

Electrical profile of ultra violet (UV) curable renewable polymer graphite (PG) composites

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ABSTRACT

The electrical profiles of the renewable polymer graphite (PG) composites upon ultra violet (UV) curing were investigated. Renewable PG films were prepared by mixing with varying weight percent of graphite (with an increment of 5 wt. % of prepared graphite) up to 30 wt.% and crosslinker. Then, the composites solution was slip casted and cured upon stimulated UV irradiation (UV accelerated weathering tester) at different time exposure (up to 1000 hours) was applied. Small changes on the functional groups of the composites were observed due to UV exposure time by Fourier Transform Infrared Spectroscopy (FTIR). Suggesting that chemical crosslink and chain scissions occurred within renewable polymer graphite composites. Further electrical profile through two point probe and four point probe method recorded visibly fluctuating values for both resistivity and conductivity within its composites range. Proposed here that the removal of organic contaminants and weak materials form both renewable polymer and graphite particles through the UV curing may have an effect on the formation of conductive network stability.

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1. INTRODUCTION

One of the fastest growing methods of surface modification is that of radiation cures. This area is divided into several types: radical ultra violet (UV) cure systems, ionic cure systems, e-beam, plasma and laser treatments [1-4]. Uniformly, all these treatments lead to the breakage of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in certain cases creation of new chemical bonds [5, 6]. UV curing significantly relies on the required application properties with the chemistry chosen to achieve the performance requirements and meet the economical aspects of coating technology. Moreover, the UV curing is much better known for its 5E characteristics (efficient, enabling, economical, energy saving and environment friendly), indicates low energy consumption.

As for the composites film, the developed films possessed phase separation structures and the filler dispersed uniformly in the polymeric phase [7, 8]. The stratification caused by the related cure of the inorganic filler and organic phases from the surface of the film downward had gave rise to the column-like

inorganic configurations. Thus, this crosslinking process had indubitably improved the electrical, thermal, and mechanical properties in polymer composites [9–11]. Previous researchers described bipolar plates consisting of synthetic graphite and milled carbon fibers as conductive filler and epoxy as a polymer matrix [12]. Likewise, the highest electrical conductivity obtained is 69.8 S/cm for the in-plane conductivity and 50.34 S/cm for the through-plane conductivity for the composite containing 2 wt.% carbon fiber (CF) with 80 wt.% filler loading. This value is 30% greater than the electrical conductivity of a typical graphite/epoxy composite with 80 wt.% filler loading, which is 53 S/cm for the in-plane conductivity and 40 S/cm for the through-plane conductivity. Moreover, the critical electrical percolation threshold for the ternary conductive polymer composites was found to be more than 8 times lower than the single phase systems [13]. It was further observed that UV treatment on the graphite or its polymer composites also played a significant role in the performance of the polymer carbon based composites [14,15].

Particularly, our free-standing renewable polymer-graphite composites cured at room temperature have been disclosed [16,17]. In this study, for the first time, we show that electrical profile of renewable polymer-graphite composites can be modified by timed UV curing. The graphite particles were incorporated into renewable monomer and Methylene Diphenyl Diisocyanate (MDI) as crosslinker through slip casting method to formulate a UV curable film formulation; 250, 500, 750 and 1000 hours upon UV exposure. The composites obtained were characterized, analyzed and investigated. In particular, the electrical profile of the composites film was a focus.

2. RESEARCH METHOD

Free-standing of renewable polymer-graphite composites were prepared via several steps.

2.1. Preparation of graphite

The flake graphite (supplied by May & Baker Ltd.) is mix with acid sulfuric acid, H₂SO₄ and placed into a flask to undergo sonication at room temperature for 60 minutes. After the sonication, yellow solution presence indicating a high oxidation of graphite. The precipitate of graphite mixture was collected and washed to neutrality with water (confirmed via pH paper), dehydrated, and dried in an oven.

2.2. Synthesis of renewable monomer

In-house catalyst was prepared by 0.6 mL of distilled water and 1.26 mL hydrogen peroxide (30% w/w). The solution was heated at 50°C and stirred (for about 30 minutes). Then let it sit at room temperature and concentrated aqueous orthophosphoric acid (90 mg, 85% w/w) (1.2 mL) was poured in. On the other hand, vegetable cooking oil of 30 gm in weight was heated at 50 °C and the in-house catalyst prepared earlier was added, followed by 50 mL of water. Furthermore, Orthophosphoric acid (15 gm, 85 % w/w) and hydrogen peroxide (18 mL, 30 % w/w) were added dropwise to the mixture. The mixture was heated up to 90 °C and stirred for 6 hours until double layers of mixture were observable. This yielded the renewable monomer.

2.3. Preparation of ultraviolet curable renewable polymer-graphite composites

By mixing of vegetable cooking oil (VCO) based monomer with Methylene Diphenyl Diisocyanate (MDI) and acid treated graphite (with 5, 10, 15, 20, 25 and 30 wt %) [18], the mixture was casted into square container which is then pre-cured at standard room temperature for 1 hour to form gelation. Further cured using Accelerate UV Weatherometer (Chamber UV Lamp Tested Model HD-703, Haida International Equipment Co., LTD) upon various time exposures (250, 500, 750 and 1000 hours) [19].

2.4. Testing characterization

The resulting composites films were subjected to functional groups identification with respect to UV curing using Perkin Elmer Fourier Transform Infrared Spectroscopy (FTIR) in the range of 600–4000 cm⁻¹ with the resolution of 4 cm⁻¹ at room temperature. Further electrical profile was measured through Two point probe method (using Keithley 6517A electrometer) and Four point probe method (using Keithley 2400 source/meter, Pro4, Lucas Labs) as in Figure 1 and equation (1) and (2). Where *w* is width, *L* is electrode distance, *t* is film thickness, *R* is the resistances determined from the slopes of the current–voltage (*I-V*) characteristics, ρ is electrical resistivity, *R_s* is sheet resistance in Ω and σ , the conductivity.

$$\rho = \sigma^{-1} R t (w/L) \quad (1)$$

$$\rho = R_s \cdot t \quad (2)$$

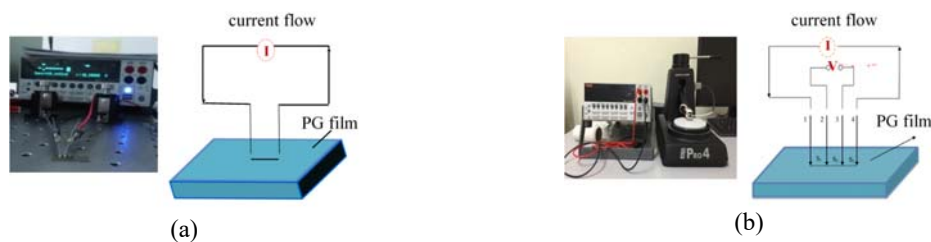


Figure 1. Schematic diagram of (a) Two-point probe method (b) Four-point probe method for I-V measurement.

3. RESULTS AND DISCUSSION

It is quite difficult to establish the correlations between the surface treatment and the electrical conductivity of composites. However, as aforementioned, the materials behavior was mainly attributed to a scattering effect of the UV curing irradiation due to the presence of the graphite particles in the polymer matrix. Therefore, throughout this section, the bulk electrical resistivity and conductivity of renewable polymer graphite composites with response to UV curing irradiation will be disclosed via four point probe and two point probe measurement.

3.1. Effects of UV curing on functional groups of renewable polymer graphite

The spectroscopy through FTIR in Figure 2 (a)- Figure 2 (g) confirmed the fingerprint of UV curable renewable polymer graphite composites did not exhibit appreciable changes upon UV irradiation, specifically for the range of 1700- 4000 cm^{-1} region. At the left side of the graph reveals a stretching of the N-H group, which strongly suggest the formation of polyuria. Moving further towards right on the graph, all typical absorbance peaks of renewable polymer, such those at 2800-3100 cm^{-1} (CH_2 and CH_3), 1724 cm^{-1} ($\text{C}=\text{O}$), 1030-1230 cm^{-1} ($\text{C}-\text{N}$), and 1110 cm^{-1} ($\text{C}-\text{O}-\text{C}$), indicate the existence of urethane in synthesized renewable polymer graphite composites. Moreover, the stretching vibration band around 2270 cm^{-1} was diminished due to the reaction of isocyanate group during polymerization which confirmed the completion of process under UV curing [20].

On the other hand, existence of peaks at 1733 cm^{-1} , 1605 cm^{-1} ($\text{C}=\text{O}$), 1540 cm^{-1} ($\text{C}=\text{C}$), and 1065 cm^{-1} ($\text{C}-\text{O}$) provide the evidence of interactions between carbonyl and hydroxyl groups from graphite particles and renewable polymer moieties. However, there are significant changes at these peaks were observed for all resulting films that subjected to UV curing. Having said that polymer composites The renewable polymer itself, Figure 2 (a) shows plateau band due to UV curing which indicate that the polymeric materials experienced chain scissions/ crosslinking at it soft segment. This could be suggested that the composites matrix undergo radical initiation at 0 to 250 hours, crosslinking above 250 hours, propagation and crosslinking at 500 and 750 hours, and chain scission beyond 1000 hours of the soft segment radical upon UV curing exposure.

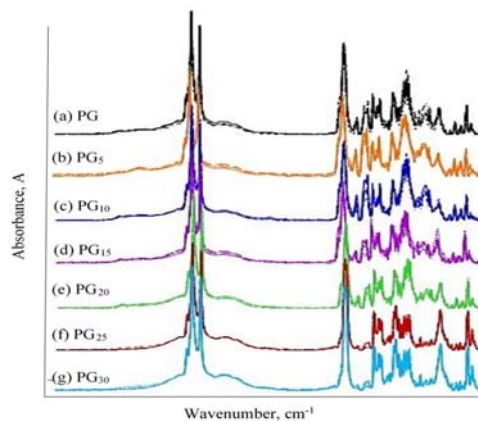


Figure 2. FTIR spectra of UV curable renewable polymer graphite composites.

Eventhough with addition of graphite particles into the matrix, Figure 2 (b), (c), (d), (e), (f) and (g), the same patterned were also observed in all resulting composites since the system is dominantly renewable polymer based. Nevertheless, as the graphite loading increased, smaller ratio of peaks beyond 1300 cm^{-1} - 1100 cm^{-1} was observed which show the limited ester formation in the composites. One possible reason is that the graphite particles absorbs the incident radiation, instead of the polyurethane leading to reduced ester formation [21]

3.2. Effects of UV curing on electrical profile of renewable polymer graphite

The electrical properties of UV curable renewable polymer graphite composites such as volume resistivity, sheet resistant and its average values were measured by fourpoint probe measurement and illustrated through Figure 3 (a)-(g). It is observed that all resulting film shows an improvement, although these decreases in resistivity appear to be marginal in accounting for the significant enhancement in electrical conductivity.

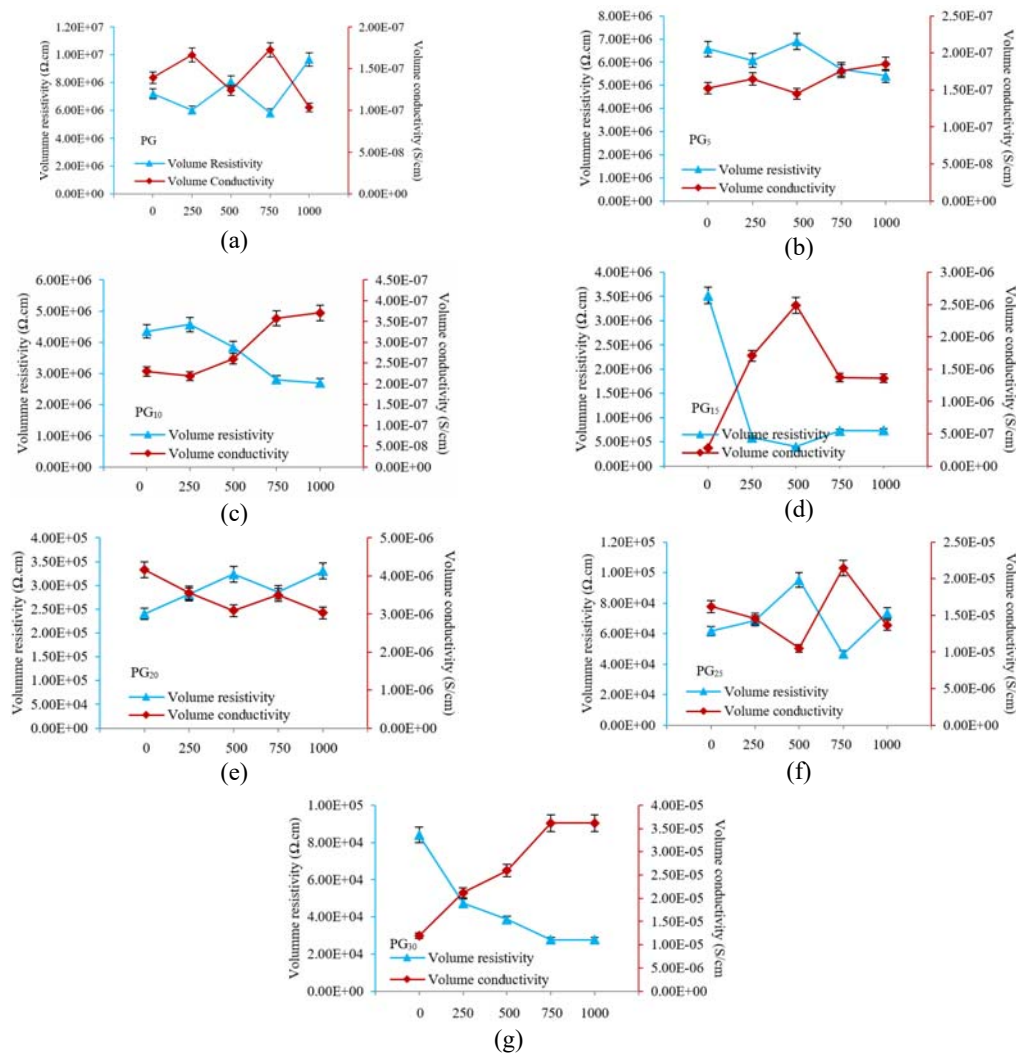


Figure 3. Electrical profile of UV curable renewable polymer graphite composites (a) PG, (b) PG₅, (c) PG₁₀, (d) PG₁₅, (e) PG₂₀, (f) PG₂₅ and (g) PG₃₀ by four point probe method

The percolation threshold was found at PG₂₀ composites onward which were noticed identical with regards of UV curing on polymer matrix. Practically, each resistivity and conductivity value visibly fluctuating within its composites range which one can say it is independent to each other. This observation is

similar with graphite nanoplatelets/ epoxy resin composites which subjected to UV treatment for 20 minutes [22]. It is recorded that the highest electrical conductivity of renewable polymer graphite composites by four point probe method was 1.19×10^{-5} at PG₃₀ composites. Therefore, this research suggested that the degree of structural changes varies with UV curing time.

The comparative observations of the above graphs (resistivity and conductivity were simplified as in Figure 4. It is found that the decreasing values of resistivity and increasing conductivity of each composite shows the response of graphite particles to UV curing irradiation. It is recorded that the highest electrical conductivity of renewable polymer graphite composites by four point probe method was 1.19×10^{-5} at PG₃₀ composites.

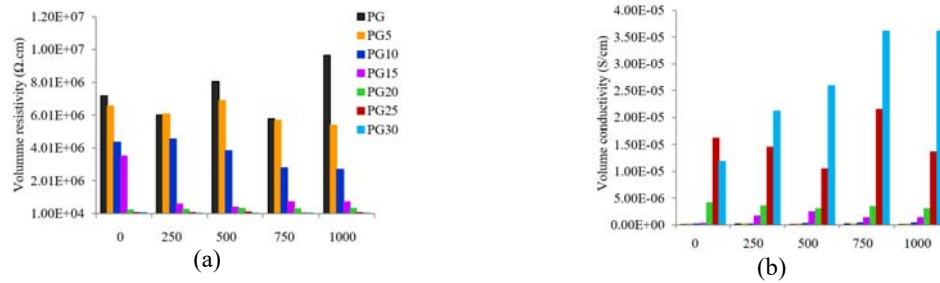


Figure 4. Electrical (a) resistivity and (b) conductivity of UV curable renewable polymer graphite composites correspond to UV curing time respectively.

Meanwhile, in Figure 5 shows I-V characterization of renewable polymer graphite composites via two point probe method. Followed the theoretical values, the volume resistivity decrease while the conductivity of the composite increase. Even upon UV curing irradiation, renewable polymer composites with lower graphite particles still does not gives any value to resistivity, results in no conductivity recorded.

As mentioned above, UV cured polymer composites are known to exhibit superior mechanical properties due to their high crosslink density. However, this limitation can be related to the presence of OH and COOH functional groups content in each consecutive matrix with addition of graphite which evident changes in FTIR spectra. The favoring PG₂₀ composites where the percolation threshold occur shows smaller resistivity values with increasing filler content lead to the conducting pathways. The electrical conductivity of 5.0×10^{-5} S/cm, 1.0×10^{-4} S/cm and 1.5×10^{-4} S/cm were calculated for PG₂₀, PG₂₅ and PG₃₀ composites respectively. Nonetheless, as the graphite particles increase, the value of electrical conductivity shall be stagnant and achieved the conductivity of graphite its self. The chemical interactions between the functional groups present on the graphite surface and renewable polymer also contributed to improving electrical conductivity by eliminating unbonded gaps or micro-voids that have high resistivity, detrimental to the formation of the conductive network with a very low volume of conductive reinforcements [23]. In this regard, it is suggested that different measurement techniques should be implied to validate the conduction composites system [24, 25].

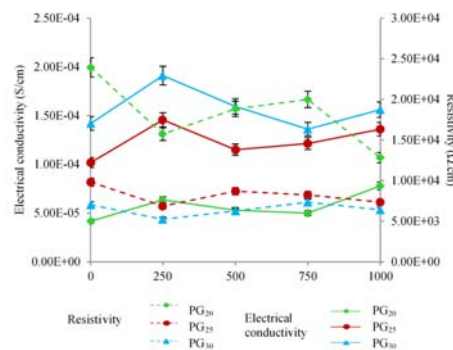


Figure 5. Electrical profile of UV curable renewable polymer graphite composites by two point probe method

4. CONCLUSION

The UV curable renewable polymer graphite was successfully fabricated. During prolonged UV curing irradiation, two competing process are expected to take place: (1) the addition and rearrangement of functional groups on graphite particles and renewable polymer resulting in increase of the materials properties and (2) deterioration of graphite particles and renewable polymer leading to quenching. These phenomena were responsible for the fluctuating values in functionality as well as the electrical profiles of the renewable polymer graphite composites.

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