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EFFECT OF HBN FILLERS ON RHEOLOGY PROPERTY AND SURFACE MICROSTRUCTURE OF ABS EXTRUDATE

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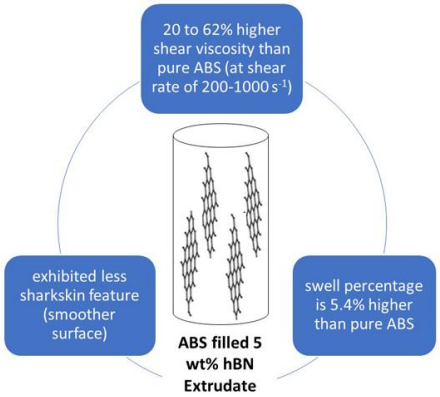
Graphical abstract



Abstract

ABS filament remains an important feeding material for fused deposition manufacturing (FDM). However, ABS tends to experience warping after printing. The current paper investigates the effect of hBN fill on rheology property and diameter of ABS extrudate. ABS filled hBN composite was prepared by a facile solution mixing method. Rheological characterisation by capillary rheometer shows that ABS filled 5 wt% hBN composite exhibited a higher shear viscosity than the pure ABS. hBN addition appears to increase the shear viscosity of ABS by 62% at the shear rate of 200 s^{-1}, but the increase was reduced to 20% at 1000 s^{-1}. ABS-hBN extrudate surface microstructure deteriorated lesser than ABS extrudate when the shear rate increased up to 1000s^{-1}. SEM micrograph of ABS-hBN extrudate's surface exhibited less sharkskin feature but its swell percentage is 5.4% higher than the ABS extrudate. The addition of hBN fillers resulted in higher shear viscosity and percentage of ABS die swell but exhibited less sharkfin feature (smoother surface) on extrudate surface than the pure ABS.

Keywords: Additive Manufacturing, Fused Deposition Modeling (FDM), Hexagonal Boron Nitride (hBN), Fused Filament Fabrication (FFF), Rheology

Abstrak

Filamen ABS tetap menjadi bahan suapan penting untuk pemodelan pengendapan terlakur (FDM). Walau bagaimanapun, ABS cenderung mengalami peledingan selepas pencetakan. Artikel ini menyiasat kesan pengisi hBN keatas sifat reologi dan diameter semperit ABS. Komposit ABS terisi hBN disediakan dengan kaedah mudah pencampuran larutan. Pencirian reologi oleh reometer rerambut menunjukkan komposit ABS terisi 5 wt% hBN mempamerkan kelikatan ricih lebih tinggi daripada ABS tulen. Penambahan hBN menampakkan peningkatan kelikatan ricih ABS sebanyak 62% pada kadar ricih sebanyak 200 s^{-1}, tetapi peningkatan ini berkurang ke 20% pada 1000 s^{-1}. Mikrostruktur permukaan semperit ABS-hBN merosot sedikit berbanding dengan semperit ABS bila kadar ricih meningkat ke 1000s^{-1}. Mikrograf SEM bagi permukaan semperit ABS-hBN mempamerkan ciri kulit jerung yang kurang tetapi peratusan ampulannya adalah 5.4% lebih tinggi daripada semperit ABS. Penambahan pengisi hBN mengakibatkan kelikatan ricih dan peratusan ampulan acuan yang lebih tinggi, tetapi mempamerkan ciri kulit jerung yang kurang (permukaan lebih licin) pada permukaan semperit berbanding dengan ABS tulen.

Kata kunci: Pembuatan Tambah, Pemodelan Pengendapan Terlakur (FDM), Boron Nitride heksagon (hBN), Pembuatan Filament Terlakur (FFF), Reologi

1.0 INTRODUCTION

3D printing is an additive manufacturing technology that builds physical parts using a layer-by-layer approach from a computer model [1]. The technology could manufacture nearly any polymer product with complex geometries at a lower manufacturing cost and shorter time than any commercially available process. Currently, the most feasible 3D printing technique for polymer products is fused deposition manufacturing (FDM).

The FDM technique requires the use of polymer feeding material in the form of a coiled filament. Among the feeding materials in the market, ABS filament remains a popular choice due to its performance reliability during printing and the durability of the printed product. However, ABS has a higher melting point than other feeding materials like PLA, and the former tends to experience warping after printing. Therefore, different approaches had been reported to resolve the warping problem, such as optimisation of printing parameters which includes adjusting the print bed temperature [2], applying adhesion on the print bed surface [2, 3], and free-form deformation compensation [4].

One of these studies claimed the warping is caused by the formation of internal stresses created by nonuniform cooling throughout the printed specimen [3]. Another possible cause of warping is nonuniform increased packing density caused by polymer melting [5]. It is believed that the root cause of the warping is inter-related due to their dependency on the temperature factor. Thus, it is more likely the ABS warping is caused by the uneven shrinking rate on the printed ABS as a result of inefficient thermal dissipation from the ABS body.

Thermal dissipation of insulating polymers can be enhanced by introducing high thermal conductive hexagonal boron nitride (hBN) [6, 7].

Recent studies show that the hBN addition exhibited improved flame retardancy reinforcement ability and suppressed toxic gas emissions from polymer composite [8]. Another study reported that the polymer filled hBN reduced the neutron attenuation through polymer up to 40% [9]. Furthermore, hBN due to its natural white colour is more appealing than a carbon-based filler for the polymer product that requires colour pigments for visual labelling.

There is increasing interest in applying 3D printing to produce polymer filled-hBN structure for thermal management applications [10, 11, 12]. A recent forecast by 360 Research Report reported the global market size of thermal management technologies is expected to reach USD 73.280 billion by the end of 2026 with a CAGR of 3.8% after considering the impact of Covid-19 [13]. Consequently, several studies on the application of polymer filled hBN as FDM filament had been reported. There were ABS filled-hBN [9, 14], Polyamide 6-polyolefin filled-hBN [11] and polyurethane filled-hBN [10]. Quil *et al.* [14] claimed that with the 5 wt% hBN concentration in ABS, thermal conductivity improved by 30 to 90% compared to pure ABS. Nevertheless, these studies did not provide insight into their polymer filled-hBN's rheology behaviour.

Rheological study is essential before the extrusion process of FDM filament, as this provides a comparison of the processability data of the composite with the pure polymer. In this case, the temperature profile and extrusion screw rotation setting need to be adjusted accordingly whenever there is a change in melt flow behaviour caused by filler addition in polymer extrusion materials [15]. It is also important that the thermal behaviour of polymer filled hBN is investigated to determine the highest use temperature as well as the lowest possible processing temperature [16]. In terms of practicality, DSC is an effective technique for identifying the polymer's processing temperature through the detection of the glass transition temperature.

The current paper investigates the effect of small amount of hBN addition (5 wt%) on the thermal, rheology property and morphology of ABS filled hBN composite prepared by the solution mixing method. Compared with melt mixing (compounding) technique which requires the usage of internal mixer, solution mixing only requires a simple technique involving organic dissolution and mechanical mixing processes. Thus, this method is cheap and possibly more feasible for scaling up for industry adoption. Previous reports claimed that the solution mixing method led to better dispersion of nanoparticles than the melt mixing method in a polymer matrix at low (<5 wt%) nanofiller concentration [17]. Another study on FDM printed polymer filled hBN composite also showed the low hBN filler concentration composite exhibited better flexural strength than high concentration composite and matched with the flexural strength of pure polymer [14]. This is particularly important as ABS filled hBN needs to maintain sufficient mechanical strength to enable the composite to undergo the extrusion process to produce long and durable filament for FDM printing. Besides reducing the cost of the material, low filler concentration filament also reduces risk of clogging at nozzle orifice during FDM printing [18].

2.0 METHODOLOGY

2.1 Materials

Acrylonitrile Butadiene Styrene pellets (ABS, POLYLAC®ABS-PA-747) were supplied by CHIMEI, Taiwan. Hexagonal boron nitride (hBN, 99.8% purity, average particle size = 0.6~1.2 μm) was supplied by Nova Scientific. Particle size and surface charge characterisations were reported in a previous paper [19]. Surface microstructure of the as-received hBN particles obtained by field emission scanning electron microscope (FESEM, Model: SU 8320, Hitachi) are shown in Figure 1.

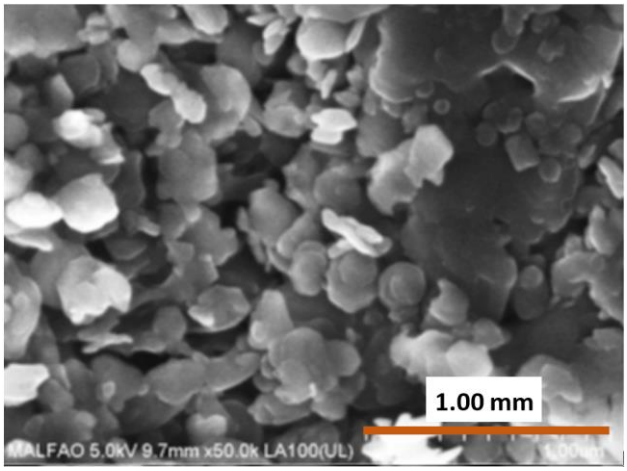


Figure 1 Surface microstructure of as-received hBN particles

2.2 Preparation of ABS-hBN Composite

As-received ABS pellets were dissolved in acetone and then mixed with hBN particles using the procedure reported by Woosley *et al*. [9]. Then, the ABS-hBN slurry was placed in a 15 cm diameter and 5 cm depth glass plate and then let dry in a drying oven at 60°C for 7 days under ambient environment. Afterwards, the dried composite was cut by a steel knife into 5 cm size and then crushed into ~0.5 cm sized granules by a cone crusher (Cheso Machinery, Singapore). The ABS-hBN composite granules were packed into a sealed plastic bag and then stored inside a sealed desiccator containing silica gel. The desiccator's whole surface area was wrapped with a commercially available aluminium foil to protect the desiccator from external UV light.

2.3 Thermal and Rheological Characterisations of ABS-hBN Composite Granules

Thermal characterisation was carried out on the composite using differential scanning calorimeter (DSC, model Jade DSC; PerkinElmer) in accordance to IPC TM-650, Method 2.4.25 standard under pure nitrogen gas environment [20]. The DSC sample was sealed in a crimping pressed aluminium crucible and then heated at 10°C/min from room temperature (25°C) to 400°C. DSC characterisation of as-received ABS pellets was also performed as reference sample. DSC sample's weight of ABS and ABS-hBN samples were 13.99 mg and 6.81 mg respectively.

A rheological test was carried out on ABS-hBN samples using INSTRON CEAST SmartRHEO model SR20 capillary rheometer in accordance with ISO 11443 standard (Method A) and ASTM D3835. A similar rheological test was also performed on as-received ABS pellets for reference purposes. Before each test, the sample was fed into the 15 mm diameter barrel. A long 1 mm diameter capillary-typed die was supported at the bottom of the barrel to maintain the geometric integrity. The ratio of capillary length to diameter (L/D) was set at 20. All the samples were subjected to a heating temperature of 230°C for a total preheating time of 300 s. After that, a constant piston loading of 100 N was applied by a hydrostatic system to drive the polymer melt through the die at increasing shear rates from 100 to 1000 s^{-1}. A transducer measured melt pressure at the long die entrances during each test and then converted into the melt viscosity values. A heating temperature at 230°C had been selected for the capillary rheometer in order to match with the barrel temperature of extruder that will be used to produce FDM filament.

2.4 Extrusion of ABS-hBN Composite Filament

The ABS-hBN composite granules were used as the feeding materials for the extrusion of ABS-hBN composite filament. The extrusion was conducted using a twin screw-typed extruder for 3D printer filament from the Zhangjiagang Friend Machinery Co. (China). Each twin screw is 22 mm in diameter with the extruder's length/diameter ratio (L/D) is 32. Barrel temperature profile of the extruder was set in degree Celsius at 200-230-230-220. A die which is designed for the fabrication of l.75 mm diameter PLA or ABS filament was fixed at the outlet of the extruder. A laser diameter measurement device (±0.05 mm tolerance, BX-1B, EECTRL, China) was fixed in front of the die to ensure the diameter stability of the extruded filament. Both the extrusion's screw speed and filament's pulling (calendaring) speed were adjusted until the required filament's diameter was achieved and was stable throughout the coiling process of extruded filament on the spool winder.

2.5 Microstructural Characterisations of ABS-hBN Composites' Extrudate

In order to estimate the mechanical behaviour of fabricated ABS-hBN filament by the extrusion process, microstructural studies were conducted on the longitudinal surface microstructure of the ABS-hBN and ABS extrudates produced by the capillary rheological characterisation and by the extruder machine. The microstructural samples were examined using scanning electron microscope (SEM, accelerating voltage = 15 kV, Model: Evo 50, Carl Zeis AG). To obtain clear SEM images, Au-Pd layer was sputtered coated onto the SEM sample before observation to avoid charging effect.

Samples from the capillary rheological characterisation and extruder machine were collected during the beginning (labelled as Head region) and the ending (labelled as Tail region) of the extrusion process. The purpose of the sampling was to investigate the stability of the mechanical property of the produced extrudates. For the capillary rheometer samples, the Head of the produced extrudate was collected at the shear rate of 200 s^{-1}, while the Tail was collected at 1000 s^{-1}. Meanwhile for the extruder machine samples, both the Head and Tail of the extrudate (also known as filament) were collected at

the same shear rate because of the screw's constant rotation speed.

3.0 RESULT AND DISCUSSION

The DSC curves of ABS and ABS-hBN (ABS filled hBN) samples (Figure 2) reveal similar thermal characteristics during the heating process from the room temperature to 250°C. Both samples exhibited similar endothermic peaks that were corresponding to the glass transition onset temperature (T_g) at ~107.5°C, and the low endothermic peaks at 220 and 230°C respectively.

T_g is a temperature at which the ABS polymer chains' glassy state are converted into the rubbery state [16]. Polymer chain motion during the rubbery state is mainly translational, when compared to the glassy state which is largely vibrational [16]. Compared to the ABS sample, the ABS-hBN sample displayed a smaller baseline jump at same T_g value. It appears that the addition of hBN decreased the degree of change of the ABS polymer chains' kinetically controlled order parameter during the glass transition process [21].

ABS is known as an amorphous polymer, and thus does not have melting temperature [16, 22, 23]. Therefore, the small endothermic peaks at 220 and 230°C) were likely contributed by a chemical additive in the as-received ABS pellet.

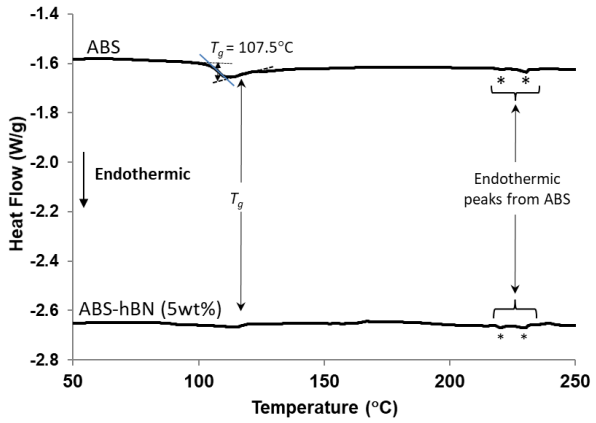


Figure 2 DSC heating curves of ABS-hBN and ABS

The shear viscosity-shear rate plot at 230°C (Figure 3) shows that ABS-hBN samples shows power-law rheological characteristic similar to the pure ABS. The decreasing shear viscosity with the increasing shear rate of these samples indicates they exhibited shear thinning behaviour [21] at a shear rate between 100 and 1000 s^{-1}. A comparison with the ABS sample indicates that the ABS-hBN samples were more viscous than the pure ABS within the studied shear rate. The finding is consistent with the rheological studies of ABS filled with natural fibre fillers [24]. Studies suggested that the presence of irregular shapes of natural filler provides an obstruction to the polymer melts of composites. This probably happened to the current ABS-hBN samples, in which hBN particles were in random orientation during the extrusion of ABS-hBN samples.

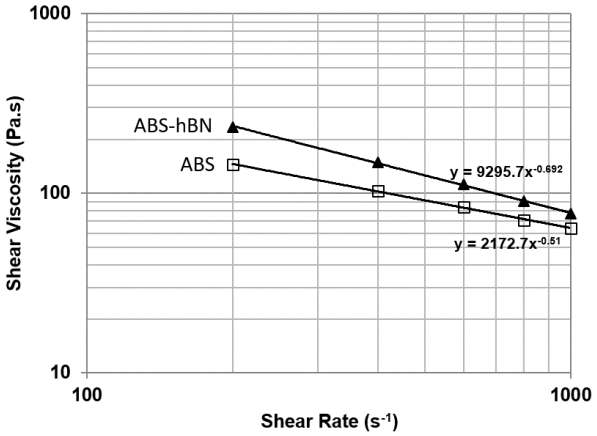


Figure 3 ABS-hBN composite's and ABS's shear viscosity as function of shear rate at 230°C

ABS-hBN extrudate appeared to be yellowish to brownish in colour, as compared to white or yellowish colour for pure ABS extrudates (see Figure 4). The measured diameter range of ABS-hBN and pure ABS extrudates obtained from the extruder machine was 1.83-1.86 mm and 1.75-1.80 mm. Calculation of percentage of die swell was done using the following equation:

$$\%\text{Die Swell} = \left(\frac{\text{measured diameter} - \text{die diameter}}{\text{die diameter}}\right) \times 100\% \text{----(1)}$$

Based on the calculation using Equation 1, ABS-hBN extrudate exhibited 5.4% die swell, larger than ABS extrudate which recorded 1.4% die swell. The swelling is caused by a significant elastic recovery of the deformed polymer when exiting from the orifice of the die [15]. In order to mitigate the die swell for ABS-hBN, the land length of the extrusion die could be increased to 10 mm [25].

Closer examination of surface morphology (refer Figure 5) of the ABS-hBN extrudates produced by capillary rheometer exhibited two distinguishing features: (i) pinhole and (ii) sharkskin microstructures.

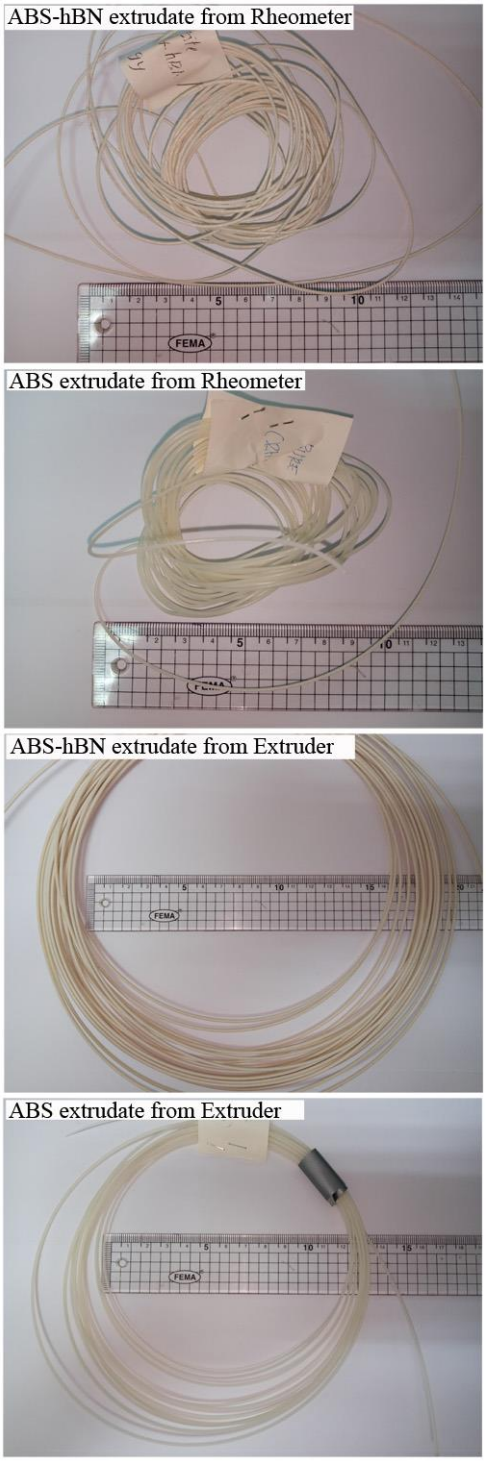


Figure 4 Photo images of ABS-hBN and ABS extrudates produced by capillary rheometer and extruder machine

A comparison of ABS-hBN extrudates' microstructure with the ABS extrudate highlighted the absence of pinhole microstructure in ABS extrudate. Previous studies reported that pin holing on the polymer occurs typically due to the volatilisation of volatile substances trapped at the interface with other materials [26]. In the current study, volatile substances refer to acetone residue trapped at the interface of ABS molecules with the hBN particles. This observation suggests that the pinhole may be formed by gas emitted from ABS-hBN during rheology test. It is possible that significant acetone residue still trapped in ABS-hBN composite after the oven drying process, resulted in significant gas emission during heating up to 230°C. The gas emission may also create less degree of laminar flow in ABS-hBN samples during capillary extrusion due to the flow resistance created by the gas emission. The absence of a pinhole microstructure in pure ABS sample suggests that gas emissions from the decomposition of ABS during melting were negligible. Microstructural comparison between the Head and Tail regions also reveals a visible outcome of the extrusion time. Pinhole size was smaller on the Tail than the Head surface for the ABS-hBN sample. This suggests the diminished effect of acetone gas emission from ABS-hBN sample as the extrusion progressed with time.

It is general knowledge in polymer extrusion that the surface of the extrudate becomes increasing wavy and less glossy due to the sharkskin phenomenon at the high shear speed [15]. Consistent with the previous study, the sharkskin feature appeared on ABS-hBN sample only at high shear rate (Tail region) and the Head region appeared smooth (free of sharkskin feature). On the other hand, only minor sharkskin feature was observed on the overall pure ABS extrudate, though the feature became more obvious at the Tail region. Less sharkskin effect on the ABS-hBN sample as compared to the ABS sample is consistent with the polymer extrusion sharkskin theory that suggests using additive in the polymer can shift the onset of sharkskin phenomenon to a higher shear stress level [27].

On the other hand, the surface microstructure (refer Figure 6) of ABS-hBN and pure ABS extrudates produced by extruder machine exhibited only sharkskin microstructure. Microstructural comparison shows ABS-hBN had minor sharkskin feature as compared to pure ABS, which shows rough sharkskin feature. A comparison between the Head and Tail regions of both samples also shows rougher microstructure on the latter region. The distinctive difference created on both ABS-hBN and ABS extrudates produced at different time indicates the stability of the extrusion and filament calendaring processes still requires further optimisation. Nevertheless, the disappearance of a pinhole in the extruder's extrudate indicates gas emission problem caused by acetone residue had been efficiently solved through the effective devolatilisation process by the extruder screw rotation [15].

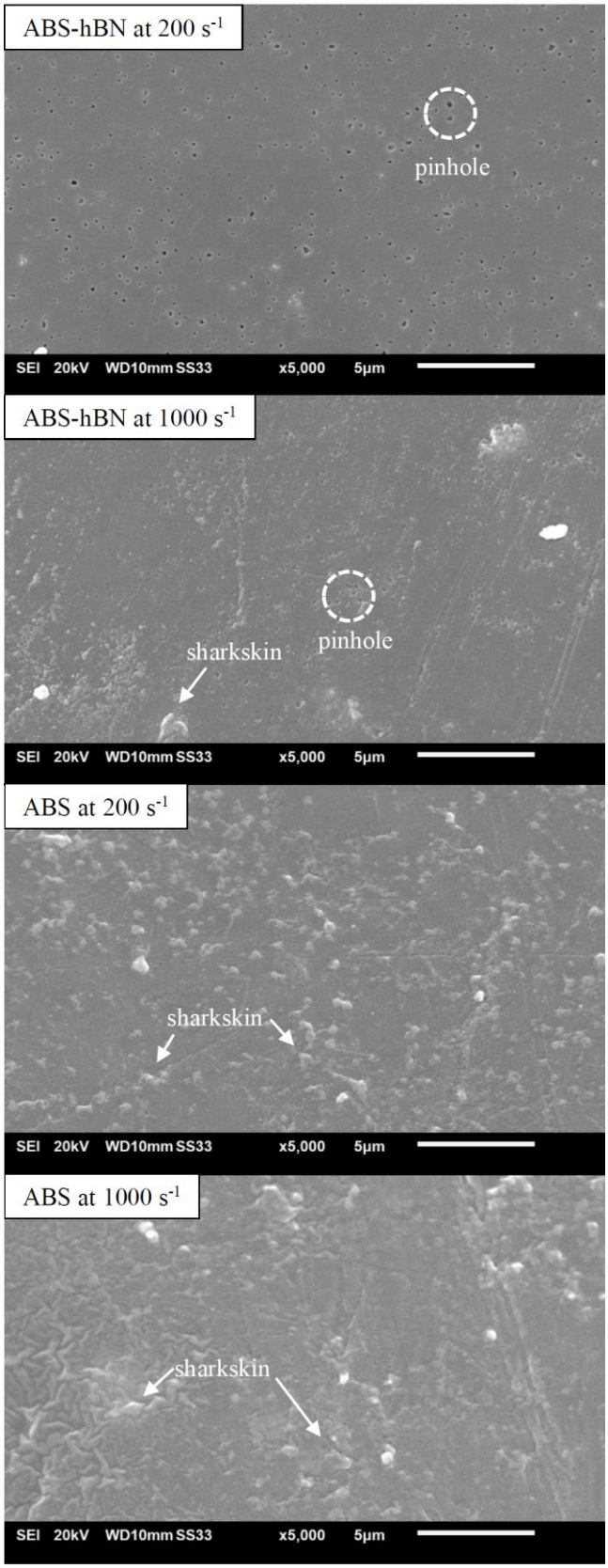


Figure 5 Surface microstructures of ABS-hBN and ABS extrudates produced by capillary rheometer at shear rate of 200 and 1000 s^{-1}

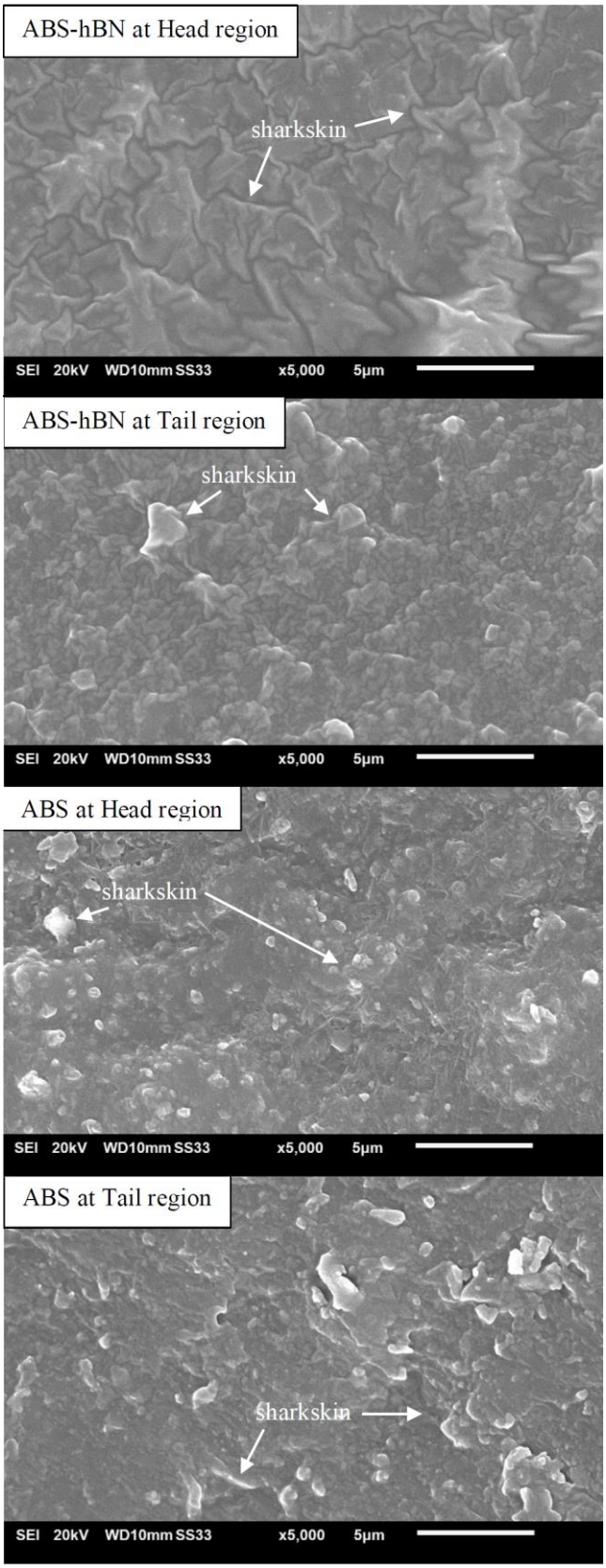


Figure 6 Surface microstructures of ABS-hBN and ABS extrudates produced by extruder at constant shear rate (indeterminate shear rate)

4.0 CONCLUSION

ABS filled hBN extrudate (filament) with a diameter range of 1.83-1.86 mm for FDM printing had been successfully fabricated by extruder machine using solution mixed ABS-hBN composite as feeding materials. The ABS-hBN extrudate exhibited less sharkskin feature but slightly higher extrudate swell percentage (5.4%) than the extrudate produced using as-received ABS pellets. Both the ABS-hBN and ABS samples did not show significant differences in thermal behaviour. However, ABS-hBN exhibited a viscosity higher than pure ABS due to flow resistance caused by hBN filler addition. The composite's viscosity was 62% higher at 200 s^{-1} but decrease to 30% at 1000 s^{-1} at the rheometer's operating temperature of 230°C. The change in rheological properties of ABS composite as a result of adding hBN resulted in a higher percentage of die swell and smoother extrudate's surface than the ABS extrudates. It is recommended that future work should focus on optimising the extrusion parameters in order to achieve consistent microstructure and reduce the die swell percentage of ABS-hBN extrudate toward the ABS's level. Previous study also showed that improving the percentage of thermal conductivity was largely influenced by the respective composite processing techniques [14].

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