Graphene nanocomposites for improved golf ball performance and lifetime

ABSTRACT

The average golfer and most professionals play with two-piece, three-piece, or four-piece layered golf balls. A typical two-layered golf ball is composed of a crosslinked rubber core (polybutadiene or polyurethane) and a rigid and glassy outer skin (poly(methacrylic acid) ionomer. A crosslinked rubber is an ideal thermodynamic material that recovers completely after extensive impact (rubber elasticity). Polybutadiene rubber has a glass transition temperature of about -73˚C, which means that it remains rubbery at extremely low winter-like conditions. A crosslinked rubber maintains form when it is struck by dissipating the mechanical energy into heat energy. The temperature where damping is highest, for most amorphous polymers (rubbers), is the glass transition temperature.

When a golf ball is struck, the hard and glassy skin receives the impact and transmits it to the rubbery core. The crosslinked rubber core absorbs and dissipates the impact energy making the golf ball highly resilient and durable. The ability to transfer the load from the skin to the core depends on their compatibility and the strength of the bond between them. The performance of the golf balls (distance traveled after striking) drops drastically under cold and wet conditions. It is reported that the hydrophilicity of the ionomers that make up the outer layer of the golf ball allows water to permeate and submerge into the rubber core, thereby causing disconnection of the two layers and disruption in load transfer from skin to core.

It is imperative to develop a golf ball capable of maintaining highest performance in all weather conditions. In this proposed project, the hydrophilicity of the outer layer of golf ball will be reduced while maintaining high impact strength by reinforcement of poly(zinc-methacrylate acid (PZnMAA)) with surface modified graphene nanosheets. Preliminary results obtained in our laboratory show that reinforcement of hybrid polymer matrix with graphene nanosheet exhibited a simultaneous increase in the storage modulus and damping ability [1,2]. It was also shown that the rubbery plateau of glassy polymers is increased by about three orders of magnitude [2]. We propose to extend this discovery to golf ball technology by reinforcing both the skin and core of a golf ball with surface modified graphene nanosheets. We expect that reinforcement of both the crosslinked rubber and PZnMAA with graphene will lead to simultaneous increase in storage modulus and impact resistance while maintaining highest damping ability over a wide range of temperature, frequencies, and time scale.

Furthermore, uniform dispersion of graphene in PZnMAA matrix and polyurethane matrix will be achieved by in-situ polymerization in the presence of the filler. Dispersion will be monitored using Raman Spectroscopy by comparing the ratio of carbon D-peak to graphite G-peak for the powder graphene nanosheets with the modified filler. Additional information about dispersion and exfoliation of graphene will be obtained from Transmission Electron Microscopy, as well as Wide Angle X-Ray Spectroscopy. The thermomechanical properties and damping behavior of the graphene nanocomposite will be determined by using Dynamic Mechanical Spectroscopy and correlated with impact strength. The high aspect ratio nanographene sheet modified with hydrophobic polyaniline will prevent wetting of PZnMAA and water permeation and toughen the system crack bridging while maintaining high storage modulus. The broader impact of the proposed research is the integration of nanotechnology in golf ball construction in order to improve their performance and lifetime.

LITERATURE REVIEW

Golf ball industries use synthetic rubbers, either polybutadiene or polyurethane, to form the inner core of the golf ball. However, while this material shows high resiliency, the compatibility of the outer skin, Surlyn, with polybutadiene is questionable especially in the spring and winter periods. It has been reported that significant degradation in performance in the form of loss of distance traveled when golfers strike golf balls under lower temperature and wet conditions. This phenomenon explains why most golfers travel to Florida during the months of October through January. Changing weather conditions affects many aspects of the golf balls' physical properties, such as resiliency, spin, and most importantly distance in the golf ball. Nowadays, distance is the key to every average golfer's game.

Furthermore, the rubber core needs to remain dry in order to maintain high resiliency, high damping ability and rubber elasticity. However, the entire reason a golf ball loses its distance throughout cold weather is due to lower elasticity from the disconnection of the inner core from the outer skin because the soft rubbery segment of the core is disconnected from the skin by water. When the golf ball is submerged, water channels its way into the core of the golf ball, through the hydrophilic polar ionomers in Surlyn. Consequently, the performance of the golf ball measured in the distance after striking the golf ball, drops drastically. It was reported that the ionomers that are typically used in the composition of golf balls are hydrophilic and allow water to freely pass into the core of golf ball [3]. The intended performance attributes of those materials are clearly affected by water by even the smallest uptake in water [3]. We propose to improve the hydrophobicity of the outer skin of the golf ball. One of the main goals of this research is to make the outer skin of golf ball hydrophobic while maintaining high modulus and resiliency. We propose to solve this problem by reinforcement of PZnMAA with surface modified 2-D dimensional nano-graphene sheets. Polymeric matrices reinforced with nano graphene sheets have been known to show remarkable improvement in their thermo-mechanical, electrical and thermal properties. Mikkal and others reported that graphene is an emerging material for producing polymer nanocomposites [4]. Graphene's heat and thermal conductivity are greater than any other known material, yet it is so dense that not even helium can pass through its honeycomb lattice structure. Graphene has emerged as a hot topic for scientific research due to its remarkable electron transport, mechanical properties, and high surface area [4-6]. The long-term transport problem associated with the ionomers present in Surlyn, will be solved by reinforcement with surface modified 2-D graphene sheets by making Surlyn electrically and thermally conductive and hydrophobic. The heat conducting nature of graphene reinforced Surlyn will enable water to dry up, prevent formation of channels, while maintaining high modulus and toughness. Literature has shown that graphene has exception thermal, mechanical, impermeability, and electrical properties and in turn, the properties of polymer matrix can be enhanced by reinforcement with graphene in accordance with the rule of mixture micromechanical model [6].

The performance of golf ball drops drastically during the winter and spring seasons due to the hydrophilic nature of the ionomer that makes up the outer skin of the golf ball. The change in weather from Fall to Winter and Winter to Spring affects the performance of the golf ball because of extended cool/wet weather conditions. Water enters the core of the golf ball through channels created by the hydrophilic ionomers. The presence of water inside the golf ball causes disconnection between the outer skin and inner core of golf ball especially during the winter season and cold/wet weather conditions. In order to control the performance of the golf ball during the extreme cold/wet weather conditions we will reinforce Surlyn with graphene nanofillers.

However, it has been proven from recent study that graphene, a two-dimensional lattice structure with exceptional mechanical and electrical properties, influenced the elastic modulus, damping ability, and the glass transition temperature of polyimide matrix. In the presence of graphene, it was determined that high elastic modulus at low damping and high glass transition temperature around 430˚C were achieved at low volume fraction of graphene of 1.18% [1]. The viscoelastic properties graphene/polyimide nanocomposites (NGS-PI) and neat-PI are shown in Figures 1 and 2, below. The figures are show the variation of storage modulus and tan delta peak height (damping ability) of neat-PI and PI containing volume percentages of NGS (graphene). The intensity of the beta transition is notably enhanced at low graphene volume fraction 1.18% (line c) as compared to the alpha transition peak intensity. It is noted that moderate damping ability was achieved at high elastic modulus at 1.18% volume. The rubbery plateau storage modulus was enhanced by 1000 times.

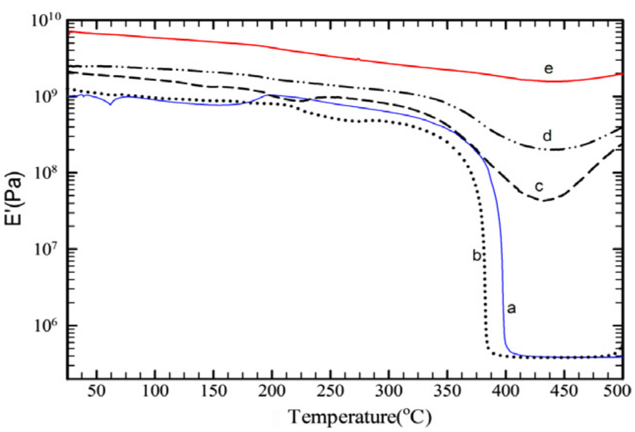

Figure 1: Storage modulus vs. Temperature

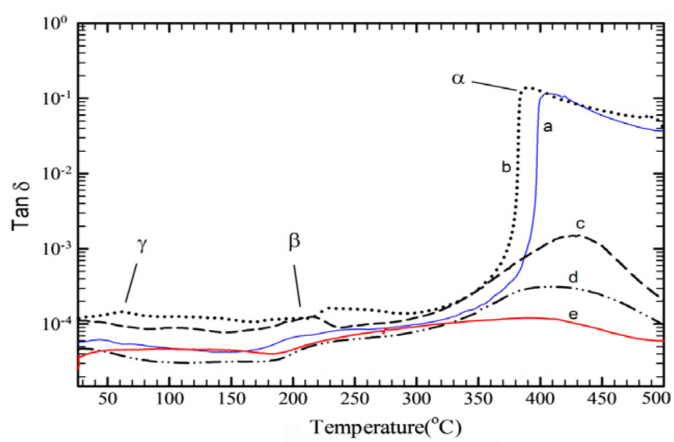

Figure 2: Damping ability vs. Temperature

In previous research in our laboratory, it was shown that reinforcement of polyimide with sulfonated polyaniline copolymer modified 2-D nanoclay platelets resulted in a simultaneous enhancement of storage modulus and tan delta damping peak height [1,2]. It was also shown that both the glassy region storage modulus and the rubbery plateau storage modulus were increased in nanocomposites containing 0.5 wt% of modified nanoclay. These results are shown in Figure 3 and Figure 4 below. Dispersion of graphene in nylon-6 was accomplished by in-situ polymerization of caprolactam in the presence of the filler, resulting in increased tensile strength and Young's modulus of the composite at about 0.1 wt. % of graphene [7]. In the proposed research, the goal is to enhance the storage modulus of Surlyn without sacrificing damping ability at desired optimal concentration of graphene. At the optimal condition to be determined, both damping ability and elastic storage modulus would be maximized. Optimal condition will be dependent on filler weight fraction, thickness of filler surface modifier and in-situ polymerization conditions.

RESEARCH INTERESTS

The innovation of this project is the successful altering of golf ball materials, the development of graphene/Surlyn nanocomposites, and creation of unique structure nanocomposite structures, enhanced performance and lifetime of golf ball. The relevance of the proposed research to space technology is the creation of a new smart nanocomposites based on nanographene sheets and Surlyn. The dispersion of graphene in Surlyn will be improved by surface modification with sulfonated polyaniline copolymer.

Furthermore, there are two main foci in this study that are intended to improve the performance of the golf ball, including prevention of diffusion of water by crack blunting and decreased wettability. Diffusion of water into the golf ball is due to the highly polar polyelectrolyte is hydrophilic. Further, the presence of water in the outer scheme of the golf ball can increase internal stress, and magnify stress at the crack edge resulting in crack propagation and physical leaking or regression of water into the center of the core. It is proposed that, the reinforcement with nanofillers can terminate crack propagation, however graphene might be susceptible to the wet conditions. Therefore, we propose to modify graphene with a hydrophobic material to bridge those cracks and prevent passages for water into enter the inside core of golf ball.

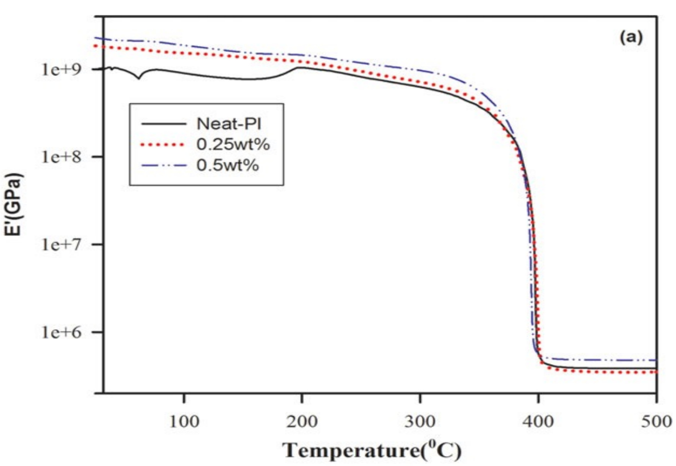

Figure 3: Elastic Modulus vs. Temperature

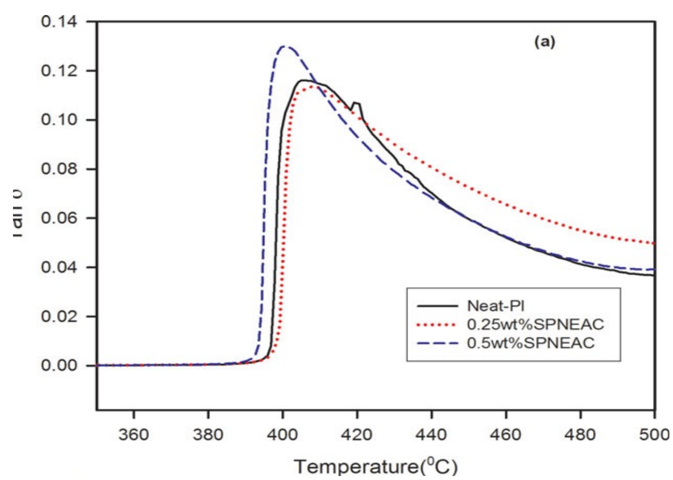

Figure 4: Storage Modulus vs. Temperature

A good candidate for preferred hydrophobicity for bridged cracking is polyaniline due to its ability to improve the damping ability without sacrificing the mechanical strength of the nanocomposite, as shown in Figure 4 [2]. In fact, the proposed nanofillers have high surface area and thermal conductivity, and if water diffuses into the core of golf ball, then it can be easily dried up, by warm it up, there-by regenerating and reinvigorating the ball. Altogether, the reinforcement with modified graphene nanofillers will improve the toughness, resilience, damping ability and prevent cracking, and water diffusion.

It was shown that reinforcement of poly(methyl methacrylate), PMMA, with 0.5 wt% of graphene nanosheets increased the glass transition temperature and storage modulus of PMMA from 119˚C to 131˚C and 1.29 to 2.0 GPa, respectively [8]. We propose to extend this discovery to golf ball technology by studying the reinforcement of Surlyn with modified graphene nanosheets of up to 5% of graphene. Graphene will be modified with polyaniline copolymer which is a hydrophobic material. The improvements that will be gained in this project will be in the transport, physical, mechanical properties and impact resistance. Drying the golf ball fabricated with conductive nanocomposite system will be more effective in preventing water ingress into the core of golf ball and allow proper drying of wet balls. In addition, our expectations are that both PZnMAA and crosslinked polyurethane rubber reinforced with modified graphene will result in a substantial increase in both storage modulus and impact resistance while maintaining highest damping ability over a wide range of temperature, frequencies and time scale.

PROPOSED RESEARCH PLAN

The technical research plan will begin with the reinforcement of PMAA matrix (golf ball-skin) by in-situ polymerization. Dispersion of graphene by In-situ polymerization will allow uniform dispersion of graphene in the matrix. Poly(methacrylic acid) will then be converted to poly(zinc methacrylic acid) by reacting graphene/PMAA suspension with zinc hydroxide followed by drying at 100°C [9]. Graphene/PZnMAA composite will be prepared by solution casting in silicon or Teflon molds or by extrusion.

INSTRUMENTAL TECHNIQUES

The techniques that would be used to study these nanocomposites include Wide Angle X-Ray Scattering, Raman Spectroscopy, Dynamic Mechanical Spectrometry, and Izod Impact Strength Testing. In-situ polymerization will be used to produce uniform dispersion of graphene in a PZnMAA matrix to form a PZnMAA/graphene nanocomposite. Wide Angle X-Ray Scattering will be used to study the structure of graphene in the nanocomposite to determine if graphene is intercalated or exfoliated or in other words if graphene is properly dispersed into the matrix polymer. In this study, we prefer graphene to be exfoliated. Exfoliated graphene will be shown in for X-Ray Diffraction testing to be randomly distribution in the matrix. Randomly distributed graphene will constitute a better reinforcement due to its higher ability to toughen the matrix material. X-Ray diffraction tests will be carried out by using a copper K-α_1 radiation at a wavelength of 1.54 angstroms. The structure of graphene in the nanocomposites, will be determined by using Raman Spectroscopy. The ratio of the intensity changes in the graphite G-band to the amorphous carbon D-band will be used to estimate the exfoliation of graphene. The impact resistance and damping ability of the composites will be studied by using Izod impact tester and Dynamic Mechanical Spectrometry, respectively, as a function of composition, temperature and frequency.

CONCLUSION

The proposed research focuses on the development of a new synthetic material constituted of graphene nanofillers and PZnMAA in order to improve the overall performance of golf ball under sever hot-wet conditions. The performance of the golf ball drops dramatically in cold and wet weather conditions and winter season because a disconnection between the skin and core of golf ball materials. However, reinforcement of graphene nanosheets modified with a hydrophobic material will improve physical and mechanical properties of the golf ball materials, and improve golf ball performance.

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