

Preparation and Properties of blends of polypropylene and Acrylonitril-Butadiene-Styrene with Thermoplastic Starch

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ABSTRACT

In the present work, the rheological and mechanical properties of polypropylene /thermoplastic starch (PP/TPS) and acrylonitril-butadiene-styrene/thermoplastic starch (ABS/TPS) blends were investigated. Starch was plasticized using glycerol, and blends were prepared using a laboratory scale with single screw extruder. Rheological properties of the prepared blends were determined using a capillary rheometer. Mechanical properties were studied in term of tensile tests, stress at break, strain at break and Young's modulus were determined. Rheological results showed that the blends are pseudo plastic in manner and the true viscosity of PP/TPS blend decreases with increasing TPS content in the blend until 10%, and at more than 10% TPS it increases with increasing TPS. In ABS/TPS, the true viscosity decreases with increasing TPS content in the blend. The mechanical results showed that in both systems, the stress at break and strain at break decrease with increasing TPS content in the blend while the Young's modulus increases with increasing TPS content. The mechanical results shown that the addition of TPS to each of PP and ABS follows the general trend for filler effects on polymer properties.

Key words ABS, PP, Thermoplastic starch, Rheology, Mechanical properties.

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(ABS/TPS)

.(PP/TPS)

TPS 10%
ABS/TPS

TPS
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TPS

PP/TPS

TPS

.TPS
ABS PP

PP ABS :

Introduction

Rising oil prices and increased activity in regards to environmental pollution prevention have pushed research and development of biodegradable plastics, where the development of plastics by using renewable resources which are naturally biodegradable and their possibility of combining their biodegradability with cost reduction and market needs have been the object of intensive academic and industrial researches. Starch is one of the most important biodegradable polymers which is used to produce and development new materials (starch – based materials) with high biodegradability, and low cost. Starch was used at first as a filler in the traditional polymers (PE, PP,..) which helps in cost reduction and rising biodegradability of resultant, in this case starch acts as filler increasing the rigidity of the material, and so, the starch concentration at which useful material can be obtained is therefore limited to a low range after which the materials properties suffer dramatically. Recently, starch was used as a main component in polymer blend, and it was not used in the native case, but it was used in plastic case, where the starch granules were plasticized by using plasticizers under heating, giving rise to a continuous phase in the form of a viscous melt which can be processed by using traditional plastic processing techniques [1], such as injection molding and extrusion. This kind of starch composite is called thermoplastic starch (TPS).

Several plasticizers have been used with starch to convert it into thermoplastic starch (TPS) to be used in polymer blends such as glycerol, ethylenbisformamide, and Urea [2,3], but the most used is glycerol [4-7]. The properties of TPS depends on the hydrogen – bond forming ability between starch and plasticizer. Also another plasticizers was used with glycerol to improve the different properties of TPS and TPS/polymer blends. Formamide was used with glycerol for preparing TPS [8], where it was found that by using formamide, the fluidity of TPS could be improved. The influence of formamide and water on the properties of TPS/PLA was studied, and it was found that the mechanical properties of the blend could be improved by substituting glycerol with formamide, where formamide could make TPS more flexible. Also the influence of citric acid on the properties of TPS/LLDPE blends [9] was studied, where it was found that the mechanical properties of TPS/LLDPE blend are greatly enhanced in the presence of citric acid. In other works [10-12] buriti oil was used as plasticizer with glycerol, where it was compared to the behavior of

glycerol and buriti oil as plasticizers in (TPS/PS) blend biodegradation. Also ethylenebisformamide was used as a plasticizer for starch, and it was found that ethylenebisformamide formed stronger and stable hydrogen bond with starch molecules [13-15].

During the last few years, biodegradable polymers with suitable mechanical and physical properties have received particular attention to replace petroleum-based plastics such as PLA. PLA belongs to the family of aliphatic polyesters which are a thermoplastic, high-strength, high-modulus polymers. PLA as a biodegradable polymer has been studied in many fields in the past few decades. Recently, PLA has been considered as a major alternative to petroleum-based plastics for disposable items, such as trash bags and food utensils. However PLA is more expensive than conventional petroleum polymers for disposable or short-term applications [16]. TPS as an inexpensive material and renewable source can be used as an alternative to PLA and to overcome the poor mechanical properties of TPS, it was blended with synthetic polymers such as LDPE [4,17], PP [6], PS [7, 10-12]. Gonzalez et al [17] prepared high performance LDPE/TPS blends under particular one-step extrusion conditions, they found that the extrusion process and the controlled deformation of the TPS phase yields an important improvement in the elongation at break of LDPE/TPS blends as a function of composition. Schlemmer et al [10-12] studied the biodegradation of PS/TPS blends and they found that the addition of TPS to PS is an effective technique to achieve biodegradability. Rosa et al [6] studied the influence of the plasticizer type on the thermal and mechanical properties of PP/TPS blends, where they blended TPS, which has 20% of plasticizer, with PP. They found that the incorporation of TPS to PP has generally reduced the mechanical properties of PP.

The aim of this work is to prepare and characterize blends of thermoplastic starch plasticized with glycerol / acrylonitrile – butadiene–styrene (TPS/ABS) and thermoplastic starch/polypropylene (TPS/PP). The prepared blends were characterized in terms of rheological and mechanical properties. Up to now, no academic works were focused on the rheological properties of these systems.

Experimental

Materials

Acrylonitrile – Butadiene – Styrene (Kumho ABS 750SW) was supplied by Korea Kumho Petrochemical Co., Ltd. (Korea), [MFR=

50 g/10 min (200 °C /21.6Kg), Density=1.04 g/cm³]. Polypropylene (PP) (PETOPL EN EH 251) was supplied by PETKIM Petrokimya Holding A.S (Turkey) [*MFR*= 24 g/10min (230 °C /21.6 Kg)]. Native corn starch is a commercial material, it was brought from local supply and used as received. Glycerol 99.5% is a commercial grade, was used without any treatment.

Thermoplastic starch (TPS) preparation

Corn starch samples were mixed manually with glycerol in different ratios Table 1, the obtained mixtures were then fed into a laboratory scale of single screw extruder (SSE) ($L/D = 25$, $D = 20$ mm) [SHAM EXTRUDER 25D, Performance: Kreem Industrial Establishment, Damascus – Syria], which could be operated at different speeds, varied from 0 to 100 RPM. The temperatures profile along the barrel of extruder were set at 90, 100, 110, 100 °C (from feed zone to die), and the screw speed was 30 RPM in TPS preparation. TPS 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 Fig.1. The TPS preparation conditions (temperature and screw speed) were selected according to the color of the granules.



Fig. 1 Thermoplastic starch granules

Blends preparation

The obtained TPS granules with different glycerol ratios were then blended with PP and ABS using the single screw extruder in different ratios. The temperatures profile along the barrel of the extruder in the PP/TPS blends were set at 125, 160, 170, 180 °C (from feed zone to die) and the speed was 15 RPM, whereas the temperatures profile along the barrel of the extruder in the ABS/TPS blends were set at 130, 140, 150, 160°C and the speed was 20 RPM. The blends were extruded through the multi holes die, left to cool in air, and the extrudates were fed into the granulator, the obtained granules were then dried in 85 °C for a 6 h before using. The compositions of TPS and the blends are shown in Tables 1 and 2.

Tensile samples preparation

Tensile samples (ASTM D638) were prepared using NEGRAI BOSSI NB25 injection machine (LEESONA CORPORATION, Italy) at 170-240 °C, the injection pressure was 90 bar and the cooling time in the mold was 30 sec. The molded samples were dog bone-shaped samples with a thickness and width of 4 mm and 10 mm respectively. The gauge length of the sample was 80 mm (Fig. 2).



Fig. 2 Tensile samples

Table. 1. The compositions of PP/TPS blends

Sample	TPS composition		TPS (wt%)	PP (wt%)
	Starch (wt%)	Glycerol (wt%)		
PP1/TPS20			10	90
PP2/TPS20	80	20	20	80
PP3/TPS20			30	70
PP1/TPS25	75	25	10	90
PP1/TPS30	70	30	10	90
PP1/TPS35	65	35	10	90

Table. 2. The compositions of ABS/TPS blends

Sample	TPS composition		TPS (wt%)	PP (wt%)
	Starch (wt%)	Glycerol (wt%)		
ABS1/TPS20			10	90
ABS2/TPS20	80	20	20	80
ABS3/TPS20			30	70
ABS1/TPS25	75	25	10	90
ABS1/TPS30	70	30	10	90
ABS1/TPS35	65	35	10	90

Rheology

Rheological properties of the blends were studied using a capillary rheometer (Davenport 3\80), it consists of a barrel into which material was loaded before start pushing by a plunger through a capillary, the load in the plunger provide the total pressure drop in the barrel and capillary, and the volume flow rate. The rheological experiments were carried out at 185, 190, 195, 200 °C for PP/TPS blends and 160, 165, 170, 175, 180 °C for ABS/TPS blends by using $L/R=8, 15, 25, 36$ capillaries. Bagley's correction was performed using the data from the four capillary dies. The true shear rate (γ_r) is given by:

$$\gamma_r = \frac{3n+1}{4n} \cdot \gamma_a \quad (1)$$

Where n is the non-Newtonian index depending on temperature, the term $\frac{3n+1}{4n}$ was the Rabinowitsch correction factor [18] and γ_a is the apparent shear rate which is given by:

$$\gamma_a = \frac{4Q}{\pi \cdot R^3} \quad (2)$$

Where R is the capillary radius and Q is the volumetric flow rate. The true shear stress (τ_r) is given by:

$$\tau_r = \frac{\Delta P}{2\left(\frac{L}{R} + e\right)} \quad (3)$$

Where ΔP is the pressure at capillary entrance, L is the capillary length, and e is the Bagley's correction factor [18,19]. True viscosity is given by:

$$\eta_r = \left(\frac{4n}{3n+1}\right) \left(\frac{\Delta P \cdot \pi R^3}{8Q\left(\frac{L}{R} + e\right)}\right) \quad (4)$$

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

$$\eta_r = A e^{\frac{E_\gamma}{RT}} \quad (5)$$

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

On-line viscosity measurements

For comparing the viscosity of TPS samples, On-line viscosity measurements were performed in the SSE. The TPS viscosity was measured directly from 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 TPS 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 TPS was directly measured with a thermocouple, which was in contact with the molten blend.

Mechanical properties

Tensile testing to study stress at break (N/mm^2), Young's modulus (N/mm^2) and strain at break (%) were performed using Testometric M350-10KN (The Testometric Company Ltd, Rochdale, UK) at room temperature, all samples were strained at 50 mm/min. Samples were conditioned at room temperature for a period of 48 h prior to testing. Results from 4-7 specimens were averaged. Relative stress at break, strain at break and Young's modulus (Relative property RP) were calculated:

$$RP = \frac{P}{P_0} \quad (6)$$

Where P is the property of the blend and P_0 is the property of the polymer (PP or ABS).

Results and discussion

Rheological properties

TPS viscosity

Figure 3 shows the effect of the glycerol content on the viscosity of TPS at 140 °C, it could be noted from fig. 3. That the viscosity of TPS decreases with increasing glycerol content in TPS, as a result of plasticizer diluting effect, reduction in TPS melt viscosity at 140 °C occurs expectedly as glycerol rises from 20% to 35% (Fig. 3), where the increasing content of glycerol in the blends causes to more arrangement of molecules, and the starch chain mobility increases as the glycerol molecules weaken the inter - chain hydrogen bonding which allows the melt blends to flow smoothly at the experimental temperature. From another side, in addition to acting as plasticizer, glycerol also served as an internal and external lubricant in the rheometer and the extruder which cause lowering the viscosity [5]. It is also evident that the TPS melt viscosity shows a power law dependence on shear rate, illustrating the ability to formulation of thermoplastic starches with viscosity and shear thinning characteristics similar to those of commercially available thermoplastics.

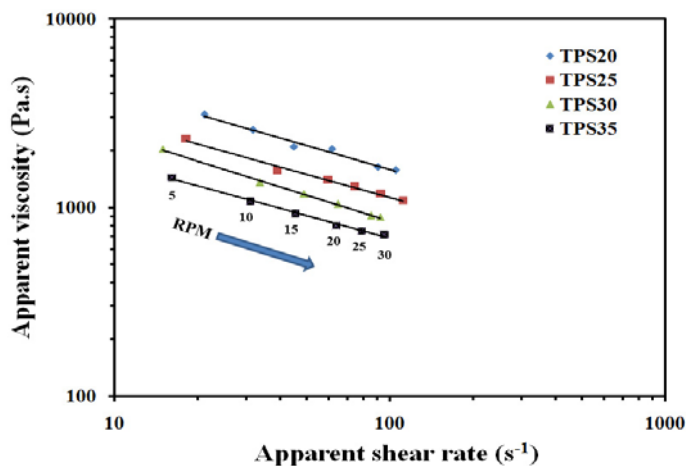


Fig. 3 Apparent viscosity versus apparent shear rate of TPS at 140 °C

Flow curves

For evaluating the processing behavior, the flow curves of these blends were determined. Figure 4 shows the flow curves of PP1/TPS25 and ABS1/TPS25. It could be noted from Fig. 4 that the shear stress increases with increasing shear rate and the relationship between shear stress and shear rate obeys the power law:

$$\tau = K\gamma^n \quad (7)$$

where K is the consistency index and n is the non-Newtonian index. The non-Newtonian index values were calculated from the slope of the fitted lines. It is well known that the value of n reflects the viscosity - sensitivity to shear rate. The obtained values of n for the blends were less than 1 implying that PP/TPS and ABS/TPS blend melts were pseudo plastic.

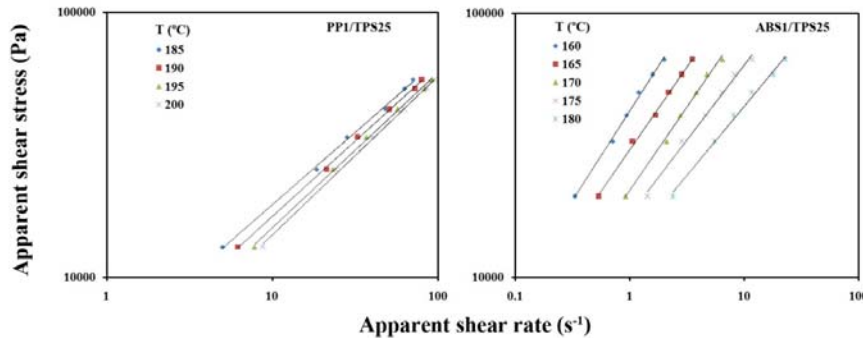


Fig. 4 Flow curves of PP1/TPS25 and ABS1/TPS25

Viscosity curves

The relationship between true viscosity and true shear rate (i.e. viscosity curves) of the blends is shown in Fig. 5. It is observed, decreasing trend of true viscosity with an increase in true shear rate, all sets of blend melts exhibited shear-thinning behavior, this behavior was attributed to the alignment or arrangement of chain segments of polymers in the direction of applied shear stress [20]. 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.

The effects of TPS content on the true viscosity of the blends are shown in Fig. 6, it could be noted from Fig. 6 that at a given true shear rate, the true viscosity of PP/TPS blend decreases with loading levels of TPS20 until 10%, where the minimum value was observed that is,

increasing TPS20 higher than 10% caused an increasing trend of the true viscosity.

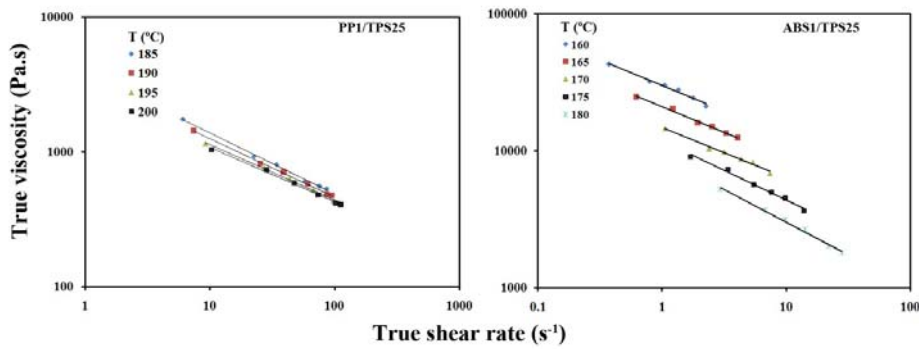


Fig. 5 Viscosity curves of PP1/TPS25 and ABS1/TPS25

Also it could be noted from Fig. 6, that the true viscosity of the blend at 10% of TPS20 indicates negative deviation blends (NDBs), while above 10% it indicates a positive deviation blends (PDBs) according to the following log additives rule [21,22]:

$$\log \eta_B = \sum w_i \log \eta_i \quad (8)$$

Where η_i and η_B are the viscosity of the *ith* component and that of the blend and w_i is the weight fraction of the *ith* component. From another side, different behaviors are noted in ABS/TPS blends where the true viscosity decreased with increasing TPS content far below the additives rule.

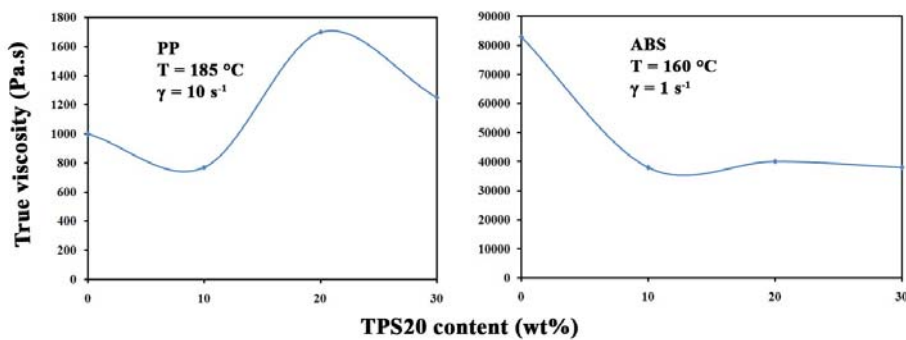


Fig. 6 True viscosity versus TPS20 content (wt%) of PP/TPS and ABS/TPS

Flow activation energy

The effects of temperature on flow behavior can be understood through the flow curves for the blend melts at different temperatures.

Figure 5, for example, shows the flow curves of PP1/TPS25 blend at 185, 190, 195, 200 °C and ABS1/TPS25 blend at 160, 165, 170, 175, 180 °C. Figure 7 shows the relationship between true viscosity and $1/T$ for blend melts at a constant shear rate (10 s^{-1} for PP/TPS, 1 s^{-1} for ABS/TPS). Flow activation energy at a constant shear rate (E_γ) can be calculated from the slopes of lines in Fig. 7 as following:

$$E_\gamma = R \left(\frac{d \ln \eta_r}{d \frac{1}{T}} \right)_\gamma \quad (9)$$

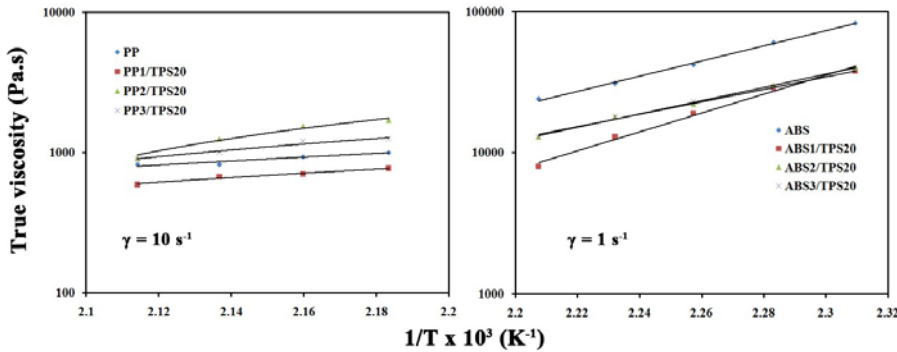


Fig. 7 True viscosity versus $1/T$ of PP/TPS and ABS/TPS

The melt viscosity of polymer was relative to the structure and free volume. The increase in temperature might result in the enhancement of free volume and improvement of chains mobility and thus lead to weakening the melt viscosity, so the viscosity decreased exponentially with the temperature rising. It is well known that the value of flow activation energy reflects the temperature sensitivity of viscosity, so the more E_γ was the more sensitive the behavior of blends were to the temperature. Figure 8 shows the effect of TPS20 content on the flow activation energy at a constant shear rate of the blends. It could be noted from Fig. 8 that the flow activation energy of PP/TPS blends is greater than that of PP. These results indicate that the flow behavior of PP/TPS blends is more sensitive to temperature compared with PP. Also it could be noted from Fig. 8 that the flow activation energy of ABS/TPS blends increases slightly with increasing TPS20 content up to 10% and the increasing TPS20 content higher than 10% caused a sharp decreasing of the flow activation energy.

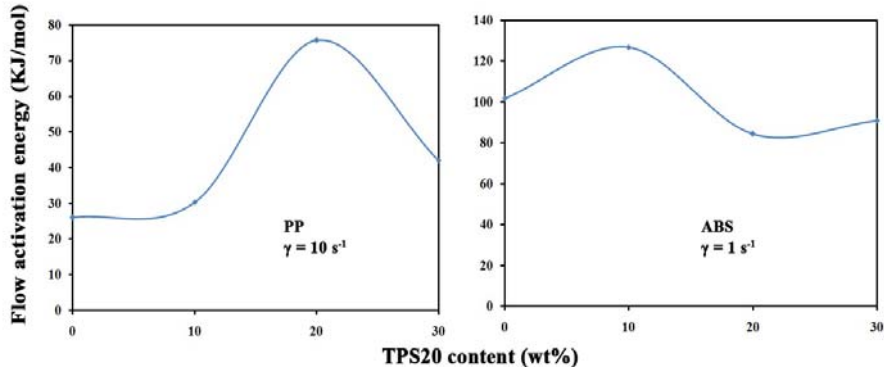


Fig. 8 Flow activation energy versus TPS20 content (wt %) of PP/TPS and ABS/TPS

Mechanical properties

Figure 9 shows the effect of TPS20 and glycerol (for 10% TPS) contents on the stress at break for the blends, it could be noted that at 10% loading of TPS, in PP/TPS blend, the stress at break of the blends increases slightly with increasing glycerol content, whereas it decreases with increasing TPS20 content, nearly the same behavior is noted in ABS/TPS blend where the stress at break of ABS/TPS blend decreases with increasing TPS20 content, while the glycerol content had a little effect on the stress at break of the blend. These unusual results might be attributed to the good levels of miscibility between both ABS, PP and TPS. The results indicate that the potential of tailoring the mechanical properties (in term of stress at break) of the blend through an appropriate glycerol content at low levels of TPS.

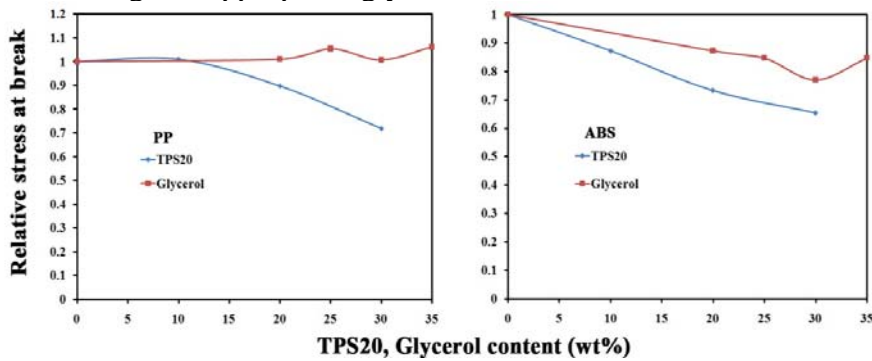


Fig. 9 Relative stress at break versus TPS20 and glycerol content (wt %) of PP/TPS and ABS/TPS

Figure 10 shows the effect of TPS20 and glycerol (for 10% TPS) contents on the strain at break for the blends, it is clearly seen from Fig. 10, that the strain at break of PP/TPS blend decreases with increasing both TPS20 and glycerol content, where the presence of 10% of TPS20 in the blend caused a steep decline in strain at break. Also, the strain at break of ABS/TPS blend decreases with increasing both TPS20 and glycerol content in the blend but the decrement in PP/TPS blend is more clearly than that in ABS/TPS blend and this behavior may be attributed to the high strain at break of PP comparing with that of ABS.

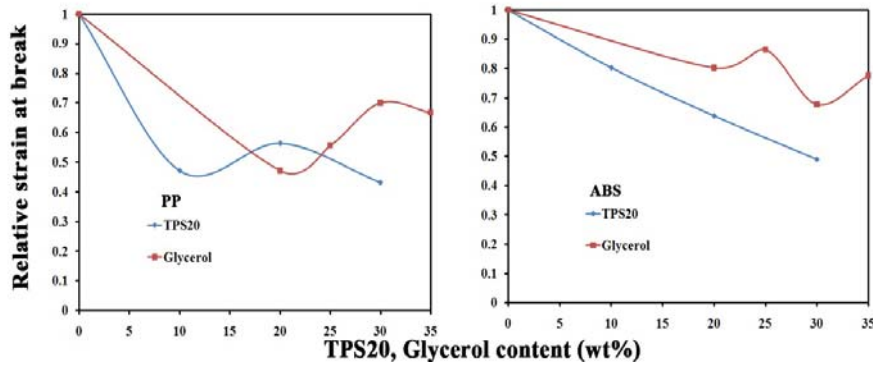


Fig. 10 Relative strain at break versus TPS20 and glycerol content (wt %) of PP/TPS and ABS/TPS

Figure 11 shows the effect of TPS20 and glycerol (for 10% TPS) contents on the Young's modulus for the blends, It could be noted from Fig. 11 that the Young's modulus of PP/TPS and ABS/TPS blends is nearly two times higher than that of the pure polymers (PP and ABS). It could be said that the addition of TPS to each of PP and ABS follows the general trend for filler effects on polymer properties [23], where the modulus increases due to stiffening effect of TPS and the strain and stress at break decrease as the TPS content is increased.

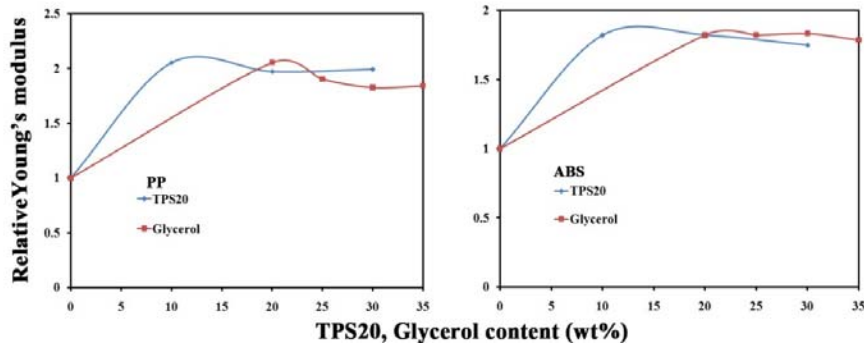


Fig. 11 Relative Young's modulus versus TPS20 and glycerol content (wt %) of PP/TPS and ABS/TPS

Conclusion

Rheological and mechanical measurements of PP/TPS and ABS/TPS blends were performed. It was found that:

1. PP/TPS and ABS/TPS blends are pseudo plastic in nature, and their viscosity decreases with increasing shear rate, similarly to most polymer and polymer blend melts.
2. The true viscosity of the PP/TPS blend decreases with loading levels of TPS20 until 10%, where the minimum value was observed that is, increasing TPS20 higher than 10% caused an increasing trend of the true viscosity. However the true viscosity of ABS/TPS blend decreases with increasing TPS20.
3. The flow activation energy of PP/TPS blends is more than that of PP, but the flow activation energy of ABS/TPS blends increases slightly with increasing TPS20 content up to 10% and the increasing TPS20 content higher than 10% caused a sharp decreasing of the flow activation energy.
4. The addition of TPS to each of PP and ABS follows the general trend for filler effects on polymer properties, where the modulus increases due to stiffening effect of TPS whereas the strain and stress at break decrease as the TPS content is increased.
5. The results of the two systems indicate that up to 30 % TPS, the blends have suitable mechanical properties and good processability (high flow activation energy).

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