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Dielectric properties and electromagnetic interference shielding effectiveness of graphene-based biodegradable nanocomposites

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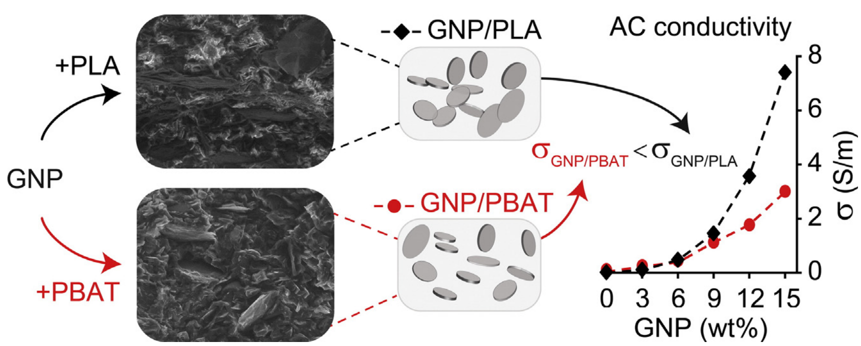
HIGHLIGHTS

- Electrical permittivity and conductivity of PLA and PBAT and therefore their EMI SE enhanced markedly with GNP embedding.
- Variations of complex permittivity of PLA and PBAT with GNP loading were successfully modelled by Sihvola's mixing rule.
- For both PLA and PBAT, electrical percolation occurred at GNP loading of between 6 and 9 wt% (3.5 and 5.3 vol%).
- PLA nanocomposites with 9 – 15 wt% GNPs had higher dielectric loss values compared to PBAT nanocomposites.
- PLA/GNP nanocomposites exhibited significantly higher potential for EMI absorption than PBAT/GNP nanocomposites.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene nanoplatelets (GNPs) were dispersed in poly lactide (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) via melt-mixing. Effect of GNP incorporation on electromagnetic properties and electromagnetic interference shielding effectiveness (SE) of PLA and PBAT was investigated and the two systems were systematically compared. Furthermore, applicability of Sihvola's mixing rule of complex electrical permittivity to these nanocomposites was studied. GNP addition significantly enhanced permittivity of both polymers. Dielectric constants of PLA and PBAT nanocomposites had comparable values. However, above 6 wt% GNPs, PLA nanocomposites showed significantly higher dielectric loss than PBAT nanocomposites, even though pure PLA had lower dielectric loss than pure PBAT. This was attributed to the dispersion state of GNPs in the two matrices, detected in morphological studies. SE of both polymers increased with GNP addition due to enhancement of their dielectric properties. The difference in dielectric loss of the two systems was revealed in their ability to attenuate the radiation by absorption. At 15 wt% GNPs, 1 mm-thick PLA/GNP nanocomposite had an effective absorbance of 70%. This value was only 43% for PBAT/GNP nanocomposite. Variations of polymers' permittivities with GNPs were successfully modelled by Sihvola's rule. While both systems returned close values for model's fitting parameters, it better fitted PBAT/GNP nanocomposites.

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1. Introduction

Incorporation of electrically conductive nanofillers into polymers has been investigated as a promising method to develop new conductive materials [1]. Electrical conductivity of such polymeric nanocomposites can be exploited in areas like electrostatic discharge protection, lightening-protection panels, solar panels, thermoelectric materials and electromagnetic interference (EMI) shielding applications [2,3].

EMI is an undesirable by-product of rapid growth of high frequency electronic systems and telecommunication devices. These radiations can interfere with the normal operation of other equipment or adversely affect human health [4,5]. Efforts have been made to reduce electromagnetic pollution by using various strategies and EMI shielding materials [5]. Such materials attenuate the signal by reflection of the wave and/or absorption of the radiation power inside the material [6]. Polymers filled with conductive particles have been explored intensively in the last decade as possible EMI shielding materials. Carbon-based particles such as carbon black [7,8], carbon fiber [9,10] and carbon nanotubes [3,4,11–13] have been demonstrated to be effective fillers for preparing conductive composites with EMI shielding properties. Lu et al. [14] demonstrated that composites with carbon-based particles can even perform well as microwave absorbers in harsh environments.

In recent years, graphene has also been embedded in polymers and has exhibited good EMI shielding performance. Various polymers including poly(dimethyl siloxane) [15], epoxy [16], wax [17], poly (ethylene–vinyl acetate) [18], poly methyl methacrylate [19] and poly aniline [20] have been used as host media for graphene and their EMI shielding effectiveness (SE) has been reported. Recently, Wen et al. [21] investigated the microwave attenuation performance of reduced graphene oxides (r-GO) composites versus that of graphite nanosheet (GN) composites and observed that r-GO composites exhibited 3–10 times higher SE than GN composites. Wen et al. [22] fabricated composites based on SiO_2 and 4–20 wt% r-GO and measured their SE over a temperature range of 323–473 K. They observed that these graphene-based composites have satisfactory shielding performance at such elevated temperatures. Dielectric and EMI shielding properties of graphene/SiO_2 composites were also investigated by Cao et al. [23] over frequency range of 8.2–12.4 GHz and temperature range of 323–473 K; Composite containing 7 wt% graphene with a thickness of 2.4 mm showed reflection loss of higher than 10 dB over the entire frequency range at the temperature of 413 K.

Graphene nanoplatelets (GNPs) are graphitic nanoparticles with layered structure which are composed of stacked 2D graphene sheets bonded together with weak Van der Waals forces [24]. As a novel nanofiller, graphene has attracted a tremendous amount of attention in industry and academia due to its excellent electrical conductivity, high mechanical properties, thermal conductivity and ability to improve barrier performance of polymers for gas and moisture diffusion [25]. High purity GNPs can be derived from the plentiful resource of natural graphite by relatively convenient methods compared to carbon nanofibers (CNFs) and carbon nanotubes (CNTs) [24]. Therefore, GNPs are more cost-effective with potential to replace high-priced CNTs in a variety of applications including EMI shielding.

The increased volume of plastic wastes in landfills has generated problems due to the non-biodegradability of most commercial polymers. Consequently, environmental concerns have resulted in an ever increasing interest in biodegradable polymers [26]. These polymers can be classified based on the origin of their monomers, whether obtained from bio-sources or derived from petroleum [27]. Prominent members of these two categories are poly lactide (PLA) and poly(butylene adipate-co-terephthalate) (PBAT), respectively [28]. The aliphatic thermoplastic polyester of PLA is synthesized by ring opening polymerization of lactides or condensation polymerization of lactic acid monomers [29]. With high strength and modulus, thermal plasticity, commercial availability and reasonable price, PLA is the most prevalent biodegradable polymer [30,31]. PBAT is another excellent biodegradable polymer. It is an aliphatic/aromatic copolyester, synthesized by esterification of 1,4 butanediol with aromatic dicarboxylic acid followed by polycondensation with succinic acid [26]. PBAT exhibits high elasticity, wear and fracture resistance as well as adhesion and compatibility with many other natural polymers [32]. Fig. 1 depicts the chemical structures of PLA and PBAT.

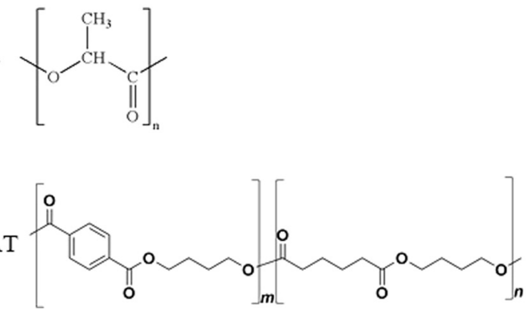

Fig. 1. Chemical structure of (a) PLA and (b) PBAT.

Extensive research has been conducted on PLA nanocomposites containing various nanofillers including conductive carbon nanofillers such as CNTs [29,33] and carbon fibers [34]. In recent years, GNPs have also been used by some researchers to reinforce PLA. Different properties of these nanocomposites have been reported including biocompatibility [35], rheology [36] and crystallinity [37]. On the other hand, PBAT has been often used as a second phase in polymer blends due to its low mechanical strength. Several researchers, however, have demonstrated that addition of nano-sized fillers such as clay and CNTs to PBAT can overcome its shortcomings such as low strength, conferring multifunctional enabling properties like enhanced mechanical, thermal and electrical properties [38,39]. Lately, effects of GNPs on crystallization and rheology [28,40,41] of PBAT have been investigated as well.

In our recent study, electromagnetic (EM) properties of PLA/GNP nanocomposites were determined [37]. The present work investigates the effect of GNP embedding on the dielectric properties of PBAT and compares the variations of EM properties of PBAT/GNP and PLA/GNP nanocomposites versus GNP loading and frequency in detail. EMI shielding performances of PBAT/GNP and PLA/GNP nanocomposites are also determined in terms of reflection, absorption and shielding effectiveness. Due to the importance of X-band frequency range (8.2–12.4 GHz) in many commercial applications [42], all the measurements were conducted over this frequency range. To the best of our knowledge, this is the first study on EM properties of PBAT/GNP system. Furthermore, the present work provides a systematic comparison between the properties of two of the most prevalent biodegradable polymers used as the host matrix for graphene-based nanocomposites with EMI shielding application. In addition, the current study investigates the applicability of Sihvola's unified mixing rule of complex electrical permittivity to graphene-based nanocomposites for the first time.

2. Experimental

2.1. Materials

PLA was purchased from NatureWorks LLC. The grade used was 4032D which exhibits a density of 1.24 g/cm^3 and a melting temperature range of 155–170 °C [43]. PBAT was Ecoflex F Blend C1200

Table 1
Composition of the nanocomposites.

GNP loading (wt%)	0	3	6	9	12	15
PLA/GNP	PL0	PL3	PL6	PL9	PL12	PL15
PBAT/GNP	PB0	PB3	PB6	PB9	PB12	PB15