



Original Article

Investigation into the effects of fillers in polymer processing

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ABSTRACT

The addition of fillers has become a common method of improving the performance of composites. Therefore, many types of fillers are commercially available while several other types are being investigated. The understanding of the effect of additives on the processing and product quality is crucial for manufacturing products economically and with the desired qualities. This study focuses on investigating the possible effects of graphene and fumed silica nanoparticle fillers on polymer processing and product properties. Three polymeric materials were processed with these two fillers *via* a Mini-Lab twin screw extruder to obtain a better dispersion, and then the properties of samples produced were explored with a number of different testing techniques (e.g., tensile testing, SEM, DSC and rheometer). The Young's modulus of amorphous materials was strongly affected by the filler content, while crystalline materials were not that sensitive to the filler content/level. The Young's modulus of polystyrene-based polymer nanocomposites (PNCs) with 8 wt% fillers at 200 °C and 50 rpm was found to be of approximately 1786 MPa. Also, as clearly recognized by the SEM images and one glass transition temperature (T_g) value rather than two T_g values, it can be ensured that the particles are finely dispersed within PNCs regardless the filler type/content. And then, the rheological results further confirmed that the properties of PNCs are affected by the filler content and set conditions, while the T_g of PNCs was mainly dependent on the matrix and have slightly influenced by the degree of filler dispersion. Moreover, the energy demand was also explored during all the experimental trials for possible comparison and indicated that the energy consumption increased with the filler content but the magnitude of increase was different with different polymer type.

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1. Introduction

Currently, polymers are one of the most widely used materials, mainly due to their properties such as high specific strength, good overall performance compared to other materials and ease of forming into complex shapes [1]. However, the characteristics of individual polymers may not be sufficient for meeting increasing demand for plastic products due to their poor mechanical/thermal properties, weak chemical tolerance, low level of working temperatures, and so forth. In order to enhance the performance of polymeric products, such as mechanical properties and thermal

resistance, as well as to broaden their applications, various additive materials such as nano-fillers have been used with wide range of polymer matrices [2]. Therefore, polymer-based nanocomposites (PNCs) have gained increasing interests in recent years [3–5]. The polymer composites filled with inorganic nanoparticles, such as calcium carbonate (CaCO_3) [6] and carbon nanotube [7], can offer their wide range of functionalities to different applications including heat distortion temperature, mechanical reinforcement and thermal conductivity [8]. This phenomenon has been investigated and confirmed previously [9] by adding silica nanoparticles into polymer *via* extrusion processes. This study focuses on examining the mechanical properties of PNCs. Three polymer materials were chosen as a matrix due to their difference in the degree of crystallinity characteristics, as this will allow to compare the effect of nanoparticles on the polymer morphology. Additionally, due to its nature in terms of whether it was brittle or not, this could reveal the effects of the nanoparticles' interfacial properties,

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dispersion state, and filler concentration on the mechanical properties of PNCs. These properties are obtained when the nanoparticles have achieved an adequate level of dispersion in the polymer matrix. Silica nanoparticle is considered to be a common but useful reinforcement for manufacturing of polymer matrix composites. For example, the incorporation of the nanoscale silica particle into a polymer matrix has shown good mechanical properties [10]. In another study, Zhang et al. [11] prepared polyurethane/silica PNCs and the results showed that the addition of a silica nanoparticle had an effect on the properties of composites. However, they claimed that the dispersion of silica nanoparticles within the polymer matrix might be difficult due to the possible incompatibilities between silica nanoparticle surface and polymer chains [12,13]. Some of the previous studies demonstrated that the use of graphene-based materials enhanced the properties of fiber or polymer-based composites [14–16]. Moreover, Son [17] suggested that only a small amount of graphene should be sufficient to form a network and an interface with polymer due to their higher surface area and aspect ratio. Thanks to their lower price, abundance, biocompatibility, and easiness of surface modification, spherical silica nanoparticles present great interest for the reinforcement of the mechanical properties of polymer matrix composites used for engineering applications. Additionally, graphene-based flakes demonstrate multifunctional properties such as large specific surface areas, high electrical and thermal conductivity, and excellent mechanical properties [18]. Therefore, graphene-based flakes and silica nanoparticles were chosen as fillers of PNCs for this study.

Moreover, it is essential to select an appropriate processing technique based on the properties of polymers and fillers. Several processing methods could be used to produce PNCs, where three main methods that are commonly used to mix nanoparticle fillers into polymers: sol-gel polymerization [19], in situ polymerization [20] and melt compounding [21]. Among these methods, in-situ polymerization is one of the best ways to disperse the nanoparticle fillers into the polymer matrix, but most of the polymers demonstrate lower viscosities than nanoparticle fillers and hence better abilities to diffuse. However, the nanoparticle filler-composites' mechanism for the in-situ polymerization is very complicated [20]. The main problem is the removal of unreacted monomers, while the maintenance of nanoparticle fillers tends to be difficult in some cases. Sol-gel polymerization, which also means solvent blending, has been the only processing method due to the limited feasibility of nanoparticle fillers, however, this method is quite expensive. In contrast, melt processing is the best method to process the nanoparticle-filled composites, since this does not require the removal of solvent and can be used through diverse melt extrusion according to the requirements. During the melt mixing, suitable shear application can minimize the aggregation of nanoparticle fillers. Melt processing is a more efficient, time saving and environmentally friendly method to disperse nanoparticles in a polymer matrix [22]. It is one of the most widely used approaches in industrial applications, because it is easier to be scaled-up [21]. Thus, the melt-mixing extrusion method is relatively time-saving and cost-saving; therefore, it is suitable for industrial applications. However, melt-mixing can suffer from the problem of poor dispersibility of fillers in the PNCs [8,23], which limits their wider application. As previously described by Thomas [24]; the poor dispersion of the nanoparticle fillers may cause deterioration of various PNC properties. Extrusion is one of the common techniques for processing polymeric materials. Mostly, most of the polymers will undergo an extrusion process at least once prior to their final production. It is one of the

potential methods used in many industries in recent years, and can be applied in automotive, aerospace, food, cosmetic processing and so forth. There are various types of polymer processing extruders including disk/drum extruders and single/multi screw extruders [25]. Among the various types of extrusion methods, twin screw extrusion is one of the most common processing methods used in melt mixing/compounding. A twin-screw extruder contains two Archimedean screws within a single barrel [22]. However, the processing mechanisms of a twin-screw extruder are quite complicated, and hence still not well-understood despite the number researches that have been carried out over the last few decades [10].

As per the authors' understanding, no previous work have been reported the correlation of the effect of fillers related to extruder energy consumption and properties of PNCs to investigate the potential ways of optimising/enhancing both of energy saving and performance of PNCs simultaneously. Increasing both energy efficiencies and performance of PNCs may be achieved *via* modifying the filler content, synchronously considering the nature of materials, set temperatures and screw speeds. This research aims to study the effect of fillers related to extruder energy consumption and properties of PNCs (e.g., mechanical, rheological and thermal properties), and then to recognise possible ways of achieving optimal energy saving and good performance of PNCs. A series of experimental trials were performed over a number of different process set conditions (three screw rotational speeds and three set barrel/die temperature conditions) using three polymeric materials and two nanoparticle fillers. A twin-screw extruder (Mini-Lab) was employed in the experimental trials as twin-screw is one of the most widely used types in processing of PNCs.

2. Experimental methods and materials

2.1. Materials

In this study two fillers were used: graphene-based flakes and fumed-silica. Graphene-based flakes (average flake size $\sim 1.45 \mu\text{m}$) were prepared using a microfluidization technique as described in the previous studies [26,27]. Fumed silica was purchased from the Sigma-Aldrich Company Ltd and this has an average particle size from 0.2 to 0.3 μm . In terms of the selection of polymer materials, a semi-crystalline material (Linear Low Density Polyethylene – (LDPE)) and two amorphous materials (polystyrene (PS) and polymethyl methacrylate (PMMA)) were chosen for this study. Among these materials, PMMA degrades *via* unzipping while PS follows a two-step degradation mechanism. Details of these polymeric materials are presented in Table 1.

2.2. Preparation of specimens

2.2.1. Extrusion of PNCs

PNCs were extruded and mixed uniformly employing a Haake Minilab II 350 micro twin-screw compounder (Thermo-Fisher-Scientific, USA). This extruder can operate at 0–360 rpm speed range, and low speeds were selected for achieving better mixing of fillers with the matrix. The set conditions used (the mixing/rotational speed, set temperatures and processing time) are described in Table 2. Before processing, the nanoparticle fillers and PMMA were dried overnight in a vacuum oven (RV5, Edwards High Vacuum International part of B.O.C LTD) at 80 °C for moisture removal. After the extrusion using Minilab, thin solid specimens of $\sim 3 \text{ mm}$ width were obtained. The amounts of the fumed silica and graphene-based flakes used in preparing the PNCs were 3 wt.%,

Table 1

Main features of the neat polymer materials used for experiments.

Polymer	PS	PMMA	LDPE
Density (kg/m ³)	1040	1200	928
Average molecular weight	35,000	120,000	2010
Volume melt-flow rate (cm ³ /10 min)	12 (200 °C/5 kg)	3 (230 °C/3.8 kg)	2.0 (190 °C/2.16 kg)
Melting or glass transition temperature	87	108	100
Melt flow index (MFI) (g/10 min)	11.538	2.5	2.15
Supplier	Styrolution	Evonik plexiglass	Lyondellbasel

Table 2

Main set processing conditions used.

Set condition	Screw speed (rpm)	Temperature (°C)	Filler content by volume	Mixing time (minutes)
Low	50	180	3% (Low), 5% (Medium), 8% (high)	10
Medium	100	200		
High	150	220		

5 wt.%, and 8 wt.%. For the purpose of comparison, pure matrix polymer materials without any filler were also processed using the same procedure and set conditions.

2.2.2. Preparation of sample for testing

After melt-mixing, PNCs were collected and brought to a Haake Mini-jet II micro piston injection moulding machine (Thermo Fisher Scientific, USA) to prepare the specimens for tensile testing which were prepared according to ISO 527-2-1BA standard. The samples were injection moulded at the same set temperature which was used for extrusion and the moulding temperature was set to be 50 °C at all times. The length and thickness of the specimen were 75 mm and 1.5 mm, respectively. The centre parallel part was 5 mm in width and 30 mm in length, and the length and width of the rectangular end parts were 15 mm and 10 mm, respectively. Tensile tests were conducted using an Instron 4301 universal tensile testing machine with Series IX software. Prior to testing, the specimens were conditioned in the test lab for 24 h in order to achieve the balance between specimens and surroundings. The lab conditions were 23 °C (± 2 °C)/50% RH (± 10 %). For each material formulation, at least three dumbbell-shaped specimens were tested and then the average of these measured values being reported. The LDPE-based specimens were tested at a crosshead speed of 5 mm/min, while the others were tested at 0.5 mm/min.

Specimens in the form of discs of thickness 1 mm and diameter 25 mm were prepared by compression moulding for rheological testing. The Small Losca machine in Tangyes Ltd was used for the moulding and aging, in which the same set temperature was used as same as that in extrusion. At least two disc specimens were produced for each set condition. The rheological properties of both the pure polymers and PNCs were then tested using an ARES-RDA 3 screw parallel-plate rheometer. During the testing, the specimens were placed between two parallel metallic plates, which were installed within a heated chamber. The lower plate was connected to a rotor while the upper plate was connected to a transducer.

For each DSC test, a 3–10 mg sample was cut from the same position of the specimens and sealed in a standard aluminium pan. Then, the effect of nanoparticle fillers on the thermal properties of nanocomposites was investigated *via* differential scanning calorimetry (DSC, Q100, TA Instruments). The samples

were tested using a heat-cool-heat cycle with a heating rate of 10 °C/min and a cooling rate of 5 °C/min over a temperature range of 80 °C–240 °C, where this range of temperatures included the expected melting and crystallization temperatures. Then, the T_m and T_g were obtained directly from the 2nd cycle (cooling) and the 3rd cycle (second heating), respectively. The purpose of the first heating cycle was the elimination of the thermal history.

The specimens prepared for scanning electronic microscope (SEM) test were obtained by fracturing the specimens, and then they were tested within a gold coating. A Hitachi S-530 SEM with an Energy Dispersive Spectrometer was also employed to have SEM graphs to analyze the morphology.

3. Results and discussion

3.1. Energy consumption

The energy consumption and power factor measured during the processing of composites at each set condition are shown in Fig. 1 and Fig. 2, respectively. Names of sub-figures are indicated as filler-material-set temperature condition, for example S-PS-200 °C denotes the processing of polystyrene with silica at 200 °C. Legend indicates the amount of loading of fillers (0%, 3%, 5% and 8%). It is clear that the energy consumption is mainly dependent upon the polymer matrix of PNCs. This phenomenon might be associated to the differences of internal heat generation during processing due to the varying frictional and viscous properties of different polymeric materials [28]. Of the three materials used in this study, an increase of power and power factor could be noticed with the increase of the set barrel temperature and processing speed with all the materials, which should be due to the fact that high set temperature or processing speed demands more energy. Moreover, the glass transition or melting temperature of these PNCs should also have influence on the power demand (the higher the T_g or T_m , the higher the demand for heat) during extrusion processing. Therefore, the results indicate that the energy demand is not only dependent upon the melting temperature or glass transition temperature of a material, and it always happens by some complex mechanism/s, including extruder/screw/die design and material's frictional/viscous properties. Also, the phase change process of crystalline materials should also be accounted for these considerations as those

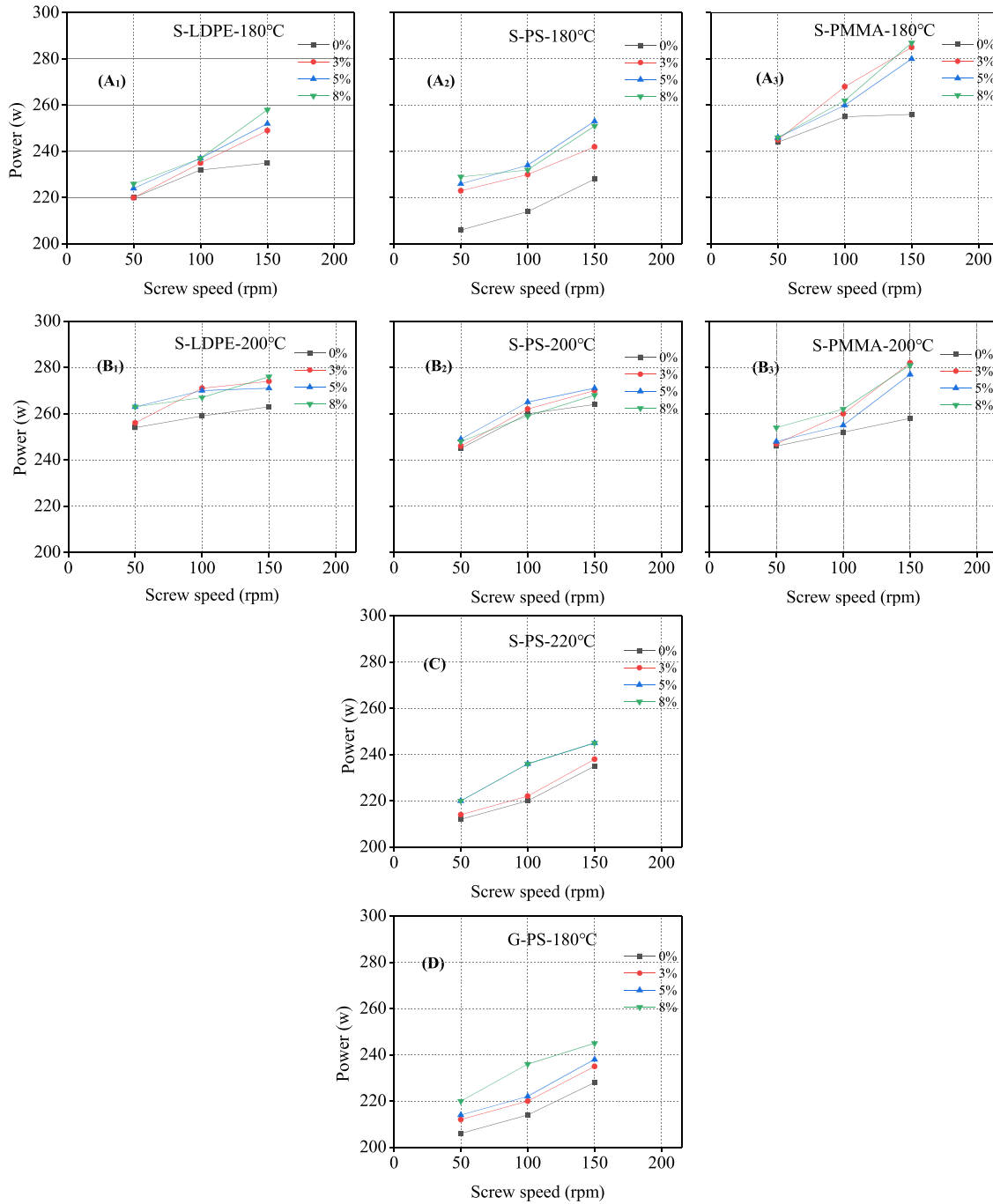


Fig. 1. The power consumption of PNCs: (A₁–A₃) – silica filled PNCs in low temperature; (B₁–B₃) – silica filled PNCs in medium temperature; (C) – PS/silica PNCs in high temperature; and (D) – PS/graphene PNCs in low temperature.

materials absorb or release a certain amount of heat (i.e., latent heat of fusion) during the phase change process with collapsing of their crystal structure.

Usually, the power factor, which can vary between 0 and 1, is an indication of the electrical efficiency of a process/component where the higher the power factor the better the electrical efficiency is. Changes to the power factor are understandable with the variations of the processing speed and set temperature. It is quite interesting to notice here that the power factor varies significantly with

polymer type as well where PMMA based PNCs indicate relatively high power factors than LDPE and PS at the same set conditions. Also, as shown in Fig. 1, the level of energy demand for processing is higher for PMMA based PNCs compared to LDPE and PS based PNCs. This could also be attributed to the frictional and viscous heat generation of different materials and also to the nature of packing (solids bed) and flow of materials with the processing unit [41,42]. However, further research should be carried out prior to making firm conclusions.

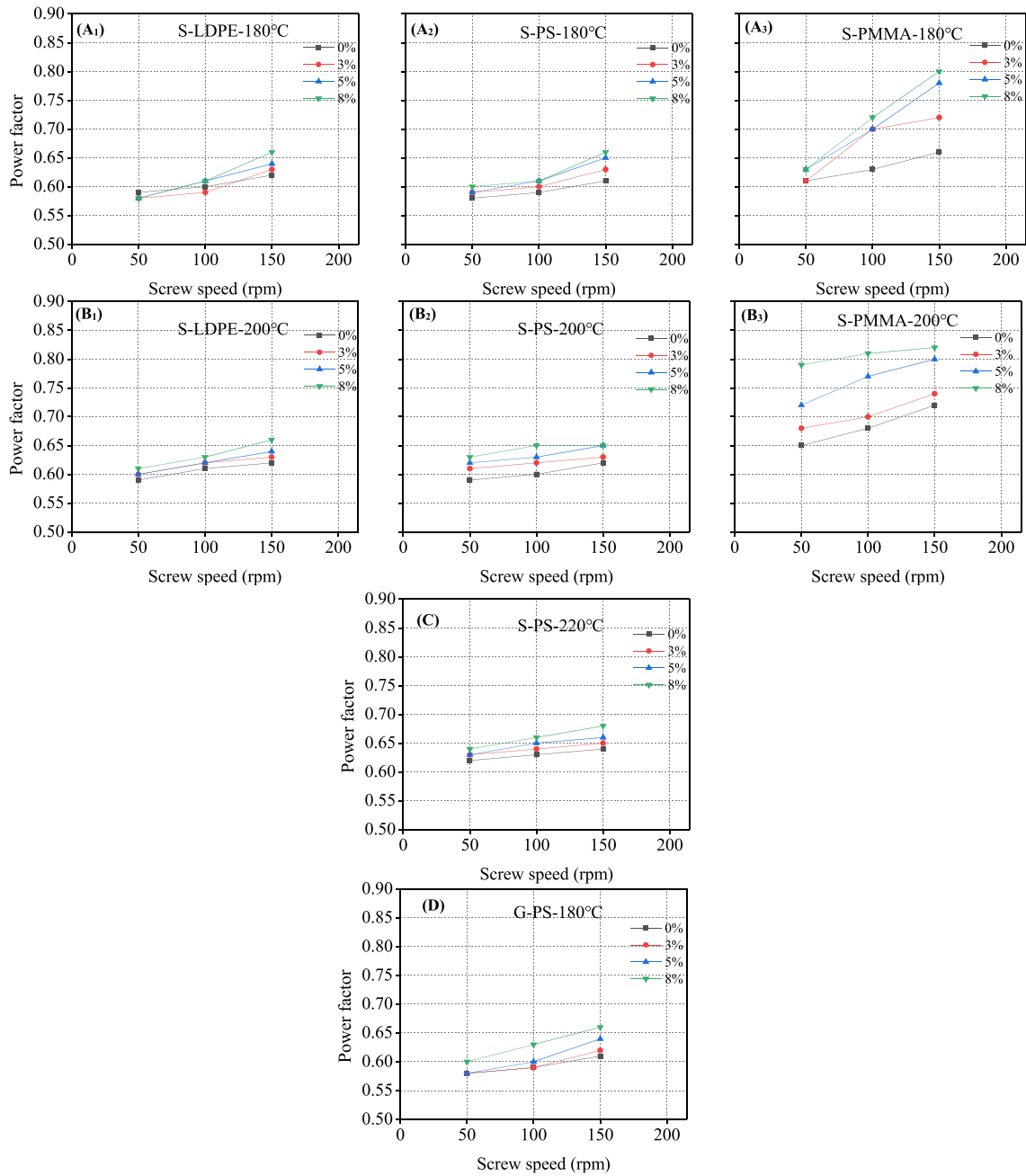


Fig. 2. The power factor during the processing of PNCs: (A₁–A₃) – silica filled PNCs in low temperature; (B₁–B₃) – silica filled PNCs in medium temperature; (C) – PS/silica PNCs in high temperature; and (D) – PS/graphene PNCs in low temperature.

3.2. Effect of fillers

3.2.1. Filler dispersion

In order to investigate whether there is good fusion between the filler and the PS matrix, the SEM images of the distribution boundary of the two fillers (silica and graphene) within the PS matrix was observed. Fig. 3 illustrates the SEM images of the cryogenic fracture surfaces of PS-based PNCs. Fig. 3-(a) shows the morphological behaviour of a PS/silica PNC while Fig. 3-(b) is related to a PS/graphene PNC. The morphology analysis shows not only the filler dispersion in the PNCs, but also the interfacial

interaction between two phases which are silica or graphene filler and the PS polymer matrix. Here, it can be clearly recognized that the particles/fillers are finely dispersed across the structure. Also, from Fig. 3-(b), it is evident that there is good dispersion of nanoparticle fillers without severe agglomeration. Furthermore, these SEM images indicate that no breaking/cracking around the filler particles occurs within the PNCs. It suggests that there is good bonding interaction between the polymer matrix and nanoparticles with no incompatibilities. Therefore, the interface between two phases can be observed as a quite vague line/boundary rather than a clear line.

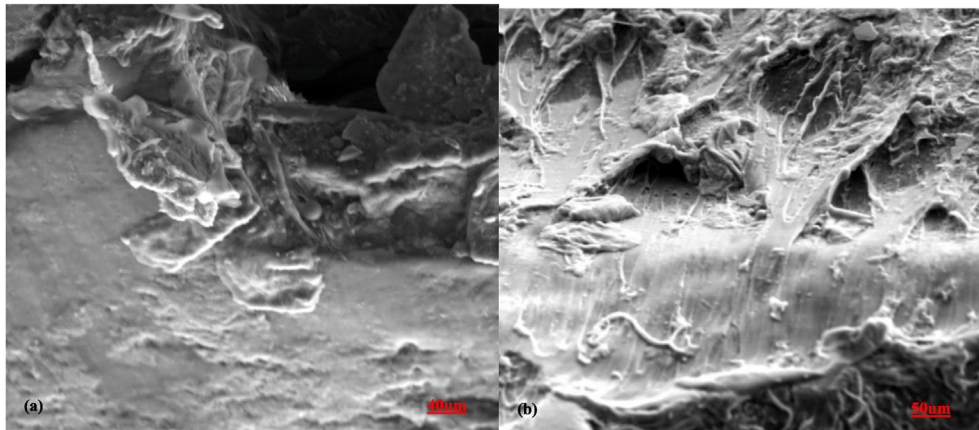


Fig. 3. SEM images: (a) a PS/silica PNC and (b) a PS/graphene PNC.

3.2.2. Mechanical properties

As shown in Fig. 4, it was found that Young's modulus of amorphous materials was affected by not only the addition of nanoparticles, but also by the parameters such as the extrusion

temperature, screw speed and filler type. For the PS-based PNCs shown in Fig. 4, the best possible set conditions are the 8 wt.% of fillers at 200 °C and 150 rpm, in which the Young's modulus of PS-based PNC has increased up to 1806 MPa from 854 MPa (where

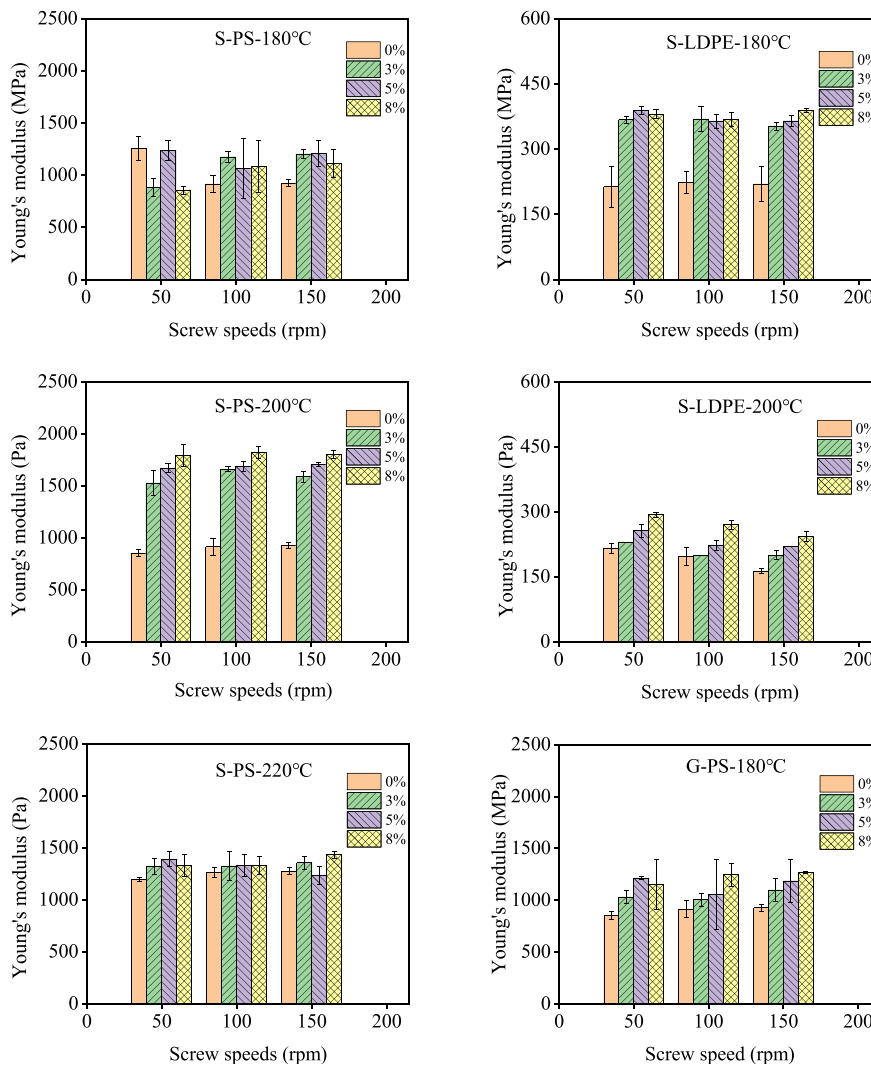


Fig. 4. Young's modulus of silica reinforced PNCs at different processing conditions.

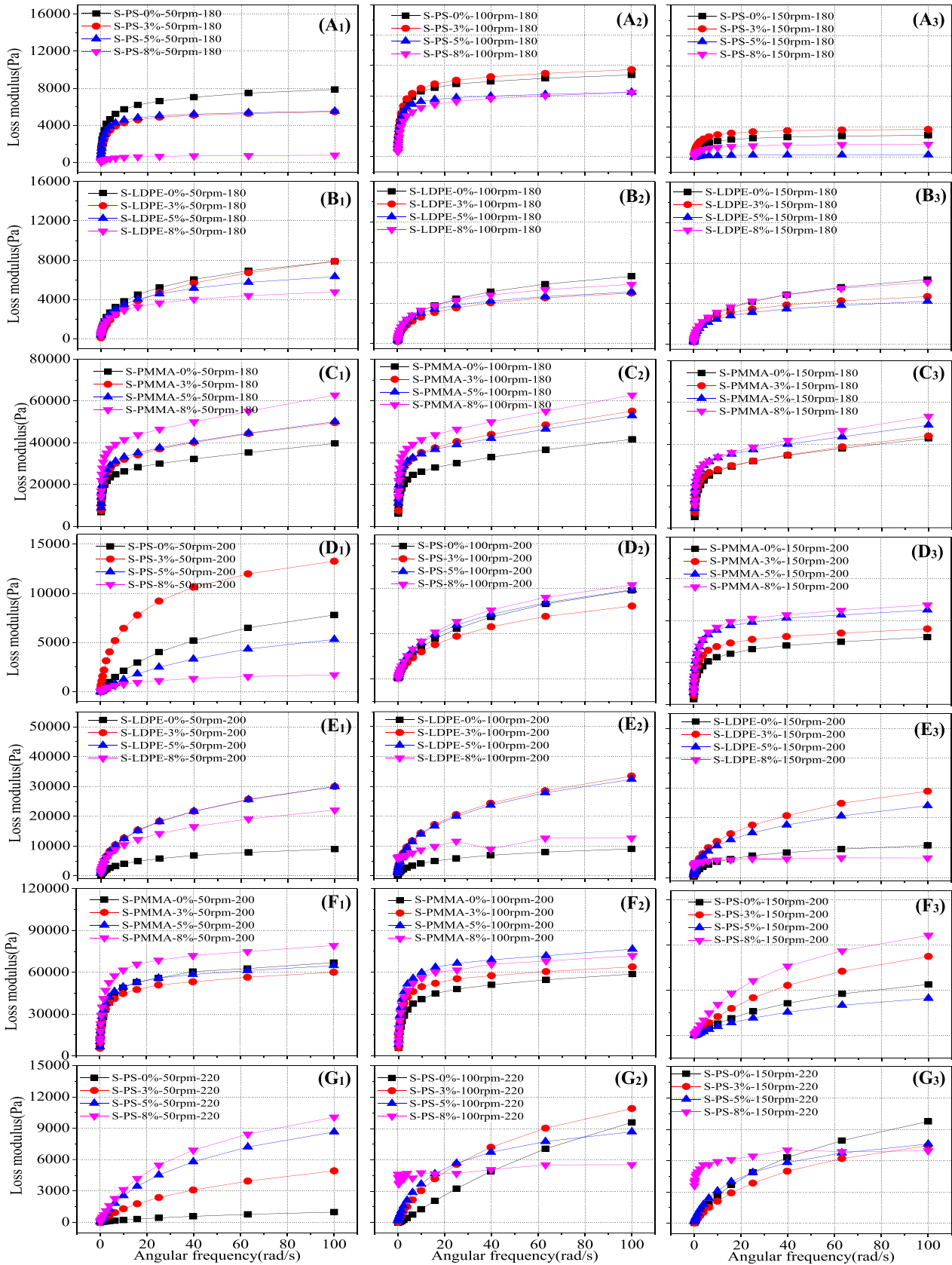


Fig. 5. The loss modulus: low temperature – (A₁-A₃): PS/silica PNCs, (B₁-B₃) – LDPE/silica PNCs, (C₁-C₃) – PMMA/silica PNCs; medium temperature – (D₁-D₃): PS/silica PNCs, (E₁-E₃): LDPE/silica PNCs, (F₁-F₃): PMMA/silica PNCs; and high temperature – (G₁-G₃): PS/silica PNCs.

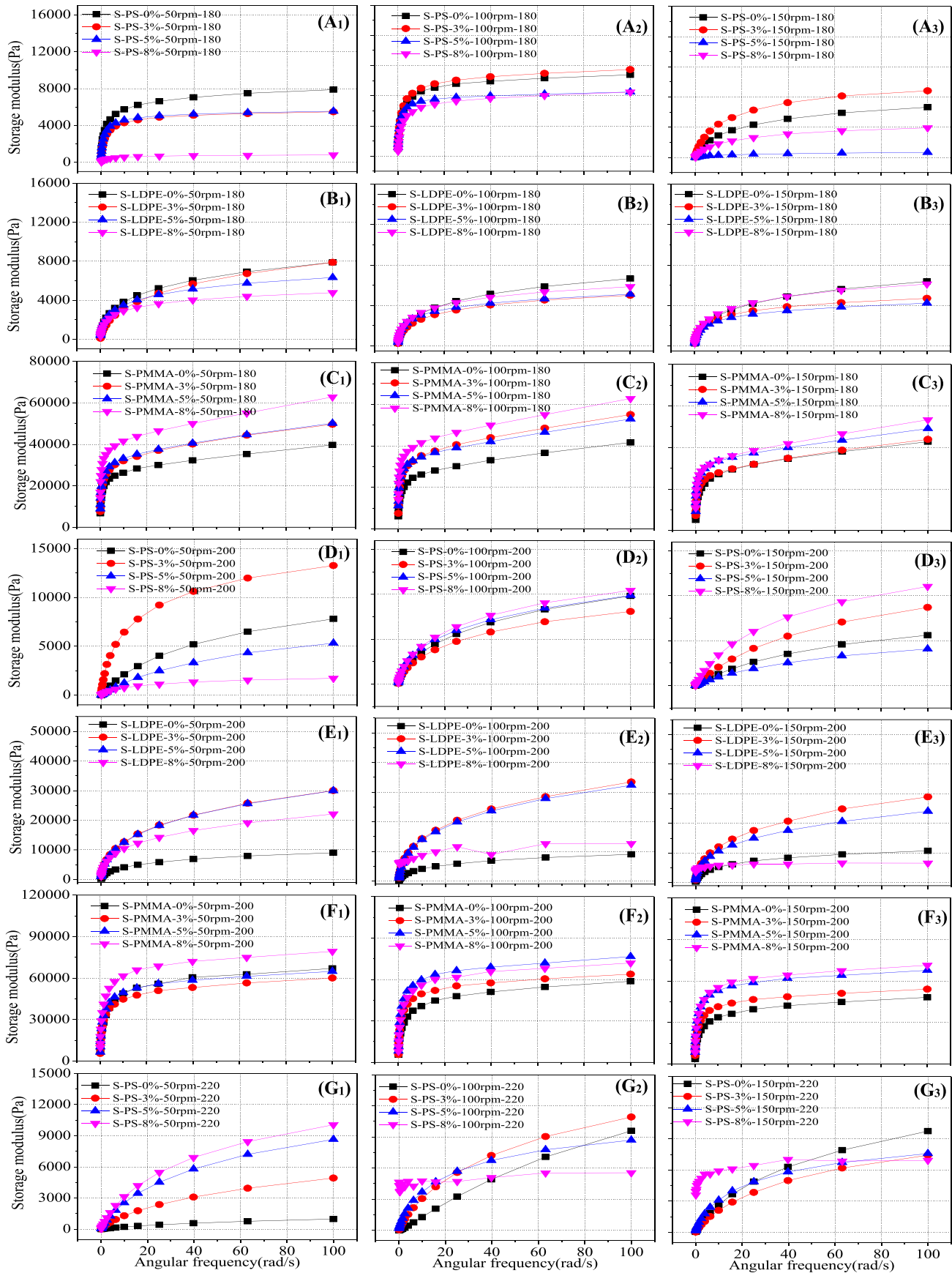


Fig. 6. The storage modulus: low temperature – (A₁-A₃): PS/silica PNCs, (B₁-B₃) – LDPE/silica PNCs, (C₁-C₃) – PMMA/silica PNCs; medium temperature – (D₁-D₃): PS/silica PNCs, (E₁-E₃): LDPE/silica PNCs, (F₁-F₃): PMMA/silica PNCs; and high temperature – (G₁-G₃): PS/silica PNCs.

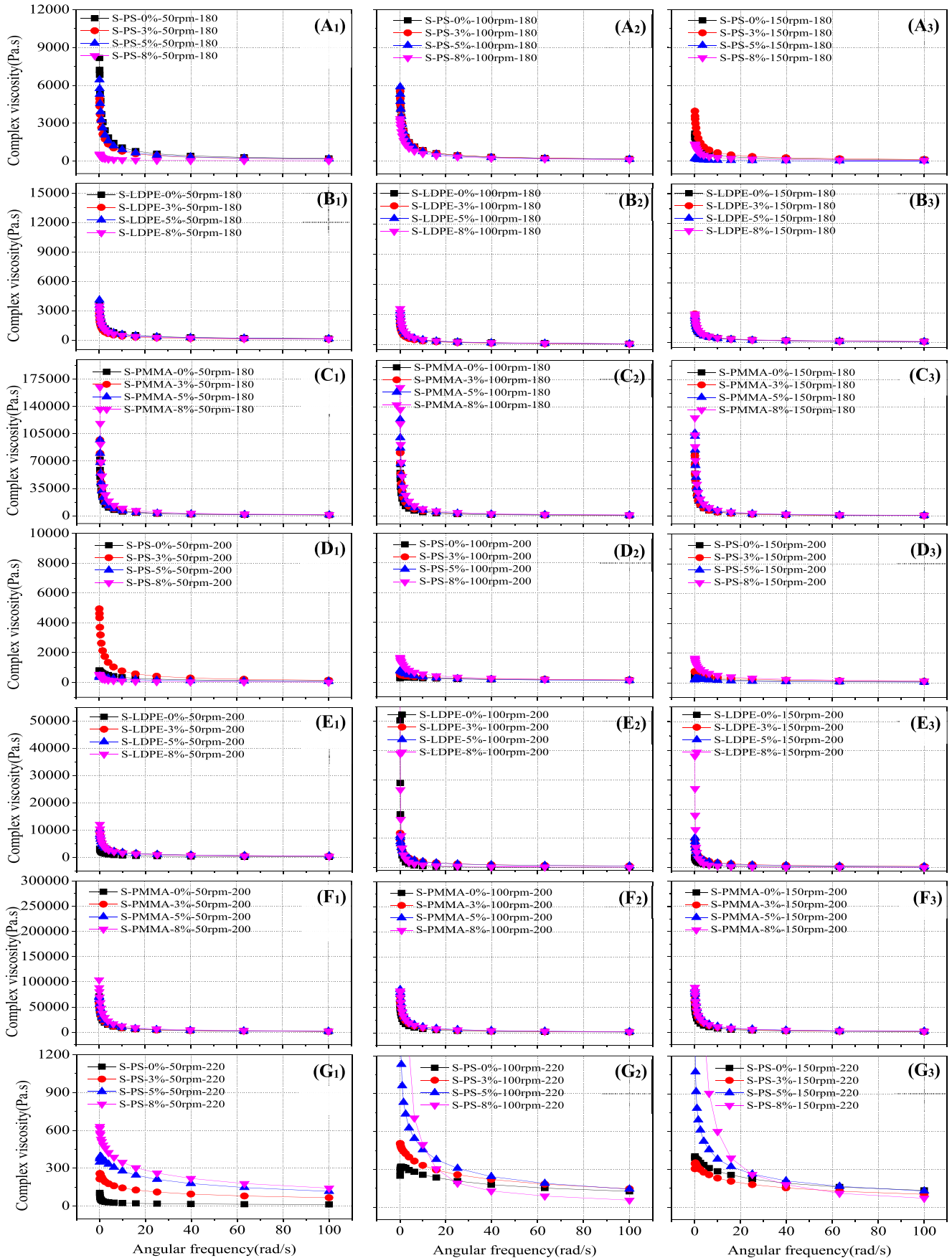


Fig. 7. The complex viscosity: low temperature – (A₁-A₃): PS/silica PNCs, (B₁-B₃) – LDPE/silica PNCs, (C₁-C₃) – PMMA/silica PNCs; medium temperature – (D₁-D₃): PS/silica PNCs, (E₁-E₃): LDPE/silica PNCs, (F₁-F₃): PMMA/silica PNCs; and high temperature – (G₁-G₃): PS/silica PNCs.

Table 3

The glass transition temperature (T_g) or melting temperature (T_m) of polymer/silica nano-composites processed with different filler loadings, screw speeds and set barrel temperatures.

Filler content (wt.%)	0			3			5			8		
Screw speed (rpm)	50	100	150	50	100	150	50	100	150	50	100	150
PMMA-180 °C (T_g)	113	112	110	111	111	111	110	109	111	111	110	110
PMMA-200 °C (T_g)	110	111	111	111	110	117	109	110	110	110	109	110
PS-180 °C (T_g)	90	98	96	92	98	97	95	98	97	98	97	98
PS-200 °C (T_g)	98	98	98	98	99	98	98	98	99	98	97	99
LDPE-180 °C (T_m)	110	112	110	108	110	110	110	110	110	110	108	110

854 MPa is for the neat material at the same set conditions with no filler). This phenomenon could be associated to the high stiffness of the included nanoparticle filler and the formation of the defects while losing the properties at break. The main reason for increasing the modulus is that the chain mobility and the intermolecular motion become more difficult in the macromolecules structure, when PNCs with higher filler content are forced with the external stresses. However, for PNCs with higher filler content, the effect of the nanoparticle filler is appeared to be less pronounced. This regulation of relationship between the materials type and the addition of nanoparticle fillers not only applied in the low screw speeds, but also fitted with the high screw speeds, but the effect of nanoparticle fillers in various screw speeds is slightly different. From the above discussion, it is obvious that silica is easy to agglomerate at 200 °C. This agglomeration phenomenon makes poor dispersion between the nanoparticles and polymer matrix, which suggests the fumed silica filling the voids around the polymer matrix uniformly. On the other hand, the effect of filler content in LDPE-based PNCs was similar as the that of PS-based PNCs, in which Young's modulus of LDPE-based PNCs with 8 wt% of fillers at 200 °C and 150 rpm increased by 80% compared to the neat LDPE. However, LDPE-based PNCs as crystalline materials, Young's modulus is not very sensitive to an increase in the filler content at the same screw speed, which proves the mechanical stability of

crystalline materials is mainly because of the ordered structure arrangement and its lower crystallization temperature. For LDPE-based PNCs, Young's modulus decreases slightly with an increase in the screw speed under the same filler content, which proves that the increase in the screw speed makes the nanoparticles fillers more uniformly dispersed in the melted LDPE matrix, but it may inhibit the crystallization process and hence may decrease the degree of crystallinity. Based on these results, it can be claimed that the processing temperature of polymer matrix is an important factor to enhance the Young's modulus of PNCs, as better melting enhances the depression of fillers. In summary, a higher Young's modulus signifies high stretch ability of the material before undergoing permanent deformation holding a good stiffness even at a low strain. The inherent characteristics of nanosilica and graphene that are being added as mechanical property enhancing fillers have encouragingly improvised the quality of the film. The results show that the Young's modulus of PNCs significantly increased with the addition of fillers. However, in higher filler content concentrations, there are more improving sites leading to a strong interface than that of the lower filler concentration PNCs. According to some published reports [9], the agglomeration of the nanoparticle fillers easily occurs at lower filler loadings, of approximately 2 wt.% – 3 wt.%. It should be noted that with the highest filler content added into the PNCs, Young's modulus of PNCs is reformed at a peak,

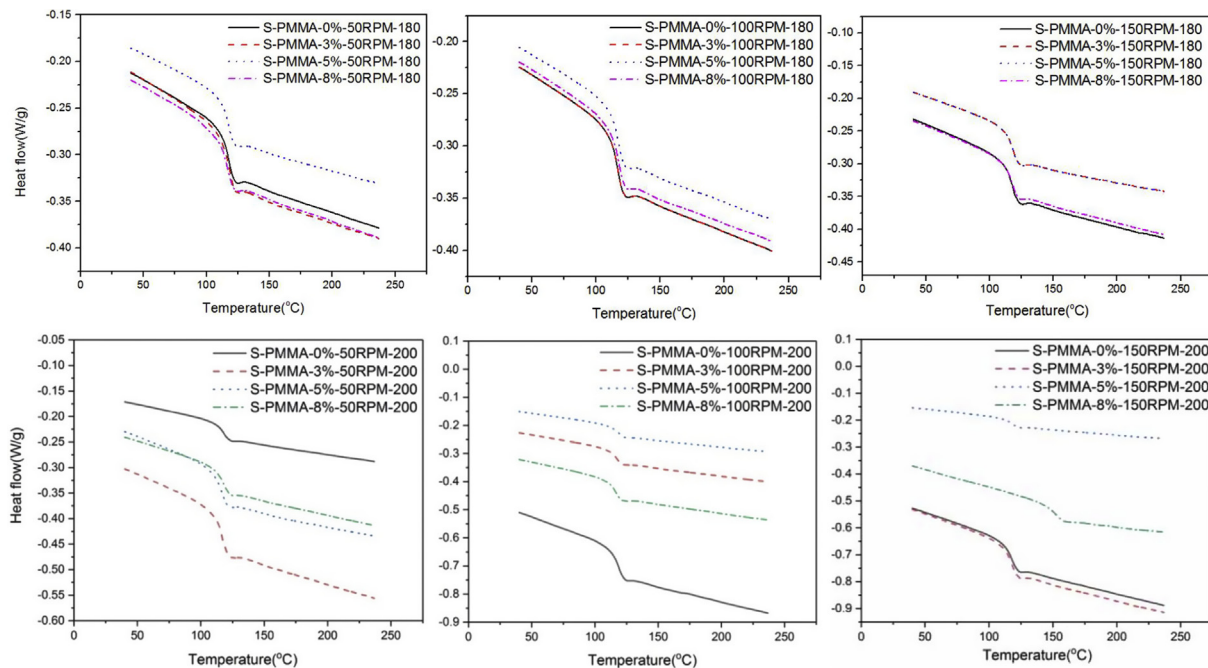


Fig. 8. DSC curves of PMMA-based silica reinforced PNCs with various filler contents under different screw speeds (50, 100, 150 rpm) and at the set temperatures (top – 180 °C, bottom 200 °C).

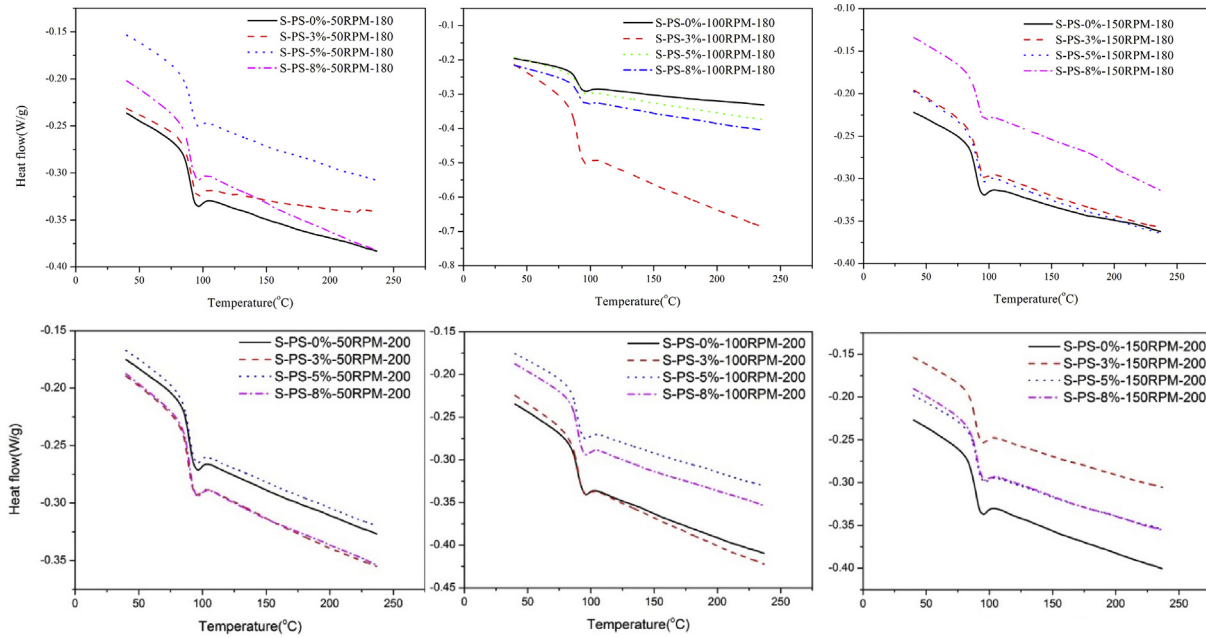


Fig. 9. DSC curves of PS-based silica reinforced PNCs with various filler contents under different screw speeds (50, 100, 150 rpm) and at the set temperatures (top – 180 °C, bottom 200 °C).

suggesting that melt extrusion is a powerful method to prepare improved PNCs with enhanced mechanical properties.

3.2.3. Rheological properties

The experimental results related to loss modulus and storage modulus of neat polymer and PNCs are shown in Figs. 5 and 6, respectively. It should be noted that the storage modulus and loss modulus are related to the elastic and viscous responses of a material, respectively. The loss modulus results of all PNCs (Fig. 5) imply that the main source of increase in loss modulus is the presence of the immobilized interface between the filler and polymer and the secondary networking which takes place through direct short-range interactions via overlapping of interfacial layers on neighbouring fillers. Furthermore, it can be seen that the addition of nanoparticle fillers (silica and graphene) leads to a remarkable rise of storage modulus of PNCs (as shown in Fig. 6) and this decreases with the increase of frequency. In addition, it is shown that the storage modulus of all PNCs declined with increasing temperature, which proves that the higher temperatures can cause relaxation of the amorphous region by enhancing motion of chains regardless the presence of the fillers. The increase of storage modulus of polymer-based PNCs in comparison to the neat

polymer is due to the higher modulus of the nanoparticle which suggests a reinforcing effect and improves the thermo-mechanical stability of the matrix. Moreover, the increase in storage modulus indicates the rise of the stiffness of PNCs [29]. Clearly, the elastic behaviour is significantly influenced by the minimum filler loading (3 wt.%), while for higher contents the rate of increase of storage modulus is becoming lower. Therefore, this consideration can be attributed to a probable increase of filler aggregates within the hosting matrix.

Finally, the complex viscosity was observed as a function of silica and graphene loading at a frequency range of 0–100 rad/s and presented in Fig. 7. According to some previous studies [30,31], the complex viscosity of PNCs is lower than that of the neat polymer. It is noteworthy that with the addition of the lower filler content at 3 wt.%, the viscosity of the system increases rapidly, which may be related to the interfacial interaction between the nanoparticles filler and polymer matrix. Also, it is accompanied by the transition from liquid-like to solid-like viscoelastic response. However, the viscosity of the system is not sensitive to the filler content at a higher nanoparticle concentration and it tends to become stable after some loading condition. A similar phenomena that a silica concentration between 5 wt% and 8 wt% can be regarded as

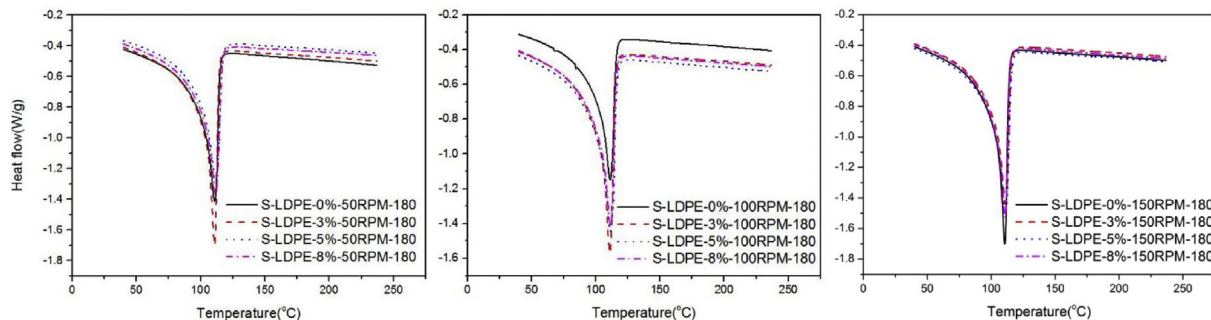


Fig. 10. DSC curves of LDPE-based silica reinforced PNCs with various filler contents under different screw speeds (50, 100, 150 rpm) and at the set temperature 180 °C.

rheological percolation threshold that have been stated within the literature [32]. Overall, it was shown that the physical properties and thermal behaviour of PNCs can be influenced by the loading ratios of the fillers with the matrix.

3.2.4. Thermal properties

The experimentally measured glass transition temperature (T_g) or melting temperature (T_m) of the composites at different processing conditions are presented in Table 3. Experimentally measured DSC curves of some of the PNCs in different set conditions and filler contents are presented in Figs. 8–10.

As can be seen, with the addition of only a small loading of nanoparticles, glass transition temperature (T_g) increases by 1–3 °C. Most of the researchers who have investigated into this field have reported almost no increase or decrease in the T_g as a variation of the filler content; however, a decrease in the T_g has also been reported previously by Wetzel [33]. However, the T_g of PNCs further decreases when introducing more nanoparticles at a higher filler concentration, and even the T_g of PNCs are lower than that of pure matrix materials without fillers. A few previous works [24,33–37] have presented a non-uniform and an unstable trend in the changes in the T_g of PNCs. In these published reports, it has been shown that the T_g of PNCs fluctuates around the T_g value of matrix polymer, rather than providing a stable trend. The main reason for the decrease or increase in T_g should be due to the respective decrease or increase in the polymer molecular mobility. However, with a high level of nanoparticle content, the T_g of the PNCs decreases to be even lower than that of the neat matrix materials. As was discussed above, nanoparticles can show an increased tendency towards the agglomeration with the increase of the filler content. Then, the agglomeration of nanoparticles can introduce a lubrication action on the molecular mobility. While the lubrication action occurred, the strength enhancing efficiency was not noteworthy. Therefore, the agglomeration of nanoparticle filler caused T_g of PNCs to be lower than that of the neat matrix materials. Without considering the nature of the materials, it might be inferred that adding silica nanoparticles at the lowest filler content to the PS polymer matrix causes the PNCs to attain more free volume and easier polymer chain mobility in which the free volume in the PNCs goes beyond that of the PS materials without a filler. Ash and colleagues [38] published an article describing a similar behaviour with an alumina/PMMA nano-composites. However, the behaviour of T_g of PNCs with the filler content/type should be further studied for better understanding. A similar trend to the PS-based PNCs (i.e., decreasing T_g with the filler content) can be observed with LDPE-based PNCs as well. This can be attributed to the addition of fillers that hinders the chain packing and spherulites formation during crystallization, so that there is less of an organized crystalline phase. Generally speaking, the surface functionalization plays an important role on the degree of crystallinity, however the introduction of nanoparticle fillers directly promotes the degree of crystallinity without any surface functionalization. This means that although the fumed silica is amorphous, its high surface area also has some nucleating effects on the polymer matrix. Obviously, this idea has been debated in some published articles, and some controversial results can be found for PE-based PNCs [39,40].

4. Conclusions

This research aimed to investigate the use of fillers with polymeric materials to prepare PNCs by optimizing set conditions and analyzing energy efficiency during processing *via* extrusion. An attempt was made to explore the possible correlation/s between the filler content and energy demand/consumption in

polymer extrusion. According to the experimental observations, the extruder power (i.e. energy demand) and power factor increase with the screw rotational speed following a linear trend in most of the cases and this behaviour is in agreement with the previously reported findings as well. Among all the test conditions, PNCs with 8 wt.% filler content had the highest power factor regardless of the filler content and set process temperature. Normally, a higher power factor is an indication of good energy efficiency, however in this case this trend has to be investigated further. Furthermore, the highest magnitude of power and power factor are associated with PMMA-based PNCs, regardless of the processing speed and extrusion set temperature, which is an indication of the effect of material properties such as the surface friction and viscos dissipation on energy consumption during processing. Moreover, the mechanical properties were increased for all the specimens produced with fumed silica for all three materials (LDPE, PS and PMMA). The rheological behaviour of the melt was dramatically affected at low filler concentrations while it shows a stabilization of the rheological behaviours at high filler loadings (above 5 wt%). The loss modulus of PNCs shows a considerable level of fluctuations at high filler contents, especially, for PMMA-based PNCs, while a similar type of trend to the loss modulus was observed with the storage modulus as well. These findings/results demonstrate the possibility of tailoring thermo-physical properties and process ability of extrusion processing by proper selection of the filler content. Finally, all the PNCs showed a significant enhancement in tensile modulus and complex viscosity with both nano-fillers and this demonstrates some strong interfacial interactions between the polymer matrix and nanoparticles. Overall, the complex viscosities of PNCs are lower than that of the neat polymer matrix without any filler. It is noteworthy that with the addition of a lower filler content at 3 wt.%, the viscosity of the composite increases rapidly and this may be related to the interfacial interaction between the nanoparticle fillers and polymer matrix. The stronger the interfacial adhesion force, it is more difficult to make the molecular movement, so the polymer molecular chains were twined closely. The compact molecular chains were difficult to separate, which caused the viscosity of PNCs to be increased. The complex viscosity of PS filled by graphene particles is different at different screw speeds. Generally, DSC analyses provided some contrasting trends in the thermo-physical characteristics for low and high filler loadings. The T_g of all PNCs is related to the T_g of neat polymers, which is mainly depended on the molecular structure of polymers. With the addition of nanoparticles, the T_g of PNCs shows a mixed behaviour in terms of the increasing/decreasing nature of T_g . For PS-based PNCs, T_g varies between 68 °C and 70 °C. Moreover, as was observed, there was only one T_g for all PNCs rather than two T_g values, which means that the polymer matrix and nanoparticle filler are mixed well and there is a good interface between these two phases in PNCs. Therefore, it indicates that the twin screw extrusion is an effective method to product PNCs.

Conflicts of interest

The authors declare that there is no conflicts of interest.

References

- [1] C. Abeykoon, A novel soft sensor for real-time monitoring of the die melt temperature profile in polymer extrusion, *IEEE Trans. Ind. Electron.* 61 (12) (2014) 7113–7123.
- [2] L.E. Nielsen, R.F. Landel, *Mechanical Properties of Polymers and Composites*, second ed., Marcel Dekker, New York, NY, USA, 1994.
- [3] A. Taguet, P. Cassagnau, J.M. Lopez-Cuesta, Structuration, selective dispersion and compatibilizing effect of (nano)fillers in polymer blends, *Prog. Polym. Sci.* 39 (8) (2014) 1526–1563.

- [4] M.S.D. Luna, G. Filippone, Effects of nanoparticles on the morphology of immiscible polymer blends – challenges and opportunities, *Eur. Polym. J.* 79 (2016) 198–218.
- [5] F. Laoutid, E. Estrada, R.M. Michell, et al., The influence of nanosilica on the nucleation, crystallization and tensile properties of PP–PC and PP–PA blends, *Polymer* 54 (15) (2013) 3982–3993.
- [6] V. Alvarez, M. Paulis, Effect of acrylic binder type and calcium carbonate filler amount on the properties of paint-like blends, *Prog. Org. Coating* 112 (2017) 210–218.
- [7] J. Gou, Z. Liang, C. Zhang, et al., Computational analysis of effect of single-walled carbon nanotube rope on molecular interaction and load transfer of nanocomposites, *Compos. Part B* 36 (6) (2005) 524–533.
- [8] P.M. Ajayan, L.S. Schadler, P.V. Braun, *Nanocomposite Science and Technology*, Wiley-VCH, Weinheim, 2003.
- [9] Yang Feng, Gordon L. Nelson, Polymer/silica nanocomposites prepared via extrusion, *Polym. Adv. Technol.* (2006) 320–326.
- [10] Y.L. Liu, C.Y. Hsu, W.L. Wei, et al., Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica, *Polym. Adv. Technol.* 18 (2003) 5159–5167.
- [11] S.W. Zhang, RenLiu, J.Q. Jiang, et al., Facile synthesis of waterborne UV-curable polyurethane/silica nanocomposites and morphology, physical properties of its nanostructured films, *Prog. Org. Coating* 70 (1) (2011) 1–8.
- [12] G. Ragosta, M. Abbate, P. Musto, et al., Epoxy-silica particulate nanocomposites: chemical interactions, reinforcement and fracture toughness, *Polymer* 46 (23) (2005) 10506–10516.
- [13] M. Bailly, M. Kontopoulou, K.E. Mabrouk, Effect of polymer/filler interactions on the structure and rheological properties of ethylene-octene copolymer/nanosilica composites, *Polymer* 51 (23) (2010) 5506–5515.
- [14] P.G. Karagiannidis, S.A. Hodge, L. Lombardi, et al., Microfluidization of graphite and formulation of graphene-based conductive inks, *ACS Nano* 11 (3) (2017) 2742.
- [15] F. Sarker, N. Karim, S. Afroj, V. Koncherry, K.S. Novoselov, P. Potluri, High-performance graphene-based natural fiber composites, *ACS Appl. Mater. Interfaces* 10 (2018) 34502–34512.
- [16] F. Sarker, P. Potluri, S. Afroj, V. Koncherry, K.S. Novoselov, N. Karim, Ultrahigh performance of nanoengineered graphene-based natural jute fiber composites, *ACS Appl. Mater. Interfaces* 11 (2019) 21166–21176.
- [17] Y.W. Son, M.L. Cohen, S.G. Louie, Erratum: energy gaps in graphene nanoribbons, *Phys. Rev. Lett.* 98 (8) (2007) 89901.
- [18] N. Karim, F. Sarker, S. Afroj, M. Zhang, P. Potluri, K.S. Novoselov, Sustainable and multifunctional composites of graphene-based natural jute fibers, *Adv. Sustainable Syst.* (2021) 2000228, <https://doi.org/10.1002/advs.202000228>.
- [19] M.M. Seraji, G. Sameri, J. Davarpanah, A.R. Bahramian, The effect of high temperature sol-gel polymerization parameters on the microstructure and properties of hydrophobic phenol-formaldehyde/silica hybrid aerogels, *J. Colloid Interface Sci.* 493 (Complete) (2017) 103–110.
- [20] Su Mi Hur, M.J. Park, H.K. Rhee, Polymer property control in a continuous styrene polymerization reactor using model-on-demand predictive controller, *Kor. J. Chem. Eng.* 20 (1) (2003) 14–21.
- [21] M. Tanahashi, Development of fabrication methods of filler/polymer nanocomposites: with focus on simple melt-compounding-based approach without surface modification of nanofillers, *Materials* 3 (3) (2010) 1593–1619.
- [22] G. Vassilatos, Polymer melt processing: foundations in fluid mechanics and heat transfer by M. M. Denn, *AIChE J.* 58 (6) (2012) 1966.
- [23] I.M. Sotirios, I. Zuburtikudis, C. Panayiotou, Solution casting versus melt compounding: effect of fabrication route on the structure and thermal behavior of poly(L-lactic acid) clay nanocomposites, *Mater. Sci.* 45 (2010) 6474–6480.
- [24] P.S. Thomas, S. Thomas, S. Bandyopadhyay, A. Wurm, C. Schick, Polystyrene/calcium phosphate nanocomposites: dynamic mechanical and differential scanning calorimetric studies, *Compos. Sci. Technol.* 68 (2008) 3220–3229.
- [25] M.J. Stevens, J.A. Covas, *Extruder Principles and Operation*, Chapman and Hall, 1995.
- [26] S. Afroj, N. Karim, Z. Wang, S. Tan, P. He, M. Holwill, D. Ghazaryan, A. Fernando, K.S. Novoselov, Engineering graphene flakes for wearable textile sensors via highly scalable and ultrafast yarn dyeing technique, *ACS Nano* 13 (4) (2019) 3847–3857.
- [27] N. Karim, M. Zhang, S. Afroj, V. Koncherry, P. Potluri, K.S. Novoselov, Graphene-based surface heater for de-icing applications, *RSC Adv.* 30 (2018).
- [28] C. Abeykoon, P.J. Martin, A.L. Kelly, E.C. Brown, Anevaluation of melt temperature sensors for polymer extrusion, *Sens. Actuators, A* 182 (2012) 16–27.
- [29] Xiaohui Liu, Qiuju Wu, PP/clay nanocomposites prepared by grafting-melt intercalation, *Polymer* 42 (25) (2001) 10013–10019.
- [30] E. Habib, R. Wang, X.X. Zhu, Correlation of resin viscosity and monomer conversion to filler particle size in dental composites, *Dent. Mater.* 34 (10) (2018) 1501–1508.
- [31] A.Y. Malkin, M.Y. Polyakova, A.V. Andrianov, et al., Viscosity and viscoelasticity of liquid nanoparticles with polymeric matrix, *Phys. Fluids* 31 (8) (2019), 083104.
- [32] Tony Mcnally, Pötschke, et al., Polyethylene multiwalled carbon nanotube composites, *Polymer* 46 (19) (2005) 8222–8232.
- [33] B. Wetzel, P. Rosso, F. Hauptert, et al., Epoxy nanocomposites – fracture and toughening mechanisms, *Eng. Fract. Mech.* 73 (16) (2006) 2375–2398.
- [34] O. Becker, G.P. Simon, 2–Epoxy nanocomposites based on layered silicates and other nanostructured fillers, *Polym. Nanocompos.* (2006) 29–56.
- [35] S.C. Tjong, Structural and mechanical properties of polymer nanocomposites, *Mater. Sci. Eng. R Rep.* 53 (3–4) (2006) 73–197.
- [36] A. Bansal, H. Yang, C. Li, et al., Controlling the thermomechanical properties of polymer nanocomposites by tailoring the polymer–particle interface, *J. Polym. Sci. B Polym. Phys.* 44 (20) (2010) 2944–2950.
- [37] A. Bansal, H. Yang, C. Li, et al., Quantitative equivalence between polymer nanocomposites and thin polymer films, *Nat. Mater.* 4 (9) (2005) 693–698.
- [38] B.J. Ash, L.S. Schadler, R.W. Siegel, Glass transition behavior of alumina/poly-methylmethacrylate nanocomposites, *Mater. Lett.* 55 (1) (2002) 83–87.
- [39] E. Kontou, G. Anthoulis, The effect of silica nanoparticles on the thermomechanical properties of polystyrene, *Appl. Polym. Sci.* 105 (2007) 1723–1731.
- [40] Kaufman L G, Cozewith C, Gadkari A C, et al. *Thermoplastic Olefin Composites*: US, US6245856. 2001.
- [41] C. Abeykoon, *Modelling and Control of Melt Temperature in Polymer Extrusion*, PhD Thesis, Queens University Belfast, UK, 2011.
- [42] C. Abeykoon, A.L. Kelly, J. Vera-Sorroche, et al., Investigation of the process energy demand in polymer extrusion: A review and an experimental study, *Appl. Energy* 136 (2014) 726–737.

List of Abbreviations

CaCO ₃ :	Calcium carbonate
DSC:	Differential scanning calorimetry
LDPE:	Linear low density polyethylene
PS:	Polystyrene
PNCs:	Polymer-based nan-composites
PMMA:	Polymethyl methacrylate
SEM:	Scanning electronic microscope