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Research on tensile strength and thermal analysis of graphene based polymer nanocomposite for food packaging

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Abstract

Polyethylene terephthalate (PET) is widely used for packaging due to its superior strength and stiffness, excellent dimensional stability, outstanding chemical and heat resistance. In this project intends to improve the mechanical, thermal and permeability of PET by adding graphene. PET/Graphene blend have been prepared by melt blending process using a co-rotating twin-screw micro compounder (X pore 15, Netherlands) attached with a mini injection molder. The processing temperature has been kept as 240, 260 and 270 °C for the three successive zones of the extruder with a screw speed of 40 rpm (acceleration rate: 50 rpm). Injection molding parameters were fixed as mold temperature at 120 °C, melt temperature at 245 °C Injection time as 4 min and injection pressure 10 bar. The aim of the present work is to study the Mechanical properties and thermal properties of PET/Graphene Nano composites.

Keywords: Graphene, nanocomposite, polyethylene terephthalate (PET)

Introduction

Polyethylene terephthalate (PET) is a widely used thermo plastic polymer. The addition of small amounts of nano fillers into a polymer matrix has proven an efficient method of improving the properties of the neat polymer. In the current project PET and PET nanocomposites reinforced with exfoliated graphene layers were prepared by melt compounding. Studies on relationships between orientation, crystallinity, permeability and mechanical properties of PET date back to as early as 1960s. They reveal that mechanical and transport properties of PET are enhanced by these orientation processes that lead to strain-induced crystallinity, preferred orientation of the chains and densification (reduction in free volume) in pure PET or its blends, which decrease permeability and increase strength of the material in the direction of stretch.

Polyester (PET) plays an important role in the packaging industry. Annual consumption of PET for beverage bottles is more than 1000×10^4 t all over the world, and its production and consumption is still increasing by 10% to 19% every year [Song B. *et. al.*, (2011); Zhang Y *et. al.*, (2006)]^[5, 10].

Over the past several years, modifications in polymers, glass, and paper packaging materials have made it possible to store, protect, and preserve food from spoiling and damage (Apendini 2002)^[1]. Though current methods for food packaging and storage are efficient, most are petroleum-based, synthetic materials that provide minimal barrier properties and mechanical support (Moosheimer 1999, Vergnaud 1998)^[7, 4]. The food packaging industry comprises almost a fifth of the net revenue of the plastic industry with the use of polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) as the main components of common food packaging plastics. Each food packaging plastic is used in a certain way due to their unique properties. A plastic such as PET has very good tensile and yield strength properties as well as being transparent after processing but melts very easily, making it ideal for cold beverages which need a strong material to contain the liquid while preventing chemical interactions (Girija 2005)^[2].

Consumption of food is one of the basic needs for human beings and its quality and safety is essential for leading a healthy life. Owing to the ever-increasing globalization of markets, foods being processed, distributed, and consumed in the same locality where they are produced are becoming less common.

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This worldwide integration of the food supply chain requires new approaches and systems for assuring food safety and quality since, during harvesting, handling, processing, and storage, food quality is compromised due to various biotic and abiotic factors. Therefore, it is important to monitor routinely the quality and safety of foods at different points in the supply chain. During the past decade or so, biosensors have been developed for detecting the presence of various deleterious analytes in foods. The sensitivity of biosensors has been significantly increased through the use of nano materials. Graphene-based nanomaterials have many unique and extraordinary properties, which make them ideally suitable for use in biosensors and other devices and techniques used in food quality analysis. These properties include high conductivity, mechanical flexibility, amenability for versatile surface functionalization, ultrahigh surface area, biocompatibility, and so on. (Sundramoorthy *et. al.*, 2018)^[6] However, increased use of engineered nanomaterials in the food industry has also raised concerns regarding their potential toxicity and impact on human health. Graphene is as a new sorbent in extraction (e.g., cocaine, adenosine, sulfonamide antibiotics, carbamate pesticides, pyrethroid pesticides, phenols, methyl parathion, squalene, and chlorophenols) from environmental, biological and food samples (Z. Huang *et. al.*, 2012)^[9].

Materials and methods

Natural flake graphite has been purchased from Sigma Aldrich (USA). Sulfuric acid, hydrochloric acid, ethanol, hydrogen peroxide and potassium Hydroxide (KOH) were purchased from MERCK, India Ltd. Potassium permanganate (oxidizing agent) and Hydroiodic acid (HI) (reducing agent) have been purchased from Sigma Aldrich (USA). All conventional chemicals were of analytical grade and were used without further purification. Ultra-pure water (18 MΩ cm) was used throughout the experiments.

Preparation of reduced graphene oxide (rGO)

In this work, we prepared mildly oxidized grapheneoxide (MOGO) by following procedure which is based on modified Hummers method (Hummers, W. S. 1958)^[3] involving a single chemical exfoliation of graphite powders within 4 h. The MOGO showed both excellent dispersibility in water (1 mg mL⁻¹) and high graphitic crystallinity. Chemical reduction of GO by HI acid was carried out through the procedures reported by Cheng and co-workers. Briefly, GO powder was prepared by vacuum filtration of GO dispersion through a membrane filter. Then the GO Powder was immersed into HI acid (55%) and the reaction system was kept at 100°C for 1 h. The obtained reduced graphene oxide (r-GO) was washed with ethanol and acetone and dried at room temperature. The electrical conductivity of reduced graphene oxide (r-GO) was measured to be 424 Scm⁻¹. The significantly improved electrical property of r-GO is attributed to its low degree of oxidation and low-defect structure.

Preparation of PET/Graphene blend and its composites

Prior to mixing, PET and Graphene were respectively dried in vacuum at 120 °C and 200 °C for 4hrs. 0%, .5%, 1%, 1.5%, 3%, 5%, And 10%wt percentage of graphene were prepared in a co-rotating twin screw micro- compounder X – Plore 15mL DSM Netherland and a screw speed of 40RPM. The mixing was carried out at a temperature of 270 °C and the specimen were injection molded into ASTM D-638 Type I tensile bars and ASTM D-25606 impact bars using an Proface

injection machine, with a maximum pressure of 10bar. Tensile properties of various compositions of PET-graphene nanocomposites were determined.

Mechanical Testing

In order to characterize the mechanical properties of the test samples, tensile, flexural and impact tests were performed. All the tests were done at ambient temperature. At least, seven test specimens were used in each type of tests. The standard deviations for all the tests were calculated and the error bars are shown in the graphs. The tensile tests were performed two times with new test samples, because tensile test results of first production batch samples had a lot of fluctuation. However, tensile tests values of the second production batch also fluctuated. The big differences between the values can be attributed to several reasons and these will be explained in the following paragraphs.

Tensile Testing

Tensile tests were performed according to ASTM D 638-03 standard (Standard Test methods for Tensile Properties of Plastics). Tensile properties were obtained with a tensile testing machine Instron 3382, using a test speed of 1 mm/min. The test specimens were prepared as Type I dimensions specified in ASTM D 638-03. Test specimen of Type I dimensions are suitable for the hard materials as epoxy and its nanocomposites. Shape of the test specimens and dimensions are given in Figure. Tests were conducted at ambient temperature. As a result of the tests; tensile strength, strain at break and Young's modulus data were obtained.

Instrumentation

Tensile testing machine applies the force to a specimen and measures the corresponding extension. In the present study Universal testing machine equipped with a constant rate of cross head movement, containing a stationary and a movable member, with a variable speed control is employed. The grips for holding the test specimen are self-aligning and move freely so as to permit the coincidence of the long axis of the test specimen with the direction of applied pull, through the center line of the grip assembly. The specimens are aligned perfectly so as to prevent slippage during the test. The straining of the specimen controls the test and the resulting force is measured. The drive system imparts uniform controlled velocity to the movable member with respect to the stationary member. The strain is accurately measured with the extensometer attached to the equipment.

Thermo-Gravimetric Analysis (TGA)

TG/DTA is a simultaneous technique that determines the weight change of a sample (TG) and measures the change in temperature between a sample and the reference as a function of temperature and/or time (DTA). Thermo gravimetric analysis (TGA) measures the mass change in a sample as a function of temperature or time. The technique provides the following valuable information on materials:

- Thermal stabilities.
- Oxidative stabilities.
- Compositional analysis.
- Moisture and volatiles content.
- Effect of reactive atmospheres on materials.
- Decomposition kinetics.
- Estimation of product lifetimes.

TGA has proven to be a useful and efficient technique of the estimation of lifetimes of polymers. Lifetime's estimations are useful in the development or selection of polymers for different applications where long-term usage is essential. The determination of lifetimes requires some form of accelerated aging. Traditional means of estimated polymer lifetimes, such as oven aging studies, are very time consuming, requiring weeks or even months of exposure.

The most TGAs are set up to scan temperature. Monitoring weight while scanning temperature will give useful results, but it must be realized that if the degradation is slow, the polymer will appear to survive to higher temperatures than it would actually survive under long-term exposure. In other words, the results will also be very sensitive to rate. The sensitivity is large because degradation rates may be slow when compared to typical scanning rates such as 10-20 °C/min. Coupling the by-products of a TGA experiment or the degradation products from the polymer to other instruments such as mass spectrometer, infrared spectrometry, gas chromatography, etc., can be useful in studying the mechanisms of polymer degradation.

The TGA kinetics approach uses the well-known variable heating method developed by Flynn and Wall. The kinetics approach starts with the following general expression:

$$da/dt = A \exp(-E/RT) (1-a)^n$$

In this equation, da/dt is the rate of mass loss, a is the fraction of material reacted, n is the reaction order, E is the Arrhenius activation energy (J/mole), T is the temperature (K), R is a

constant (8.314 J/mole K) and A is the pre-exponential factor (sec⁻¹). Under the application of a constant heating rate, f , and assuming a first order reaction ($n = 1$), the rate expression becomes:

$$da/(1-a) = \{A/f\} \exp(-E/RT) dt$$

With the TGA decomposition kinetics approach, the sample is heated at several different heating rates ranging between 40 and 1°C/min.

Results and Discussion

Tensile strength

Tensile strength of PET/ Graphene nano composite was observed to be greatly increased, ie, the tensile strength of PET+0.5wt%, PET+1wt%, PET+1.5wt %, PET +5wt% and PET+10wt% are 39.57MPa, 43.67MPa, 38.63 MPa, 38.50MPa, 37.22MPa respectively which are 70.8%, 88.5%, 66.7%, 66.2%, and 60.6% respectively higher than that of virgin PET with 23.16MPa. It was observed that tensile modulus was not changed very much but decreased slightly to a maximum of 9% for PET+0.5wt% and decreased gradually upto 5% for PET+5wt% and for PET+10% it was 4% increased with comparison to that of virgin PET. And there is very negligible change in strain percentage and are almost same. The increases in tensile strength must be caused by very high stiffness of the filler & strong interaction between the polymer & filler due to the large interfacial surface area between nanoparticles.

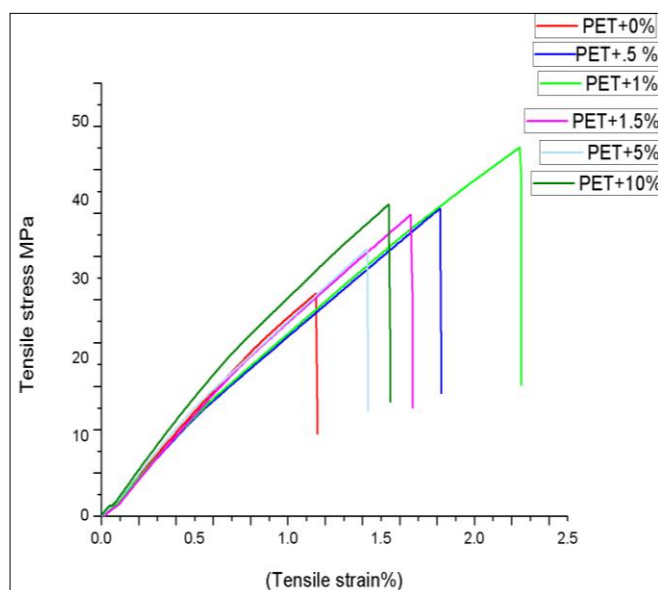


Fig 1: Tensile strength of PET

Thermal Analysis

Thermo gravimetric analysis (TGA) was performed to obtain information on thermal stability of the virgin PET, PET/Graphene Nano composite in nitrogen atmosphere. In the below table 1 shows the TGA of the composite. The thermal degradation of the composite occurs in two stage. In first stage, the rate of degradation of the PET virgin and the Composite various randomly. This is because of the presence of entrapped air molecules or condemnation in the sample. In second stage, PET virgin tends to degrade at faster rate compared with that of the composite. This shows that the thermal stability of the composite is improved by means of adding rGO filler to the PET matrix. The increase in thermal

stability of the polymer in the presence of filler is due to inhibition of molecular mobility of polymer chains. Also composite at 800°C have some amount of residual char due to presence of Graphene particles.

Table 1: Thermo gravimetric analysis (TGA) of the virgin PET, PET/Graphene

Sample	T _{int}	T _{10%}	T _{50%}	T _{D1}	T _{D2}	T _{END}
PET Virgin	365	408	452	370	500	630
PET+1%rGO	345	420	448	390	485	-
PET+3%rGO	357	446	460	402	530	-
PET+5%rGO	362	436	450	360	476	-

Conclusion

The chemistry of PET is simple and its intrinsic properties do not rely on the presence of additives. As PET can be used in many packaging forms ranging from wrapping films to bottles, it constitutes a valuable basic packaging material for a variety of foodstuffs. Within the field of chemical and biological sensors, graphene has already received a significant amount of attention. More recently, graphene-based hybrid materials are of particular interest owing to the unique and advantageous properties of each individual material and their synergism for use in sensing applications (Y. Shao, *et. al.*, 2010)^[8]. The thermal stability of the composite is improved by means of adding rGO filler to the PET matrix. The increase in thermal stability of the polymer in the presence of filler is due to inhibition of molecular mobility of polymer chains. The increases in tensile strength must be caused by very high stiffness of the filler & strong interaction between the polymer & filler due to the large interfacial surface area between nanoparticles. The future of food security may depend on the technological advancement of graphene-based nanosensors, integration of a graphene sensor in a food container, and generating breakthroughs in smart packaging solutions.

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