Preparation of PTFE/graphene nanocomposites by compression moulding and free sintering: A guideline

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ABSTRACT: This work was aimed at preparing polytetrafluoroethylene (PTFE) nanocomposites filled with graphene nanoplatelets and investigating how the graphene nanoplatelets and the preparation techniques influenced the physical properties. Graphene was incorporated up to 4 vol % of the total PTFE system by dry and solvent assisted blending. The powder compaction was evaluated using the Kawakita/Ludde model to describe the compressibility of the powder blends. The nanocomposite billets were prepared using cold compression moulding by applying preform pressures between 12.7 and 140 MPa and the preform billets were sintered at 380°C using a specific sintering cycle. The changes in the physical dimensions, billet mass, density, and void content of the billets, pre and post sintering, were analyzed with experimental design to evaluate the influence of the precompaction pressure and graphene loading. From the evaluation it was concluded that the ideal compaction pressure was at 12.7 MPa and the solvent assisted blending was superior to the mechanical blending method. Furthermore, the compression creep tests confirmed the ideal processing temperature and graphene loading range to improve the mechanical properties. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43369.

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a fluoropolymer which exhibits very high crystallinity and molecular weight which gives it a range of outstanding physical properties. These properties include good chemical resistance, high thermal stability, dielectric properties, mechanical properties, and low coefficient of friction. Therefore, PTFE is used extensively in high-end applications in various industries. However, PTFE can be vulnerable to deformation under load (creep) and high wear rates.[1] These limitations of PTFE can be improved through the incorporation of specific filler materials when the standard properties might not be sufficient in specific applications.[2]

The incorporation of nanofillers into PTFE has received a lot of attention in the past few years and has shown to be effective in improving the tribological properties[1,3–6] and the thermal conductivity[7] of PTFE. Yan *et al.*[8] showed that expanded graphite combined with other nanofillers give a synergistic effect to improve the mechanical properties of PTFE composites. However, there exists limited information regarding PTFE composites filled with graphene nanoplatelets and how it influences the physical properties of the PTFE.[5,7,9,10] Furthermore, the

proper fabrication methods of these nanocomposites are also relatively unestablished and very few articles address the preparation of nanofilled-PTFE composites. Most of the guidelines are provided by the manufacturers recommending the correct processing conditions regarding preform pressures and the sintering cycles for filled and unfilled PTFE.

Because PTFE possesses such a high molecular weight, it also exhibits a high melt viscosity, which makes it difficult to process finished articles with the usual polymer processing methods like extrusion and injection moulding.[11,12] Therefore, PTFE is usually processed using powder metallurgy methods like cold compaction and free sintering.[11–13] With the incorporation of a nanofiller material, the fabrication process would also need to be altered.

Therefore, the aim of this paper was to prepare graphene filled PTFE nanocomposites and evaluate how the powder blending (dry and solvent-assisted), fabrication method (conditions of preform compaction and sintering), and the graphene concentration influence the physical properties. Furthermore, the information gained from the results should act as some form of guideline to prepare graphene filled PTFE with conventional methods.

Table I. PTFE/Graphene Powder Blends Volume Fractions

Sample	Graphene (g)	TFM 1700 PTFE powder (g)	Calculated volume fraction (vol %)
Reference	0	5	0
0.25	0.012	5	0.25
0.75	0.036	5	0.75
1	0.050	5	1
2	0.100	5	2
4	0.200	5	4

## EXPERIMENTAL

Materials and Dispersion Methods

The PTFE moulding powder (Grade TFM 1700) was obtained from 3M Dyneon (Nuess, Germany) which is a non-free flowing modified PTFE that exhibits a specific gravity of 2.16 g cm^{-3} and very fine particle size of 25 μm. This modified PTFE is a copolymer composed of tetrafluoroethylene and a perfluoro (alkyl vinyl ether) monomers. The amount of the latter in this PTFE copolymer is less than 2 wt %.[14,15] The graphene nanoplatelets (XGNp M-25) were obtained from XG Sciences (East Lansing, WV) which exhibits an average diameter of 25 μm; thickness of 6 to 8 nm and specific gravity of 2.2 g cm^{-3}. The particles were blended by two different methods, namely mechanical and solvent, to prepare the blended powder mixtures according to volume fraction (vol %) of the total blended system. The volume fraction of the incorporated graphene was determined from the density and mass of the graphene in the total PTFE/graphene
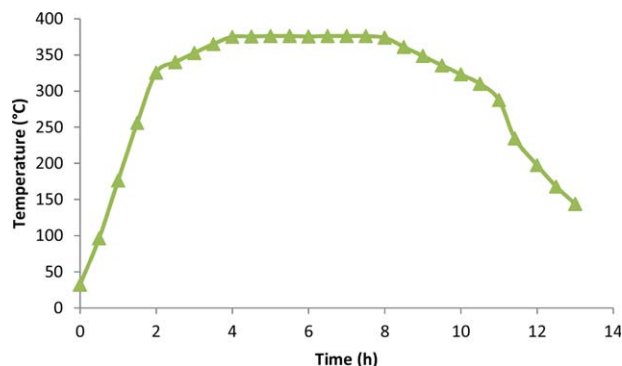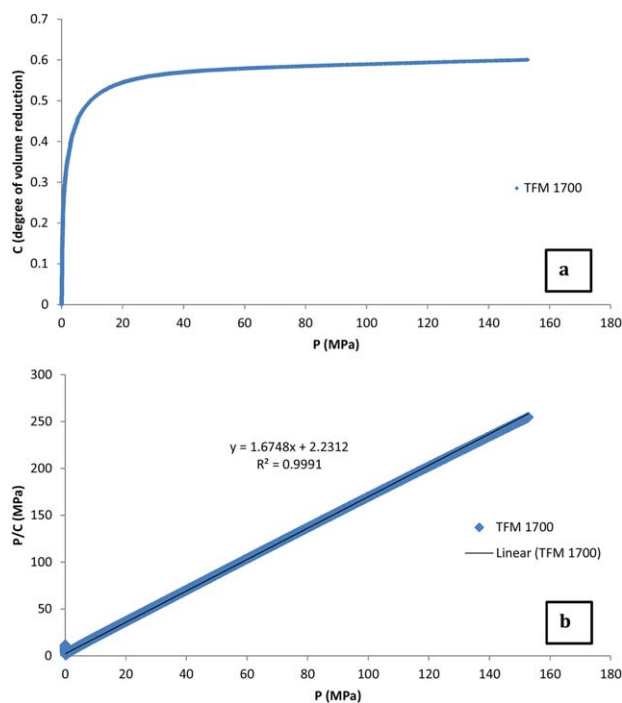

Figure 2. Sintering profile used to process the preform billets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

powder system. The graphene/PTFE batches were prepared with graphene concentrations at 0.25; 0.75; 1; 2; and 4 vol % and each batch consisted of a total mass of 5 g (Table I). The mechanical blending was performed with a blender (Russel Hobbs, RHCG 120) where the dry particles were dispersed together for 2 to 3 min and the blended powder collected.

Solvent blending was performed by dispersing the graphene and the PTFE powder, separately, in perfluoroheptane (Pelchem) in an ultrasonic bath (Scientech 702; 100 W) for 1 h where the temperature was set at 30°C. The PTFE and graphene dispersions were combined and stirred for another hour to prepare a homogenous blend. The PTFE/graphene powder was filtered to remove and recycle the PFH. The blended powder was dried in a vacuum oven (Instruvac, OV-11) at 70°C for 24 h to remove any remaining solvent. The agglomerated PTFE/graphene
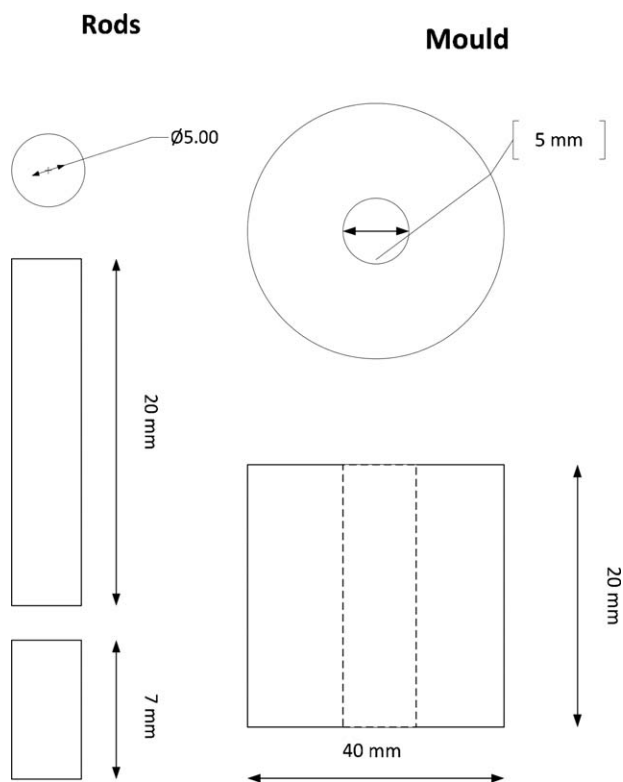
Figure 1. Drawing of stainless steel mould with base plate and plunger rods.

Figure 3. Example of the (a) compression curve and the related (b) linear Kawakita plot of the TFM 1700 PTFE powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
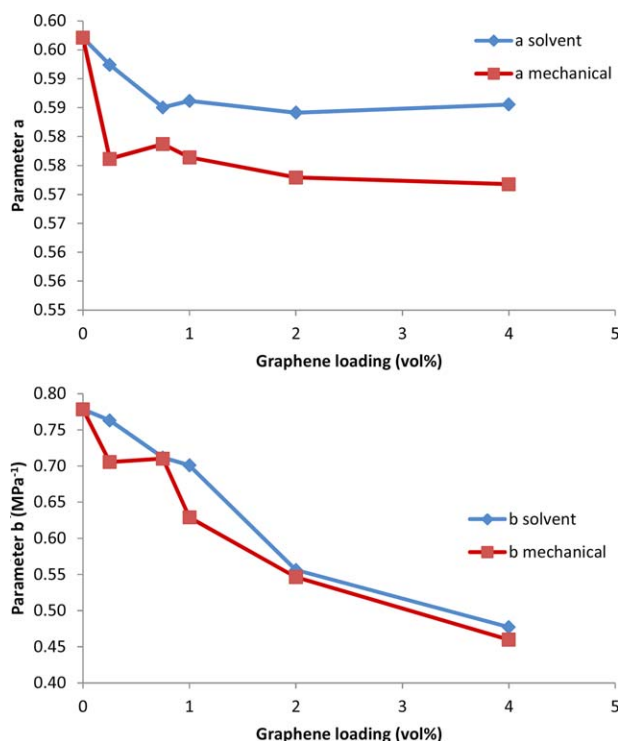
Figure 4. Influence of graphene on Kawakita parameters (a and b) for mechanical and solvent blended powders. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

powder was de-agglomerated into finer form in the blender at a slower blending speed setting for 10 s.
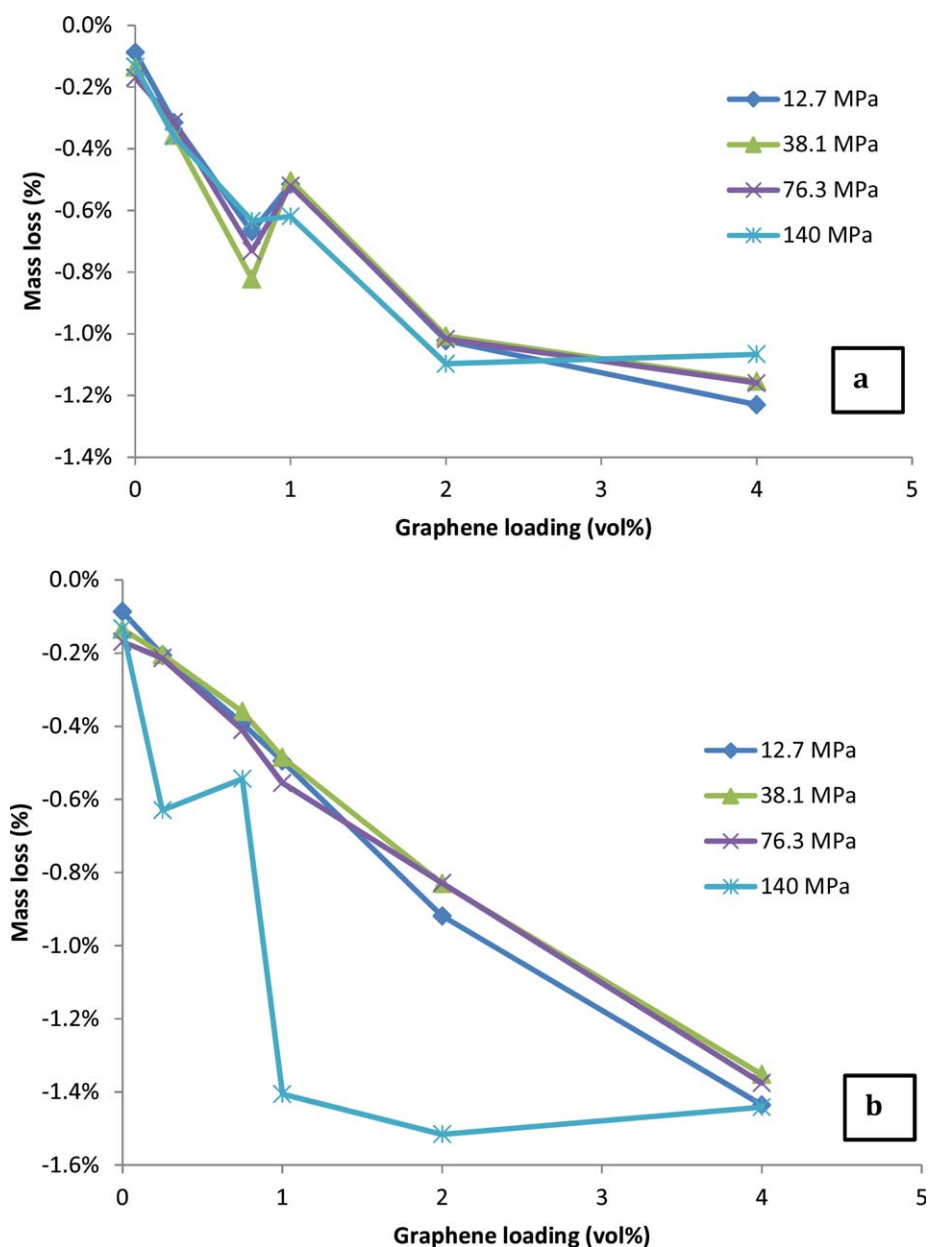
Powder Compaction

An Instron 5900R mechanical tester was used to measure how the prepared graphene/PTFE blended powders respond during compaction in a stainless steel mould (Figure 1) over an increasing pressure range up to 152 MPa. The generated data was evaluated according to the Kawakita/Ludde model[16] to describe the compressibility of the powder blends. The powder (250 mg) was loaded into the mould and compressed at a fixed rate of 1 mm/min until the load cell (5
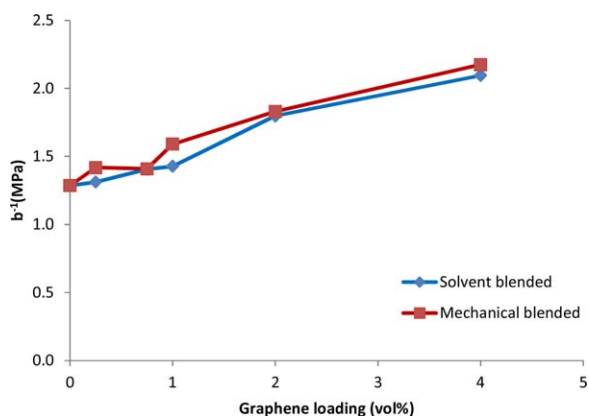
Figure 5. Inverse of parameter b (b^{-1}) which denotes the yield strength of the powder blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Change in Physical Properties of Graphene/PTFE Composite Billets after Sintering

Graphene loading (vol %)	Blending method	Change in billet diameter (%) Preform pressure (MPa)				Change in billet height (%) Preform pressure (MPa)				Change in density (%) Preform pressure (MPa)			
		12.7	38.1	76.3	140	12.7	38.1	76.3	140	12.7	38.1	76.3	140
0	Reference	−4.81	−4.40	−4.21	−3.21	7.37	9.80	10.82	12.65	2.70	−0.48	−1.82	−5.36
0.25	PFH	−3.94	−3.05	−4.16	−4.20	8.86	11.32	11.23	13.04	−0.75	−4.76	−2.42	−3.94
0.75	PFH	−4.65	−3.78	−3.80	−4.17	9.27	11.78	11.74	13.18	−0.01	−4.17	−4.00	−4.39
1	PFH	−4.75	−3.87	−4.44	−3.67	8.27	7.24	12.08	10.92	1.27	0.40	−2.80	−3.44
2	PFH	−4.39	−4.31	−3.23	−3.83	6.68	9.02	9.13	7.97	1.50	−0.84	−3.14	−0.96
4	PFH	−4.22	−3.94	−4.07	−3.95	4.27	7.41	8.46	9.42	3.26	−0.27	−0.97	−1.99
0.25	Mechanical	−5.41	−4.60	−4.62	−4.19	8.31	10.31	10.00	10.22	2.98	−0.60	−0.29	−1.79
0.75	Mechanical	−5.22	−4.61	−4.80	−4.81	6.81	9.37	9.69	10.43	3.81	0.13	0.18	−0.61
1	Mechanical	−5.41	−4.61	−5.20	−4.42	7.34	9.97	9.93	10.73	3.61	−0.55	0.65	−2.54
2	Mechanical	−5.40	−4.81	−5.00	−4.61	7.22	8.89	9.81	10.12	3.26	0.51	0.07	−1.71
4	Mechanical	−5.20	−4.61	−4.61	−4.60	5.54	7.81	8.86	7.79	3.92	0.56	−0.43	0.47

Figure 6. Change in mass of composite billets made with (a) solvent and (b) mechanical blended powders. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

kN) reached the maximum required pressure. The maximum load exerted on the mould was 3 kN as not to damage the load cell. The data collection was done with Blue Hill software.

Composite Billet Preparation and Sintering
The prepared graphene/PTFE blended powders were also compressed into Ø 5 × 6.5 mm billets (approximately 250 mg) in the same stainless steel mould (Figure 1) using a CEAST (Italy) creep tester which is fitted with a mechanical arm and rod to exert a required preform pressure. The preform pressures chosen were 12.7; 38.1; 76.3; and 140 MPa and exerted on the mould for 3 min. The pressed preform billets were accurately weighed (Sartorius, BP210D, Germany) and the dimensions measured with a digital Vernier calliper (QCW, China). The

prepared preforms were sintered in a sintering oven (Carbolite HT) at 380°C according to a programmed cycle (Figure 2). This temperature was chosen based on the observations made by Hambir et al.[17] After sintering, the billets were weighed and measured the same way as the preforms. The difference in the height, diameter, density, and the mass was recorded.

Composite Characterization
The PTFE/graphene composite sample structures were examined with the aid of microscopic and microfocus X-ray techniques. X-ray tomography was performed using a Nikon Metris XT H 225L (Japan) at the South African National Centre for Radiography and Tomography (SANCRAT) which is located at Necsa.[18] Micro-focus X-ray tomography is a nondestructive
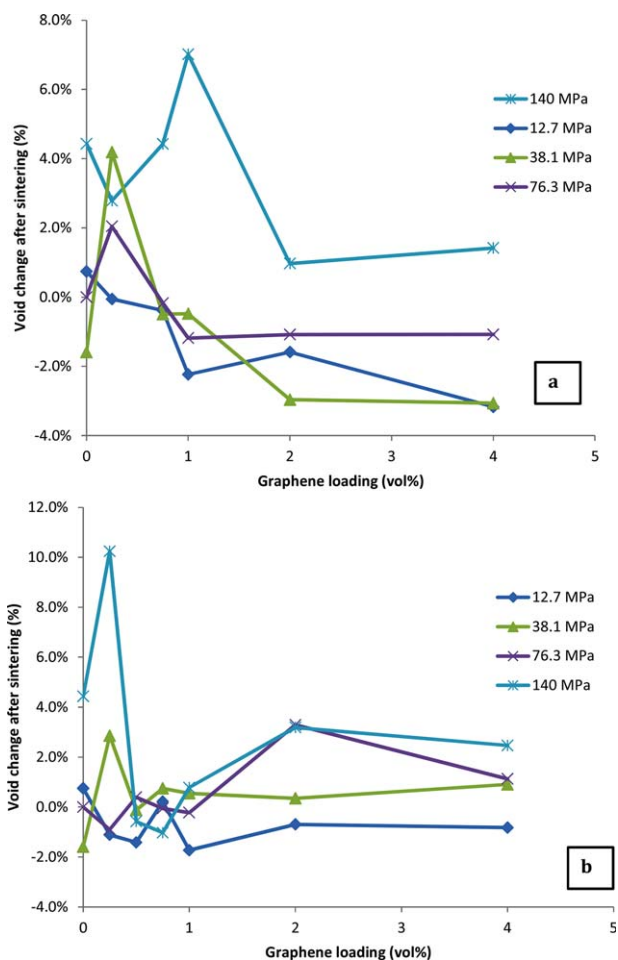
Figure 7. Void content of composite billets made with (a) solvent and (b) mechanical blended powders after sintering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

three-dimensional (3D) imaging technique which enabled the interior examination of the morphology of the graphene/PTFE composite samples. Furthermore, it also has shown potential to optimize processing parameters and to determine the porosity of composite materials.[19–21] This technique was mainly used to determine the void content of the billet and to visually assess how the preform pressure influenced the billet structure. Full revolution (0–360°) scans were performed on the preform and sintered billets using a 0.36° scan rate with the power settings set at 90 kV for the tube voltage and 120 μA current for the tungsten target. The lowest detectable pixel resolution for a sample was ca 4.5 μm and the scan duration was for approximately 33 min. The dispersion state of the graphene in the composite billets was examined using a Motic® (Hong Kong) K-400L optical microscope.

Deformation under Load

To measure the deformation under load a modified version of ASTM D621 was used where 3 mm pressed discs (Ø 5 mm) were subjected to a constant load of 12.7 MPa at 50°C for 3 h. The height of the composite disc samples were measured before and after testing with a digital micrometer (QCW, China).

RESULTS

PTFE/Graphene Powder Properties

The blending of fillers with PTFE is normally done to enhance the mechanical, thermal, and electrical properties. However, due to the inertness of PTFE, fillers might not interact with the polymer matrix and this makes uniform mixing of fillers difficult with PTFE.[2] The mixing of the graphene was successfully performed with both the mechanical and solvent-assisted blending up to 4 vol %. The mechanical blending easily dispersed the graphene up to 1 vol % with the PTFE powder, but higher concentrations (above 4 vol %) became more difficult to disperse effectively using this technique. The solvent-assisted blending dispersed all the concentrations of graphene with ease. Hence, to compare the efficacy of both blending techniques a maximum graphene concentration of 4 vol % was used.

The preform pressure applied during the compaction of PTFE powder is essential to prepare finished articles that exhibit specific properties.[17] When fillers are added to PTFE the required preform pressure must also change in order to prepare a composite with optimum properties. Therefore, with the incorporation of graphene as filler in the PTFE it was considered essential to evaluate how the filler influenced the PTFE powder during volumetric compaction.

The Kawakita/Ludde model[16] has been used to describe the compaction of powder particles in a closed system and is mainly used in the pharmaceutical and metallurgical industries. The Kawakita/Ludde equation is best used to describe the compaction of fluffy powders and assumes that during compression of powder particles in a confined space that the system is in equilibrium[16,22];

$$C = \frac{V_0 - V}{V_0} = \frac{abP}{1 + bP} \tag{1}$$

where C is the degree of volume reduction, V_0 the original volume of die; and V is the die volume at pressure (P) in the die. The compression parameters are listed as a and b, which are constants. These parameters were derived from the linear expression of the Kawakita equation;

$$\frac{P}{C} = \frac{P}{a} + \frac{1}{ab} \tag{2}$$

The Kawakita parameters were determined from the linear regression in eq. (2) and the statistical deviation ($R^2 > 0.9991$) produced very good fits from the measured data (Figure 3).

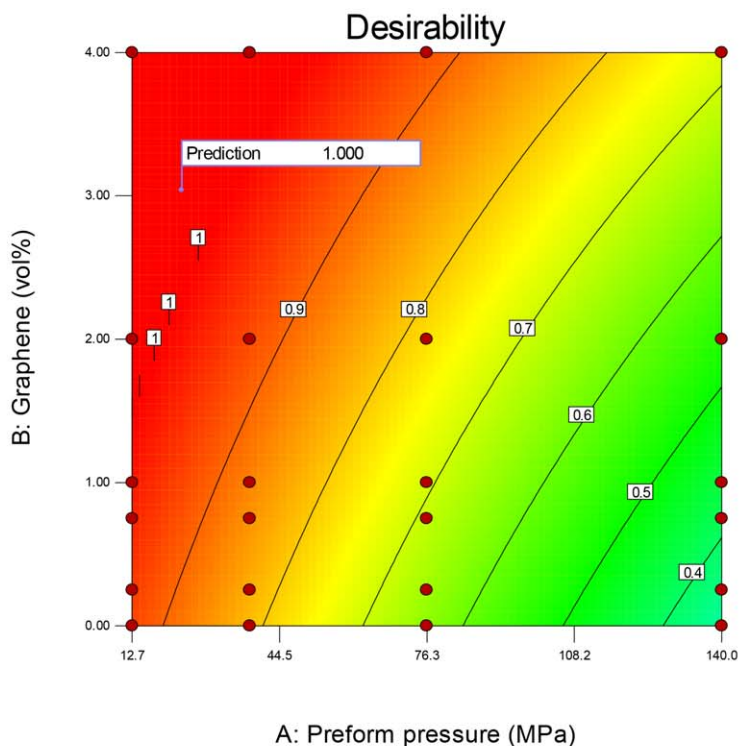**Table III.** Optimization Parameters for the Processing of the Graphene/PTFE Billets

Parameter	Goal
Preform pressure	In range
Graphene loading	In range
Change in height	Minimise
Change in density	Maximise
Change in diameter	Minimise
Change in void	Minimise
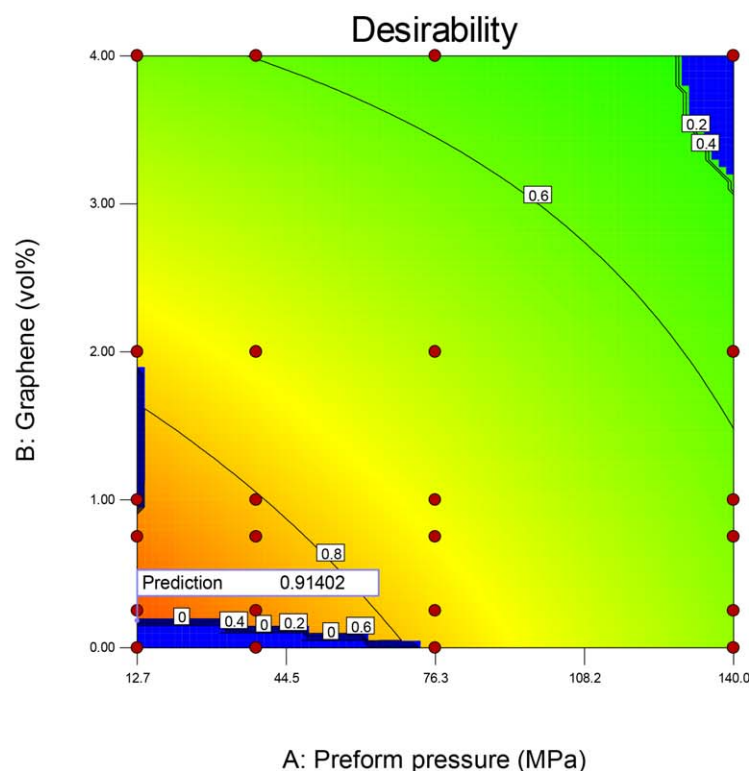
Figure 8. Prediction from design of experiments data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The parameter *a* is an indication of the maximum volume reduction and compressibility of the powder. Parameter *b* is inversely related to the yield strength of the resin particles which effectively describes the pressure at which the granules deform to create a cohesive *green* article. From the results it can be seen that the incorporation of graphene reduces the *a* and *b* parameter values (Figure 4). The solvent blended powder showed to be more compressible which indicated that the graphene distribution was more uniform than with the mechanical blended powder (Figure 4). Furthermore, from the inverse of
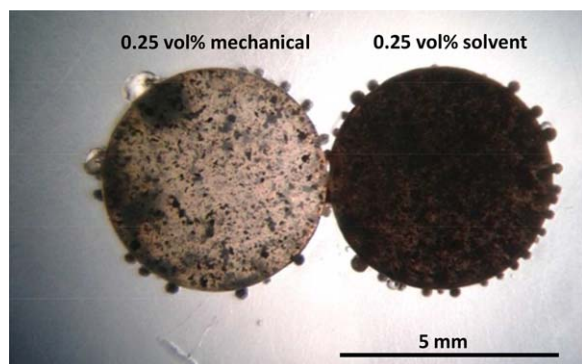
Figure 9. Micrograph of 0.25 vol % billets prepared by mechanical and solvent blended powders. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parameter b (b^{-1}) it can be seen that the yield strength of the powder composite increased with higher loadings of graphene (Figure 5). This phenomenon might be explained due to the presence of the graphene which exhibits a significantly higher modulus and distributes the applied stress between the graphene nanoplatelets and resin particles.[23]

### Influence of Preform Pressure and Graphene Content on Sintered PTFE Composites

The influence of the preform pressure and the graphene loading is compiled in Table II to show how the properties changed pre and post sintering. The solvent blended samples showed some improvement in the shrinkage as the filler loading increased compared with the unfilled PTFE. The shrinkage of the billet diameter is higher at lower preform pressures and with the mechanical blended technique (Table II). The height of the samples increased with higher preform pressures; however, the height change became less with increased loadings of graphene (Table II). The density of the samples showed an increase at a preform pressure of 12.7 MPa which indicated a lower porosity for the samples pressed at that preform pressure after being sintered (Table II).

After being sintered, the composite billets showed a decrease in mass with increasing graphene loading (Figure 6). This mass loss was independent from the blending technique and the preform pressure. Only the mechanical blended sample showed excessive mass loss at a preform pressure of 140 MPa due to excessive cracking of billets [Figure 6(b)]. It is known that unfilled PTFE does experience mass loss during processing due to slight degradation of PTFE at temperatures above its melting point.[24] The higher mass loss shown with increasing graphene loading might be explained due to the increased thermal conductivity attributed by the graphene nanoplatelet shape and presence[7] which also accelerate thermo-oxidative decomposition of the PTFE. Analysing the void content was only taken from a section (Region of interest, ROI) from the centre of each sample due to the amount of voids that would need to be processed. VGStudio Max 2.2 software (Volume Graphics GmbH, Germany) was utilized to calculate the total voids for the specific region of interest which was 20 mm^3. The total volume (mm^3) of the voids in the ROI was used to calculate the relative porosity. From the void content analysis it could be seen that the solvent blended samples had significantly lower void content when compared with the mechanical blended samples (Figure 7). The
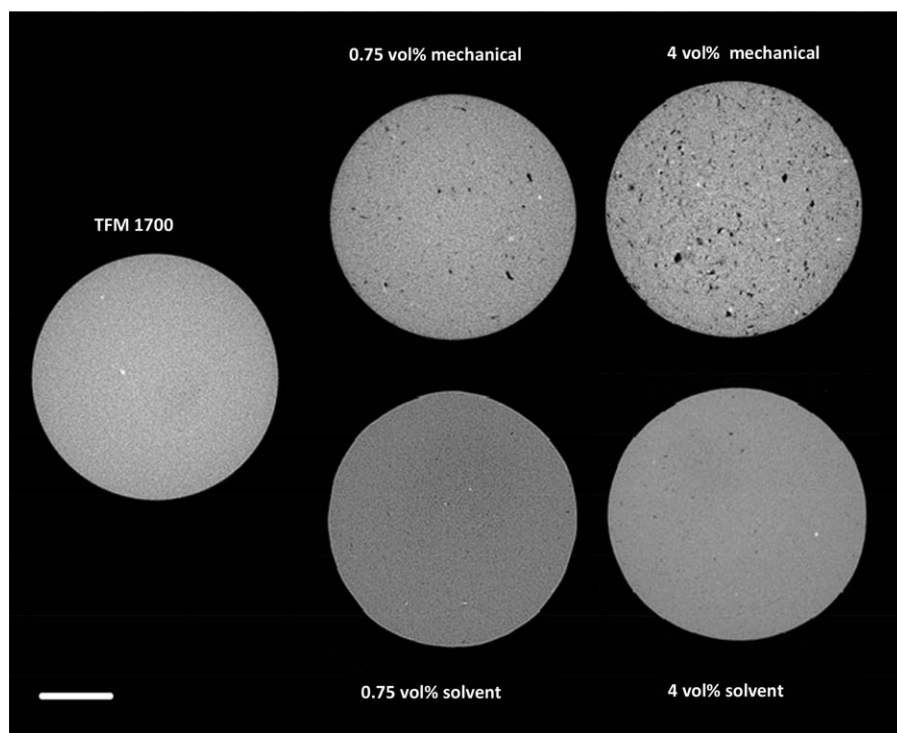
Figure 10. Micro-CT slides of sintered mechanical and solvent blended billets prepared at a preform pressure of 12.7 MPa. The reference sample is also included for comparison reasons. Scale bar is 1.5 mm.
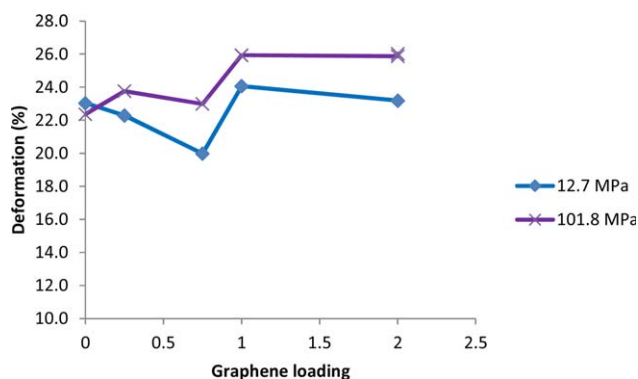
Figure 11. Deformation under load results for solvent blended samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lower preform pressure showed to be the best option with both dispersion techniques to produce samples with low void content. Random samples from the data sets of the solvent and mechanical blended samples were repeated to confirm the physical changes pre- and post sintering and the standard deviation was found to be negligible.

The data sets from both the solvent and the mechanical blending were compiled in Design Expert 9 (Stat-ease Inc.) as historical data to evaluate how the preform pressure and graphene loading influenced the billets, pre and postsintering. The optimization parameters were adjusted according to the conditions listed in Table III for both blending methods. According to the data optimization, using a quadratic model, the composite billets prefer lower preform pressures with both blending techniques (Figure 8). However, the mechanical blending prefers lower graphene loadings whereas the solvent blending effectively

dispersed higher loadings of graphene. The use of a solvent dispersed the graphene more uniformly than the mechanical blending. This was confirmed with microscopic investigation of billets incorporated with 0.25 vol % graphene which were mounted in epoxy and polished down to 1 mm thickness. The sample which was prepared with the solvent dispersed powder showed uniform dispersion as opposed to the mechanical blended powder (Figure 9). Apart from the improved dispersion, micro-CT slices of the sintered billets prepared with the solvent blended powder exhibited lower amounts of voids when compared with the billets prepared with the mechanical blended powder (Figure 10). This was also observed by Vail et al.,[6] where solvent blending with isopropanol improved the dispersion of carbon nanotubes and the mechanical methods (dry air jet-milling) did not improve the dispersion as expected which exhibited highly agglomerated regions. Therefore, the improved dispersion of the graphene nanoplatelets and the application of lower preform pressures were found to be the critical parameters when preparing graphene filled PTFE.

Deformation under Load and Sintering Time Evaluation

Seeing that the solvent blending had the superior dispersion ability, the deformation was evaluated with these powders to optimize the processing parameters. Deformation under load is still applied in industry as a qualitative method, even though ASTM D621 has been withdrawn. The modified test method has been applied successfully at Necsa since 1980 to determine the creep of PTFE flat seals. With the incorporation of graphene nanoplatelets, the resistance to deformation improved at loadings up to 0.75 vol % (Figure 11). Above this loading the creep resistance became gradually worse. A reason for this can be due to slippage between the layers of the graphene platelets, which consist of multilayers and the polymer matrix. This has also been observed
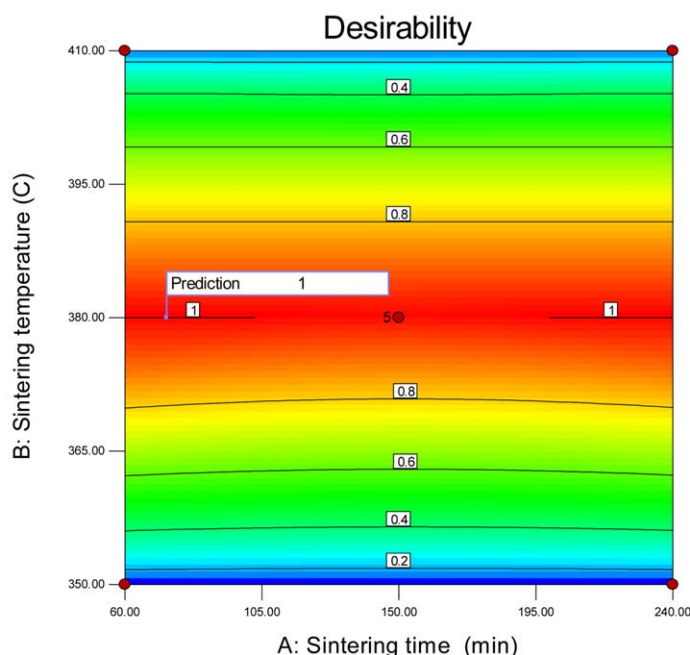
Figure 12. Deformation under load as factors of sintering temperature and dwell time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with aluminium composites which contain graphene nanoplatelets.[25] However, this was only the case with the preform pressure at 12.7 MPa. The higher preform pressure at 101.8 MPa exhibited worse resistance to deformation when compared with the unfilled PTFE, regardless of the graphene loading.

To confirm whether 380°C was the optimum sintering temperature, a set of experiments were compiled in Design Expert 9 which evaluated the sintering temperature and the dwell time factors. The graphene loading was kept constant at the 0.75 vol % loading of graphene, seeing that the 0.75 vol % samples showed the best results at reducing the deformation under load. From the response it could be seen that 380°C is the ideal temperature to sinter the samples at and the dwell time is not the critical factor (Figure 12). This sintering temperature was also observed by other researchers[17] to improve the mechanical strength of PTFE as compared with samples sintered in the region of 365°C.

CONCLUSIONS

In this study, graphene filled PTFE composites were prepared and the influence of the preform pressure and the graphene loading on the physical properties was evaluated. The incorporation of the graphene with the PTFE resin powder was achieved with mechanical and solvent-assisted blending up to 4 vol %. The Kawakita/Ludde model was successfully applied and showed that the compressibility of the powders decreases with the incorporation of the graphene nanoplatelets and the yield strength increases the powder compact. The solvent blended powders showed to be more compressible than the mechanical blended powders which indicated better dispersion of the graphene nanoplatelets.

The sintered billets showed to be directly influenced by the presence of graphene and the preform pressure when the physical properties were evaluated. Through optimization of the results it was clear that the solvent blended powders showed improved dispersion of the graphene in the PTFE and the ideal preform pressure is at 12.7 MPa. Closer investigation of the composite matrices confirmed that the solvent blending improved the dispersion which also reduced the void content. The mechanical blending is not advised to prepare quality fabricated articles and the solvent blending allows for higher loadings of graphene. The mechanical properties were also improved up to a loading of 0.75 vol % and the processing temperature range was confirmed at 380°C.

From the obtained results the ideal processing conditions were determined and the methodology that was applied may be used as a guideline to prepare graphene filled PTFE nanocomposites. Furthermore, the methodology should be applied when producing other nanofilled PTFE composites to determine the ideal processing conditions.

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