A NOVEL APPROACH TO LIGHT WEIGHT AND COST EFFECTIVE AUTOMOTIVE TRIM PRODUCTION BY INTEGRATION OF GRAPHENE FROM RECYCLED WASTE TIRE

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Abstract

In the present work, graphene-like nanoplatelets were produced from recycled carbon obtained by pyrolysis process of waste tire at mild conditions. New type of graphene was used as a reinforcing agent in thermoplastic compounds to produce light weight and cost effective automotive plastic interior and exterior trims. After the production and characterization of graphene samples, interior and exterior trims of vehicles were determined by Farplas Co. (one of the leading companies producing plastic trim parts for passenger and commercial vehicles) for the integration of graphene in compound formulation and lightening the components and decreasing the cost. The chosen polymers were compounded with graphene materials by thermokinetic mixing in a short time at different graphene/polymer ratios to attain better performance in mechanical and thermal properties of composites. High shear rates during compounding process provided high exfoliation and proper dispersion of graphene layers in polymer matrix. As a result, more reliable, value-added and long lasting composite production is possible by using graphene obtained from recycled carbon as a matrix reinforcement in polymeric materials.

Introduction and Background

Graphene has been attracting great interest due to its extraordinary electronic, thermal, and mechanical properties, resulting from its two-dimensional structure, and to its potential applications such as energy, wind turbines, construction, defense, automotive, aeronautics and aerospace applications. In last decades, there are numerous works about graphene synthesis and its applications in laboratory scale but mass production of graphene has still doubts and obstacles. These methods can be categorized into four main groups: micromechanical cleavage, chemical exfoliation, epitaxial growth on SiC and other substrates, and chemical vapor deposition technique. Among these methods, chemical vapor deposition (CVD) and epitaxial growth techniques are promising methods for the synthesis of large-area graphene whereas chemical exfoliation offers the production of graphene in large amounts.

With the appropriate surface treatments, single graphene sheets can be separated from the graphite material and the layer-to-layer distance can be extended. [1,2] One of the applicable methods is graphite oxidation to reduce the strong bonding between graphene sheets in graphite and obtain single layer graphene.[3] However, in this method, strong oxidizing agents (e.g. potassium permanganate) and strong acids (sulphuric acid and nitric acid) are used to exfoliate layers in graphitic structure and produce graphene oxide. This process carries risk and can be explosive as reaction volume increases. At this point, alternative approaches for graphene

production accelerate the commercialization of graphene based products.

Instead of graphite as a starting material for the synthesis of graphene, chars and carbonized chars produced from lignocellulosic biomass or oxygen rich precursors were used to obtain graphitic structures and these materials had structural similarities with thermally reduced graphene oxide.[4] In one of the recent studies, porous graphene-like nanosheets with a large surface area were synthesized by a simultaneous activation–graphitization route from renewable biomass waste coconut shell by using the graphitic catalyst precursor ($FeCl_3$) and activating agent ($ZnCl_2$).[5] In another work, a hybrid of graphene flakes and tubular shape nano carbon was produced from the pyrolysis of a salt milled solid carbon source under unoxidizing environment using a specific Fe relative catalyst.[6] Also, a coal slurry after grinding was pulverized with an electrolyte containing a proton carrier and a catalytic salt and electrolysis process led to the formation of gelatinous film on coal particles and then the reduction by H_2 caused the formation of graphene.[7] Therefore, these attempts open up a new direction in graphene synthesis and alternative production techniques have gained an attention in the literature. Furthermore, nanocomposites reinforced by graphene based materials even at very low loadings have shown great influence on mechanical performance, thermal, electrical conductivity and flame retardancy in comparison of unmodified polymers.[8,9]

Results and Discussions

Recycled carbon obtained by pyrolysis of waste tire contains impurities and has low carbon ratio. Therefore, this material could not find the right place in the market and not act as carbon black or active carbon. At this point, Nanografen Co. developed technology to remove the impurities, increase carbon content and decrease particle size and form graphene-like structures by applying chemical and heat treatments at mild conditions and this know-how is preserved as trade secret. Figure 1 summarizes Nanografen's technology.
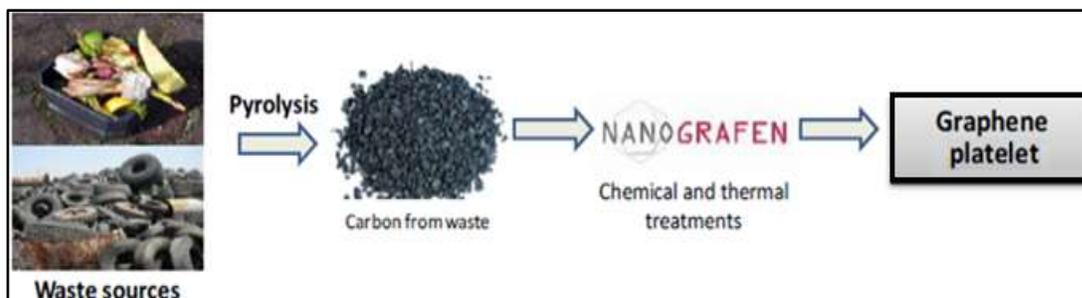

Figure 1: Graphene manufacturing process

Carbon/oxygen ratio has significant importance to control the dispersion of graphene layers in polymer matrix. Graphene from recycled carbon has approximately 8 wt% surface oxygen groups in its structure obtained from X-ray photoelectron spectroscopy. Surface oxygen functional groups carry significant importance to interact with polymer chains and provide better distribution of graphene layers. Raman spectroscopy allows a qualitative and quantitative characterization of graphene samples and determines the number of graphene layers. There are two main characteristic peaks in Raman spectrum of graphene from recycled carbon which are D band at around 1360 cm^{-1} and G band at 1580 cm^{-1} belonging to as seen in Figure 2a. Raman analysis confirmed the formation of graphene layer by applying recycling process. Figure 2b represents high resolution transmission electron microscope (TEM) image of graphene platelets. The plate size is about 50 nm. The results confirmed the formation of graphene-like structures by applying Nanografen's technology by using recycled carbon produced by the pyrolysis of waste tire.
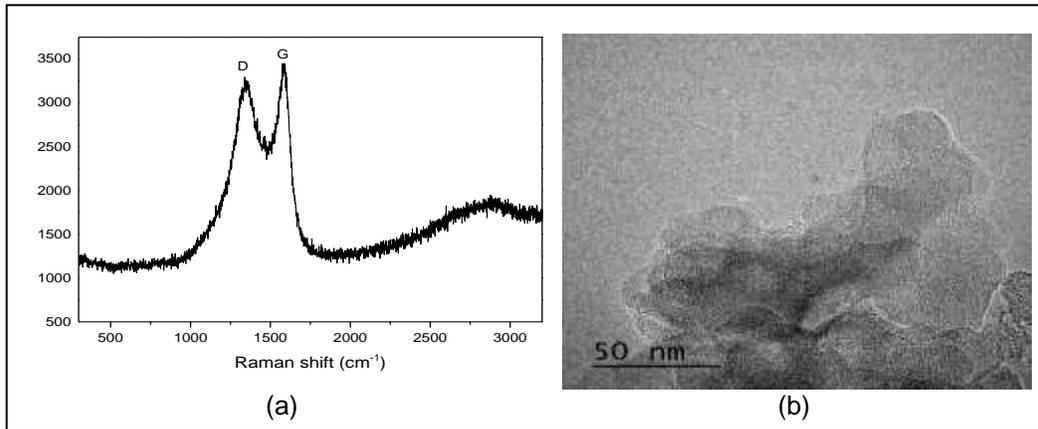
Figure 2: (a) Raman spectrum and (b) TEM image of graphene platelet produced recycled carbon

In composite production, graphene was mixed with polypropylene by custom-made Gelimat Thermokinetic Mixing/Compounding Machine at shear rate of 5000 rpm at 180°C for 45 seconds. Graphene loadings were adjusted as 1, 3 and 5 wt%. Dogbone shaped composite specimens for tensile tests were prepared by DSM injection moulding machine. Mechanical behaviors of specimens were investigated by ZWICK Proline 100 Universal Test Machine (UTM) with 10 kN load cell at constant cross-head speed of 20 mm/min.

Table 1 summarizes tensile test results of homopolymer and copolymer polypropylene (PP) composites by integrating graphene in the range of 1 to 5 wt%. It is seen from results that neat homo-PP possess higher modulus yield strength and strain at the breakage compared to copo-PP which is due to the higher crystallinity of homo-PP specimens.

Table I: Summary of tensile test results of graphene reinforced homo- and copo-PP composites

Specimens	Modulus [MPa]	Improvement (%)	Tensile Strength [MPa]	Yield Strength [MPa]	Tensile Strain at Break [%]
Neat Homo-PP	1240±38	----	40.6±0.07	27.3	790±3
PP-Homo-1wt%graphene	1470±70	18.5	39.8±0.56	28.9	730±33
PP-Homo-3wt%graphene	1580±75	27.4	36.4±1.01	30.9	620±22
PP-Homo-5wt%graphene	1870±3009	50.8	32.4±1.01	32	380±169
Neat Copo-PP	780±5	----	22.6±0.10	16.3	640±7
PP-Copo-1wt%graphene	785±10	0.6	20.5±1.72	18	520±74
PP-Copo-3wt%graphene	966±40	23.8	22±0.5	19.8	545±70
PP-Copo-5wt%graphene	1020±109	30.8	19.1±0.83	18.5	410±167

Flexural properties are key parameters for the evaluation of mechanical performance and understanding the interactions between matrix and reinforcement.[10] Two flexural properties indexes were obtained from mechanical tests: that is to say, flexural modulus as a parameter for the tendency of the composite material to bend, and flexural strength as a factor indicating the resistance of materials against the fracture. Table 2 shows the improvement percentages of flexural modulus and flexural strength of graphene reinforced homo- and copo-PP composites. The flexural test results showed that flexural strength and strength values of graphene reinforced composites are notably higher than those of neat homo-PP and copo-PP specimens. In addition, it is seen that both flexural modulus and strength values of both homo-PP and copo-PP composites by increasing graphene amount.

Table 2: Summary of flexural test results of graphene reinforced homo- and copo-PP composites

Specimens	Chord Modulus (0.5% - 1.0%) [MPa]	Improvement (%)	Flexural Strength [MPa]	Improvement (%)
Neat Homo-PP	1010±35	---	34.7±0.95	---
PP-Homo-1wt%graphene	1200±24	18.8	39.1±0.77	12.7
PP-Homo-3wt%graphene	1270±21	25.7	40.2±0.48	15.9
PP-Homo-5wt%graphene	1350±33	33.6	42.5±1.00	22.5
Neat Copo-PP	576±5	---	19.2±0.2	---
PP-Copo-1wt%graphene	670±34	16.3	21.7±0.87	13.0
PP-Copo-3wt%graphene	685±3	18.9	21.8±0.09	13.5
PP-Copo-5wt%graphene	760±17	31.9	23.2±0.41	20.8

Non-isothermal crystallization behavior of neat PP and the effect of exfoliated graphene loading on the crystallinity of PP composites were investigated at different cooling rates by Differential Scanning Calorimetry (DSC). Table 3 summarizes the changes in melting point and crystallization peak of composite specimens. In both homo- and copo-PP composites, melting temperature increased by the addition of graphene as well as crystallization temperature increased.

Table 3: Summary of DSC analysis of graphene reinforced homo- and copo-PP composites

Specimens	Melting point (ºC)	Crystallization peak (ºC)
Neat Homo-PP	163	113
PP-Homo-1wt%graphene	166	124
PP-Homo-3wt%graphene	166	127
PP-Homo-5wt%graphene	170	126
Neat Copo-PP	161	111
PP-Copo-1wt%graphene	164	118
PP-Copo-3wt%graphene	164	120
PP-Copo-5wt% graphene	164	121

A fractographic analysis was conducted to observe the effect of graphene on the cross sectional area of flexural test specimens. Figure 3 shows SEM images of fracture areas of flexural test specimens of homo-PP and 1 wt% graphene reinforced homo-PP composite after breaking in liquid nitrogen. SEM analysis showed that surface roughness of composite sample increased by the integration of graphene. Figure 4 represents SEM images of fracture areas of neat copo-PP and 1 wt% graphene based copo-PP composite specimens. As seen in Figure 4, porosity increased and pore size decreased down to 1 microns after the dispersion of graphene in copo-PP polymer matrix. This work will bring a new insight in mucell applications since graphene improves modulus and strength values and decrease the pore size due to its platelet structure.
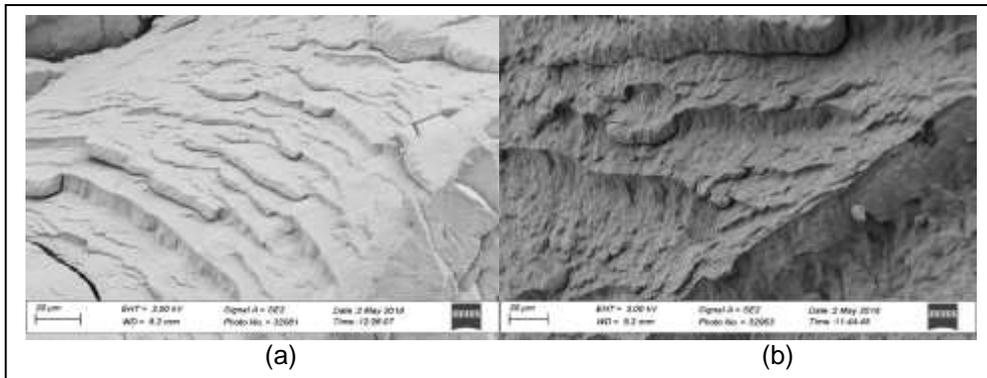
Figure 3: SEM images of fracture area of (a) homo-PP polymer and (b) 1 wt% graphene reinforced homo-PP composite specimens
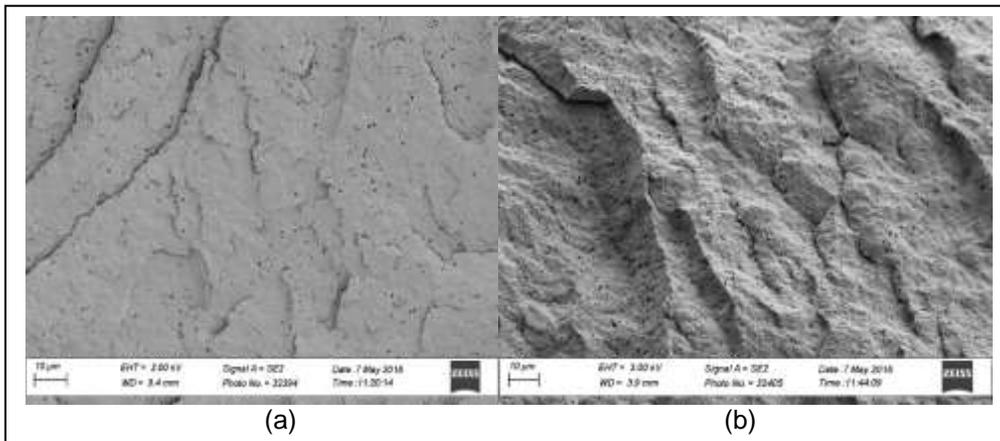

Figure 4: SEM images of fracture area of (a) copo-PP polymer and (b) 1 wt% graphene reinforced copo-PP composite specimens

Summary and Next Steps

In the present work, heat treatment process is used to synthesis graphene sheets from carbon-rich solid residues. At this point, Nanografen developed a technology and used recycled carbon to synthesize graphene. Nanografen's approach is

 ➢ Cost-down
 ➢ Large volume production capacity
 ➢ Robust, reliable, and fast processes
 ➢ Green recycling technique
 ➢ More reliable and long lasting graphene reinforced composite production
 ➢ Hinder graphene agglomeration.

With the proposed technology, the mechanical and thermal properties of the materials were improved and significant weight reduction was provided by the addition of graphene from recycled carbon as a reinforcement in matrix material at low loadings ranging from 1 to 5%. Also, crystallinity of polymer composites increased by adding graphene because graphene acts as nucleating agent. Furthermore, graphene has a significant influence on the porosity and this can be applicable in mucell applications. Consequently, Nanografen's corporation with Farplas Automotive Company accelerates the commercialization of graphene in commodity products and thus certification process of nanographene as an automotive grade material.

Acknowledgements

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