Preparation and Characterization of Acrylonitrile – Butadiene – Styrene/ Corn Starch Composites

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ABSTRACT

In this work, Rheological and mechanical properties of acrylonitrile – butadiene – styrene/ corn starch composites (ABS/starch) were studied. The composites were prepared using a laboratory scale single screw extruder. Rheological properties were determined using the single screw extruder, and apparent shear rate (γ), apparent shear stress (τ), apparent viscosity (η), non-Newtonian index (n) and flow activation energy at a constant shear rate (E_γ) and constant shear stress (E_τ) were determined. Mechanical properties in term of tensile tests were performed using Testometric M350-10KN, stress at break, strain at break and Young's modulus were determined. Rheological results showed that the composites are pseudo plastic in behavior, and the apparent viscosity of the composites increases with increasing starch content above the additive rule which indicates a partial compatibility in the composite, also it was found that the flow activation energy of the composite increases with increasing starch content. Also it was found that the activation energy value at a constant shear stress is more than that at a constant shear rate. The mechanical results showed that the strain at break of the composite decreases sharply by the presence of starch, whereas the young's modulus increases with increasing starch content.

Key words: Corn starch, ABS, Polymer composites, Rheology, Extruder.

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الملخّص

(ABS)   –   –

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(n)   (η)   (τ)   (γ)

.(E_τ)   (E_γ)

Testometric   M350-10KN

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:   ABS   .

Introduction

Acrylonitrile – butadiene – styrene copolymer (ABS) is an engineering polymer used extensively in industry owing to its good mechanical and processing properties, to enhance its tensile strength, impact toughness, and stiffness further as well as to reduce the production cost, ABS is usually filled with rubber particles [1] or rigid inorganic particles (RIP), such as calcium carbonate ($CaCO_3$) [2], kaolin and glass bead [3], and talcum powder [4]. In the last two decades, the mechanical properties of ABS, its blends, and composites have been intensively studied [3-10]. Usually, the tensile strength of ABS–RIP composites decreases with the increase of RIP content [4, 5]. The mechanical properties of filled polymer composites depend, to much extent, on the filler shape, size, and its distribution, the interfacial morphology, etc.

Fillers have been widely used in polymer materials for several decades. It is well established that the source and size of inorganic filler and the interaction between the filler particle and polymeric matrix will affect the structure and mechanical properties of the composites [11]. Inorganic substances are the main filler materials employed during the past decades. However, with an increasing interest in biodegradable polymers, more natural fillers are being incorporated in the development of new biodegradable polymer composites.

One of the most common biodegradable fillers used in plastic formulations is starch [12, 13]. Raw starch is considered to be a cost effective additive and meets the requirement of minimum interference with flow properties, and minimum disturbance of product [14]. Rigid fillers, such as granular starch, are added to polymers to improve certain physical properties, such as dimensional stability and stiffness. In general, some undesirable consequences are associated with the addition of starch as a filler, including the need for more complex fabrication techniques or a reduction in some mechanical properties such as toughness or impact strength.

In plastics containing blends of polyethylene with starch, microbes initially attack starch resulting in an increase in the porosity and surface to volume ratio of the polymer blend and a consequent enhancement of its biodegradability. In order to attack the starch, the microbes, should first adhere to the surface of the polymer, so polymers that have a rougher surface finish are more prone to microbial attack. Scanning electron microscopy analysis have shown

that starch based polymers have a textured surface whereas PE has a smooth surface [15].

Numerous studies have shown that the addition of dry starch granules to low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) follows the general trend for filler effects on polymer properties [16-22]. Lim *et al* [20] studied the effect of starch granule size on physical properties of starch- filled polyethylene and reported that the film containing small particle corn starch exhibited greater elongation and tensile strength compared with a film containing large particle corn starch. Jagannth *et al* [18] found that addition of 5wt% of starch into LDPE caused water vapor transmission to increase from 7.9 to 36.85 g/m^2 in 24 h at a temperature of 38ºC. Also, Starch-filled linear low density polyethylene (LLDPE) composites films were studied and it was found that the tensile strength of the films containing crosslinked starch were generally higher than those of the films containing native starch [21,22]. Siddaramaiah and Somashekar [23] reported that starch-filled polyvinyl alcohol (PVOH) was slightly higher in tensile strength than the pure polymer.

In this paper ABS/ starch composites were prepared and the aim of this work is to study the rheological and mechanical properties of the composites, such works are very important in solving the plastics waste problem.

Experimental

Acrylonitrile – Butadiene – Styrene (Kumho ABS 750SW) was supplied by Korea Kumho Petrochemical Co., Ltd. (Korea), [*MFR* = 50 g/10 min (200 °C /21.6 Kg), Density = 1.04 g/cm^3]. Native corn starch is a commercial material, it was brought from local supply and used as received.

Composites preparation

ABS granules and starch powder were mixed manually and dried at temperature 85 ºC for a 6 h. ABS/starch composites were prepared using a laboratory scale single screw extruder (SSE) (*L/D = 25, D = 20mm*) [SHAM EXTRUDER 25D, Performance: *Kreem Industrial Establishment*, Damascus – Syria] which could be operated at different speeds, varied from 0 to100 rpm. The screw has a fluted type mixing section located before the metering zone [24], in this type of mixers the material is forced to pass at a high shear stress. This brings in some level of dispersing action besides reorienting the interfacial area, and increasing the imposed total strain. The flight depth of screw

in the metering zone was 1.5 mm, and the helix angle 17.7°. The temperatures profile along the barrel of extruder were set at 160,160,160,170 °C (from feed zone to die), and the screw speed was 30 RPM. The composites were then extruded through a multi holes die (3 mm) and the extrudates were left to cool in air and then fed into a granulator which converted them into granules. The obtained granules were then dried at temperature 85°C for 6 h before using. The prepared composites and ABS were compressed and the molding temperature for the composites and ABS were 195, 170 °C respectively. The Molded specimens were then cooled to 80 °C before removal from the mold and cut into dog bone - shaped sample (ASTM D638) under the air pressure for mechanical testing. The compositions of ABS /starch composites are shown in Table 1.

Table 1. Compositions of ABS/starch composites.

Sample	S10%	S15%	S20%
ABS (wt %)	90	85	80
Starch (wt %)	10	15	20

On-line rheological measurements

On-line rheological measurements were performed using the SSE. The ABS\ starch composites rheology was determined using the SSE by replacing the multi holes die used for granules preparation with a capillary die $L/R = 37$. PT124G-124 melt pressure transducer (Shanghai Zhaohui Pressure Apparatus Co., Ltd - China) was placed at the die entrance. Pressure values were measured each 5 sec while the ABS\ starch composites mass flow was determined at intervals of 30 sec once the pressure was stable; this process was repeated at different speeds (5, 10, 15, 20, 25 and 30 RPM). The temperature of ABS\starch composites was directly measured with a thermocouple, which was in contact with the melt.

The apparent shear rate (γ) is given by:

$$\gamma = \frac{4Q}{\pi.R^3} \qquad (1)$$

Where R is the capillary radius, Q is the volumetric flow rate. The apparent shear stress (τ) is given by:

$$\tau = \frac{\Delta PR}{2L} \qquad (2)$$

Where, ΔP is the pressure at capillary entrance, L is the capillary length. Apparent viscosity is given by:

$$\eta = \frac{\tau}{\gamma} \qquad (3)$$

Flow activation energy at a constant shear rate (E_γ) and constant shear stress (E_τ) was determined by using Arrhenius equation:

$$\eta = A.e^{\frac{E}{RT}} \qquad (4)$$

Where A is the consistency related to structure and formulation, R is the gas constant (8.314 J/mol.K).

Mechanical properties

Tensile testing to study stress at break (N/mm^2), strain at break (%) and Young's modulus (N/mm^2) were performed by using Testometric M350-10KN (The Testometric Company Ltd, Rochdale, UK) at room temperature, all samples were strained at 5 mm/min. Samples were conditioned at room temperature for a period of 48 h prior to testing. Results from 3 to 5 specimens were averaged

Results and discussion

Rheological properties

Flow curves:

Figure 1 shows the relationship between apparent shear stress and apparent shear rate at 180 °C and $L/R = 37$, for the composites over the range of the studied shear rate. It is clearly seen from Fig. 1 that the linearity of these lines is good and they obey the power law at a certain range of shear rate.
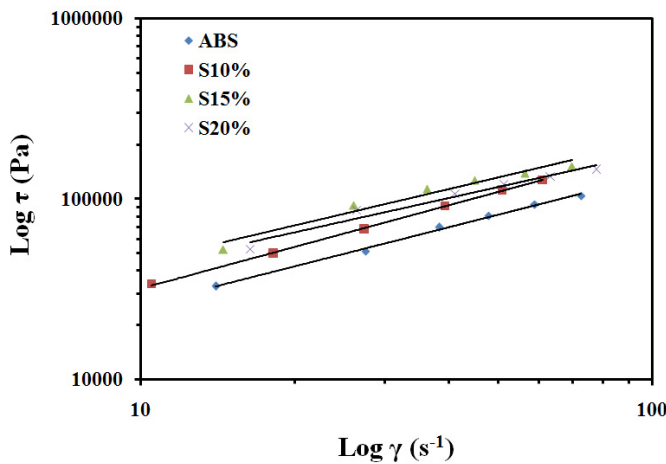
$$\tau = K\gamma^n \qquad (5)$$

Fig. 1 Flow curves of ABS/ Starch composites at 180 ºC.

Where K is the viscosity coefficient and n is the non-Newtonian index. n values were calculated from the slope of the fitted lines in Fig. 1.

$$n = \frac{d \log \tau}{d \log \gamma} \qquad (6)$$

All the values of n were less than 1, implying that ABS/starch composite melts were pseudo plastic; similar to most of the polymeric melts.

The effect of composition ratio on n is shown in Fig.2. It could be noted from Fig. 2 that the n value increases with increasing starch content in the composite in the range of 0-10%. where the maximum value was observed. Increasing starch higher than 10 % caused a decreasing trend of the non-Newtonian index this indicates the greater pseudoplasticity in the flow for the melts of ABS/starch composites at a loading level of starch higher than 10%.

The value of n describes the deviation from the Newtonian fluids about flow behavior, so it is also called the flow behavior index. A higher value of n reveals less influence of shear rate on flow behavior. In other words, the changes in viscosity upon shear rate are not obvious, that was to say that the flow behavior of the ABS/starch composites with a loading level of starch greater than 10% is more sensitive to shear rate.
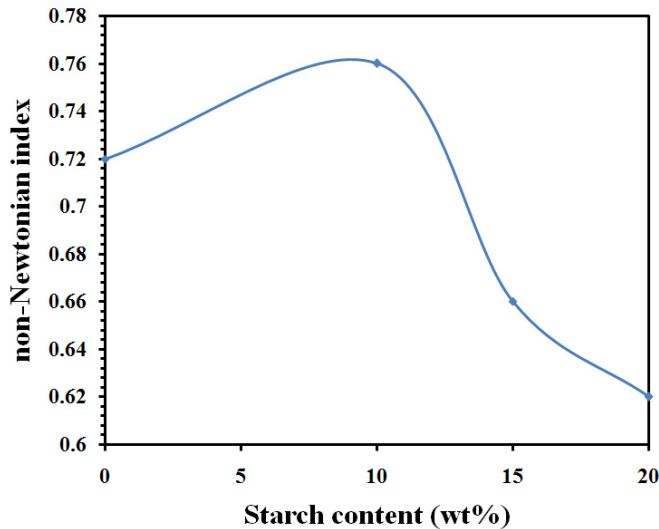

Fig.2 Non-Newtonian index versus starch content (wt%) at 180 ºC

Viscosity curves

For evaluating the processing behavior, the viscosity curves of these composites were determined. Figure 3 shows the viscosity curves of the composites at 180 ºC and *L/R* = 37. It could be noted from Fig. 3 that the composites show a typical shear – thinning behavior over the range of the studied shear rates, this behavior was attributed to the alignment or arrangement of chain segments of polymers in the direction of applied shear stress [25]. The high viscosity at a low shear rate provide the integrity of the extrudate during extrusion, and the low viscosity at a high shear rate enables low injection pressure and less time of the injection cycle.
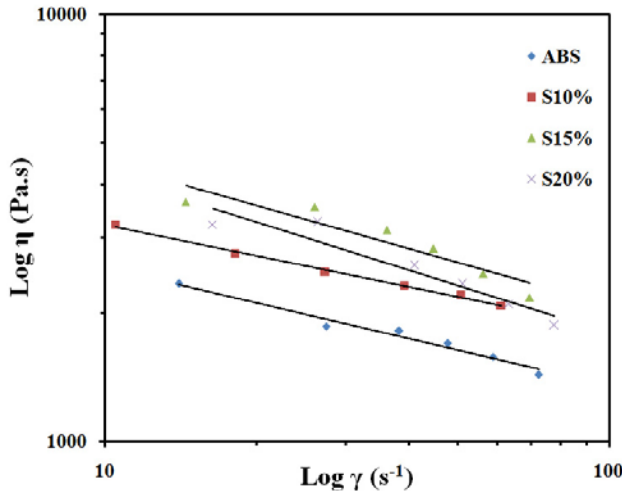

Fig. 3 Viscosity curves of ABS/ Starch composites at 180 ºC.

Figure 4 shows the relationship between apparent viscosity (at a constant shear rate and constant shear stress) and starch content in the composites at 180 ºC. It could be noted from Fig. 4 that the apparent viscosity increases with loading levels of starch until 15 % where the maximum value was observed, and the increasing starch higher than 15% caused a decreasing trend of the apparent viscosity. Also it could be noted that the viscosity of the ABS/starch composites indicates positive deviation composites, according to the following log additive rule [26, 27]:

$$\log \eta_c = \sum_i w_i \log \eta_i \qquad (7)$$

Where η_i and η_c are the viscosity of the *i*th component and that of the composite and w_i is the weight fraction of the *i*th component. Compatible or partially compatible composites normally lead to a positive deviation in rheological properties, such as the viscosity, die swell, etc. It is, therefore, concluded that ABS/starch composites were partly compatible composites.
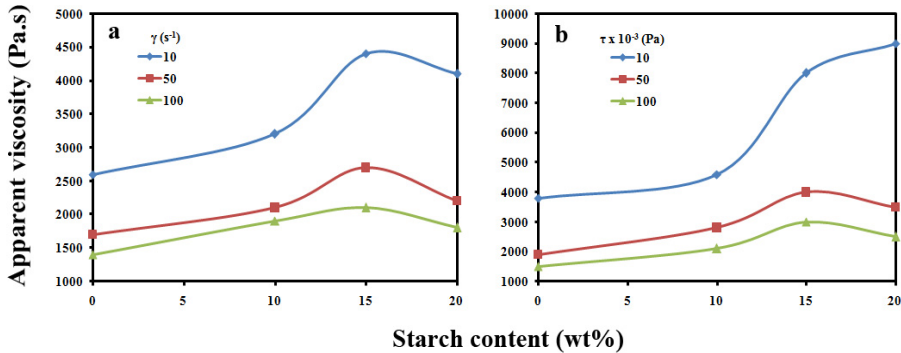

Fig. 4 Apparent viscosity versus starch content (wt%) (a) at a constant shear rate (b) at a constant shear stress.

Flow activation energy

The effects of temperature on flow behavior can be understood through the viscosity curves for the composite melts at different temperatures. Figure 5, for example, shows the viscosity curves of S15% melts at three temperatures: 180, 190 and 200 ºC.
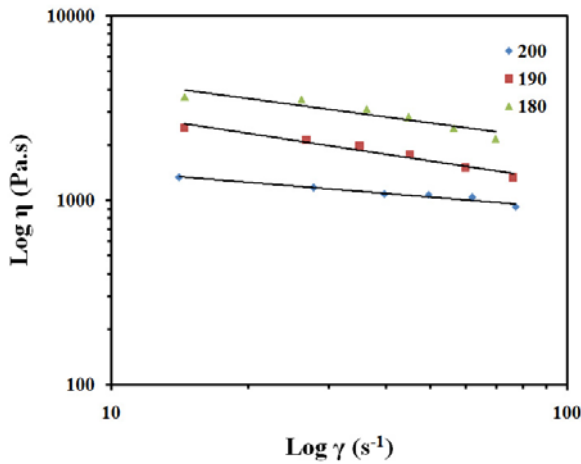

Fig. 5 Viscosity curves of S15%

Figure 6 shows the relationship between apparent viscosity and *1/T* for composite melts at a constant shear rate and constant shear stress. Flow activation energy at a constant shear rate (E_γ) and constant shear stress (E_τ) can be calculated from the slopes of lines in Fig. 6,

$$E_\gamma = R \left(\frac{d \ln \eta}{d \frac{1}{T}} \right)_\gamma \tag{8}$$

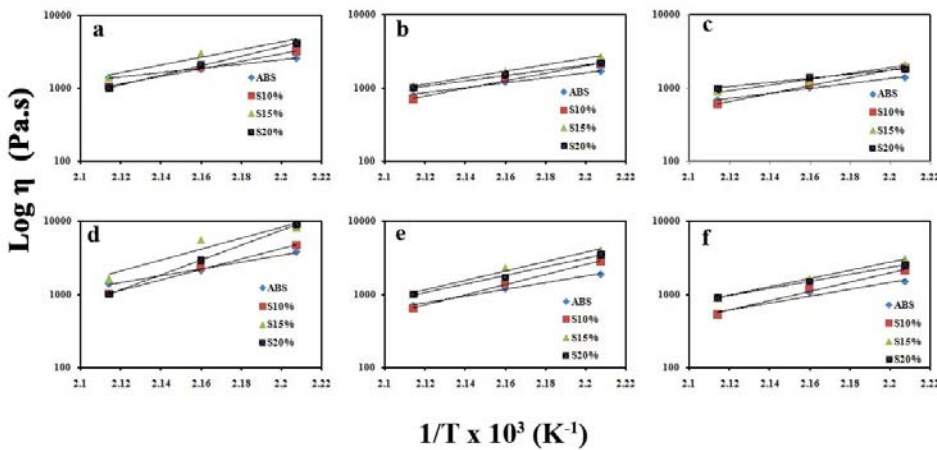$$E_\tau = R \left(\frac{d \ln \eta}{d \frac{1}{T}} \right)_\tau \tag{9}$$

Fig. 6 Apparent viscosity versus *1/T* of the composites (a) γ =10 s^{-1} (b) γ =50 s^{-1} (c) γ =100 s^{-1} (d) τ =10^4 Pa (e) τ = 5x10^4 Pa (f) τ =10^5 Pa

Figure 7 shows the effect of starch content on the flow activation energy at a constant shear rate and constant shear stress of the composites. The flow activation energy represented the effect of the temperature on the flow behavior of material. The more *E* was, the more sensitivity of the composite was to the temperature. According to the values of the flow activation energies at a constant shear rate and shear stress presented in Fig. 7, it could be noted that at a low shear rate and shear stress the flow activation energy increases with increasing starch content in the composites, so it could be said that the

sensitivity of the flow behavior of the composites to the temperature increases with increasing starch content at a low shear rate and shear stress, whereas at a higher shear rate and shear stress, the flow activation energy increases with loading levels of starch until 10 % where the maximum value was observed, and the increasing starch higher than 10% caused a decreasing trend of the flow activation energy.

Also it could be noted that the flow activation energy of the composites increases with increasing shear rate and shear stress and that of pure ABS is almost independent of shear rate and shear stress. The variation of the activation energy with shear rate and shear stress of the composites depends on the starch content in the composites: the higher the content of starch, the sharper the variation.
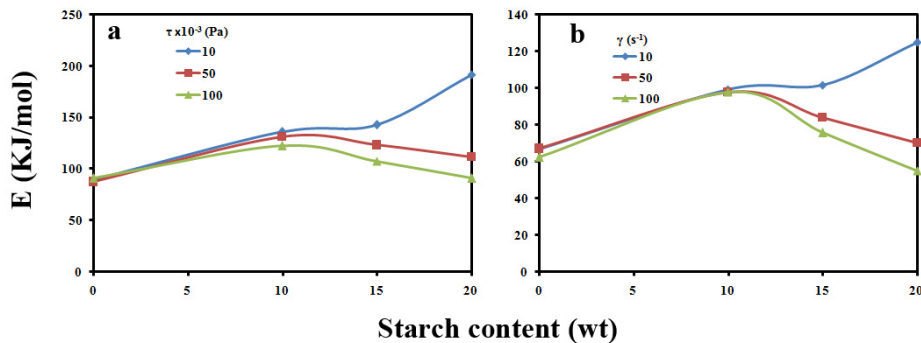

Fig.7 Flow activation energy versus starch content (wt%) (a) at a constant shear rate (b) at a constant shear stress.

Mechanical properties

For all samples, no yield phenomenon is existed. Figure 8 shows the effect of starch content on the stress at break of the composites. It could be noted from Fig. 8, that the stress at break increases slightly with increasing starch content up to 10%. The increasing starch content higher than 10% caused a sharp decreasing of the stress at break. Figure 9 shows the effect of starch content on the strain at break of the composites, it is clearly seen in Fig. 9, that the strain at break of the composites get worse with the addition of starch where it decreases with increasing starch content, and the presence of 10% of starch in the composite caused a steep decline in strain at break.
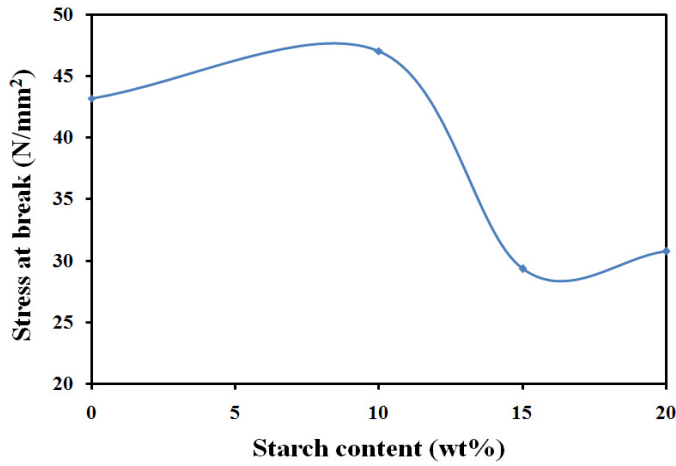
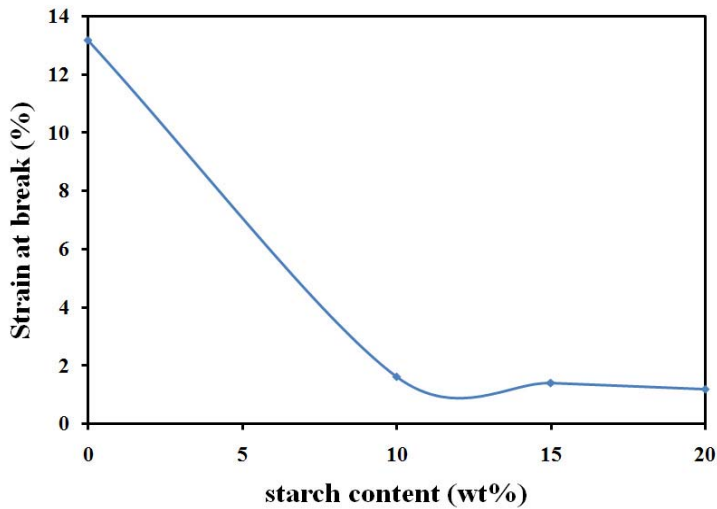**Fig. 8 Stress at break versus starch content (wt%)**

Fig. 9 Strain at break versus starch content (wt%).

Figure 10 shows the effect of starch content on the Young's modulus for the composites, It could be noted from Fig. 10, that the Young's modulus of the composites is nearly four times higher than that of pure ABS. It could be said that the addition of starch to ABS follows the general trend for filler effects on polymer properties [19]. The modulus increases due to stiffening effect of starch and the strain at break decreases sharply as the starch content is increased.
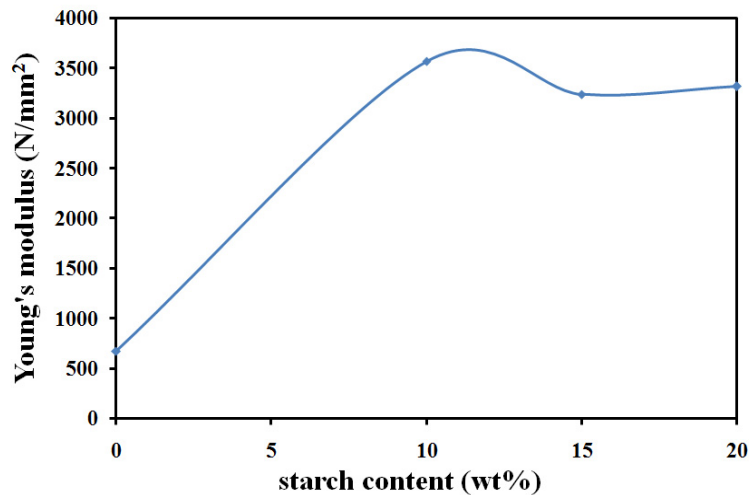
Fig. 10 Young's modulus versus starch content (wt%)

Conclusion

It could be concluded from the above discussion:

- ABS/starch composites are pseudo plastics in behavior, and the shear sensitivity of the composites is more than that of pure ABS.
- The apparent viscosity of the composites increases with increasing starch content up to15% starch, and the viscosity results shown here strongly support the notion that ABS/starch composite is a partial compatible composite.
- The flow behavior of the composites is more sensitive to temperature than that of pure ABS where the flow activation energy at a constant shear rate and shear stress of the composites increases with increasing starch content at a low shear rate and shear stress.
- Mechanical results show that the strain at break of the composites decreases sharply with increasing starch content, and the same behavior is noted in the stress at break in starch levels higher than 10%, whereas Young's modulus of the composites is nearly four times higher than that of the pure polymer.
- The results indicate that up to 20% starch, the composites have suitable mechanical properties, and good processability (high flow activation energy).

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