Material Properties

Graphene-reinforced elastomeric nanocomposites: A review

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ABSTRACT

The development of graphene nanosheets and/or their derivatives (GSDs) has sparkled worldwide overwhelming industrial and academic research interests, due to their unique and potentially useful properties. This review is written to highlight the state of art of GSDs/elastomer nanocomposites and their applications in various fields of technologies. It begins with reviewing the recent progress made in GSDs/elastomer nanocomposites in comparison to elastomer nanocomposites based on carbon nanotubes. The role of GSDs structures, functionalization, type of matrices, and content of fillers on properties of GSDs/elastomer composites has been reviewed systematically. The basic properties of various GSDs/elastomer nanocomposites including; morphology, curing behavior, mechanical properties such as Young's modulus (E), tensile strength (σ_s) and elongation at break (E_b), electrical percolation threshold, and thermal stability have been discussed in details. Finally, an attempt has been made to identify the critical challenges, which still need to be addressed for improving the processing of GSDs/elastomer nanocomposites and to explore their prospects for advanced applications. The article has been concluded by summarizing the key facts of GSDs that play significant role in developing GSDs/elastomer nanocomposites for technological applications.

1. Introduction

Over the years, various types of fillers such as talc, glass fibers, carbon black, layered silicates and calcium carbonate have been used to enhance the properties of polymers and to reduce the cost of polymer products. Fillers below 100 nm provide a high level of reinforcement to control the physico-mechanical properties of the composites. Amongst the various fillers, the carbonaceous nanofillers such as carbon nanotubes (CNTs) and graphenes nanosheets (G) have contributed significantly in controlling the mechanical, thermal, and electrical properties of polymers due to their high mechanical strength and high aspect ratio [1]. The extraordinary properties of graphene and its ability to disperse in various polymeric matrices have provided an opportunity to develop new class of polymeric nanocomposites [2–22]. The graphene is a flat monolayer of carbon atoms, tightly packed into a two-dimensional (2D) honeycomb lattice having conjugated sp^2 hybridized planar structure [23]. A flat monolayer of carbon atoms is a basic building block of graphitic materials with all other dimensions. The graphene was discovered in 2004 by Novoselov and co-workers who initially thought the material was thermodynamically unstable in ambient conditions [23]. The graphene is a naturally occurring material but with the discovery of synthetic methods, efforts are being made to study its properties and applications. Recently, various methods have been used for the production of graphenes, which are classified either as bottom-up or top-down methods. The bottom-up methods include; chemical vapor deposition (CVD), epitaxial growth on SiC, arch discharge chemical conversion, reduction of CO, unzipping carbon nanotubes, and self-assembly of surfactants. Whereas, by top-down methods, the graphene or modified graphene is produced by applying separation/exfoliation of graphite (GR) or graphite derivatives [1,24]. Graphene

has shown a significantly high and useful mechanical strength. A single-layered graphene has shown Young modulus of ~1 TPa, ultimate strength of 130 GPa, thermal conductivity of 5000 Wm^{-1}K^{-1}, high flexibility, and a very high electrical conductivity up to 6000 Scm^{-1} [25,26]. CNTs are the one-dimensional tubular structures, which are possibly made through the rolling of one-atomic thick sheet of graphene [25,27]. Unlike CNTs, the chirality in graphene is not considered so important to influence its electrical conductivity and mechanical properties. The extremely high surface area (theoretical limit: 2630 m^2/g) seems to be an outstanding properties that makes graphene useful and desirable nanomaterials to improve the properties and processing of polymer nanocomposites. Polymer chemists and material scientists are already ahead of time by incorporating graphene and/or graphene sheet derivatives (GSDs) in polymer matrices to produce composites for various applications. Like CNTs, graphene and GSDs have been used frequently to make various polymer composites such as; GSDs/polystyrene [28], GSDs/epoxy [29], and GSDs/natural rubber (NR) [30], which showed significantly improved physical and chemical properties in comparison to pristine matrices.

In graphene/polymer nanocomposite technology, one of the greatest challenge is to get homogeneous dispersion of graphene sheets into matrices due to presence of weaker interfacial interactions with matrices and strong attractions between graphene sheet surfaces [31]. Unless these problems are addressed to a greater extent, it is quite difficult to obtain homogeneously dispersed graphene/polymer nanocomposites [25] to harness the maximum benefits for advanced applications. However, meticulous efforts have been made to address these issues but still there is scarcity of reliable methods to prepare defects free and purified graphene nanosheets. To overcome various challenges of graphene/polymer nanocomposites, rigorous studies are still needed to get significant insight to over come the existing problems.

Although a considerable amount of work on the advancement of CNTs [27,32–35] and GSDs-polymer nanocomposites [36,37], is reported but challenges and future scope for graphene/elastomer nanocomposites are not yet addressed properly. This review is written to target the ambiguous issues associated with GSDs reinforced elastomer or rubbery polymer nanocomposites as promising advanced materials for fabrication of domestic devices and industrial components that are used for energy, electronics, medical, automobile, and aerospace industries.

During last one decade, there has been a significant growth (Fig. 1) in literature reports dealing with the development and advancements
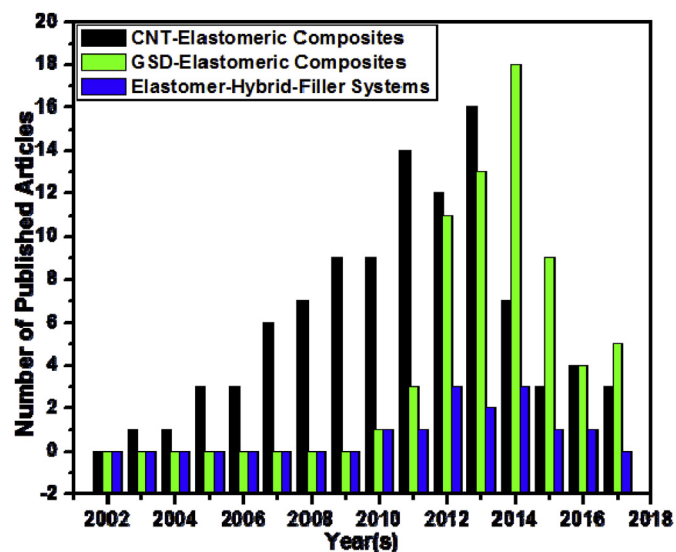
for CNT/elastomer compounds [38–63], [64–77], [56,78–89], [90–102], [103–122], [123–138] and their hybrid composites [139–141] or dealing with GSD/elastomer nanocomposites [2–22], [142–157], [158–171], and their hybrid nanocomposites [172–174]. This has clearly indicated that a significant amount of research has been carried out to develop CNTs-, and GSDs-reinforced elastomeric nanocomposites.

Considering the properties and applications of CNTs-, GSDs, and reinforced polymer nanocomposites, a significant amount of research has been reported by enthusiastic researchers around the world to explore the potential of nanofillers and nanocomposites, but the results are scattered, inconsistent and sometime controversial. Additionally, the role and influence of various factors such as; CNTs chirality, aspect ratio, types of CNTs (SWCNT, MWCNT etc.) or GSDs (graphene nanoplatelets (GnP), expanded graphites (EGs), reduced graphene oxides (RGOs), etc.), functionalization, choice of rubber matrices, processing methods, morphology, structure and state of dispersion to improve the properties of nanocomposites are hardly discussed sufficiently.

In this review, effort has been made to present a streamlined state of art on GSDs-based elastomeric nanocomposites and their hybrids by considering issues exclusively related to processing, functionalization, and characterization techniques. The elastomeric matrices reinforced with different kinds of GSDs and their combinations with other nanoparticles have been used to highlight the role of matrices and nanofillers in controlling the properties of nanocomposites. The performance of elastomer composites fabricated with functionalized nanofillers and different type of matrices has been discussed to analyze the role of matrices and fillers in controlling the properties of nanocomposites. The improvements in physical properties of GSDs-based elastomeric nanocomposites, such as mechanical strength (ultimate tensile strength, elongation at break and Young's modulus), thermal stability, electrical property, and percolation threshold, are presented in this article.

Finally, the review has been concluded stating the current challenges, future scope for research, and potential applications of GSDs/elastomer composites. The presentation of existing issues (merits and challenges) relating to GSDs/-elastomer nanocomposites, will play a significant role in achieving the goal of polymer nanoscience and technology in technical applications and to overcome the gaps that need immediate attention to improve the properties of GSDs/-elastomeric nanocomposites to utilize their full potential in near future.

2. Synthesis of graphene sheet derivatives (GSD)

Although, the production of graphene nanosheets (GS/G/GE/GS) is traced back to 1970 but free-standing single-layer graphene sheet was first produced in 2004 by applying a micromechanical cleavage method to graphites (GR). However, recent methods have been found to be more attractive than the conventional method of micromechanical cleavage for the production of graphene for fundamental studies and electronic applications [1,24]. The dispersion of graphene nanosheets in polymer matrix has shown dependence on sheet size and its functionality. To increase the extent of dispersion of graphene nanosheets, the surface modification has played a significant role. Graphenes without functional groups interact with polymer matrix through van der Waals forces, $\pi - \pi$ stacking and hydrophobic interactions, which are very weak and unable to cause significant variation in electronic properties of nanocomposites. To obtain a modified graphene sheet (RGO), the crystalline GR flake needs to be exfoliated, which is normally achieved by using either mechanical/chemical or thermal method [27] of exfoliation. For this purposes, both of Hummer's [7,9,144,175] and Brodie's approaches [142,152,176] are found to be quite useful for the production of graphene oxide (GO) and subsequent formation of RGO by hydrazine reduction [25,27]. The oxygen functionalities in GO create electrostatic repulsion and reduced van der Waals forces between interlayers of GR, which help in exfoliation of GO in water. A typical process for production of modified graphene sheets

Fig. 1. Survey of research publications on CNTs-/GSDs reinforced elastomeric matrices, and their hybrid nanocomposites during 2002–2017.