

# Effect of Recyclate PTFE/GF Laminate Incorporation on the Dielectric and Mechanical Properties of PTFE/GF Composites Using a Novel Manufacturing Process

Zhoutian Xi, Oana R. Ghita, Ken E. Evans

College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK

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**ABSTRACT:** This study examines the recycling of polytetrafluoroethylene (PTFE)/glass fiber (GF) printed circuit boards (PCB) laminates through mechanical grinding and the re-manufacture of new composites incorporating PTFE/GF recyclate using sintering processes with and without pressure (SWOP and SWP). The PTFE/GF recyclate was tested for mechanical and dielectric performance. Experimental data were fitted to modified Lichtenecker and Effective-Medium Theory (EMT) theoretical equations to estimate the dielectric constant of PTFE/GF recyclate subsheets for

further use in new PTFE/GF laminates. It was found that the experimental values were inside of the Wiener bounds and fitted well the two theories for both manufacturing methods proposed. Overall, the results showed that PTFE/GF recyclate could be used as replacement for virgin PTFE/GF when incorporated in specific concentrations. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2467–2477, 2011

**Key words:** recycling; PTFE/GF reuse; dielectric; mechanical

## INTRODUCTION

Polytetrafluoroethylene (PTFE) and glass-filled PTFE are known to exhibit unique properties, such as excellent dielectric performance, low friction, excellent chemical resistance, and high temperature stability.<sup>1–3</sup> In addition, glass-filled PTFE has been shown to have improved performance in wear and creep and are used widely in engineering applications for gaskets, bearings, piston rings, and radio frequency PCBs.<sup>3–5</sup>

PTFE/glass fiber (GF) composite is extensively used for manufacturing of PTFE laminates, which are further utilized in PTFE PCBs for broadcast and cellular base-station antennae. PTFE/GF laminate consists of several layers of PTFE films and PTFE coated glass fabric, with a copper foil attached to the outer surfaces. PTFE PCBs are then produced by etching away the unwanted copper to form the required circuit.

The majority of printed circuit board laminates are made of epoxy, polyimide, and cyanate ester. These PCBs are commonly found in consumer electronics. Two studies<sup>6,7</sup> have reviewed the recycling process for these types of PCB. The conventional recycling process for these materials involves three stages: pulverizing/grinding, separation, and refining/recovering. After

the disassembling process has removed all the reusable and hazardous components, the PCB wastes are normally pulverized or ground to fine powders, with the aim of refining and recovering the precious metals' fraction. Unlike the conventional PCB recycling process, PTFE PCBs contain very little precious metal and therefore have received no attention in terms of recycling. However, considering that PTFE itself is an expensive engineering material, it is crucial for the PTFE PCB manufacturers to address the recycling issue. Current analysis of PTFE PCB waste stream has revealed that approximately 25 wt % waste is currently generated during the PTFE/GF laminate and PTFE PCB manufacturing processes (Trackwise internal report). In addition, recycling legislation (Waste electrical and electronic equipment directive 2008/35/EC), shortage of landfill capacity, and cost of disposal are increasing the pressure for development of suitable recycling approaches.

Although the recycling and reuse of PTFE/GF laminates and PTFE-PCBs seems relatively straight forward, the reuse of PTFE cannot be easily achieved. PTFE exhibits a high viscosity during melting ( $10^{11}$ – $10^{12}$  poise at 380°C)<sup>3</sup> due to its very high molecular weight ( $10^6$ – $10^7$ ).<sup>3</sup> As a result, melted PTFE is in a gel state and cannot flow easily like other thermoplastics. For this reason, PTFE cannot be processed using the conventional melting process methods, such as injection molding, or extrusion. Currently, PTFE is manufactured by a unique preforming–sintering approach. PTFE is firstly compressed to a very dense “preform” at ambient temperature in a mold. After

Correspondence to: O. R. Ghita (O.Ghita@exeter.ac.uk).

removal from the mold, the dense "preform" is sintered between 360 and 380°C to form a homogenous and strong structure.

The direct use of mechanically ground PTFE as a feedstock to replace the virgin PTFE may lead to reduced mechanical properties. Virgin PTFE is manufactured by polymerization of tetrafluoroethylene (TFE), which exhibits an extended chain crystal structure and a high melting temperature (342°C). In comparison with virgin material, the recycled PTFE is sintered PTFE, which exhibits a folded-chain crystal structure and a relatively low melting temperature (327°C). The recycled PTFE exhibits a harder surface due to its folded-chain crystal structure, thus a "preform" with more interparticle voids will be produced in the presence of recycled PTFE, which might lead to an inhomogeneous structure and reduced mechanical properties. Furthermore, the PTFE/GF laminate recyclate contains GFs, which are harder to compress and bond to PTFE matrix. As a result, the presence of glass will introduce even more "voids" in the preform. Due to these difficulties, many manufacturers avoid the reuse of mechanically ground PTFE and glass-filled PTFE recyclate as a feedstock to replace the virgin PTFE. In addition, PTFE exhibits a large volume expansion (approximately 10%) during melting. The different melting temperatures will lead to different expansion ratios at 327°C, which might induce internal stress in the sintered part and produce minor crack.

However, few studies have addressed PTFE recycling by breaking down the PTFE molecular chains to produce PTFE micropowder, i.e., low molecular weight PTFE. Hartwimmer<sup>8</sup> developed a pyrolysis process to break the PTFE chains by heating the PTFE to 700°C under high pressure in an inert gas, like nitrogen. Dillon<sup>9</sup> tried to recycle PTFE waste using electron beam irradiation to break down the PTFE molecular chains. The PTFE micropowders produced using these methods can be added to plastics, inks, oils, lubricants, and coatings to impart PTFE properties such as reduced friction. These methods showed great success, and nowadays a large quantity of scrap PTFE from industry is converted into micropowder.<sup>3</sup>

Although the recycling of PTFE has proved to be successful, only one study<sup>10</sup> has tried to recycle PTFE/GF composite. Lehmann and Hupfer<sup>10</sup> used 200 kGy electron beam irradiation to break down the PTFE molecular chains and yield glass-filled PTFE micropowders. The glass-filled PTFE micropowder was extruded together with Polyamide 6. It is reported that the yield compound exhibited excellent wear resistance and a low coefficient of friction. Although it showed some degree of success, this recycling process will not be easily accepted by industry due to the fact that it involves an expensive irradiation process.

The general conclusion of the foregoing work is that there is no current recycling and reuse technology available for PTFE PCBs. This paper will now describe a novel re-manufacturing, through mechanical recycling, process for PTFE PCB waste. The resulting recyclate PTFE/GF composites were investigated for dielectric and mechanical performance. It is well established that the dielectric properties of PTFE/GF composites is critical to be used in high frequency and electric packaging applications. Hence, it is important to predict the dielectric properties of the recycled PTFE/GF composites. However, the dielectric constant (Dk) of a composite not only depends on the dielectric constant of the matrix and the inclusion but also is affected by the size, shape, and orientation of the inclusion, the porosity, the interface between the matrix and inclusion, and the extent of filler dispersion. This makes the precise prediction of dielectric properties very difficult.

Several studies<sup>11–19</sup> have addressed the dielectric constant prediction of random heterogeneous mixtures, such as Clausius–Mossotti theory,<sup>12</sup> Jayasundere theory,<sup>13</sup> Poon–Shin theory,<sup>14</sup> Fricke theory,<sup>15,16</sup> Effective-Medium Theory (EMT),<sup>17</sup> Lichtenecker theory,<sup>18</sup> and modified Lichtenecker theory.<sup>19</sup> Clausius–Mossotti theory is one of the earliest studies that describes the simple situation of conducting spherical particulates uniformly dispersed in a dielectric medium. However, in reality, the inclusions are not always spherical and uniformly distributed, and the inclusion is surrounded by a mixture rather than by the component, when the concentration of the inclusion is high. In addition, this theory did not consider the shape and the orientation of the filler, and the interaction between the matrix and the filler. A number of studies were then carried out to derive better formulae by expanding the assumptions of the Clausius–Mossotti theory. The Fricke theory and EMT take the shape and the orientation of the inclusion into account. Jayasundere theory<sup>13</sup> and Poon–Shin theory<sup>14</sup> considers the interaction between the matrix and filler, whereas Lichtenecker theory<sup>18</sup> and modified Lichtenecker theory<sup>19</sup> consider the random inclusions that follow a statistical distribution. Among all these theories, modified Lichtenecker model<sup>18</sup> and EMT model<sup>17</sup> are the two theories that have gained the most support based on the experimental data. It was found that the dielectric constant of PTFE/ZnAl<sub>2</sub>O<sub>4</sub>-TiO<sub>2</sub>,<sup>20</sup> Barium strontium titanate and thermoplastic cyclic olefin copolymer,<sup>21</sup> and poly(methyl methacrylate) (PMMA) and BaTiO<sub>3</sub><sup>19</sup> mixtures could be precisely predicted using the modified Lichtenecker model. The EMT model<sup>17</sup> was also supported by several experimental data, such as PTFE/Sr<sub>2</sub>Ce<sub>2</sub>Ti<sub>5</sub>O<sub>16</sub>,<sup>22</sup> PTFE/TeO<sub>2</sub>,<sup>23</sup> and epoxy/silica mixtures.<sup>24</sup>

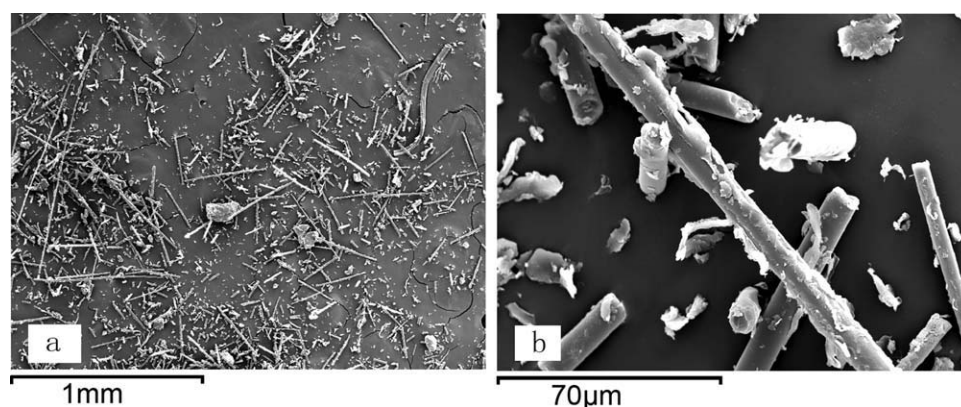


Figure 1 SEM photos of recycled PTFE/GF recyclate.

## MATERIAL PREPARATION AND EXPERIMENTAL METHODS

### Recyclate preparation

The PTFE PCB manufacturing waste used in this study was supplied by Trackwise (Tewkesbury, UK).<sup>25</sup> Manufacturing waste with no copper circuits was selected and was initially pregranulated using a hammer mill to reduce size to approximately 2–3 mm. The pregranulated waste was then finely ground in a cryogenic Microtec turbomill.<sup>26</sup> This turbomill is a mechanical mill with an adjustable grinding gap, using high speed particle turbulence. Liquid nitrogen was introduced for cooling during the milling process, and thus the PTFE become brittle and easy to grind to fine particles.

### Recyclate analysis

Scanning electron microscope of recyclate PTFE/GF (R-PTFE/GF)

Figure 1 shows an scanning electron microscope (SEM) image of the PTFE/GF laminate recyclate. The ground powder was examined using a Hitachi S-3200N SEM. All samples were coated with a 4 nm layer of gold to reduce surface charging, and sec-

ondary electron images were taken with an accelerating voltage of 25 keV. It can be seen from Figure 1(a) that the laminate waste material was fully ground to fine powder using the cryogenic grinding. Figure 1(b) shows that some of the GFs in the recyclate are still coated with PTFE. The PTFE left on the GFs is thought to help the interfacial bonding between the glass and PTFE during the next sintering stage.

### Particle/fiber size analysis of R-PTFE/GF

As can be seen in Figure 1, the granulated PTFE/GF exists in a wide range of shapes. Some of the recyclate was ground to such a small size that it can be considered as a particle, whereas some of it had high aspect ratio as it retained the original fiber shape. For this reason, particle and fiber size analysis was carried out and is presented in Figures 2 and 3. Particle size analysis was performed using a Mastersizer 2000<sup>27</sup> particle size analyzer. Water was used as the dispersing agent. Figure 2 shows the particle size distribution after cryogenic grinding. Eighty-three percent powder with a particle size <100 µm was achieved. The particle size distribution

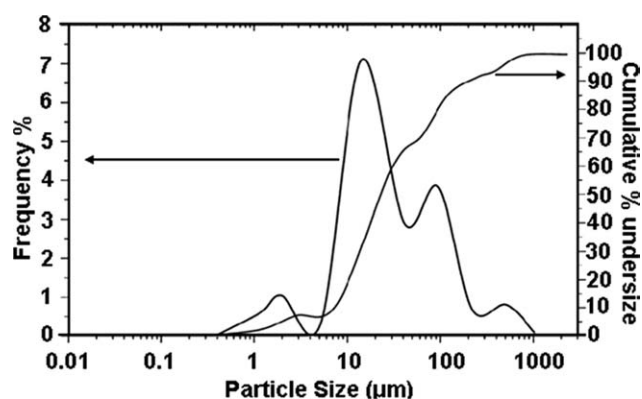


Figure 2 Particle size distribution of PTFE/GF recyclate.

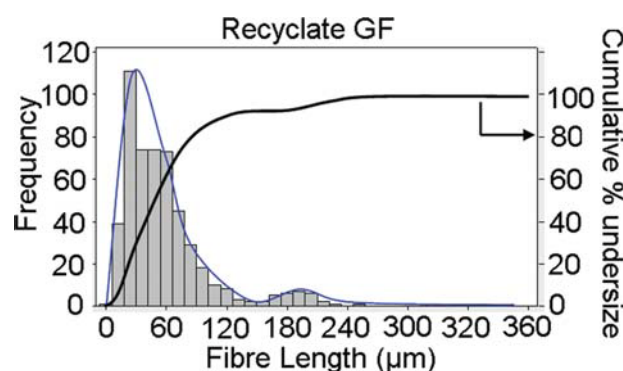
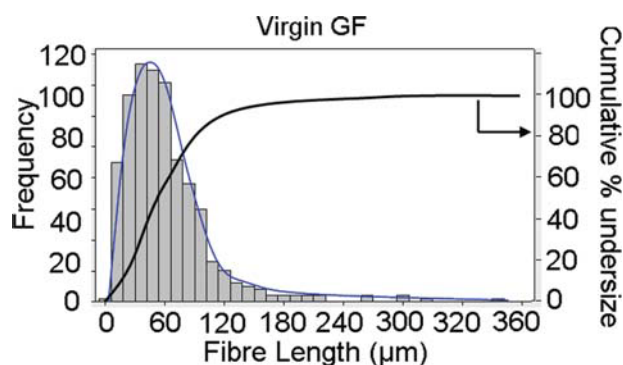


Figure 3 Fiber length distribution of PTFE/GF recyclate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 4** Fiber length distribution of virgin glass fiber. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shows a multi-modal distribution pattern (see the presence of multiple peaks in Fig. 2). This may be caused by the wear of the cutting tool caused by the GF, which is a very abrasive material. This is confirmed by the examination of the cutting tool, which became dull at the end of the grinding process.

Fiber length distribution analysis was performed by measuring 500 fiber lengths using ImageJ software based on the SEM photos. Minitab was then applied to plot the fiber length distribution and median fiber length distribution. In Figure 3, approximately 85% of fibers in the PTFE/GF recyclate powder exhibits lengths smaller than 100  $\mu\text{m}$  and a small percentage (<10%) retained fiber length longer than 180  $\mu\text{m}$ . The median fiber length was calculated to be 47.8  $\mu\text{m}$ .

In this study, PTFE and virgin GF composites were also prepared for comparison. The virgin GF was supplied by Owens Corning (Lancaster, UK) under the trade name OC<sup>TM</sup> Milled Fiber 739DC. It is an unsized E-glass type fiber specifically formulated for mixing with PTFE. Fiber length distribution was also performed on the virgin glass and is included in Figure 4. Compared with the recyclate PTFE/GF, the virgin GF exhibits a wider fiber length distribution and a longer medium length of 107  $\mu\text{m}$ . Ninety percent of the milled GFs has a length smaller than 250  $\mu\text{m}$ .

#### Gravimetric analysis of R-PTFE/GF

The aim of the gravimetric analysis was to identify the PTFE/GF ratio in the recycled regrind. The final reconstituted laminates should have a fixed dielectric constant. In principle, dielectric constant is determined by the PTFE and GF ratio. If the PTFE/glass ratio is known, and the relationship between the dielectric constant and the PTFE/GF ratio is determined, it is possible to calculate how much virgin PTFE powder needs to be added into PTFE/GF recyclate to achieve a desired dielectric constant. The gravimetric analysis was based on the principle of

burning the PTFE and weighing of the remaining GFs. The recyclate was placed into a preheated oven at 700°C and burnt for 20 min. The waste powder was weighed before and after burning to an accuracy of 0.1 mg. The pyrolysis of pure PTFE has been also carried out, and no residual weight was found. The composition of the recycled powder is listed in Table I.

#### Sample formulation

Different weight fractions (10, 20, 30, 40, 50, and 60 wt %) of PTFE/GF recyclate and virgin PTFE were mixed using a Kenwood blender for 15 min. The virgin PTFE was TF 1750 (average particle size 25  $\mu\text{m}$ ) supplied by Dyneon<sup>28</sup>

For comparison purposes, virgin PTFE/GF samples were also prepared. Virgin GF (10, 15, 20, 25, and 30 wt %) and virgin PTFE powder were mixed using the same approach as the recyclate. It is important to emphasize that the weight fractions of GF within virgin samples and recyclate samples are similar. The weight fractions incorporated in recyclate samples include a mixture of PTFE and GF recyclate (46.5/53.5% see Table I).

It is expected that the lower size distribution obtained for recyclate PTFE/GF regrind is going to be an advantage and help the overall performance of any new PTFE/GF composite manufactured. Higher fiber length distribution (such as the one given by virgin GF) is successfully used in combination with PTFE for various electronic applications.

#### Sample manufacturing

The mixtures were compacted into 60  $\times$  80  $\times$  1.6 mm preforms under 40 MPa pressure for 2 min in a stainless steel mold. After preforming, two sintering methods were used: (1) sintering without pressure (SWOP) and (2) sintering with pressure (SWP). For the SWOP process, the preforms were placed in a compression mold, gradually heated in a furnace to the sintering temperature of 375°C, kept for 2 h, and then cooled down to room temperature, without any pressure in the furnace, at a cooling rate of 30°C/h. For the SWP process, the preforms were sintered within the mold in the furnace at 375°C for 2 h. The sintered preform was then cooled in air on a preheated hot press with a temperature of 375°C under

**TABLE I**  
Composition of the PTFE/GF Laminate Recyclate

	PTFE/GF laminate recyclate fraction	
	By weight	By volume
PTFE	46.55 $\pm$ 0.7%	50.60 $\pm$ 0.7%
GF	53.45 $\pm$ 0.7%	49.40 $\pm$ 0.7%

15 MPa pressure. The pressure was released after 30 min during cooling, and the preform continued to cool in the hot press. It is expected that the pressure applied during cooling will improve the interface between the recycled glass and PTFE matrix, decrease the voids amount of air, and improve the mechanical properties. The authors did some preliminary investigations into homogeneity of the composite and adhesion between fiber and polymer using SEM, and no strong correlation between the manufacturing method for presented results and SEM images was noticed.

### Sample experimental methods

#### Porosity measurement

The aim of the porosity measurements is to determine the air entrapped in each specimen. The air entrapped in the specimens is expected to have a big effect on the tensile properties and the dielectric properties. The volume fraction of air entrapped in the specimens (porosity) was calculated using the following equation:

$$V_A = 1 - \frac{\rho_S}{\rho_T} \quad (1)$$

where  $V_A$  is the volume fraction of air entrapped in the specimen, and  $\rho_S$  and  $\rho_T$  are the actual and theoretical density for each specimen.

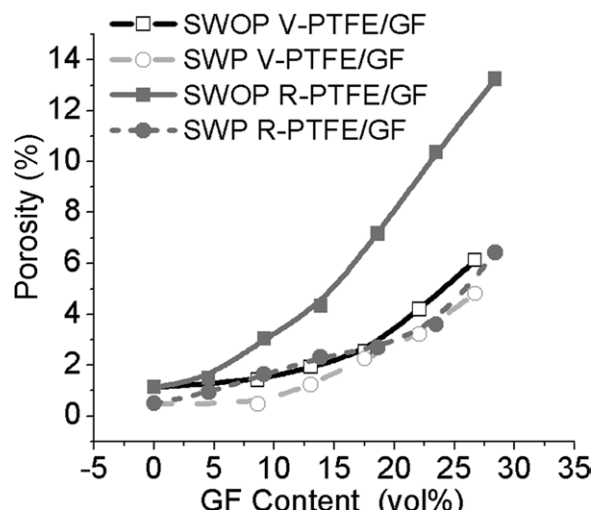
The theoretical density of PTFE/GF composite was determined using the following equation:

$$\rho_T = \rho_{PTFE} V_{PTFE} + \rho_{GF} V_{GF} \quad (2)$$

where  $\rho_{PTFE}$  and  $\rho_{GF}$  are the density of PTFE and GF, respectively.  $V_{PTFE}$  and  $V_{GF}$  are the volume fraction of PTFE and GF, respectively. The densities of the specimens were determined using the immersion density technique based on British standard BS EN ISO1183-1 : 2004,<sup>29</sup> where deionized water was used as the immersion medium at room temperature.

#### Differential scanning calorimetry

The differential scanning calorimetry (DSC) experiments were carried out using a Mettler-Toledo (Leicester, UK)<sup>30</sup> DSC 821e calorimeter under a nitrogen flow of 60 mL/min using dynamic scans at a heating rate of 10 K/min from 0 to 400°C. Three repeat cycles were performed with each sample. The degree of crystallinity is then given by dividing the heat of fusion of melting by the heat of fusion for 100% crystalline PTFE (known as 77.1 J/g<sup>31</sup>). The melting temperatures were also recorded.



**Figure 5** Comparison of porosity of the virgin and recycle sample (V-PTFE/GF and R-PTFE/GF) with and without pressure (SWP and SWOP).

#### Dielectric testing

The dielectric properties were measured according to the IPC-TM-650 2.5.5.5<sup>32</sup> at the frequency 10 GHz using HP 8510 vector Network Analyzer (HP Agilent Technologies, Berkshire, UK). Measurements were made using a resonant element pattern card, which is separated from the ground planes by two sheets of the material to be tested. For each recycled waste fraction, three measurements were performed.

#### Tensile testing

For each fraction of PTFE/GF laminate recycle, 8 samples with a dimension of 22 mm × 5 mm × 1.6 mm were cut from two panels. Tensile tests were preformed using a LLOYD EZ20 tensile testing machine.<sup>33</sup> The cross-head displacement rate was 50 mm/min according to ASTM D\_3294.<sup>34</sup>

#### Scanning electron microscope

Tensile fracture surface were examined using a Hitachi S-3200N SEM. All samples were coated with 4 nm gold layer to reduce surface charging, and secondary electron images were taken with an accelerating voltage of 25 keV.

## RESULTS AND DISCUSSION

### Porosity measurement

Figure 5 shows the comparison of the porosity of the virgin V-PTFE/GF samples and recycle R-PTFE/GF samples made using SWP and SWOP methods. Compared with the V-PTFE/GF sample, for both SWP and SWOP manufacturing methods, the R-PTFE/GF samples exhibit higher porosities due to

**TABLE II**  
Crystallinity and Melting Temperature of the V-PTFE/GF and R-PTFE/GF Obtained with and Without Pressure

	SWOP V-PTFE/GF	SWP V-PTFE/GF	SWOP R-PTFE/GF	SWP R-PTFE/GF
GF contents (vol %)	22.1%	22.1%	23.4%	23.4%
Crystallinity	65.8 ± 1.1%	62.0 ± 1.7%	71.6 ± 1.6%	66.7 ± 1.1%
Onset melting temperature (°C)	324.9 ± 0.2	342.6 ± 0.2	325.6 ± 0.1	325.0 ± 0.3

the change in the molecular structure of PTFE at the preform stage. The recycled PTFE exhibits a folded-chain crystal structure as it is sintered PTFE, whereas the virgin PTFE exhibits an extended chain crystal structure. Due to the folded-chain crystal structure, PTFE exhibits a harder surface, and it is much more difficult to compress into a dense preform.

Therefore, a "preform" with more interparticle voids will be produced, which leads to a higher porosity in the sintered samples. Although the low molecular mass weight of recycled PTFE would be expected to reduce porosity during sintering, the effect is limited due to the large volume fraction of voids in the recycled preforms. Therefore, the recycled samples made using SWOP approach still showed high porosities than virgin samples. Compared with the SWOP R-PTFE/GF samples, the SWP R-PTFE/GF samples exhibit much lower porosities. This is attributed to the pressure added during the cooling stage for the SWP samples, which helps the air exhausting and the bonding of the recycle PTFE and GF with virgin PTFE.

#### Differential scanning calorimetry

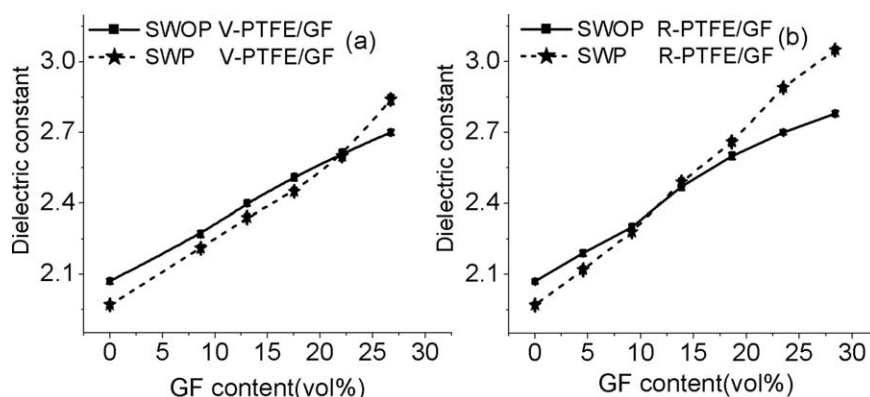
Table II shows the crystallinity results of the V-PTFE/GF and R-PTFE/GF as well as the melting temperatures. As expected, the SWOP samples exhibit a higher crystallinity due to the slower cooling rate applied during the manufacturing process, which allowed more time for re-crystallization. R-PTFE had shorter chains due to the breakage of

the molecular chains during the grinding process and allowed formation of several crystallization domains, nonuniformly distributed across the sample. In comparison, V-PTFE requires much longer time for its long molecular chains to align and allows formation of a lower but uniform crystallization structure across the entire sample. The recycled PTFE, which exhibit shorter chains, could re-crystallize easier in comparison with virgin PTFE, and thus exhibit a higher crystallinity. The effect of changes in crystallinity on the density and volume fraction was calculated to be negligible for the studied samples.

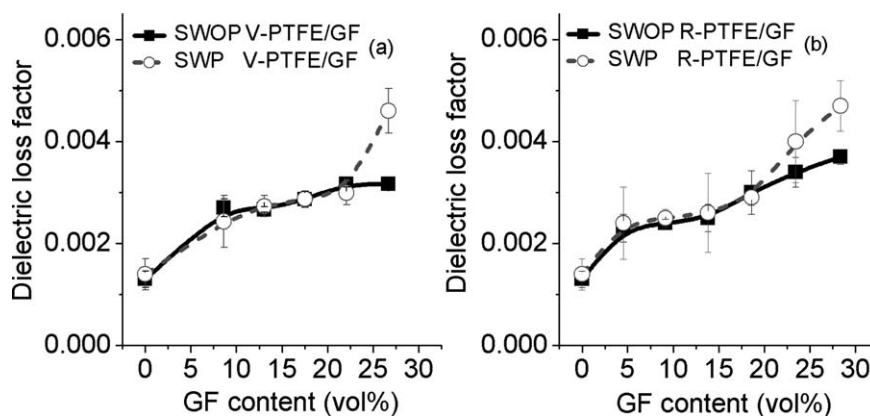
#### Dielectric testing results of the PTFE/GF recycle

Figure 6 shows the dielectric constants of V-PTFE/GF and R-PTFE/GF samples made using SWP and SWOP methods. The standard deviation of the dielectric constant has been included, but it is too small to be noticed. For both samples, the dielectric constant increased with the increase of the GF fraction. This is not surprising considering that glass exhibits a higher dielectric constant than most polymers, and it is known to be 6 for glass and 2.1 for PTFE at 10 GHz.<sup>35</sup>

Slightly higher dielectric constant values had been obtained for the V-PTFE/GF samples manufactured without any pressure when GF is lower than 20 vol %. One of the possible reasons is the different crystallinity of the PTFE samples made using SWOP and SWP, as shown in Table II. Koizumi et al.<sup>36</sup> reported that the PTFE with a lower crystallinity exhibits a slightly lower dielectric constant at frequencies of



**Figure 6** Comparison of dielectric constant of the PTFE/GF sample manufactured with and without pressure (SWP and SWOP). (a) V-PTFE/GF and (b) R-PTFE/GF.



**Figure 7** Comparison of dielectric loss factor of the PTFE/GF sample manufactured with and without pressure (SWP and SWOP). (a) V-PTFE/GF and (b) R-PTFE/GF.

10–300 kHz. As the GF content increases, the pressure becomes more important in the manufacturing process, and its effect is noticed in the dielectric constant values obtained. When pressure is applied at GF content higher than 25%, more air trapped in the sample is eliminated, and hence the dielectric constant is increased. It is well established that air exhibits a very low dielectric constant (approximately 1<sup>37</sup>) and has a detrimental effect on the dielectric properties of samples, hence the porosity measurements help predict and understand the dielectric behavior of samples.

The dielectric constants of R-PTFE/GF follow similar trends to the V-PTFE/GF samples. At low GF concentrations, there are slight differences in the gradual increase of dielectric values, whereas at higher GF contents, the pressure applied during manufacturing steps has a significant impact. It is interesting to notice that the effect of pressure becomes important much earlier than in the case of V-PTFE/GF, as more air is entrapped in the SWOP R-PTFE/GF (as shown in Fig. 5). Therefore, the effect of the air elimination by the pressure becomes significant at lower GF contents. The different in manufacturing methods is noticeable at GF contents higher than 25% in virgin samples and at 15% in recycle samples.

The virgin PTFE/GF laminate normally exhibits dielectric constants in the range of 2.2, 2.5, 3.0, and 3.2 depending on the application. It can be seen from Figure 6(b) that the dielectric constants of recycled PTFE/GF samples exhibit a similar range and can be controlled to a specific value by varying the recycle fraction in the recycled samples.

Figure 7 shows the dielectric loss factor (Df) values of V-PTFE/GF and R-PTFE/GF samples manufactured with and without pressure. For all types of samples, the dielectric loss factor increased with the increase of GF content due to the relatively high dielectric loss factor of the glass and the increase of

the porosity.<sup>38</sup> The dielectric loss is also affected by the contamination and the orientation of the GF, which could explain the large standard deviation noticed. Similar to the dielectric constant values, the pressure introduced in the manufacturing process seems to increase the dielectric loss factor values at higher GF contents.

It is important to predict the dielectric constant of this recycled composite as it could be used in high frequency PCB or electronic packaging applications, which generally requires a fixed dielectric constant. Wiener<sup>11</sup> published one of the earliest studies on the permittivity prediction of the heterogeneous mixtures. Wiener's theory describes the two extreme anisotropic situations of the materials' arrangement, the series and parallel connected cases, namely, Wiener's upper bound and Wiener's lower bound, respectively. For a heterogeneous system of two-phase composite dielectric, irrespective of the shape, size, or orientation of different phases, the effective dielectric response of mixture should always lie within these two specified limits.

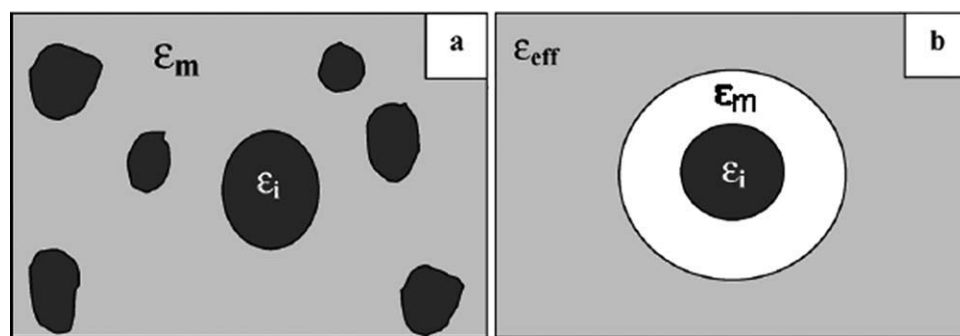
As previously discussed in the literature, modified Lichtenecker model<sup>18</sup> and EMT model<sup>17</sup> are the two theories that gained the most support from the experimental data. The equations used for prediction of the dielectric constant of the composites for the two theories are presented as follows:

$$\begin{aligned} \text{Modified Lichtenecker theory : } \log \epsilon_{\text{eff}} \\ = \log \epsilon_1 + (1 - k)v_2 \log \frac{\epsilon_2^2}{\epsilon_1} \end{aligned}$$

$$\begin{aligned} \text{Effective - Medium Theory (EMT) : } \epsilon_{\text{eff}} \\ = \epsilon_1 \left[ 1 + \frac{v_2(\epsilon_2 - \epsilon_1)}{\epsilon_1 + nv_1(\epsilon_2 - \epsilon_1)} \right] \end{aligned}$$

where  $\epsilon_{\text{eff}}$ ,  $\epsilon_1$ , and  $\epsilon_2$  are the dielectric constant of composite, the host medium, and inclusion, respectively, and  $v_1$  and  $v_2$  are the volume fraction of the





**Figure 8** (a) Schematic diagrams of composite structure and (b) structure of random unit cell.<sup>22</sup>

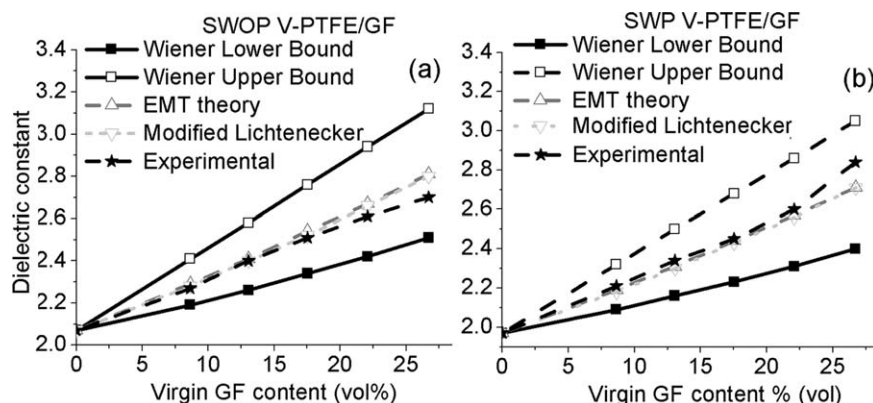
host medium and inclusion, respectively.  $k$  and  $n$  are fitting factors.

The modified Lichtenecker equation is developed from the Lichtenecker equation by introducing a fitting factor  $k$ , which represents the interaction between the polymer matrix and the filler. The Lichtenecker equation considers the stochastic element into the dielectric mixture for the first time.<sup>18</sup> The mixture forming process is complicated due to the statistical nature of the random inclusion location and the orientation of the inclusion.<sup>18</sup> Therefore, the dielectric properties of the mixture will be essentially subjected to statistical distribution and correspond to a probability.

Figure 8(a) shows the microstructure of a composite with particles embedded in a matrix as proposed by the EMT. The particles shown in Figure 8(a) were treated as round inclusions surrounded by matrix shells, as shown in Figure 8(b) (where  $\epsilon_i$ ,  $\epsilon_m$ , and  $\epsilon_{eff}$  represent the dielectric constant of the inclusion, matrix, and composite, respectively).<sup>17,22</sup> This structure is defined as a random unit cell (RUC), the ratio of the inclusion volume to the matrix shell volume is equal to the volume fraction of the inclusion shown in Figure 8(a).<sup>17</sup> This theory assumes that RUC has a same dielectric properties as that of the effective medium.

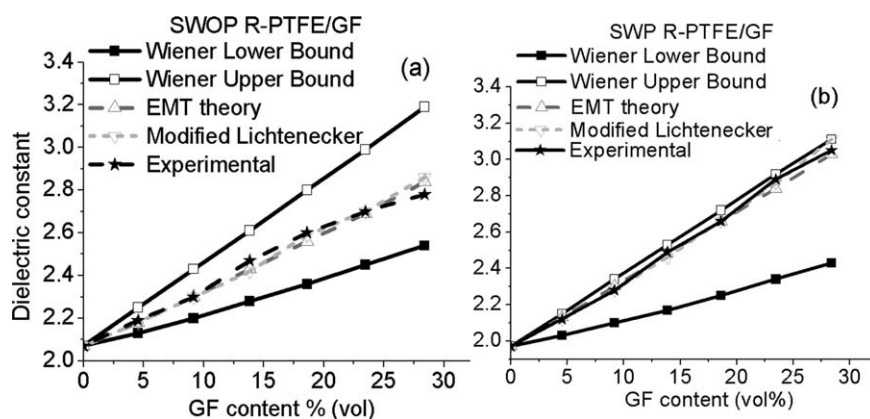
Predicted models for the modified Lichtenecker and EMTs together with the Wiener's upper and lower bounds were plotted against the experimental data and are presented in Figures 9 and 10. Figure 9(a,b) shows the comparison of the experimental results and the prediction models for dielectric constant for the V-PTFE/GF SWOP and SWP samples, respectively. For both types of samples, virgin and recycle, the EMT and modified Lichtenecker theory showed good agreements with each other and the experimental results at lower GF fractions. At high GF content, considerable deviation of the predicted value and the experimental value were noticed for both prediction theories. This deviation might be attributed to the imperfect dispersion of the GF and considerable air entrapped in the sample at high GF fractions. For both SWOP and SWP V-PTFE/GF samples, the fitting factors were found empirically, to be 0.3 for the EMT and  $-0.07$  for the modified Lichtenecker theory. Similar values for the EMT fitting factor were reported previously in the literature.<sup>23</sup>

Figure 10(a,b) shows the comparison of the experimental results and the prediction models for dielectric constant for the R-PTFE/GF SWOP and SWP samples. For the samples manufactured without pressure, there was a good correlation between the



**Figure 9** Comparison of experimental and theoretical dielectric constants of V-PTFE/GF samples without (a) and with (b) pressure.





**Figure 10** Comparison of experimental and theoretical dielectric constants of R-PTFE/GF samples without (a) and with (b) pressure.

predicted values and experimental results, for all recycle GF fractions. The fitting factors for both theories were noticed to be similar as those obtained from the virgin samples. However, in the case of R-PTFE/GF samples manufactured with pressure, the fitting factors were found to be significantly different than previously recorded (0.05 for the EMT and  $-0.44$  for the modified Lichtenecker theory). Smaller fitting factors shift both predictions towards the Wiener upper bound as it can be noticed in Figure 10(b). The experimental data follow the same trend as the EMT and Lichtenecker predictions. This is somehow surprising considering that the inclusions used in this study are fibers and during the manufacturing process, due to the way the pressure is applied, the fibers and the matrix are expected to behave as a lower bound system.

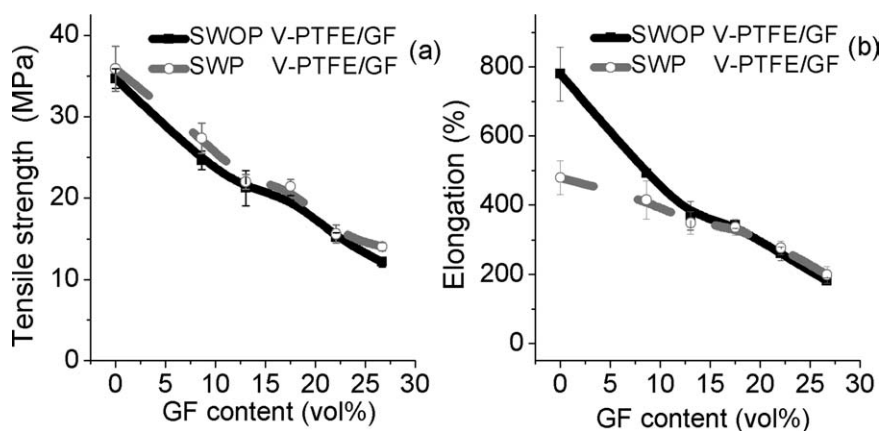
The different fitting factor could be explained by interphase zone theory introduced by Vo and Shi.<sup>39</sup> This theory suggests that the interphase between the matrix and inclusions could exhibit unique properties and shift the dielectric constant of the composites. Although both manufacturing methods use GF coated with PTFE, the effect of interphase zone

appears in samples manufactured with pressure only. This is not surprising as the pressure is expected to enhance the bonding properties.

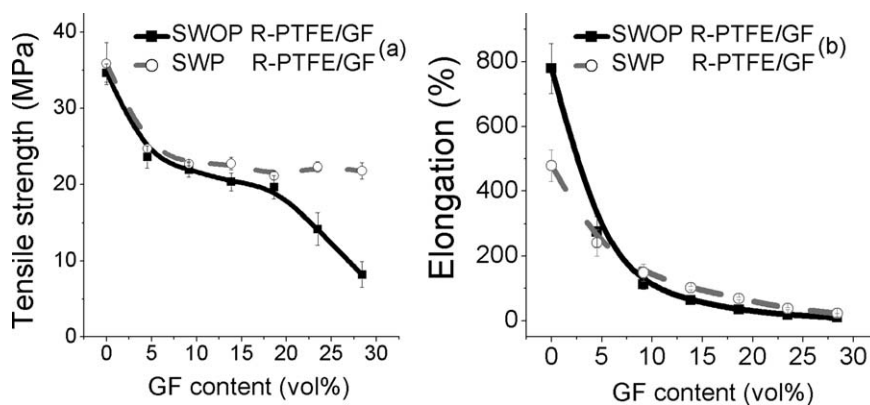
### Tensile testing

Another important property required for PCBs and electronic packaging applications is mechanical performance. The tensile strength and elongation of the recycled samples were tested and are shown in the Figures 11 and 12, respectively. As expected, in the case of V-PTFE/GF samples, there is a general trend of decrease of tensile strength and elongation at break with increase of GF content. In the case of R-PTFE/GF samples, although the overall trend is similar, pressure becomes an important factor for tensile strength at high GF contents. An increase from approximately 10–23 MPa has been noticed in the case of 28.4 vol % GF.

In comparison with virgin samples, the tensile stress of the recycled samples produced with pressure is improved at high GF fraction, from approximately 15–23 MPa in case of the 28.4 vol % sample, whereas the elongation at break for SWP R-PTFE/GF



**Figure 11** Mechanical properties of V-PTFE/GF samples manufactured with and without pressure. (a) Tensile strength and (b) elongation.



**Figure 12** Mechanical properties of *R*-PTFE/GF samples manufactured with and without pressure (a) Tensile strength and (b) Elongation.

GF samples becomes negligible at high GF contents dropping from 200% to 25%. This observation could be related to the better interface of *R*-PTFE/GF, as some of the recycled GF remained coated with PTFE after grinding (see Fig. 1). In comparison, the virgin GF used in this study is unsized GF, which provides a poor interface and could move more freely during tensile testing. As a result, the *R*-PTFE/GF samples exhibit an improved tensile stress and a reduced elongation, as the bonding between the GF and PTFE will restrict the PTFE elongation and lead to the stress concentration. In addition, the drop in elongation of *R*-PTFE/GF could also be explained by the chain length and crystallinity structure of recycle and virgin PTFE. The short molecular chains of *R*-PTFE will lead to several crystalline domain sites weakly bonded between themselves spread nonuniformly across the entire sample, where *V*-PTFE will have a uniform crystalline structure distributed uniformly across the entire sample. During tensile testing, the *R*-PTFE breaks in between the crystal domains in a brittle manner, where *V*-PTFE exhibited a ductile structure due to the uniform crystalline structure. Similar finding were noticed previously by Xiang and Tao<sup>40</sup> on 20 wt % recycled PTFE-filled virgin PTFE. He found that the elongation reduced massively to 28.3%, in comparison with 363% of the virgin PTFE.

### CONCLUSIONS

A new PTFE/GF composite incorporating PTFE/GF recycle has been developed. PTFE/GF waste was cryogenically ground to fine powder, which was then reconsolidated to a PTFE/GF recycle with the addition of virgin PTFE powder. In general, a good correlation between the experimental and predicted dielectric properties has been noticed. The two manufacturing methods proposed here (with and without pressure) had an effect on the mechanical and dielectric properties of the new PTFE/GF composite

at high GF contents. Although the tensile strength was maintained within a similar range for standard and recycle structures, the elongation at break was significantly affected by the use of recycle PTFE.

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