Polym. Bull. (2012) 68:1079–1091
DOI 10.1007/s00289-011-0611-z

ORIGINAL PAPER

Rheological and mechanical properties of polypropylene/thermoplastic starch blend

Mosab Kaseem · Kotiba Hamad · Fawaz Deri

Received: 16 August 2010 / Revised: 24 May 2011 / Accepted: 20 August 2011 /
Published online: 26 August 2011

Abstract Starch as an inexpensive and renewable source has been used as a filler for environmentally friendly plastics for about two decades. In order to improve the compatibility between hydrophilic starch granules and hydrophobic polypropylene (PP), glycerol used as a plasticizer for starch to enhance the dispersion and the interfacial affinity in thermoplastic starch (TPS)/PP blend. In this study, PP was melt blended with thermoplastic starch (TPS) using a single screw extrusion process and molded using injection molding process to investigate the rheological and mechanical properties of these blends. TPS viscosity measurements were performed on the single screw extruder. Rheological properties were studied using a capillary rheometer and the Bagley's correction was performed. Mechanical analysis (stress–strain) was performed using Testometric M350-10KN. The rheological properties showed that the viscosity of TPS decreases with increasing glycerol content in TPS. Also, it was found that PP/TPS blends are pseudo plastic in nature and the flow activation energy of the blends is greater than that of PP. Mechanical results showed that strain at break of the blends is lower than that of PP, whereas the Young's modulus of the blends is higher than that of PP.

Keywords TPS · PP · Blend · Mechanical properties · Rheological properties

Introduction

Research in biodegradable and bioresorbable polymers has received increased attention in recent years because of their wide applications in environmental and clinical medicine (e.g., dental/orthopedic surgery). The most popular and important

M. Kaseem (✉) · K. Hamad · F. Deri
Department of Chemistry, Faculty of Science, Laboratory of Materials Rheology (LMR), University of Damascus, P.O. Box 31513, Damascus, Syria
e-mail: mosabkaseem@yahoo.com

biodegradable polymers, poly lactic acid (PLA), polycaprolactone (PCL), polyethylene oxide (PEO), poly(3-hydroxybutyrate) (PHB), polyglycolic acid (PGA), and thermoplastic starch (TPS). TPS is considered one of the most attractive materials for short-life products due to its low cost and because it is a biodegradable material obtained from renewable resources. In addition, it can be produced by traditional processing techniques commonly used in plastics industry (injection, extrusion,…) [1]. TPS is produced by the plasticization of native starch [2] in the presence of hydroxyl or amid rich plasticizers, such as glycerol [3–5], sorbitol [6], ethylene-bisformamide [7–9], and formamide [10]. The chemical nature of plasticizers and the amount used plays an important part in TPS performance and several plasticizers have been investigated for this purpose, including water and polyols. Other compounds such as urea [11, 12] and citric acid have also been used for starch plasticization. However, TPS has two main disadvantages compared to most plastics currently in use, i.e., it is highly water soluble and has poor mechanical properties. These features can be improved by mixing it with certain synthetic polymers.

Synthetic polymers produced from petrochemicals, such as polystyrene (PS), polypropylene (PP), and polyethylene (PE), are widely used in packaging, automotive, healthcare application, and communication or electronic industries. However, as these conventional synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, they may accumulate in the environment and represent a significant source of environmental pollution potentially harming wildlife.

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 [13]. 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 [14, 15], PP [16], PS [17–20]. Gonzalez et al. [14] 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. [18–20] 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. [16] 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 in PP.

In this study, PP was melt blended with TPS which was plasticized with different ratios of glycerol (20, 25, 30, and 35%). The prepared blends were characterized in term of rheological and mechanical properties. Up to now, no academic works were focused on the rheological properties of this system.

Experimental

Materials

Polypropylene (PP) (PETOPLEN EH 251) was supplied by PETKIM Petrokimya Holding A.S (Turkey) [MFR = 24 g/10 min (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 used without any treatment.

Thermoplastic starch (TPS) and TPS/PP blends preparation

Corn starch samples were mixed manually with glycerol in different ratios Table 1, the obtained mixtures were then fed into a laboratory scale single screw extruder (SSE) ($L/D = 25$, $D = 20$) [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 obtained TPS granules with different glycerol ratios were then blended with PP by using the single screw extruder in different ratios Table 1. 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. Also, the blends were extruded through the multi holes die, left to cool in air, and the extrudates were fed into the granulator, the

Table 1 The compositions of PP/TPS blends

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

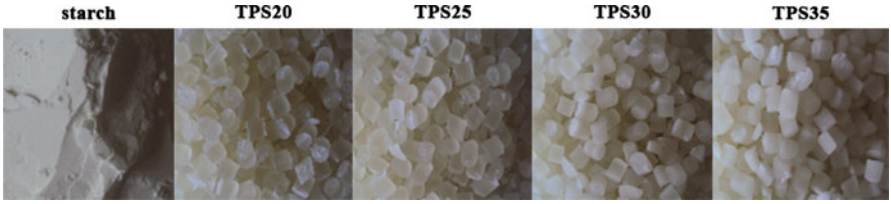

Fig. 1 Thermoplastic starch granules

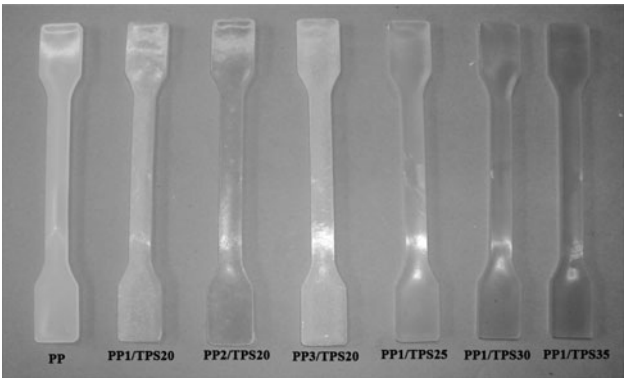

Fig. 2 Tensile samples

obtained granules were then dried in 85 °C for a 6 h before using. The compositions of TPS and the blends are shown in Table 1.

Tensile samples preparation

Tensile samples were prepared using NEGRAI BOSSI NB25 injection machine (LEESONA CORPORATION, Italy) at 170–240 °C, the injection pressure was 9 MPa and the cooling time in the mold was 30 s. The molded samples were dog bone-shaped samples with a thickness and width of 4 and 10 mm, respectively. The gauge length of the sample was 80 mm (Fig. 2).

On-line viscosity measurements

For comparing the viscosity of TPS samples, On-line viscosity measurements were performed in 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 s, while the TPS mass flow was determined at intervals of 30 s 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 polymer.

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 begin pushed 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, and by using $L/R = 8$, 15,

25, 36 capillaries. Bagley's correction was performed by using the data from the four capillary dies. The true shear rate (γ_r) is given by:

$$\gamma_r = \left(\frac{3n+1}{4n}\right) \cdot \frac{4Q}{\pi R^3} \tag{1}$$

where R is the capillary radius, n is the flow index depending on temperature, and Q is the volumetric flow rate. The term ($\frac{3n+1}{4n}$) was the Rabinowitsch correction factor [21]. The true shear stress (τ_r) is given by:

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

where ΔP is the pressure at capillary entrance, L is the capillary length, and e is the Bagley's correction factor [22]. True viscosity is given by:

$$\eta_r = \frac{\tau_r}{\gamma_r} \tag{3}$$

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

$$\eta_r = A.e^{\frac{E_\gamma}{RT}} \tag{4}$$

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

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 before testing. Results from four to seven specimens were averaged. Relative stress at break, strain at break and Young's modulus (Relative property RP) were calculated:

$$RP = \frac{P}{P_0} \tag{5}$$

where P is the property of the blend and P_0 is the property of PP.

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

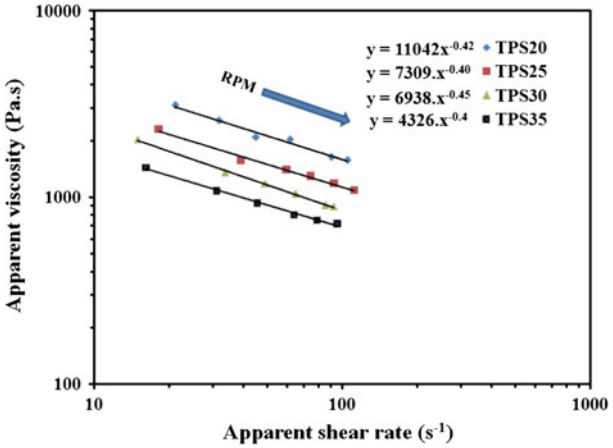

Fig. 3 Apparent viscosity versus apparent shear rate of TPS at 140 °C

melt viscosity at 140 °C occurs expectedly as glycerol rises from 20 to 35% (Fig. 3). 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. The values of the non-Newtonian index (n) of TPS samples, which could be obtained from Fig. 3, were less than 1 (between 0.55 and 0.6), implying that TPS samples were pseudo plastic; similar to most of the polymeric melts [14].

Flow curves

Figure 4 shows the flow curves of PP1/TPS25 at 185, 190, 195, and 200 °C. It could be noted from Fig. 4 that the shear stress for PP1/TPS25 increases with increasing

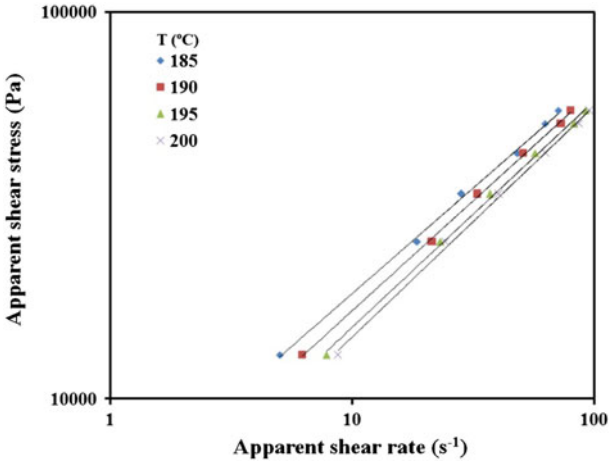

Fig. 4 Flow curves of PP1/TPS25

shear rate and the relationship between shear stress and shear rate obeys the power law:

$$\tau = K\gamma^n \tag{6}$$

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. The values of n of PP/TPS blends were less than 1, implying that PP/TPS blends were pseudo plastic [10]. It is well known that the value of n reflects the viscosity–sensitivity to shear rate.

Viscosity curves

The relationship between true viscosity and true shear rate (i.e., viscosity curves) of PP1/TPS25 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. 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 [23].

The effect of composition on the true viscosity of the blend is shown in Fig. 6, it could be noted from Fig. 6 that at a given true shear rate, the true viscosity of the blend decreased 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. 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:

$$\log \eta_B = \sum_i w_i \log \eta_i \tag{7}$$

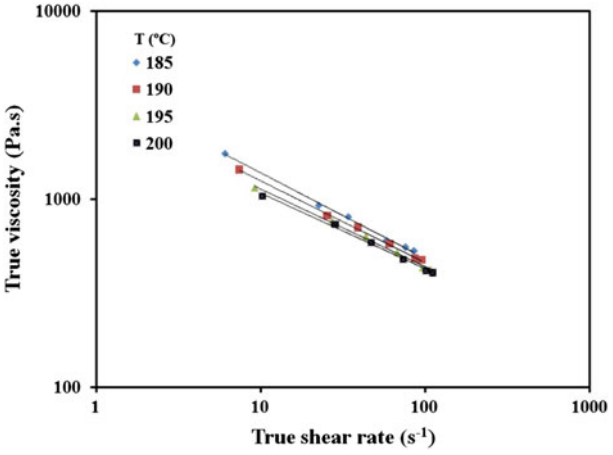

Fig. 5 True viscosity versus true shear rate of PP1/TPS25

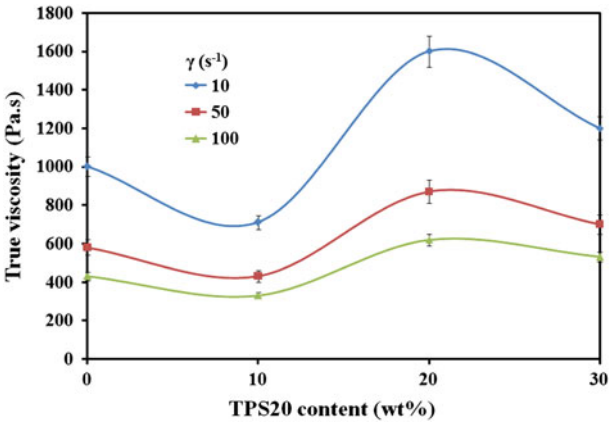

Fig. 6 True viscosity versus TPS20 content (wt%) at 185 °C

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.

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 melts at four temperatures: 185, 190, 195, and 200 °C.

The viscosity of the blend melts varied more widely with increasing temperature than PP. The decrement of viscosity with temperature differed for different blends. This shows that the flow behavior of the blend melts was more sensitive to temperature than PP.

Furthermore, the influence of temperature on viscosity can be seen in Fig. 7 where the viscosities at shear rate $= 10\ s^{-1}$ are plotted against the blending ratios at various temperatures. It can be seen that the viscosity decrements with temperature in different blending ratios show that the dependences of viscosity on temperature varied with the blending ratio. In other words, blend melts with different proportion of TPS20 and PP display distinct viscosity temperature-sensitivity, which can be evaluated by calculating the flow activation energy of blend melts.

Figure 8 shows the relationship between true viscosity and *1/T* for blend melts at shear rate $= 10\ s^{-1}$. Flow activation energy at constant shear rate (E_γ) can be calculated from the slopes of lines in Fig. 8. Figure 9 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. 9 that the flow activation energy of PP, PP1/TPS20, and PP2/TPS20 blends decreases with increasing shear rate whereas it increases with increasing shear rate in PP3/TPS20 blend. There is little attention paid to the dependence of the flow activation energy on shear rate in the literature and the reason for this dependence is not yet clear [24]. It could also be noted that the flow

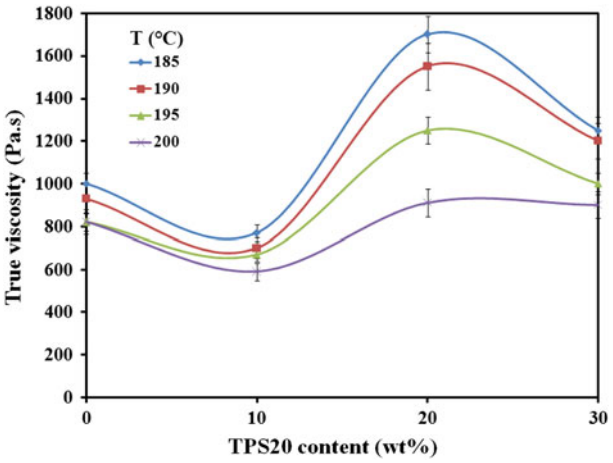

Fig. 7 True viscosity versus TPS20 content (wt%) at shear rate = 10 s^{-1}

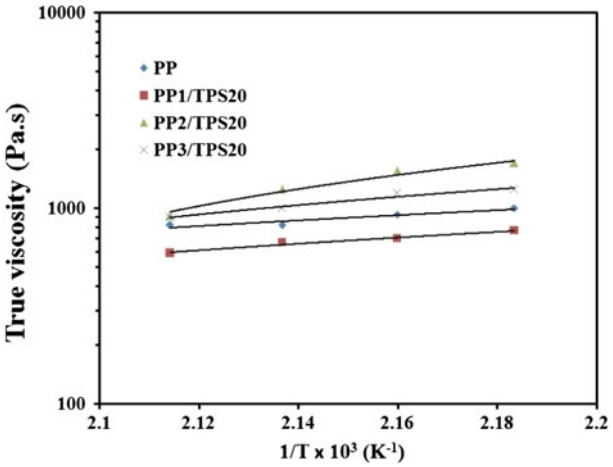

Fig. 8 True viscosity versus *1/T* for PP/TPS20 blends at shear rate = 10 s^{-1}

activation energy of the blends is greater than that of PP. These results indicate that the flow behavior of the blends is more sensitive to temperature compared with PP.

Mechanical properties

Figure 10 shows the effect of TPS20 and glycerol (for 10% TPS) contents on stress at break for the blends, it could be noted that at 10% loading of TPS the stress at break of the blends increases slightly with increasing glycerol content whereas it decreases with increasing TPS20 content. This behavior could be attributed to the good internal contact in the blend at a high level of glycerol. The results indicate the

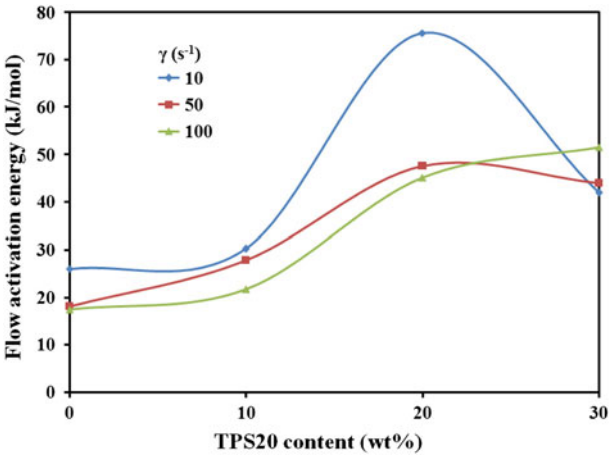

Fig. 9 Flow activation energy versus TPS20 content (wt%)

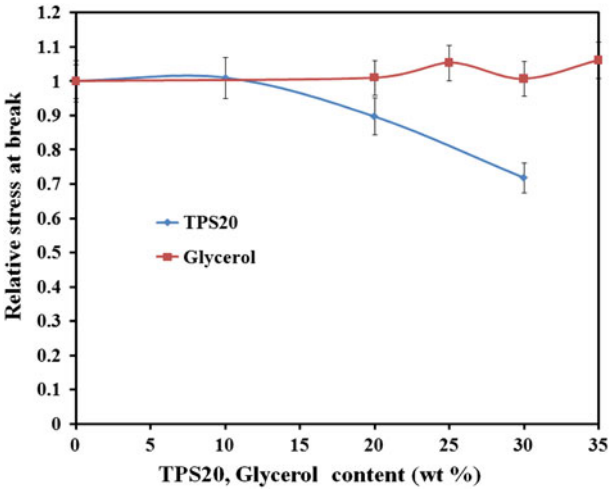

Fig. 10 Relative stress at break versus TPS20 and glycerol content (wt%)

potential of tailoring the mechanical properties of the blend through an appropriate glycerol content at a low content of TPS [14].

Figure 11 shows the effect of TPS20 and glycerol (for 10% TPS) contents on the strain at break for the blends, it is clearly seen in Fig. 11 that the strain at break of the blends decreases with increasing both TPS20 and glycerol content. Presence of 10% of TPS20 in the blend caused a steep decline in strain at break [4].

Figure 12 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. 12 that the Young's modulus of the blends is nearly two times higher than that of neat PP. It could be said that the addition of TPS to PP follows the general trend for filler effects on

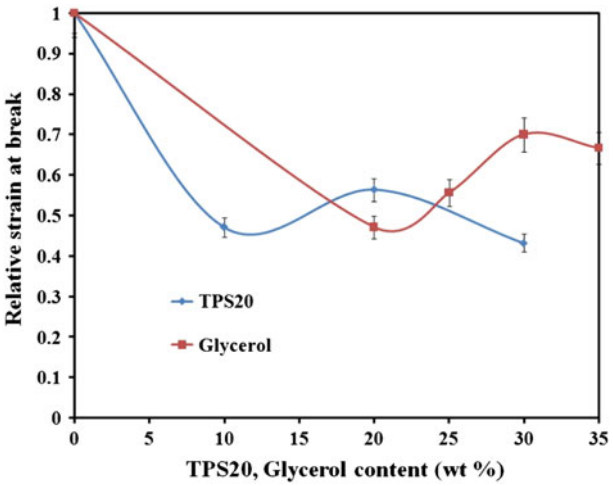

Fig. 11 Relative strain at break versus TPS20 and glycerol content (wt%)

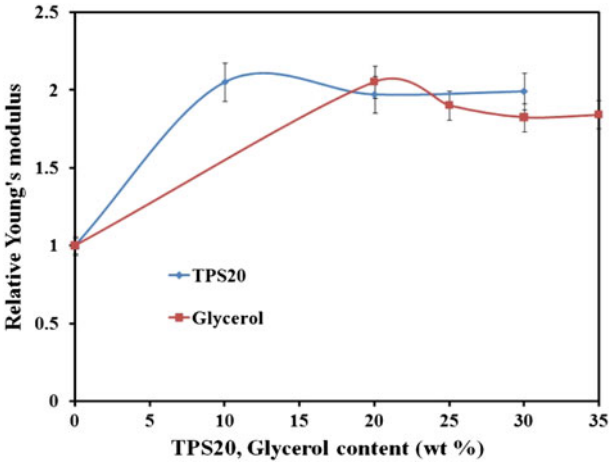

Fig. 12 Relative Young's modulus versus TPS20 and glycerol content (wt%)

polymer properties [25]. The modulus increases due to stiffening effect of TPS and the strain at break decreases as the TPS content is increased.

Conclusion

PP/TPS blends were prepared using a single screw extruder, rheological tests showed that PP/TPS blends were pseudo plastic and exhibited shear-thinning behavior where the viscosity decreased with increasing shear rate and the flow behavior of the blends is more sensitive to temperature compared with PP. Also it

was found 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). Mechanical tests showed that stress at break of the blends decreases with increasing TPS content, whereas it increases slightly with increasing glycerol content. Also, it was found that the strain at break decreases with increasing both TPS and glycerol content.

References

1. Liu H, Xie F, Yu L, Chen L, Li L (2009) Thermal processing of starch-based polymers. Prog Polym Sci 34:1348–1368
2. Carvalho AJF, Job AE, Alves N, Curvelo AAS, Gandini A (2003) Thermoplastic starch/natural rubber blends. Carbohydr Polym 53:95–99
3. Gonzalez FJ, Ramasy BA, Favis BD (2004) Rheological and thermal properties of thermoplastic starch with high glycerol content. Carbohydr Polym 58:139–147
4. Rosa DS, Guedes CGF, Carvalho CL (2007) Processing and thermal, mechanical and morphological characterization of post-consumer polyolefins/thermoplastic starch blends. J Mater Sci 42:551–557
5. Teixeira EM, Roz Da, Carvalho AJF, Curvelo AAS (2007) The effect of glycerol/sugar/water and water mixtures on the plasticization of thermoplastic cassava starch. Carbohydr Polym 69:619–624
6. Bourtoom T (2008) Plasticizer effect on the properties of biodegradable blend film from rice starch–chitosan. Songklanakarin J Sci Technol 30:149–165
7. Yang JH, Yu JG, Ma XF (2006) A novel plasticizer for the preparation of thermoplastic starch. Chin Chem Lett 17:133–136
8. Yang JH, Yu JG, Ma XF (2008) Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). Carbohydr Polym 63:218–223
9. Yang JH, Yu JG, Ma XF (2006) Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS). Carbohydr Polym 66:110–116
10. Wang N, Yu J, Chang P, Ma X (2008) Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. Carbohydr Polym 71:109–118
11. Ma XF, Yu JG, Wan JJ (2006) Urea and ethanolamine as a mixed plasticizer for thermoplastic starch. Carbohydr Polym 64:267–273
12. Ma X, Yu J (2004) The plasticizers containing amide groups for thermoplastic starch. Carbohydr Polym 57:197–203
13. Auras R, Harte B, Selke S (2004) An overview of polylactides as packaging materials. Macromol Biosci 4:835–864
14. Gonzalez FJ, Ramsay BA, Favis BD (2003) High performance LDPE/thermoplastic starch blends: a sustainable alternative to pure polyethylene. Polymer 44:1517–1526
15. Salcido CS, Gonzalez FJ, Hernandez ML, Esquivel JC (2008) Effect of morphology on the biodegradation of thermoplastic starch in LDPE/TPS blends. Polym Bull 60:677–688
16. Rosa DS, Bardi MAG, Machado LDB, Dias DB, Silva LGA, Kodama Y (2009) Influence of thermoplastic starch plasticized with biodiesel glycerol on thermal properties of PP blends. J Them Anal Calorim 97:565–570
17. Mihai M, Huneault MA, Favis BD (2007) Foaming of polystyrene/thermoplastic starch blends. J Cell Plast 43:215–236
18. Schlemmer D, Sales M, Resck IS (2009) Degradation of different polystyrene/thermoplastic starch blends buried in soil. Carbohydr Polym 75:58–62
19. Schlemmer D, Oliveira ER, Sales M (2007) Polystyrene/thermoplastic starch blends with different plasticizers, preparation and thermal characterization. J Them Anal Calorim 87:635–638
20. Pimentel T, Duraes J, Drummond A, Schlemmer D, Falcao R, Salas M (2007) Preparation and characterization of blends of recycled polystyrene with cassava starch. J Mater Sci 42:7530–7536
21. Han CD (2007) Rheology and processing of polymeric materials (Polymer Rheology). Oxford University Press, New York
22. Bagley EB (1957) End corrections in the capillary flow of polyethylene. J Appl Phys 28:624–627

23. Sinthavathavorn W, Nithitanakul M, Grady B, Mangaraphan R (2009) Melt rheology and die swell of PA6/LDPE blends by using lithium ionomer as a compatibilizer. Polym Bull 63:23–35
24. Xu S, Zhu L, Xie J, Jiang M (1999) Melt rheology of compatibilized polystyrene/low density polyethylene blends. Polym Int 48:1113–1120
25. Willet JL (1994) Mechanical properties of LDPE/granular starch composites. J Appl Polym Sci 54:1685–1695