

Morphology and Tensile Properties of High-Density Polyethylene/Natural Rubber/Thermoplastic Tapioca Starch Blends: The Effect of Citric Acid-Modified Tapioca Starch

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ABSTRACT: The effect of citric acid on the tensile properties of high density polyethylene (HDPE)/natural rubber (NR)/thermoplastic tapioca starch (TPS) blends was investigated. The ratio between HDPE/NR was fixed at 70/30 and used as the matrix system. TPS loadings, after modification with citric acid (TPSCA) and without modification (TPS), were varied from 0 to 30 wt %. The morphologies and tensile properties of HDPE/NR blends were evaluated as a function of TPS loadings. The tensile strength, Young's modulus, and elongation at break were found to decrease with increasing TPS loading. However, a slight improvement in the tensile

strength of HDPE/NR/TPSCA blends at 5 and 10 wt % TPS loadings were observed. TPS can be partly depolymerised to produce a low viscosity product when processed with citric acid. TPS with low viscosity can easily disperse in the thermoplastic natural rubber (TPNR) system and reduce the surface tension at the interphase of TPS-HDPE/NR as shown by scanning electron microscopy (SEM). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 768–775, 2012

Key words: polyethylene; rubber; biocompatibility; blends; morphology

INTRODUCTION

Environmental problems associated with the disposal of plastics and the need for environmental-friendly products has resulted in the significant use of starch. Starch is a low cost, biodegradable material, which makes it an attractive option for manufacturing sustainable products. The incorporation of starch into some synthetic thermoplastics can enhance its environmental degradation. The use of starch in blends to enhance the biodegradability of conventional plastics has been reported by many researchers.^{1–6} Currently, research is being conducted to produce newer plastics based on thermoplastic starch and starch-synthetic polymer blends.

The use of starch at higher loadings requires certain specific properties. To use in blends, the starch must be disrupted to form a continuous phase in the blends. Thermoplastic starch can be prepared with the addition of plasticizer, such as glycerol, at a high temperature and in high shear conditions.^{4,7–9} However, TPS has some limitations such as poor

mechanical properties and sensitivity to water absorption. To overcome these drawbacks, the processing of TPS is always carried out with other synthetic polymers (e.g., polyolefin and poly vinyl alcohol) to attain the required properties of the blends.⁸ Several previous studies showed the effects of incorporating TPS into thermoplastics systems or blends with natural rubber.^{10–16} However, no work has been carried out on starch-thermoplastic natural rubber blends. Therefore, this work was devoted to exploring the possibility of producing TPNR composed of high density polyethylene (HDPE), natural rubber (NR), and thermoplastic tapioca starch (TPS) blends. In the TPNR system, the NR plays a functional role in improvement of impact resistance and overcome the problem of brittleness in thermoplastic products. Whereas, HDPE which possesses good tensile properties, plays the role as a rigid phase in TPNR system. TPNR which is composed of hard and soft domains are able to be versatile products which are having wide field of application. Unlike any conventional rubber products, TPNR were produced without involving vulcanization process, and thus TPNR can be reprocessed to avoid the wastage.

TPS can be partially depolymerised to produce a low viscosity product when processed with a carboxylic acid: namely, citric acid and ascorbic acid.^{4,17} Decreasing the molecular weight of starch by adding

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TABLE I
The Weight Proportion of HDPE/NR/TPS Blends
Modified with and without Citric Acid

Sample	Sample (weight proportion)		CA (relative to TPS content)
	(HDPE/NR)	TPS	
Matrix	100	0	–
5%TPS	95	5	–
10%TPS	90	10	–
20%TPS	80	20	–
30%TPS	70	30	–
5%TPSCA	95	5	1
10%TPSCA	90	10	1
20%TPSCA	80	20	1
30%TPSCA	70	30	1

carboxylic acid has been reported to improve the wettability with a second polymer.^{5,8} However, some researchers also reported that adding citric acid (CA) yields starch ester, which upon further reaction leads to crosslinking in starch chains.^{18,19} Therefore, the aim of this work is to use TPS modified with CA in the melt blending of a HDPE/NR blend and to investigate its effect on the tensile properties of the HDPE/NR/TPS blend. The main objective of decreasing the starch molecule weight (M_w) is to improve the adhesion at the interphase of TPS-HDPE/NR blends.

MATERIALS

High density polyethylene (HDPE) granulates with a density of 0.96 g/cm³ was supplied by Titan Chemicals, Malaysia. Natural rubber (NR) grade SMR L was obtained from Lembaga Getah Malaysia. The tapioca starch used was food grade. Reagent grade glycerol and citric acid were obtained from Merck, Darmstadt, Germany.

Preparation of thermoplastic tapioca starch (TPS)

A kitchen blender was used to premix, tapioca starch (with and without 1% citric acid) and 35% glycerol to obtain a homogenous mixture. Then, the mixture was stored overnight in a dry place. Later, the mixture was processed using a heated two-roll mill at temperature of 150°C and the mixing time was 10 min.

Preparations of HDPE/NR/TPS blends

The blends were prepared by melt blending of HDPE/NR/TPS in a Haake Rheomix 600 mixer equipped with roller rotors. The mixing was carried out at a temperature 150°C, and the rotor speed was fixed at 55 rpm. The HDPE was first charged into the mixing chamber for 3 min and followed by NR.

Then, the mixing time was continued for 4 min before mixing with TPS and processed until plateau torque was reached. The duration of the whole process was 12 min. The blend was converted into a 1 mm sheet using a hydraulic hot press Gotech Testing Machine. The hot press procedures involved preheating at 150°C for 6 min, and followed by 2 min of compression at the same temperature and, subsequent cooling under pressure for 4 min.

Table I shows the weight proportion of HDPE/NR/TPS blends modified with and without citric acid. The ratio between HDPE/NR was fixed at 70/30, and TPS content was varied from 5 to 30% relative to the overall weight of the blends. The percentage of citric acid was fixed at 1% relative to the TPS content.

Tensile properties

Measurements of the tensile properties were performed with an Instron Universal Testing Machine (model 3366), with a crosshead speed of 50 mm/min. Dumbbell samples (1 mm thick) with a 50 mm gauge length were tested according to ASTM D 638. The mean value out of five samples was reported with standard deviation to show the error range.

Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectra of TPS and TPSCA were measured using a Perkin Elmer System 2000 to characterize the possible reaction between TPS and citric acid. Unreacted CA and excess glycerol were extracted from TPS samples through Soxhlet extraction in acetone for 3 days. The transmittance spectra regions were obtained between 4000 cm⁻¹ and 800 cm⁻¹ with a 4 cm⁻¹ resolution.

Scanning electron microscopy (SEM)

Fracture surface of the samples were examined with a Leo Supra—3SVP field emission scanning electron microscope at an acceleration rate of 20 kV. The fracture surfaces of the specimens were mounted on aluminum stubs and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

FTIR spectroscopic analysis

The FTIR spectra of TPS prepared with and without 1% CA are shown in Figure 1(a). The IR spectra were used to confirm the changes in the TPS structure. Furthermore, they were also used to determine the hydrolysis of the starch backbone and the

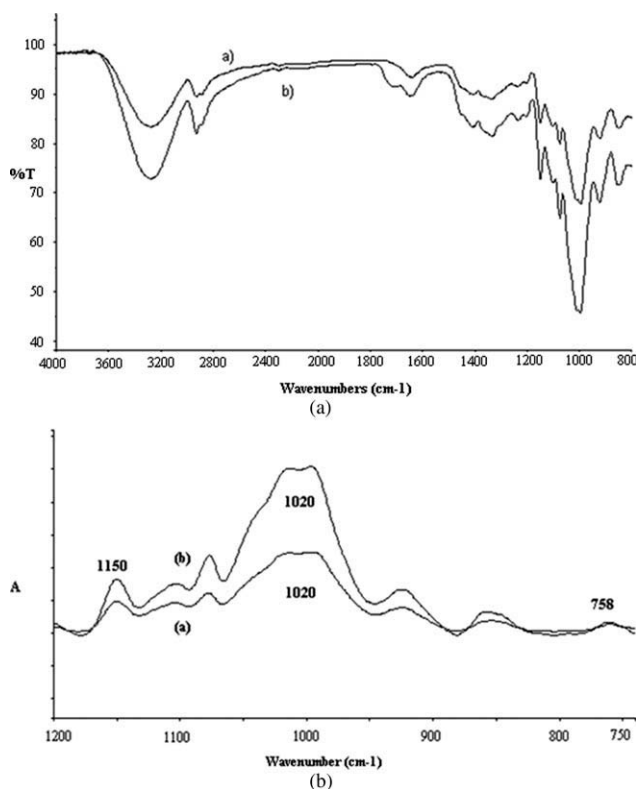


Figure 1 The FTIR spectra of (a) TPS and (b) TPSCA. (b) The effect of modification TPS with CA on the peak's height at 1150 cm^{-1} (a) TPS and (b) TPSCA.

esterification process between starch and CA. The band range from 3200 to 3400 cm^{-1} corresponds to the vibration stretching of inter- and intramolecular hydrogen bonds of starch. The peak appearing at 2930 cm^{-1} is attributed to the formation of inter- and intramolecular bonds between starch and glycerol hydroxyl groups.⁶ For TPSCA, the additional shoulder peak was observed at around 1729 cm^{-1} and was identified as the peak of the ester group. Shi et al. (2007)⁴ also reported that the peak at 1729 cm^{-1} demonstrates ester bonding due to the esterification process between starch and citric acid. Before the FTIR test, the extraction process was carried out in acetone to remove unbound CA and excess glycerol. The ester derivation from the reaction between CA and glycerol also been extracted out since they determined to be soluble in acetone.⁶

A schematic reaction of the esterification of starch with citric acid is shown in Figure 2. When citric acid was heated, the carboxyl group in the citric acid dehydrated to form citric anhydride and later reacted with hydroxyl groups in the starch to form starch acetate [Eq. (1)].¹⁸ On further reaction [Eq. (2)] which happened at another end of the citric acid yielded crosslinked starch acetate.¹⁹ This reaction can be controlled to maximize reaction efficiency, minimize crosslinking, and maximize carboxyl content. The appearance of an absorption peak at

1729 cm^{-1} indicates an effective acetylation process occurred between the hydroxyl groups of starch and citric acid.

The peak at 1020 cm^{-1} is the vibration stretching in C—O—C, and the peak near 1150 cm^{-1} is attributed to the vibration stretching of C—O in C—O—H groups.²⁰ The peak height at 1150 cm^{-1} for TPSCA is higher than the peak that was observed in TPS [Fig. 1(b)]. The peak's height was measured from the baseline for which the unchanged peak at 758 cm^{-1} was used as the reference peak. The peak at 758 cm^{-1} is reflected to C—O—C ring vibrations on starch²¹ and this peak was not influenced by the reaction between starch with CA. The increase of the peak height at 1150 cm^{-1} was due to the increase of C—O—H groups, which resulted from the hydrolysis of glycosidic bonds in the starch to form new hydroxyl groups.

Adding citric acid to the TPS preparation caused partial depolymerisation between C1 and glycosidic oxygen in starch. Ning et al. (2007)⁵ reported that adding citric acid made granular starch destructured, plasticized, melted, and also partially depolymerised. Calvalho and coworkers (2005)⁸ used ascorbic and citric acids as the catalysts for the controlled hydrolytic cleavage of starch macromolecules through melt processing. They found that adding carboxylic acid caused a severe decrease in starch molar mass. The proposed hydrolysis mechanism in the starch chain is shown in Figure 3. This acidic hydrolysis occurs at glycosidic bonds and is induced by the residual moisture that is available in excess in starch. In the presence of citric acid (represented by $\sim\sim\sim\text{A—H}$), the glycosidic oxygen is protonated, and the resulting glycosyl is further hydrolyzed by water molecules to form a stable product which is the same as the substrate.²²

Processing characteristics

The melt processing characteristics of the HDPE/NR/TPS blends were studied from processing torque-time curves. Figure 4(a) shows the processing torque of the melt mixed HDPE/NR and HDPE/NR with different TPSCA loadings. The first and second peaks correspond to shear torque before the melting of HDPE and NR. The different peaks were obtained for all cases and are related to the different amounts of HDPE and NR charged into the mixing chamber. The percentage of HDPE and NR were reduced when TPSCA loading increased from 5 to 30 wt %. The third peak appearing at around 7 min corresponds to the introduction of TPS. After 10 min, the blends became homogeneous with dispersions of TPS into the HDPE/NR system, and then the processing torque stabilized indicating that a good level of mixing was achieved.

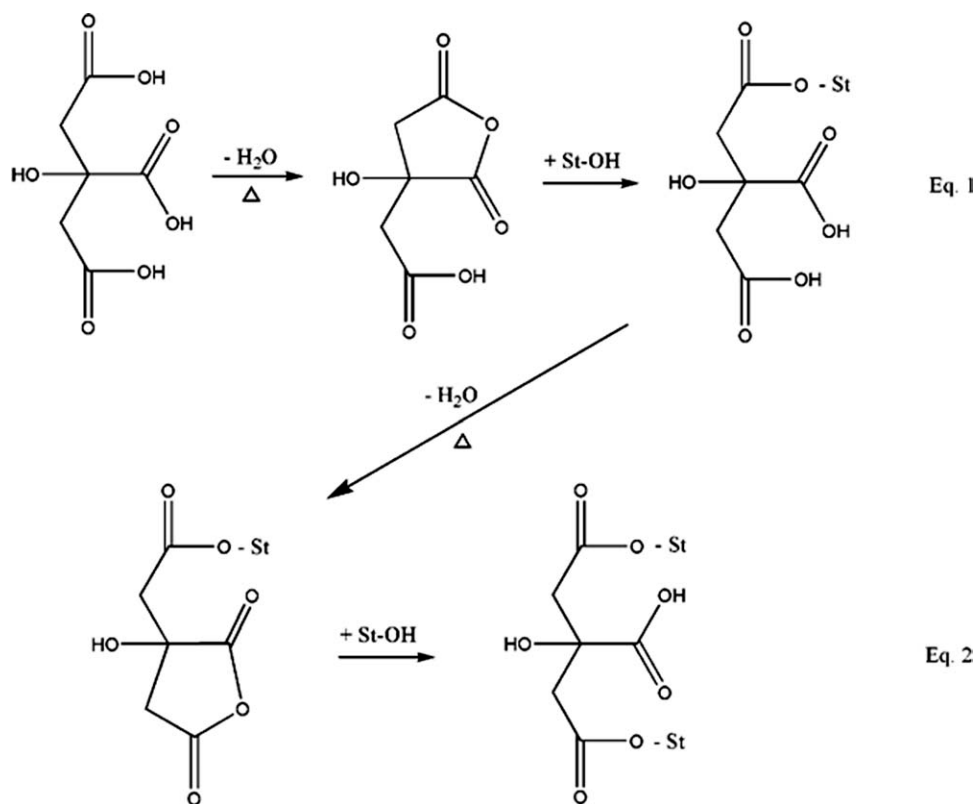


Figure 2 The possible crosslink reaction between citric acid and starch.

The stabilization torques for different TPS loadings with and without modification with citric acid is given in Figure 4(b). It can be seen that the stabilization torque decreased with increasing TPS loading.

Meanwhile, HDPE/NR/TPS modified with citric acid showed lower stabilization compared with the HDPE/NR/TPS blends with unmodified TPS. The stabilization torque clearly indicates that the

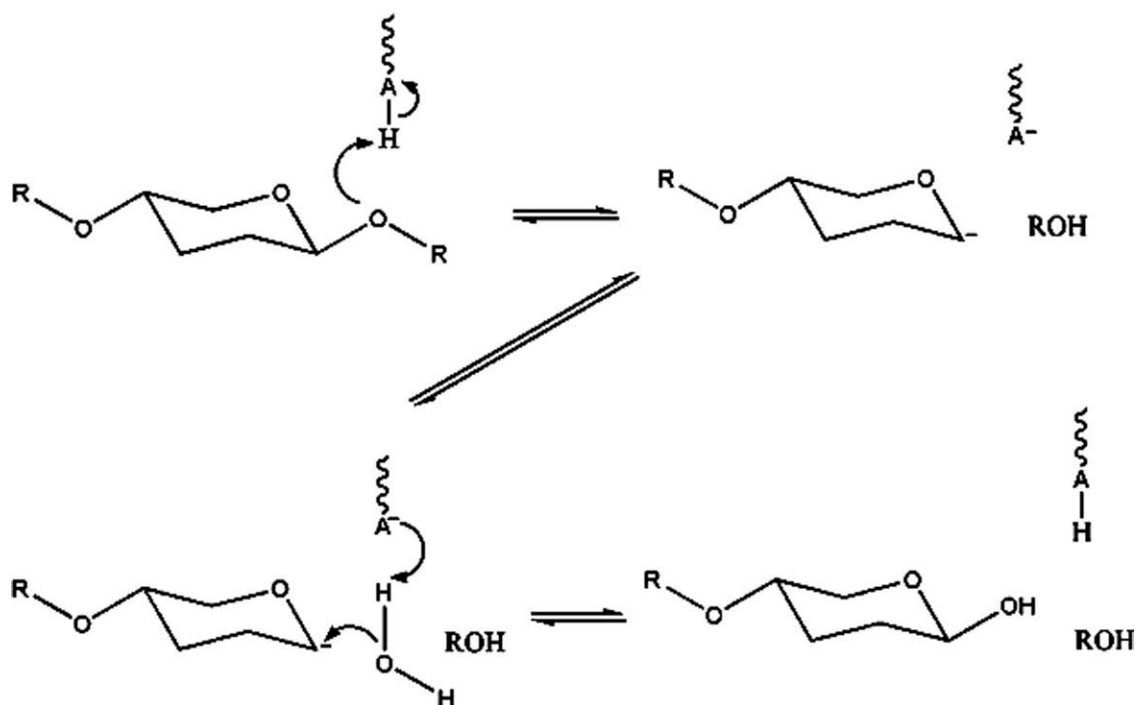


Figure 3 The proposed mechanism of starch hydrolysis with citric acid.

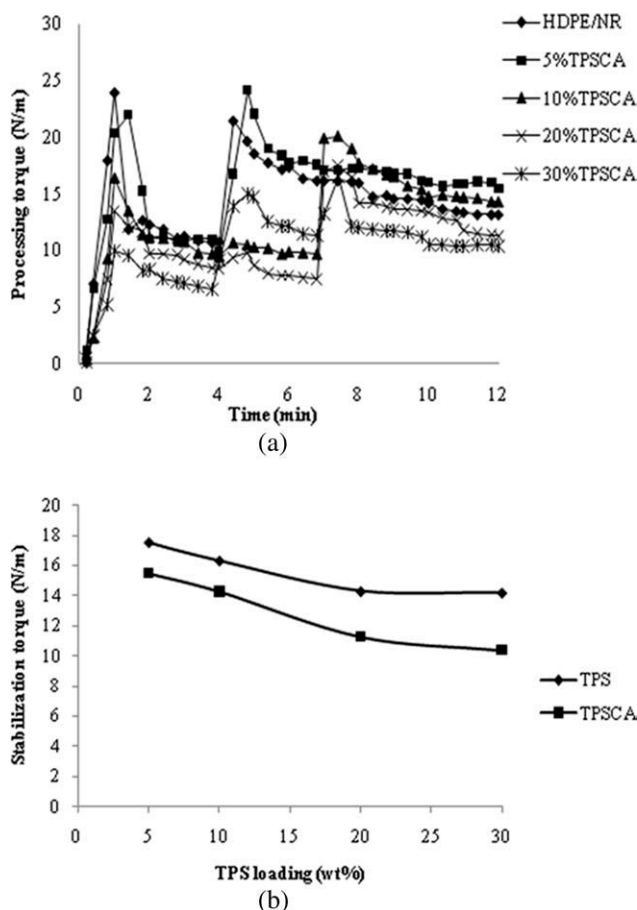


Figure 4 (a) The processing torque of HDPE/NR blend and HDPE/NR/TPS blends. (b) The effect of citric acid on the stabilization torque of HDPE/NR/TPS blends as a function of TPS loading.

molecular weights of the blends modified with citric acid were reduced. The same finding has been observed by Carvalho et al.⁸ They mentioned that the decrease of TPS molecular weight depends on the type of acid used, the acid concentration, and the processing time.

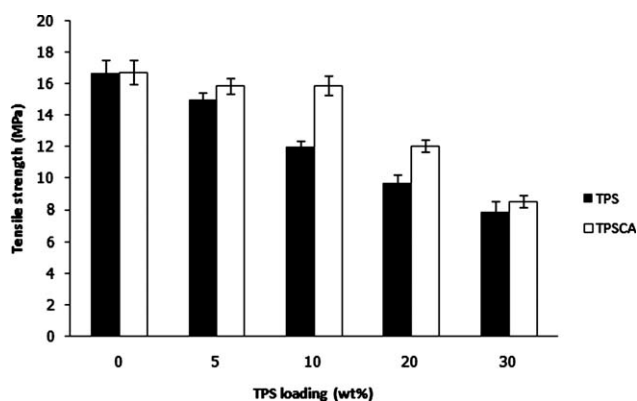


Figure 5 Tensile strength of the HDPE/NR/TPS blends with and without citric acid as a function of TPS loading.

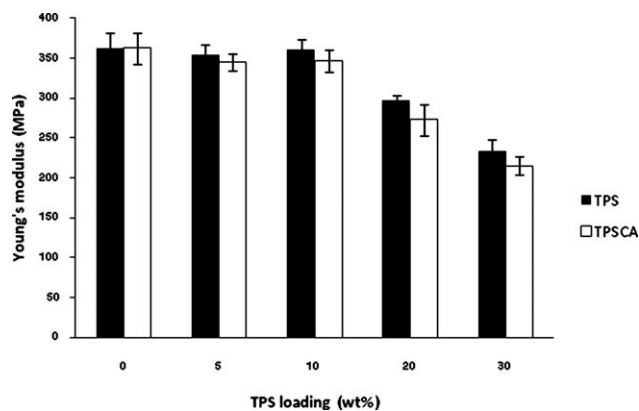


Figure 6 Young's modulus of the HDPE/NR/TPS blends with and without citric acid as a function of TPS loading.

Tensile properties

The tensile properties of HDPE/NR/TPS blends with and without modification with citric acid are shown in Figures 5–7. The addition of TPS causes a decrease in the tensile strength, Young's modulus, and elongation at break of HDPE/NR/TPS blends. This was due to the incorporation of nonreinforcing material into the blend and the inability of TPS to support stress transfer from the HDPE/NR matrix phase. The tensile properties of these blends depend on how TPS is well dispersed in the HDPE/NR matrix. However, an increase in tensile strength was observed in the HDPE/NR/TPS blends when TPS was modified with citric acid compared with the blends without citric acid (Fig. 5). The tensile strengths at 5 and 10 wt % TPSCA are almost the same as the tensile strength for the HDPE/NR blend: it is about 16.7 MPa. The increases in tensile strength for 5 and 10 wt % of TPS loading as a result of modification with CA were observed to be about 0.9 MPa and 3.9 MPa compared with the blends without CA.

For incompatible blends, such as incorporating hydrophobic starch into the HDPE/NR system, the

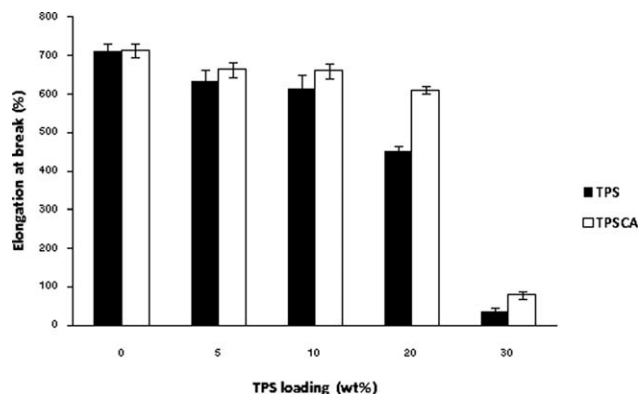


Figure 7 Elongation at break of the HDPE/NR/TPS blends with and without citric acid as a function of TPS loading.

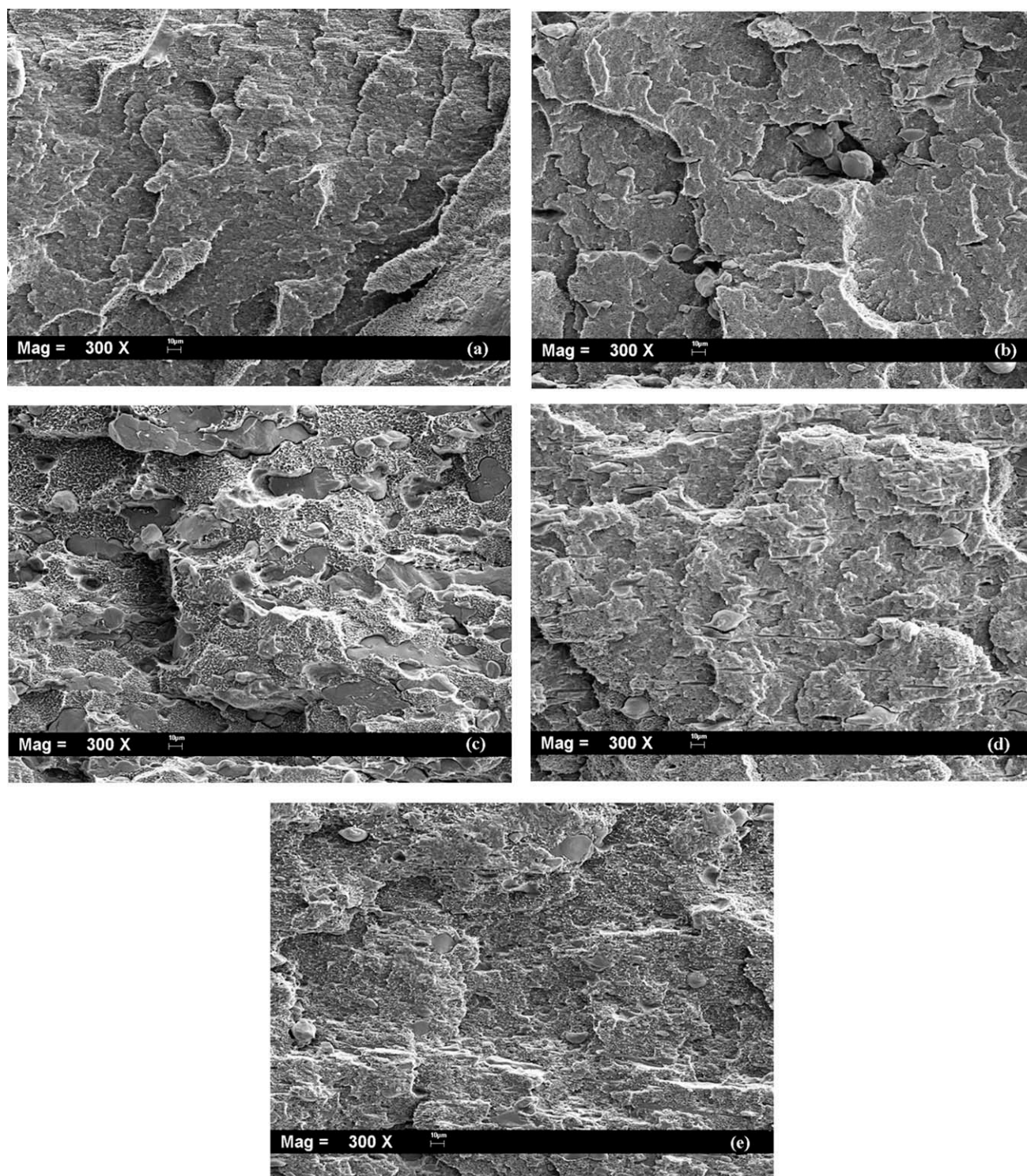


Figure 8 SEM micrographs of (a) HDPE/NR/TPS blends, (b) 10% TPS loading, (c) 30% TPS loading, (d) 10% TPSCA loading, and (e) 30% TPSCA loading.

mechanical properties of the blend depend mainly on dispersion of the dispersion phase.² Liu et al. (2009)²³ reported that the acidity of citric acid deteriorates the chain entanglement in the starch and weakens the interactions between the starch molecules, which improve the fluidity of the TPS.

Furthermore, modification of TPS with citric acid can cause hydrolytic cleavage of the starch chain and thus decrease the starch viscosity.⁸ Low TPS molecular weight and the increase of TPS fluidity are important for TPS dispersion when blending in the HDPE/NR system. It has also been reported that

lowering starch molecular weight via the hydrolysis process in dilute acid can improve adhesion at the interphase,²⁴ and thus improved the compatibility between TPS and HDPE/NR system. Further increasing the TPS content to 20% and 30%, a marked decrease in the tensile strength for both series was observed. This observation was attributed to the increased particle size of TPS in the HDPE/NR blend. The addition of TPS at higher loading leads to particle agglomeration, and the large TPS particles increased the stress-concentration points in the blend, which caused the tensile strength failure.²⁵

The changes of the Young's modulus with different starch loadings are shown in Figure 6. After adding TPS to the HDPE/NR blend, there were no significant changes in Young's modulus observed for the first 10 wt % TPS loading for both series. When the TPS loading increased to 20% and 30%, the Young's modulus decreased due to the effect of the incorporation soft materials into the HDPE/NR system. This is similar case as incorporating NR phase into the HDPE matrix for this system. Furthermore, TPS was prepared with 35 wt % of glycerol, which had a softening effect on the blend. Taquet and coworkers (2009)²⁶ found that the blend with a higher amount of glycerol was overplasticized and that glycerol softens the blends. Similar results were reported by Godbole et al. (2003)²⁷ and Reis et al. (2008),²⁸ which found that starch addition in thermoplastics systems decreased the Young's modulus. For all blend compositions, HDPE/NR/TPS blends without CA exhibited better Young's modulus compared with TPS modified with CA. As described before, adding CA caused starch degradation through the hydrolytic cleavage of starch chains. According to Wang et al. (2009),²⁹ the polymer chain cleavage due to the hydrolysis reaction ultimately leads to the reduction in Young's modulus.

Figure 7 shows that the elongation at break of HDPE/NR/TPS blends decrease with increasing TPS content. At 5 and 10 wt % TPS content, there was a slight decrease in elongation at break for both series but HDPE/NR/TPSCA blends showed better flexibility than the HDPE/NR/TPS blends. Upon further increase of the TPS content to 20% and 30%, HDPE/NR/TPS blends showed major decreases in elongation at break, which can be attributed to agglomeration of the TPS phase. Agglomeration of TPS will create weak points in the blends that will easy break when the force is applied. Meanwhile, for the HDPE/NR/TPS modified with citric acid blend, incorporation of TPS up to 20% showed better elongation at break. The improvement of elongation at break arises from the finer dispersion of the TPS in HDPE/NR blends due to the smaller size of the TPS phase.²

Blends morphology

Figure 8(a) shows SEM micrographs for the fracture surface of HDPE/NR blend with NR as the dispersion phase in the HDPE matrix. Although HDPE/NR is an immiscible blend, it can be seen that NR particles are well distributed in the HDPE matrix. To investigate the effect of citric acid on the dispersion of TPS in HDPE/NR blends, the fracture surfaces of HDPE/NR/TPS blends and HDPE/NR/TPSCA are shown in Figure 8(b–e). Previous works have reported that to incorporate a higher amount of starch in the HDPE or NR matrix, starch granules must be disrupted to form thermoplastic material by adding plasticizer.^{4,8,9} It can be seen in the SEM micrograph shown in Figure 8(b) that the interfacial adhesion between TPS and the HDPE/NR matrix is relatively weak. In Figure 8(c), SEM image shows a clear separation at the interface between the TPS and HDPE/NR matrix due to the incompatible blend between hydrophobic TPS and hydrophilic HDPE/NR.

When comparing HDPE/NR/TPS [Fig. 8(b,c)] with HDPE/NR/TPSCA blends [Fig. 8(d,e)], the dispersion level of TPS is improved by modification with CA. For HDPE/NR/TPS blends, the size of TPS particles for the 10% TPS loading ranged from 10 to 100 μm , and upon further addition of TPS loading to 30%, the TPS particles tend to agglomerate. However, fine TPS particles (ranging from 10 to 30 μm) are observed in both 10 and 30% HDPE/NR/TPSCA blends, indicating an increase in adhesion between the TPS and HDPE/NR blends.

CONCLUSIONS

TPS was modified with citric acid to improve its interaction with the HDPE/NR matrix. Accordingly, FTIR analysis showed the occurrence of both starch hydrolysis and the acetylation process between the starch and citric acid. Compared with HDPE/NR/TPS, the modified TPS blends exhibited increased tensile properties and improved surface morphology. The HDPE/NR/TPSCA blends with 5% and 10% TPS loading possessed improved tensile strength, which was almost the same value as that of the HDPE/NR blend. This is attributed to the low viscosity of TPS, which allowed it to easily disperse when blended with the HDPE/NR matrix. SEM studies of the tensile fracture surfaces showed that the blends with modified TPS have better dispersion in the HDPE/NR matrix compared with HDPE/NR/TPS blends.

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References

1. Chandra, R.; Rustgi, R. *Polym Degrad Stab* 1997, 56, 185.
2. Bikiaris, D.; Prinos, J.; Koutsopoulos, K.; Vouroutzis, N.; Pavlidou, E.; Frangi, N.; Panayiotou, C. *Polym Degrad Stab* 1998, 59, 287.
3. Huang, C.; Roan, M.; Kuo, M.; Lu, W. *Polym Degrad Stab* 2005, 90, 95.
4. Shi, R.; Zhang, Z.; Liu, Q.; Han, Y.; Zhang, L.; Chen, D.; Tian, W. *Carbohydr Polym* 2007, 69, 748.
5. Ning, W.; Jiugao, Y.; Xiaofei, M.; Ying, W. *Carbohydr Polym* 2007, 67, 446.
6. Raquez, J.; Nabar, Y.; Srinivasan, M.; Shin, B.; Narayan, R.; Dubois, P. *Carbohydr Polym* 2008, 74, 159.
7. van Soest, J. J. G.; Benes, K.; de Wit, D.; Vliegthart, J. F. G. *Polymer* 1996, 37, 3543.
8. Carvalho, A. J. F.; Zambon, M. D.; Curvelo, A. A.; Gandini, A. *Carbohydr Polym* 2005, 62, 387.
9. Teixeira, E. M.; da Ro'z, A. L.; Carvalho, A. J. F.; Curvelo, A. A. S. *Carbohydr Polym* 2007, 69, 619.
10. Yang, Z.; Bhattacharya, M.; Vaidyat, U. R. *Polymer* 1996, 37, 2137.
11. Mani, R.; Bhattacharya, M. *Eur Polym J* 1998, 34, 1467.
12. Averous, L.; Moroa, L.; Dole, P.; Fringant, C. *Polymer* 2000, 41, 4157.
13. Ramis, X.; Cadenatoa, A.; Sallaa, J. M.; Moranchoa, J. M.; Valle's, A.; Contat, L.; Ribes, A. *Polym Degrad Stab* 2004, 86, 483.
14. Wu, Y.; Qi, Q.; Liang, G.; Zhang, L. *Carbohydr Polym* 2006, 65, 109.
15. Liu, C.; Shao, Y.; Jia, D. *Polymer* 2008, 49, 2176.
16. Mondragon, M.; Hernandez, E. M.; Rivera-Armenta, J. L.; Rodriguez-Gonzalez, F. J. *Carbohydr Polym* 2009, 77, 80.
17. Hirashima, M.; Takahashi, R.; Nishinari, K. *Food Hydrocolloids* 2005, 19, 909.
18. Ma, X.; Chang, P. R.; Yu, J.; Stumborg, M. *Carbohydr Polym* 2009, 75, 1.
19. Tharanathan, R. N. *Crit Rev Food Sci Nutr* 2005, 45, 371.
20. Fang, J. M.; Fowler, P. A.; Tomkinson, J.; Hill, C. A. S. *Carbohydr Polym* 2002, 47, 245.
21. Jayasekara, R.; Harding, I.; Bowater, I.; Christie, G. B. Y.; Lonergan, G. T. *Polym Test* 2004, 23, 17.
22. Davies, G.; Henrissat, B. *Structure* 1995, 3, 853.
23. Liu, H.; Xie, F.; Yu, L.; Chen, L.; Li, L. *Prog Polym Sci* 2009, 34, 1348.
24. Comyn, J. *Chemistry of Adhesives which Harden without Chemical reaction*. In *Adhesion Science*; The Royal Society of Chemistry: Thomas Graham House, United Kingdom.
25. Nawang, R.; Danjaji, I. D.; Ishiaku, U. S.; Ismail, H.; Mohd Ishak, Z. A. *Polym Test* 2001, 20, 167.
26. Taquet, A.; Huneault, M. A.; Favis, B. *Polymer* 2009, 50, 5733.
27. Godbole, S.; Gote, S.; Latkar, M.; Chakrabarti, T. *Bioresour Technol* 2003, 86, 33.
28. Reis, K. C.; Pereira, J.; Smith, A. C.; Carvalho, C. W. P.; Wellner, N.; Yakimets, I. *J Food Eng* 2008, 89, 361.
29. Wang, Y.; Han, X.; Pan, J.; Sinka, K. *J Mech Behav Biomed Mater* 2010, 3, 14.