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High performance polyethylene/thermoplastic starch blends through controlled emulsification phenomena

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ABSTRACT

The emulsification efficacies of a range of compatibilizers for polyethylene/thermoplastic starch blends have been studied and a detailed morphological and mechanical analysis has been conducted. It is shown that polyethylene–maleic anhydride terpolymers containing elastomeric segments provided excellent emulsification of PE/TPS blends with a fine morphology (volume diameter of 1.4 μm; number average diameter of 600 nm). The blends compatibilized with these copolymers exhibit a very high elongation at break of about 800%, the highest value ever reported for PE/TPS systems. Also, significant improvement in notched impact strength performance at interfacial saturation was found for these systems leading to specimens with an equivalent performance to pure polyethylene. An excellent correlation was found between the critical concentration for interfacial saturation and the mechanical properties, indicating the key role of morphology.

1. Introduction

Starch is a natural carbohydrate storage material accumulated by green plants in granular form and is composed of amylose (linear molecules) and amylopectin (branched molecules). It is a renewable, inexpensive natural polymer that can be blended with synthetic polymers in order to decrease their relative amount and to lower the cost of the final product. Griffith was one of the pioneers who prepared a starch-filled polyethylene (PE) composite (Griffin, 1977). However, the addition of starch to PE resulted in a drastic decrease of its tensile strength and elongation at break (Evangelista, Nikolov, Sung, Jane, & Gelina, 1991; Willett, 1994).

The crystalline structure of starch can be disrupted by a process called gelatinization (French, 1984). In that process, starch is first mixed with water and is subsequently stirred and heated, resulting in the disruption of the crystalline structure due to the formation of hydrogen bonds between water molecules and the free hydroxyl groups of starch. In this state, starch can flow. Otey and co-workers (Otey, Westhoff, & Doane, 1980, 1987) produced gelatinized starch/ethylene acrylic acid (EAA) cast films that showed good transparency, flexibility and mechanical properties. Gelatinized starch can then be subsequently plasticized by the addition of a suitable plasticizer such as glycerol. This material, known as thermoplastic starch (TPS), can flow at elevated temperatures and shows good ductility, which makes it convenient for melt processing.

TPS can be melt-blended with polyolefins (Bikiaris et al., 1998; Favis, Rodriguez-Gonzalez, & Ramsay, 2003; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Taguet, Huneault, & Favis, 2009) or with biodegradable polymers (Averous & Fringant, 2001; Averous, Fauconnier, Moro, & Fringant, 2000; Ma, Hristova-Bogaerds, Schmit, Goossens, & Lemstra, 2012, Teixeira et al., 2012; Sarazin, Li, Orts, & Favis, 2008; Walia, Lawton, & Shogren, 2002). In a previous work from this laboratory, (Favis et al., 2003; Rodriguez-Gonzalez et al., 2003) developed a one-step melt extrusion process for LDPE/TPS blends that permitted an effective control over the morphology as well as the continuity level of the TPS phase, resulting in good mechanical properties. The authors obtained 96% of the elongation at break and 100% of the modulus of LDPE in a 71/29 LDPE/TPS blend. It should be underlined that a high level of plasticizer is required in the TPS in order for it to be sufficiently fluid to undergo the phase deformation/disintegration phenomena required for morphology deformation. These authors also examined the effects of coalescence and particle deformation during melt drawing of these blends systems.

Binary blends of TPS and polyolefins have a relatively high interfacial tension due to the high incompatibility of the non-polar polyolefin and the highly polar TPS (Chandra & Rustgi, 1997; Willett, 1994). It is possible to improve their compatibility through the addition of a suitable interfacial modifier (Bikiaris, Prinos, &

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Table 1
Description and properties of the materials used for the blends.

Material	Density (g/cm^3)	MFI at 190 °C (g/10 min)	Wt.% of R_x	Wt.% of MA	M_n; M_w (g/mol)
HDPE (Sclair® 2710)	0.951	17	–	–	–
Wheat starch (Supergell® 1203-C, ADM)	1.4	–	–	–	$M_v \sim 70{,}000$[c]
Glycerol (Labmat)	1.26	–	–	–	92.09; –
PP-g-MA[a]	–	–	–	~3	~32,000; 77,000
PE-g-MA[a]	0.95	12	–	3.9[d]	31200; 112,500
PE-R_1-MA[b]	0.94	6	High	~3	12,700; 88,000
PE-R_2-MA[b]	0.94	3	Medium	~3	~16,800; 92,000
PE-R_3-MA[b]	0.94	9	Low	~4	11,400; 73,800

[a] Polypropylene and polyethylene grafted with maleic anhydride.
[b] Polyethylene-R_x-MA where the R_x groups are elastomeric segments containing is a $-OCH_3$, $-OC_2H_5$ and $-OC_4H_9$ respectively. The maleic anhydride, as the R_x groups, is not grafted but randomly distributed on the polymer chain.
[c] Measured by intrinsic viscosity (M_v: average viscosity molecular weight).
[d] Measured by elementary analysis.

Panayiotou, 1997; Bikiaris et al., 1998; Girija & Sailaja, 2006; Sailaja & Chanda, 2000; Sailaja, Reddy, & Chanda, 2001). One of the most common modifiers used for the compatibilization of TPS/PE blends is polyethylene grafted with maleic anhydride (PE-g-MA) (Bikiaris et al., 1997, 1998; Sailaja & Chanda, 2000; Wang, Yu, & Yu, 2005a, 2005b). The esterification reaction between the maleic anhydride groups of the PE-g-MA and the hydroxyl groups of the starch results in the in situ formation of a grafted copolymer that improves interfacial interactions, leads to a decrease of the dispersed phase size and improves the mechanical properties (Bayram, Yilmazer, Xanthos, & Patel, 2002; Bikiaris & Panayiotou, 1998; Ramkumar, Bhattacharya, & Vaidya, 1997; Wang et al., 2005a, 2005b).

In a previous work from this laboratory (Taguet et al., 2009), it has been demonstrated that glycerol-rich domains in the TPS dispersed phase tend to migrate to the PE/TPS interface. This results in a very thin glycerol-rich layer at the interface. The optimum mechanical properties were obtained when 36% of glycerol was used for the blends. A PE-g-MA interfacial modifier was used to compatibilize the PE/TPS interface and it was suggested that a portion of the copolymer was not finding its way to the interface.

The main objective of this work is to examine the efficacy of various polyethylene-based copolymers on their ability to emulsify PE/TPS blends. The use of copolymers here is motivated by the desire to develop high performance bioplastics that can be used in the semi-durable and durable application fields. Detailed characterization of the emulsification phenomena will be determined through the use of an emulsification curve which tracks the size of the dispersed phase evolution with the wt.% of copolymer. The copolymer efficacy will be related to the chemical composition, molecular weight, interfacial saturation and areal density of the copolymer at the interface. Finally, the relationship between these various parameters and the mechanical properties will be studied in detail.

2. Experimental part

2.1. Material

The high-density polyethylene (HDPE) was supplied by Nova Chemicals (Sclair® HDPE 2710, MFI = 17). The native wheat starch (20–28% amylose, 72–80% amylopectin (Averous, 2004; Tester & Morrison, 1990), Supergell 1203-C) and the pure glycerol (99.5% purity with 0.5% water) were obtained from ADM and Labmat respectively. Five different interfacial modifiers with maleic anhydride (MA) were tested: polypropylene grafted maleic anhydride (PP-g-MA); polyethylene grafted maleic anhydride (PE-g-MA); and three different random ethylene-R_x-maleic anhydride interfacial modifiers. R_x is an elastomeric segment containing –OR groups. These latest compatibilizers (PE-R_x-MA) used in this study are denoted as PE-R_1-MA, PE-R_2-MA and PE-R_3-MA where R_1 refers to an elastomeric segment containing $-OCH_3$ groups, R_2 to $-OC_2H_5$ groups and R_3 to $-OC_4H_9$ groups respectively. Note that the maleic anhydride and the R_x elastomeric segments are not grafted but are randomly distributed in the polymer chain. The characteristics of all the materials are given in Table 1. The compatibilizers used in this study were not made in-house, but are proprietary materials supplied by industry.

2.2. Blend preparation

Starch granules were gelatinized, plasticized with glycerol and water and blended with HDPE and compatibilizer in a one-step extrusion process. Blends were prepared containing 20 wt.% of TPS and 80 wt.% of HDPE. The TPS contains 36% of glycerol. The compatibilizer was added with the HDPE, at various rates. All compatibilizer concentrations are based on the TPS content.

The processing of the polyethylene/thermoplastic starch blends was based on a process developed previously in this laboratory (Favis et al., 2003). More detailed information related to the process is given in those articles. The extrusion system was composed of a single-screw extruder (SSE) connected midway to a co-rotating twin-screw extruder (TSE). A starch/glycerol/water suspension was fed in the first zone of the TSE. Native starch was gelatinized and plasticized and volatiles were extracted in the first part of the TSE. Molten HDPE and copolymer ($T = 160\,°C$) were fed from the SSE to midway on the TSE. TPS, HDPE and copolymer were then mixed in the latter part of the TSE. The TSE screw speed was 150 rpm for all blends. A three-hole strand die (diameter 3 mm) was used and strands were water cooled, followed by air cooling and then pelletized.

Note that the TPS with 36% of glycerol is prepared from a suspension containing 28.1 wt.% glycerol. The 36% in the TPS corresponds to the weight of glycerol divided by the weight of glycerol and starch (including ambient water in the as-received starch, but not including any added excess water). After plasticization of the starch, water was removed using a venting process. Under such conditions, virtually all of the water was removed (including native water within the as-received starch).

2.3. Scanning electron microscopy and image analysis

Prior to the blends being cut into 3 mm pellets, some strand were taken out and cut into 1 cm long cylinders. Samples were then cryogenically microtomed at −150 °C with a glass knife perpendicular to the extrusion direction using a Leica RM 2165 microtome equipped with a Leica LN 21 cryochamber. The TPS phase was subsequently extracted from the samples using 6 N HCl for 3 h at room temperature. The samples were subsequently washed with water, dried under air overnight and coated with a gold–palladium alloy by plasma sputtering for 45 s. The SEM observations were carried

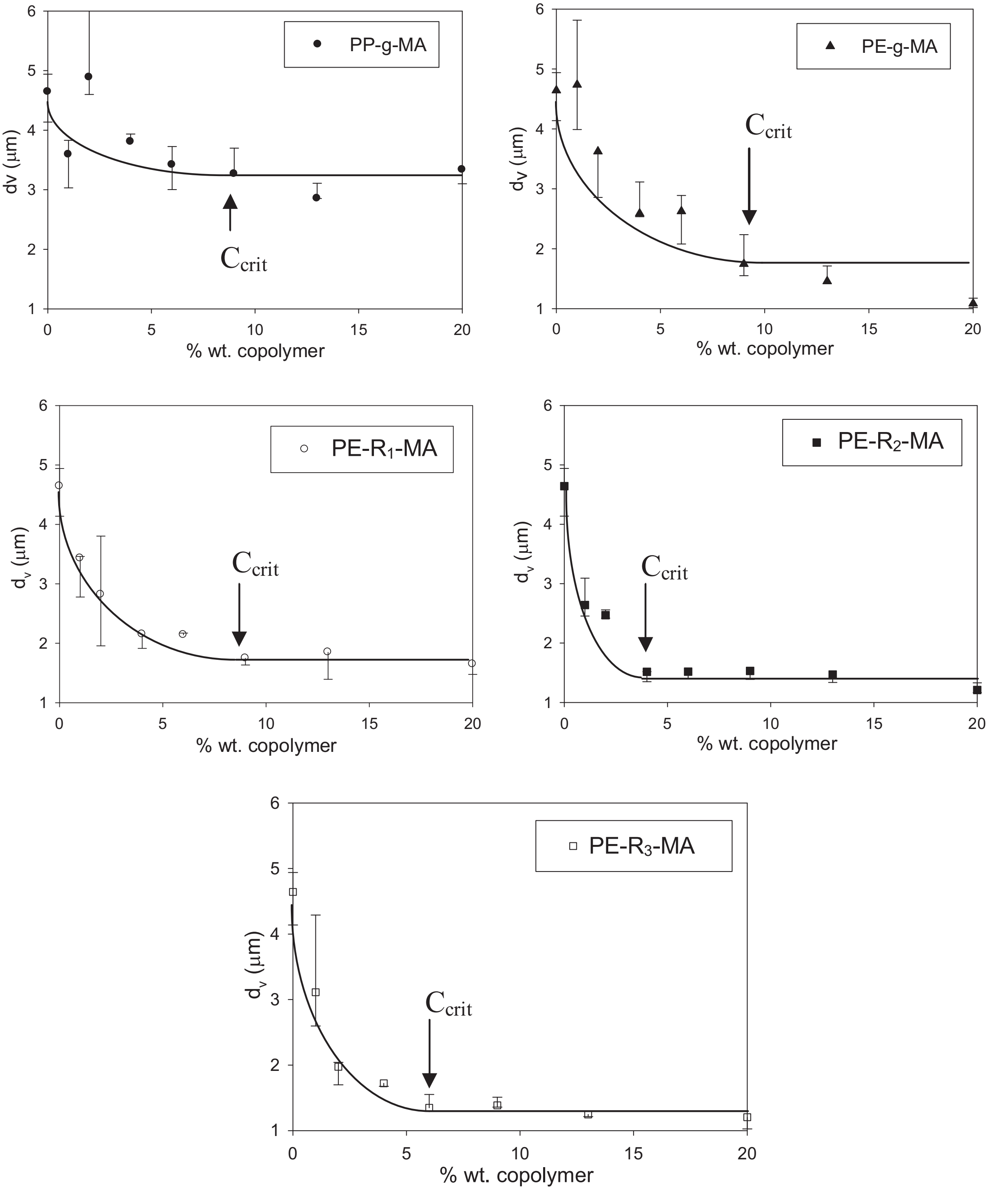

Fig. 1. Influence of the wt.% of interfacial modifier on volume average diameter of the dispersed phase for TPS/PE blends containing: (•) PP-g-MA, (▲) PE-g-MA, (○) PE-R$_1$-MA, (■) PE-R$_2$-MA and (□) PE-R$_3$-MA. Lines are guides for the eyes, and the bars for each point represent the particle size distribution.

out using a Jeol JSM 840 Scanning Electron Microscope operated at a voltage of 10 kV and a current of 3×10^{-11} A.

To obtain the emulsification curves, the SEM micrographs were analyzed with a semi-automatic image analysis method, using a digitizing table, SigmaScan v.5.0.0 software and an in-house developed program described elsewhere (Favis & Chalifoux, 1987). For each sample, around 500 diameter measurements were made from which the volume, surface and number average diameters d_v, d_s and d_n were calculated. The Saltikov correction procedure (Saltikov, 1967; Underwood, 1970) was used to take into account the particle size polydispersity and the fact that the droplets of the dispersed phase are generally not cut at the equator. The emulsification curves are obtained by plotting the volume average diameter measurements as a function of the copolymer content in the blends.

2.4. Tensile tests

Blend pellets were injection molded into dumbbell-shape specimens with dimensions of 57.00 mm × 9.70 mm × 3.05 mm with a Sumitomo SE 50S injection press (temperatures were set between

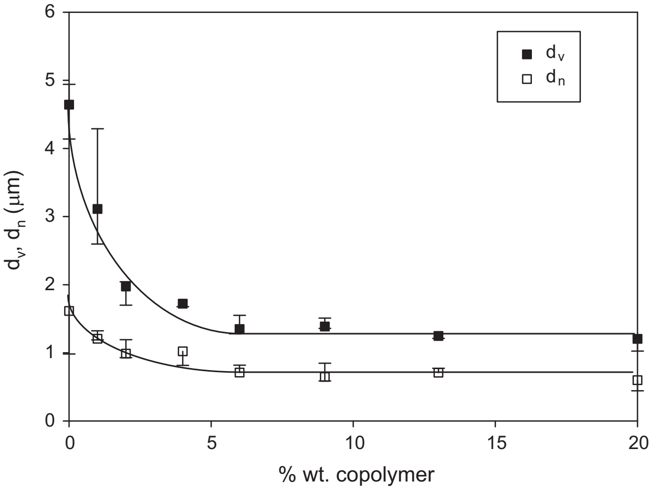

Fig. 2. Influence of the wt.% of interfacial modifier on (■) volume average diameter and (□) number average diameter of the dispersed phase for TPS/PE blends containing PE-R_2-MA. Lines are guides for the eyes, and the bars for each point represent the particle size distribution.

150 and 180 °C, holding pressure between 15 and 20 MPa and cooling time at 10 s). Tensile measurements were performed according to the ASTM D638 standard with an Instron 4400R universal testing machine at a crosshead speed of 50 mm/min. The elongation at break ε_b (%) was determined from the stress–strain curves of each sample. Eight specimens of each blend were tested and the elongation at break average value was reported with error bars indicating the minimum and the maximum obtained values.

2.5. Notched Izod impact test

Injection molding was also used to prepare 62.10 mm × 12.40 mm × 4.62 mm rectangular bars for impact testing. Forty-five degree angle notches were made according to the ASTM D256 norm. The impact measurements were then performed with a CS-137C-176 CSI Custom Scientific Instrument impact machine according to the ASTM D256 standard on notched specimens. Eight specimens were tested for each blend and the average value of the notched impact energy (kJ/mm^2) was reported with error bars indicating the minimum and the maximum obtained values to show the distribution of the results.

2.6. Photoacoustic Fourier transform infrared spectroscopy

Photoacoustic FTIR spectroscopy was used to investigate the extent of the maleic anhydride reaction with the starch and/or glycerol of the TPS phase. After the extrusion process, sample pellets were pressed into films for analysis using two parallel hot plates at 160 °C and then cooled. The Photoacoustic FTIR spectroscopy analysis was carried out with a digilab FTS6000 FTIR spectrometer equipped with a Photoacoustic cell (MTEC Model 300 Detector, MTEC Photoacoustics, Inc.) filled with Helium gas.

3. Results and discussion

3.1. Emulsification phenomena

In binary immiscible polymer blend, the modification of the interface serves to reduce the interfacial tension between the two components and brings about a significant diminution of the dispersed phase particle size (Liang, Favis, Yu, & Eisenberg, 1999) leading to a better dispersion of the dispersed phase and better properties of the blends. Tracing the evolution of the dispersed phase particle size with the amount of added interfacial modifier, known as the emulsification curve, is a very useful method to determine key-parameters such as the critical concentration (C_{crit}) for the interfacial saturation in interfacial modifier or the apparent areal density of the copolymer molecules at the interface (A_{app}) (Favis, 1994). Emulsification curves are usually characterized by an initial rapid decrease of the average diameter of the dispersed phase droplets at a low concentration of interfacial modifier, until a levelling-off is reached at a certain amount. This concentration is known as the critical concentration C_{crit} (Favis, 1994; Lomellini, Matos, & Favis, 1996) and marks the point at which there is no subsequent decrease of the droplet size. The interface is saturated by the copolymer, the interfacial tension reaches a minimum and the remaining interfacial modifier forms micelles within the bulk phases (Adedeji, Lyu, & Macosko, 2001; Israels et al., 1995; Macosko et al., 1996; Noolandi & Hong, 1982; Vilgis & Noolandi, 1990).

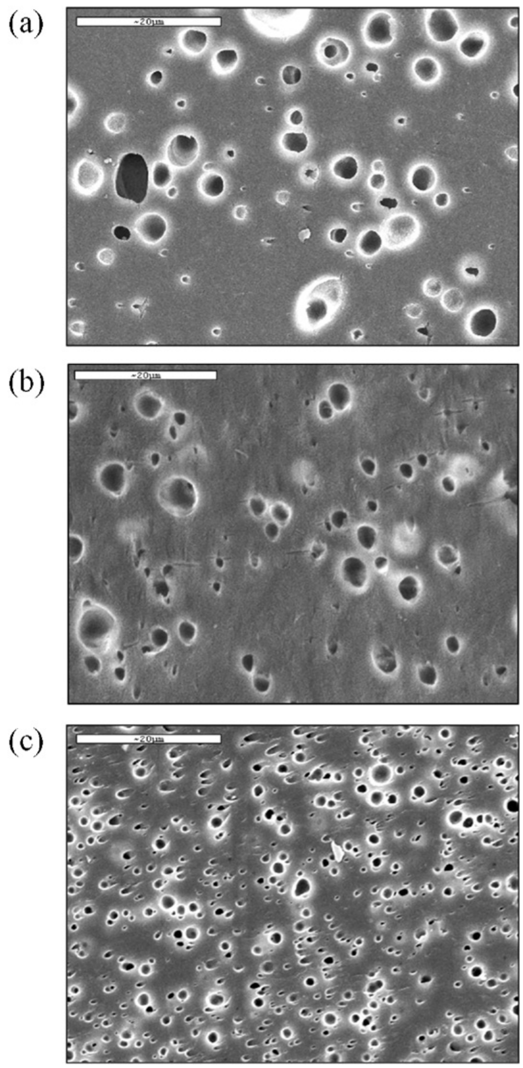

Fig. 3. SEM micrographs of transverse direction strand samples: (a) TPS/PE, (b) TPS/PE compatibilized with PP-g-MA 20% and (c) TPS/PE compatibilized with PE-R_3-MA 20%. The white bar indicates 20 μm.

Emulsification curves illustrating the decrease of the volume-average diameter, d_v, of the TPS dispersed phase domains, as a function of the interfacial agent concentration (wt.% based on TPS concentration), are reported in Fig. 1. Only d_v is represented since it is known to best indicate interfacial saturation (since it takes into account the larger dispersed phase particles). Both d_n, the number average diameter, and d_v for one of the blends are shown in Fig. 2 and is it clear that the two trends are the

Table 2
Critical concentration, number, surface and volume average diameters of dispersed phase at C_{crit}, calculated interfacial area occupied per molecule of interfacial modifier (A_{app}) and areal density of copolymer Σ obtained for HDPE/TPS (80/20 wt.%) blends compatibilized with PP-g-MA, PE-g-MA, PE-R_1-MA, PE-R_2-MA and PE-R_3-MA.

Interfacial modifiers	C_{crit} (wt.%)	d_n; d_s; d_v (at C_{crit}, μm)	A_{app} (nm^2/mol)	Σ (mol/nm^2)
PP-g-MA	9	1.4; 2.6; 3.3	0.8	1.3
PE-g-MA	9	0.55; 0.84; 1.5	2.5	0.4
PE-R_1-MA	9	0.8; 1.5; 1.7	0.6	1.7
PE-R_2-MA	4	0.6; 1.3; 1.5	2	0.5
PE-R_3-MA	6	0.7; 1.2; 1.4	1	1

same. The copolymer is formed by the esterification reaction between the maleic anhydride MA groups of the interfacial modifier and the hydroxyl groups of the thermoplastic starch (Bikiaris & Panayiotou, 1998; Wang et al., 2005a, 2005b; Ramkumar et al., 1997).

All of the tested interfacial modifiers provide a significant decrease of the particle size. From Figs. 1 and 3, we can see that, in the absence of compatibilization, the TPS particle size is quite high ($d_v \sim 4.7$ μm). Note that in Fig. 3, we only show the SEM images of PE-R_3-MA and PP-g-MA compatibilized blends, but the SEM images

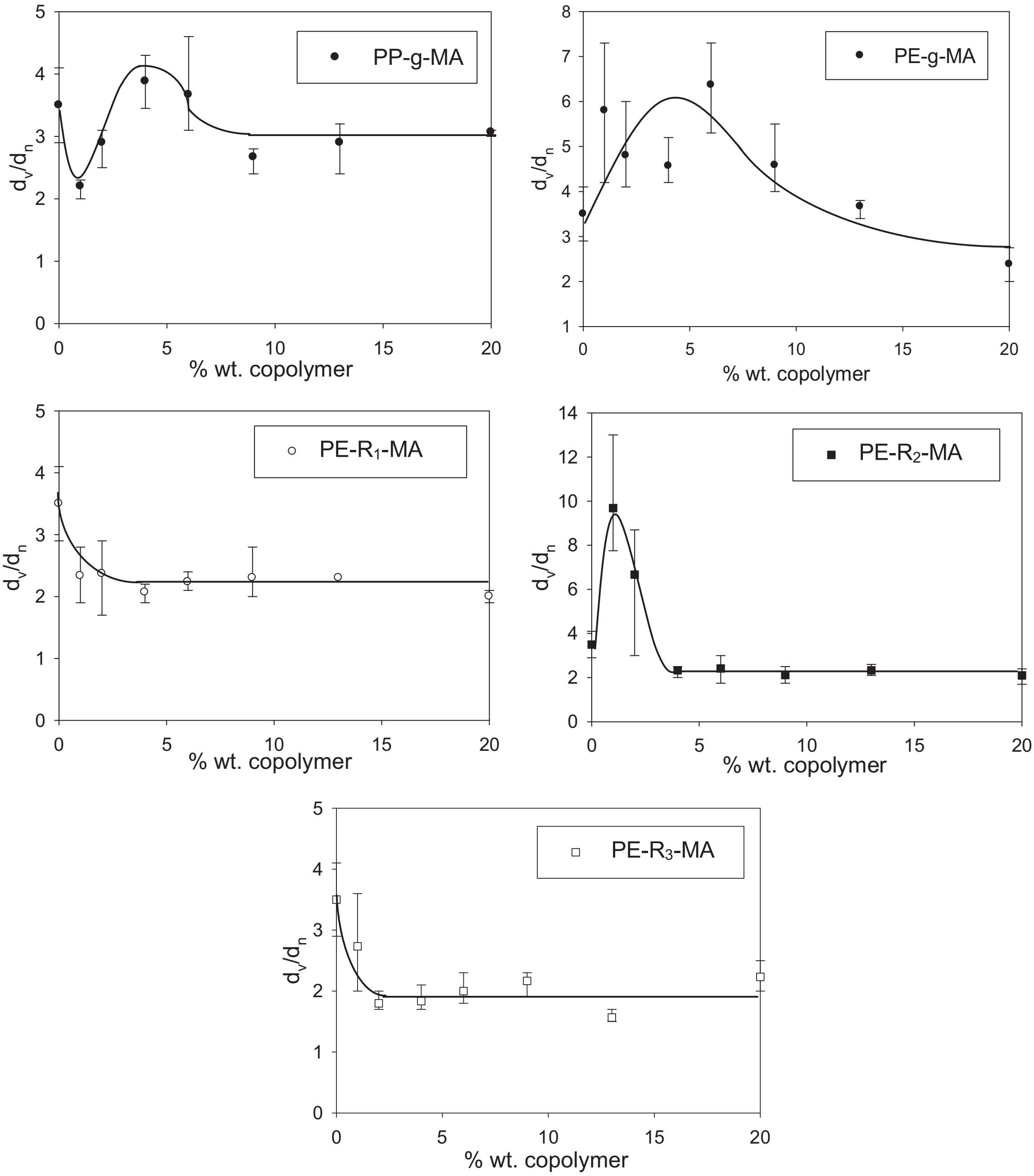

Fig. 4. Influence of the wt.% of interfacial modifier on polydispersity for TPS/PE blends containing: (•) PP-g-MA, (▲) PE-g-MA, (○) PE-R_1-MA, (■) PE-R_2-MA and (□) PE-R_3-MA. Lines are guides for the eyes, and the bars for each point represent the particle size distribution.

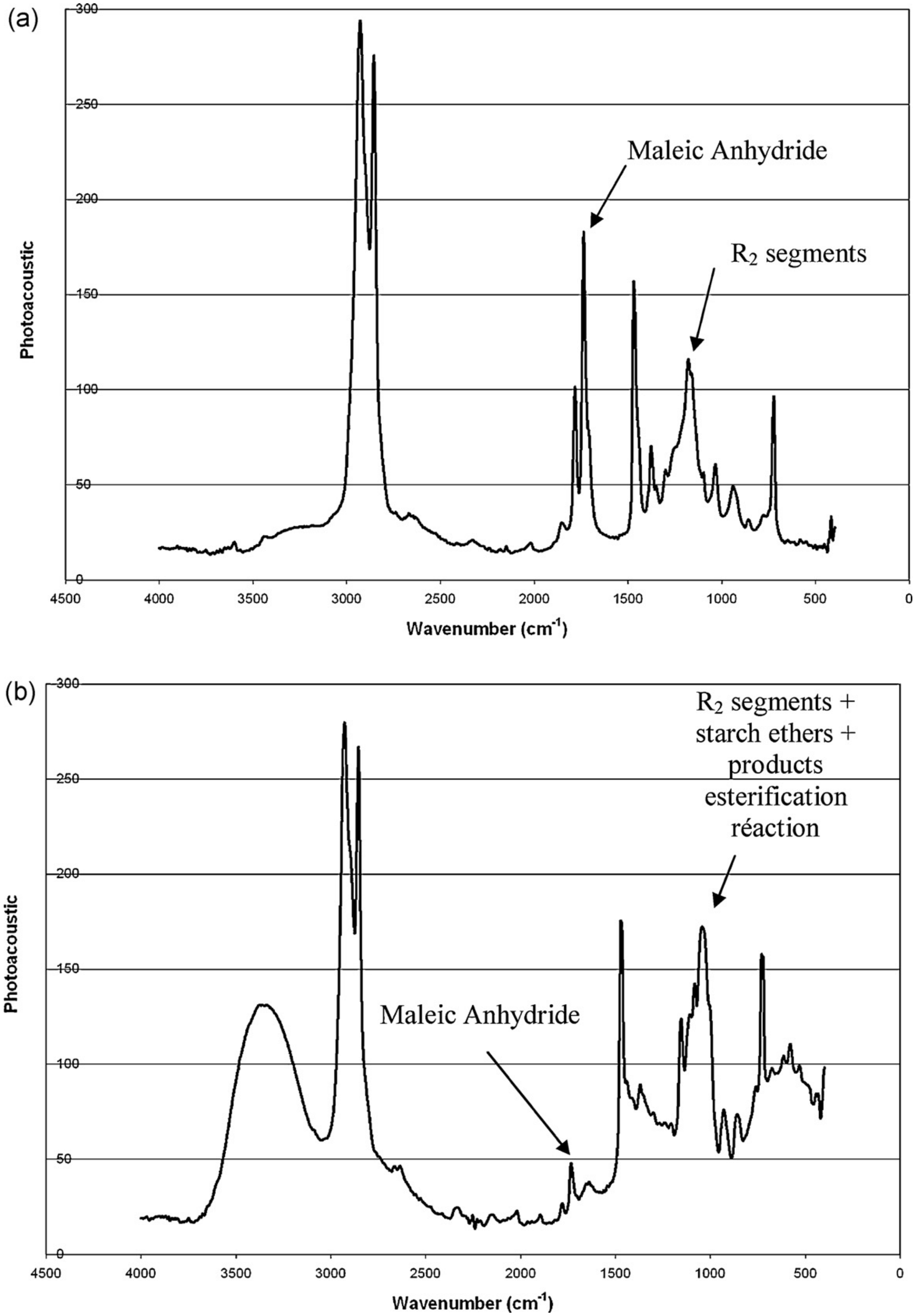

Fig. 5. Photoacoustic Fourier transform infrared spectroscopy for pure (a) PE-R_2-MA and (b) for TPS/PE compatibilized with PE-R_2-MA (20% of TPS).

for PE-g-MA, PE-R_1-MA and PE-R_2-MA were also performed and demonstrated a similar behavior. However, to avoid repetition and for better clarity we did not show all images, but only the most significant ones. The PE-g-MA, PE-R_1-MA, PE-R_2-MA and PE-R_3-MA interfacial agents have a more significant effect on the dispersed phase size as compared to the PP-g-MA. This is likely due to the PP backbone being less miscible with the PE. Fig. 1 shows that a levelling off is observed in each case and the critical concentration values, C_{crit}, for each interfacial modifier are reported in Table 2 as well as the droplet average diameters at C_{crit}.

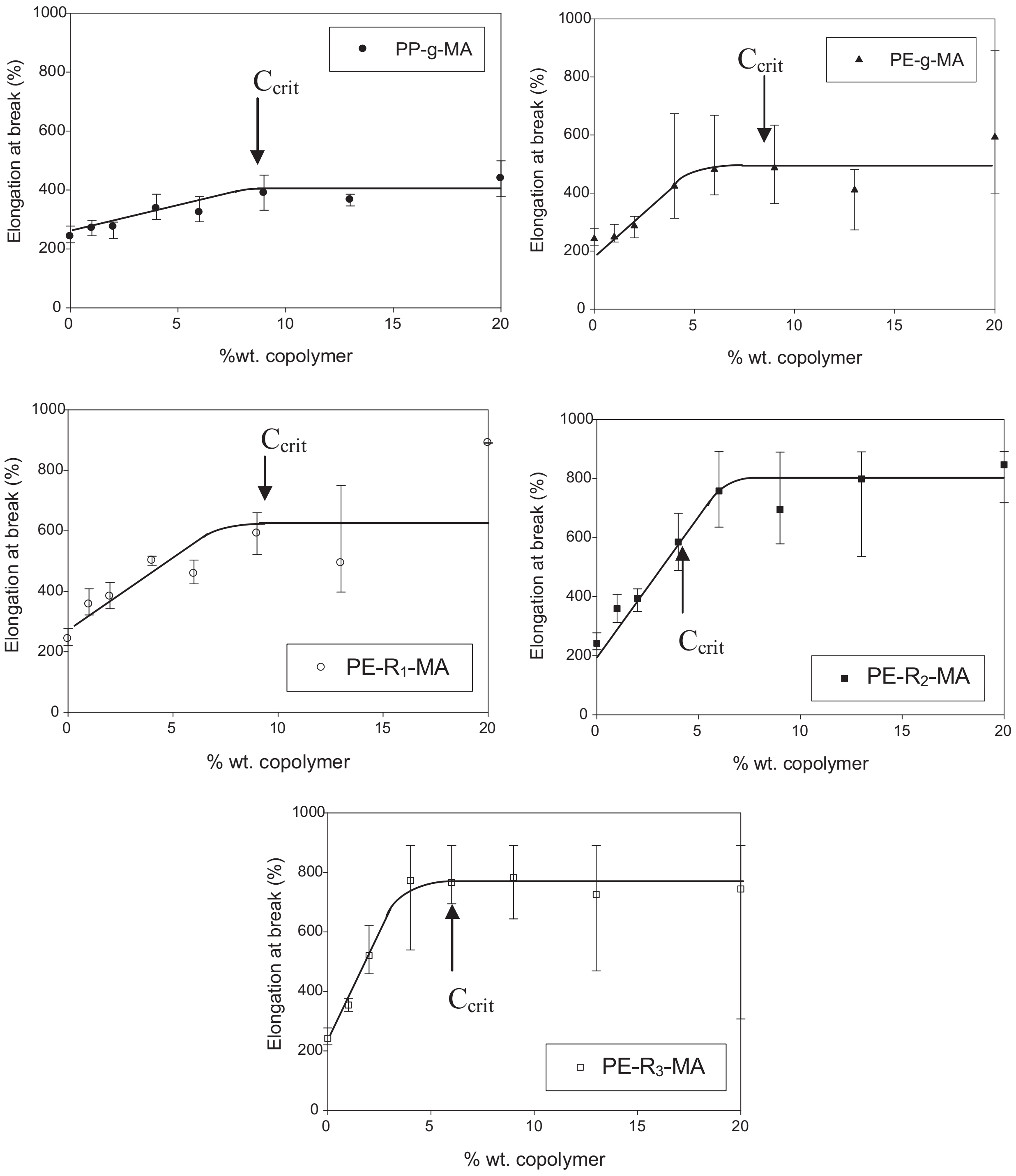

Fig. 6. Influence of the wt.% of interfacial modifier on elongation at break of TPS/PE blends containing: (•) PP-g-MA, (▲) PE-g-MA, (○) PE-R$_1$-MA, (■) PE-R$_2$-MA and (□) PE-R$_3$-MA. Lines are guide for the eyes and the bars for each point represent the particle size distribution. The C_{crit} value shown here is taken from the emulsification curves.

The PE-R$_2$-MA and PE-R$_3$-MA interfacial modifiers show the lowest C_{crit} (4 wt.% and 6 wt.% respectively) and resulting average particle size ($d_v = 1.5$ and 1.4 μm respectively). They seem to be the best candidates to both reduce the amount of the copolymer and obtain a fine morphology. In comparison, PE-g-MA interfacial modifier results in a particle size of 1.5 μm but the obtained C_{crit} is 9 wt.%. This latter result was already observed in another work from this laboratory (Taguet et al., 2009) where a C_{crit} of 9 wt.% with and an average particle size of 1.0 μm were reported. In this work, using a PP-g-MA provides a C_{crit} of 9 wt.% and an average particle size of 3.3 μm. The PE-R$_x$-MA modifiers thus clearly appear to be more efficient modifiers compared to PE-g-MA and PP-g-MA from a C_{crit} (interfacial saturation) standpoint.

The polydispersity (d_v/d_n) of the blends as a function of the copolymer concentration is also shown in Fig. 4. The final polydispersity of the blends is about 3 for the blends compatibilized with PP-g-MA and PE-g-MA and about 2 for the blends compatibilized with PE-R$_x$-MA. Thus, with these latter terpolymers, it is also possible to achieve a smaller dispersity in particle size. Furthermore this low polydispersity for the PE-R$_x$-MA copolymers is

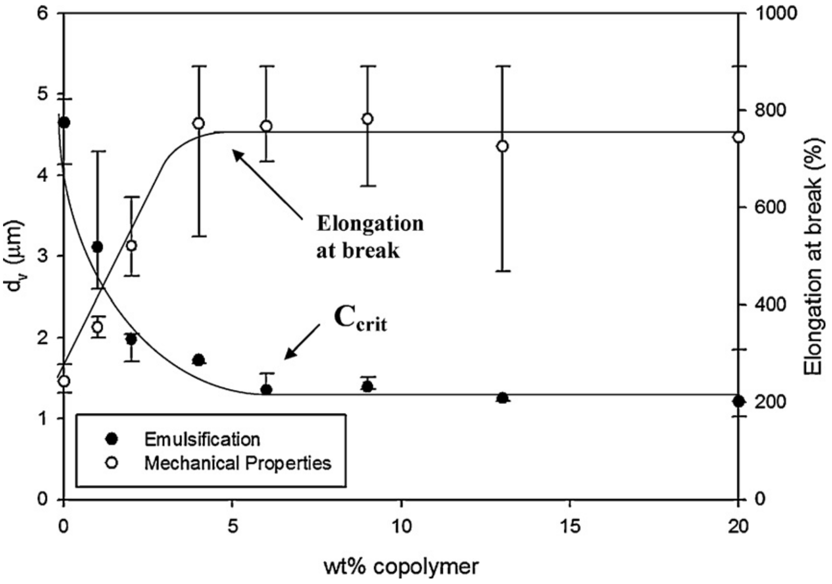

Fig. 7. Comparison between (•) the emulsification curve and (○) the mechanical properties curve as a function of interfacial modifier content for 20/80 TPS/PE blends compatibilized with PE-R_3-MA. Lines are guide for the eyes and the bars for each point represent the particle size distribution.

achieved at a lower wt.% of copolymer which is also a strong indication of emulsifier efficacy. Note the absence of any d_v/d_n increase for PE-R_1-MA and PE-R_3-MA. An increase of d_v/d_n indicates some particles in the blend system are emulsified while others are not. Note also that the d_v/d_n value for the PE-g-MA is still high even after the addition of 13 wt.% copolymer. Clearly, the d_v/d_n results in Fig. 4 support a conclusion that the PE-R_x-MA copolymer series are superior emulsifiers to PP-g-MA and PE-g-MA.

One possible explanation for the improved efficacy of the PE-R_x-MA modifiers could be explained by the presence of the randomly distributed R_x segments within the chains. These segments cannot react chemically with the starch or the glycerol of the TPS (although their –OR groups have the possibility of forming hydrogen bonds with the hydroxyl groups present in both starch and glycerol). However, they may allow for a more efficient migration of the PE-R_x-MA interfacial modifiers to the interface since they provide some further immiscibility with the PE phase into which they are added. This enhanced immiscibility with the PE phase may drive these modifiers more effectively to the interface.

Perhaps even more importantly, the PE-R_x-MA copolymers have lower molecular weights than the other interfacial modifiers. This will also allow the copolymers to migrate to the interface more readily. Other work in the literature has also observed that a low molecular weight copolymer can lead to a more effective migration to the interface (Adedeji et al., 2001; Macosko et al., 1996).

In the PE-R_x-MA copolymer series, the PE-R_2-MA interfacial agent seems to be the most efficient copolymer to decrease C_{crit} whereas the PE-R_3-MA results in the lowest particle diameters. From Table 1, one can notice that PE-R_3-MA contains somewhat more maleic anhydride that can react with the TPS phase than PE-R_2-MA and it is possible that more effective reactions result in the lower dispersed phase size. However, it is PE-R_2-MA which contains more R_x segments on its chain which result in a more effective migration to the interface and thus a lower C_{crit}.

3.2. Interfacial areal density

The emulsification curve can also be used to estimate the apparent interfacial area occupied per molecule of copolymer (A_{app}) and the interfacial areal density of the copolymer at the interface Σ which is the reciprocal of A_{app} (Li & Favis, 2002; Paul, 1978). If all the interfacial modifier has migrated to the interface, the interfacial area occupied per copolymer molecule can be estimated using the following equation (Li & Favis, 2002):

$$A_{app} = \frac{6M_n}{d_v Na_{\rho_C} C_{crit}} \tag{1}$$

ρ_C and M_n are the density of the copolymer and the number-average molecular weight of the copolymer; d_v and Na are the volume-average diameter of the dispersed phase at C_{crit} and the Avogadro number respectively. The values of the calculated interfacial areas and the interfacial areal densities Σ for the interfacial modifiers tested in this paper are given in Table 2. The values of A_{app} range from 0.6 to 2.5 nm^2/molecule (corresponding to areal densities of 1.7–0.4 molecules/nm^2). These values are relatively low compared to results from previous studies conducted in PS/EPR blends compatibilized with various SEB and SEBS diblock and triblock copolymers (Cigana & Favis, 1998). In that work, it was shown that a diblock copolymer occupied 5.6 nm^2/molecule (areal density of 0.18 molecules/nm^2) and a triblock occupied 27 nm^2/molecule. Since grafted copolymers have multiple reacting sites (maleic anhydride sites), the interfacial area occupied per molecule of graft copolymers should normally be higher than 5 nm^2/molecule for a similar molecular weight system. It could mean that either a significant quantity of the interfacial modifier is not finding its way to the interface, or multiple grafting does not occur. In fact, depending on the configuration (Gaussian or stretched) of the copolymer at the interface, some MA groups may not be able to react with the TPS. These hypotheses appear to be confirmed by Photoacoustic Fourier Transform Infrared Spectroscopy (FTIR) analysis performed on blends samples. In Fig. 5, pure PE-R_2-MA and a blend of TPS/PE containing 20% of PE-R_2-MA spectra are shown. The MA C=O bond is observed at around 1755 cm^{-1} and is characterized by two peaks, the first one being of higher intensity than the second one. The other peaks can be assigned to the polyethylene (C—H bond at 2800–3000 cm^{-1} and at 1470 cm^{-1}) and to the R_2 elastomeric segments. On Fig. 5(b), one can observe another large peak at around 3200–3500 cm^{-1} corresponding to the OH group of the starch and glycerol, but also from the esterification reaction between the starch (or the glycerol) with the MA. The ester–ether group is still also observable at 1290 cm^{-1} and corresponds to the esterification process between the starch or the glycerol with the

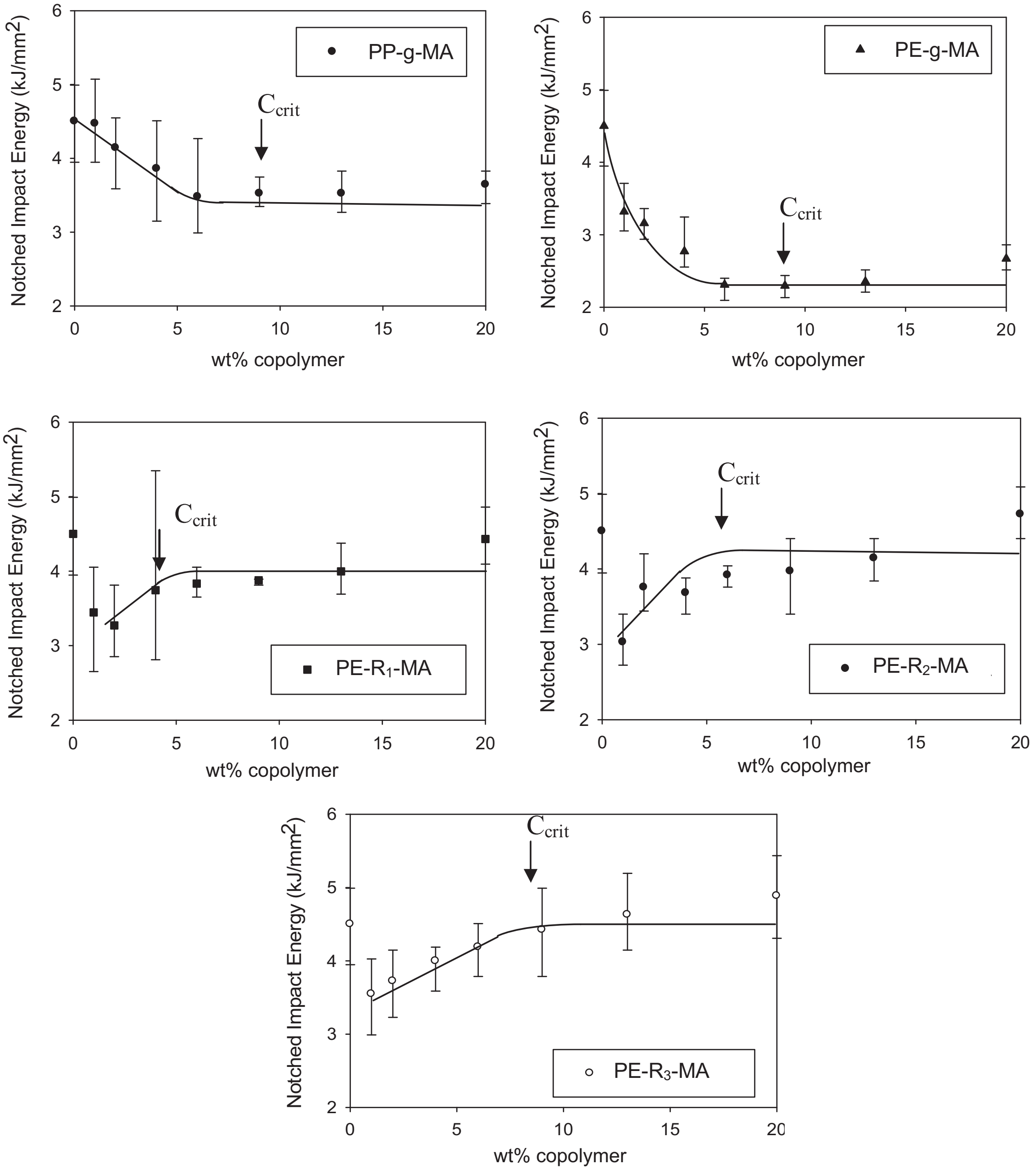

Fig. 8. Influence of the wt.% of interfacial modifier on notched impact energy of TPS/PE blends containing: (•) PP-g-MA, (▲) PE-g-MA, (○) PE-R$_1$-MA, (■) PE-R$_2$-MA and (□) PE-R$_3$-MA. Lines are guide for the eyes and the bars for each point represent the particle size distribution. The C_{crit} value shown here is taken from the emulsification curves.

MA and to the ether groups present in the starch. The MA two peaks are clearly visible in the pure PE-R$_2$-MA spectrum but are also still visible, although less intense, in the blend spectrum, Fig. 5(b). This clearly suggests that either some MA groups did not react at the interface and/or that there is some interfacial modifier lost in the PE matrix.

The interfacial modifier molecular weights M_n used in this study could also explain the relatively low values of A_{app} (or high values for Σ) found in this study. Eq. (1) shows that A_{app} (so Σ as well) is directly proportional to M_n, so that lower molecular weight modifiers should give lower A_{app} values. It appears that if one wants to decrease the C_{crit} and decrease the quantity of the copolymer used, one needs to consider a copolymer with a lower molecular weight. Note however that a high enough molecular weight will be required to ensure that sufficient entanglements occur between the phases of the blend for good mechanical properties. A compromise is needed here to optimize both emulsification and mechanical properties.

3.3. Mechanical properties – elongation at break

In classical polymer blends, unmodified high interfacial tension systems typically display very poor interfacial interactions. Under such circumstances even a blend of two highly ductile components will display brittle fracture even at low concentrations of minor phase (Ishikawa & Narisawa, 1983; Kinloch & Young, 1983; Narisawa, Ishikawa, & Ogawa, 1980). This is principally due to an inability to effectively transfer stress at the interface resulting in the interface becoming the weakest part of the blend system. With an interfacial modifier at the interface of the blend, the stress transfer between the matrix and the dispersed phase is possible which contribute to significantly improve the mechanical properties of the blend. Fig. 6 shows the elongation at break for the blends compatibilized with each interfacial modifier tested. The elongation at break is significantly increased for the five tested interfacial modifiers compared to the elongation at break obtained for the PE/TPS blend without any compatibilization (about 200%), with values ranging between 400% for PP-g-MA to almost 800% for PE-R_3-MA. This is the highest elongation at break value ever reported for PE/TPS blends. With the modification of the interface, the low molecular weight of the modifier allows a better deformation of the interface under a stress. The stress is then effectively transferred from the HDPE matrix to the dispersed phase. The PP-g-MA gives good results, but it is the least effective interfacial modifier. Similar values of the elongation at break obtained with PE-g-MA have already been observed in another paper (Taguet et al., 2009). From Fig. 6, it is evident that the best results are obtained with the PE-R_3-MA interfacial modifier. The effect of this interfacial modifier is already significant at 6 wt.% copolymer and remains stable for higher concentrations. In Fig. 7, the emulsification curve and the mechanical properties for the system compatibilized with PE-R_3-MA are compared as a function of %copolymer. There appears to be a close correspondence of the maximum elongation at break with interfacial saturation (C_{crit}). The same correlation can be established with the other interfacial modifiers. Again, these result points to a close relationship between the state of the interface after compatibilization, the resulting microstructure and the mechanical properties. It is interesting to note that the poorest performance with respect to emulsification (obtained with PP-g-MA) also results in the lowest increase in elongation at break.

The good results for the blend containing PE-R_x-MA terpolymers may be explained by the fact that the R_x segments in the PE-R_x-MA copolymers are quite elastic, leading to a better elasticity and deformation of the interface for PE/TPS blends. The stress will be transferred more easily via an 'elastic' and 'deformable' interface than via a rigid one (obtained for PP-g-MA or PE-g-MA).

3.4. Mechanical properties – Impact resistance

The impact resistance results obtained for all five interfacial modifiers as a function of their concentrations are reported in Fig. 8. The notched impact energy is found to be 4.5 kJ/mm^2 for the TPS/PE blend without any interfacial modifier. The value obtained for the pure PE is 4.8 kJ/mm^2. So PE/TPS blends behave in a similar way than pure PE in terms of impact resistance. This result is very interesting showing that a part of HDPE can be replaced by TPS without any loss of impact properties.

Fig. 8 shows two significant trends in the compatibilized blends results. The first trend is observed in the PP-g-MA and PE-g-MA containing blends and is characterized by a decrease in the impact energy from 4.5 to 3.5 kJ/mm^2 and 2.3 kJ/mm^2 respectively. A levelling off is observed at 9% copolymer, which corresponds to a stabilization of the energy required to break the sample. The stabilization of the energy corresponds to the appearance of the plateau on the emulsification curve. A completely different trend is observed for the three PE-R_x-MA copolymers. An impact energy drop is first observed, but is then followed by an increase that eventually levels off. The PE-R_1-MA demonstrates the best results and the impact energy reaches the same value measured for the uncompatibilized TPS/PE blend and for pure PE.

Fig. 9 compares the emulsification curve and the impact resistance as a function of the PE-R_1-MA interfacial modifier content. It is quite clear that the stabilization of the impact resistance corresponds to the point where C_{crit} is reached. The same correlation can be established with the other interfacial modifiers. Again, as for elongation at break results, these results strongly suggest that there is a close relationship between the microstructure, the state of the interface and the impact resistance (reduction of the size and interfacial modification occur at the same time). The critical concentration and hence, interfacial saturation, is directly linked to the maximum impact strength obtained.

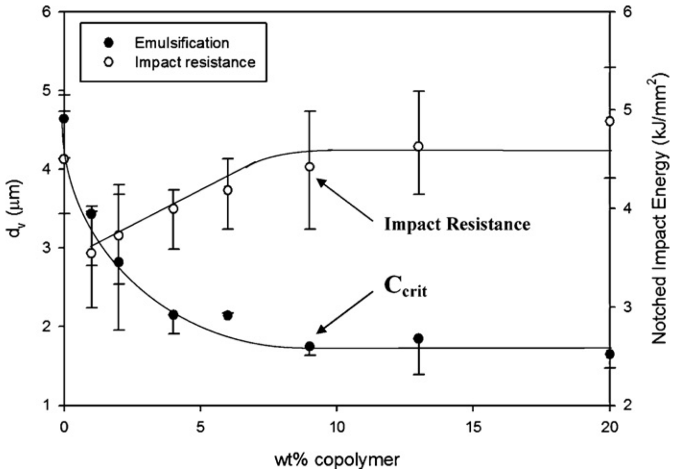

Fig. 9. Comparison between (●) the emulsification curve and (○) the impact resistance curve as a function of interfacial modifier content for 20/80 TPS/PE blends compatibilized with PE-R_1-MA. Lines are guide for the eyes and the bars for each point represent the particle size distribution.

The presence of the elastic R_x segments on the PE-R_x-MA terpolymers can provide some elasticity at the TPS/HDPE interface as mentioned previously. This grafting provided by the PE-R_x-MA is enough to provide good emulsification and allows for elasticity and deformation of the interface leading to improved impact energy values. This deformability of the interface could also explain the good results obtained for PE/TPS without compatibilizer. The glycerol, a small molecule, migrates to the interface between TPS and PE and forms a glycerol-rich layer (Harkin's theory for three component polymer blends) (Harkins, 1941; Harkins and Felman, 1922; Torza & Mason, 1970) as explained in another work of this laboratory (Taguet et al., 2009). The glycerol-rich layer around the TPS particles can provide good deformation at the interface and allow better impact properties.

In the case of PE-g-MA, the phase size is quite small and yet its properties are inferior to the PE-R_x-MA systems. It is possible in this case that the PE-g-MA system is forming a highly reactive, but rigid interface.

4. Conclusions

Using the emulsification curve, the efficacy of five compatibilizers for polyethylene/thermoplastic starch blends was studied. In this way, it was possible to compare the different interfacial modifiers, to estimate the interfacial areas occupied per copolymer molecule at the interface and to report the concentration required to saturate the interface known as the critical concentration. Fine morphologies were obtained for the PE-R_x-MA (d_v = 1.4 μm). This emulsification efficacy was then compared with both tensile mechanical and notched impact strength properties. The PE-R_x-MA copolymers provided very high elongations at break in the range of 700%, the highest values ever reported for PE/TPS systems. Furthermore those copolymers reversed the classic tendency of compatibilized PE/TPS blends, which show a decrease in impact strength with compatibilizer content, and instead resulted in significantly improved notched impact resistance. The critical concentration for saturation of the interface closely corresponds to optimum mechanical properties, indicating the key role of the morphology.

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