frequency for flexible PU nanocomposite foams.

Conclusions

The present work demonstrates the greater improved thermal stability and EMI shielding properties of functionalized graphene sheets compared to both MWCNTs and f-MWCNTs. The study showed that the functional groups on the surface of the nanofillers interacted directly with the urea hard segments and decreased the degree of phase separation of the matrix. The thermal stability of the nanocomposite foams has been improved due to the presence of the carbon nanoparticles in particular for those filled with graphene sheets. An enhancement of the EMI shielding effectiveness is observed due to the inclusion of the carbon nanofillers.

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