

# Morphology and properties of compatibilized polylactide/thermoplastic starch blends

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## Abstract

This paper investigates the properties and interfacial modification of blends of polylactide (PLA) and glycerol-plasticized thermoplastic starch (TPS). A twin-screw extrusion process was used to gelatinize the starch, devolatilize the water to obtain a water-free TPS and then to blend into the PLA matrix. The investigated TPS concentration ranged from 27 to 60 wt%. In the absence of interfacial modification, the TPS/PLA blend morphology observed through scanning electron microscopy was very coarse with TPS particles sizes between 5 and 30  $\mu\text{m}$ . Interfacial modification was achieved by free-radical grafting of maleic anhydride (MA) onto the PLA and then by reacting the modified PLA with the starch macromolecules. Blends comprising MA-grafted PLA showed much finer dispersed phase size, in the 1–3  $\mu\text{m}$  range and exhibited a dramatic improvement in ductility. The paper discusses the effects of two interfacial modification strategies on the blend morphology and tensile properties and investigates the compatibilization efficiency for glycerol plasticizer contents between 30 and 39 wt% and for starches from three different sources: wheat, pea and rice.

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## 1. Introduction

Poly(lactide) (PLA) and thermoplastic starch (TPS) are two of the most promising bio-based materials currently available on the market. The expected rise in the cost of petroleum-based commodities in the next decades opens bright perspective for these materials. Their biodegradability and compostability can also be an asset in applications that are difficult to recycle. PLA production is derived from renewable resources and has therefore gained attention as an alternative to conventional synthetic polymers. It is in many ways similar to poly(ethylene terephthalate) (PET). It is a highly transparent and rigid material with a relatively low crystallization rate that makes it a promising candidate for the fabrication of biaxially oriented films, thermoformed containers and stretch-blown

bottles. Instead of controlling the crystalline content with co-monomer content as in PET, the PLA crystallisable content can be controlled by the ratio between the L and D isomers of lactic acid used in its synthesis. The crystallisable content in PLA is typically smaller than in PET and the melting point and glass transition temperatures are lower. Many of PLA's properties are highly suited for high-volume packaging applications [1]. It exhibits good barrier properties to aromas and the permeability to carbon dioxide, oxygen and water vapor is only slightly higher than that of PET. In terms of food contact, PLA has the advantage that the residual monomers are naturally occurring and non-toxic chemicals. PLA is thus safe for use in food-contacting articles.

Contrarily to PLA, starch is a naturally occurring polymer. It consists of amylose and amylopectin, two types of polysaccharide based on  $\alpha$ -D-glucose monomeric units. The ratio between amylose and amylopectin is dependent on the starch sources but amylose is typically the minor component of natural starch. It is a linear macromolecule with a molar mass in

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the range  $10^5$ – $10^6$  g/mol. Amylopectin is a branched polysaccharide with a larger degree of polymerization and a molecular mass about  $10^8$  g/mol. The crystalline starch structure disappears when it is subjected to temperatures greater than 70–90 °C in the presence of plasticizers such as water or glycerol. This transformation is named gelatinization and leads to the so-called thermoplastic starch (TPS). Because of its high molecular weight, relatively high plasticization levels are necessary for gelatinized starch to flow. Gelatinization along with some molecular weight reduction can easily be achieved using extrusion technology, which provides a closed pressurized environment with sufficient heat and shear stress to break down the crystalline structure of the semi-crystalline starch and render it completely amorphous. Once the starch is gelatinized and properly plasticized, the TPS can flow just as any synthetic polymer and is therefore suited for conventional molding and extrusion technologies.

Early work in starch/PLA blends has focused on the incorporation of dry starch into PLA to reduce the cost of the material while maintaining biodegradability [2,3]. In this case, the starch acts as a filler increasing the rigidity of the material but at the same time further increasing the intrinsic brittleness of the PLA. The starch concentration at which useful materials can be prepared is therefore limited to a low range after which the composite properties suffer dramatically. This has prompted investigations on PLA plasticization as a mean to decrease the brittleness of the composites. This avenue decreases the glass transition of the PLA and can increase the crystallinity level that can be achieved over time in the PLA crystallization temperature range. The use of potential plasticizers such as poly(ethylene glycol) [2], poly(propylene glycol), citrates, glycerol and sorbitol [3] have been investigated in concentrations up to 25%. Acetyl triethyl citrates and triethyl citrate were shown to be the most effective in decreasing the glass transition of the PLA. At starch concentrations of 40 wt%, the elongation at break of the blends was shown to be very low, below 5% for the materials plasticized with the polyols. For the ones plasticized with 20–25% citrates, elongation at break reached 15% but only at the expense of a 10-fold decrease in tensile modulus and a 4-fold decrease in tensile strength. It is therefore clear that plasticization of the PLA/starch blend offers a relatively limited property range for the resulting composites. This situation was virtually unchanged by using starches with varying amylose content or moisture content [4].

The tensile strength and elongation at break of composites are directly linked to interfacial adhesion between the solid particulate and the polymer matrix. In this context, surface modification of starches by chemically linking them to the polymer matrix is expected to greatly improve the composites properties. The different strategies available to compatibilize granular starch with different polymer matrices have recently been reviewed by Kalambur and Rizvi. [5]. A first potential route is to use difunctional molecules that have the potential to chemically link the polymer matrix to the starch grain surface. This route was explored in starch/PLA composite using small amount of diisocyanates and was shown to improve

the tensile strength of the composite but still led to relatively brittle materials [6]. A second approach consists in chemically bonding the starch grain surface with polymeric side chains that are miscible in the polymer matrix. This has been reported in starch/PCL composites where  $\epsilon$ -caprolactone monomer was polymerized onto starch in the presence of proper catalysts [7–9]. The resulting properties of the PCL-modified starch composites were relatively poor however when compared to those of the pure PCL matrix [5]. The approach was also reported recently for composites involving PLA-grafted starch [10]. Properties of composites containing 50% starch were greatly improved when 10–20% of the starch was substituted by PLLA-grafted starch. In the best case, the tensile strength of the composite reached almost 70% of the pure PLA value, but the elongation at break was still very low, around 3.6% compared to 6% for pure PLA.

Even though the starch grafting route yields significant improvement when compared to non-modified composites, it is not yet easily amenable to an economical commercial production. It generally involves expensive catalysts, relatively long reaction times, and a large quantity of solvents to prepare the starch and to purify the modified products. Currently, a more promising interfacial modification route may come from the modification of the polymer matrix itself. This can be achieved by grafting a reactive moiety onto the polymer matrix and then having this moiety react in some way with the starch macromolecules. The grafting of maleic anhydride (MA) onto polyolefin is a well-known reaction [11]. It is carried out in the melt using a free-radical initiator such as an organic peroxide and is easily amenable to large-scale production through continuous extrusion technologies. MA-grafted polyolefins are extensively used to compatibilize the non-polar polyolefins with common minerals such as glass fibers, talc and mica. In polyethylene–starch blends, the use of MA-grafted PE was shown to increase the tensile properties of composites [12] and of blends with slightly plasticized starch [13]. Other moieties such as acrylic acid, oxazoline, and glycidyl methacrylate can be grafted to confer reactivity to otherwise non-reactive polymers but MA grafting is generally preferred because of MA's easier handling, low toxicity and because it does not tend to homopolymerize in normal free-radical melt grafting conditions. The grafting of maleic anhydride onto PLA was first reported by Carlson et al. [14] and Mani et al. [15] in 1999. The maleation was carried out in a twin-screw extruder using 2 wt% of MA and up to 0.5% of a peroxide initiator. The achieved grafting level onto PLA was around 0.5 wt%. The compatibilization efficiency of the PLA-g-MA in granular starch/PLA composites was assessed through microscopy analysis which showed improved interfacial adhesion [14]. Later, the tensile strength and to a much lesser extent the elongation at break of starch/PLA composites were shown to be improved by the presence of MA-grafted PLA [16].

One potential avenue to increase the ductility of PLA could be the use of thermoplastic starch (TPS) rather than granular starch. TPS offers a greater potential in terms of material processability and final morphology as the thermoplastic starch

phase can be deformed and dispersed to a much finer state than the dry native starch. The typical drawbacks of thermoplastic starch are its moisture sensitivity, low temperature resistance, plasticizer migration and starch recrystallisation over time leading to embrittlement. These problems can be partially circumvented by blending the TPS into a hydrophobic polymer matrix. Blends of TPS with biodegradable and non-biodegradable polymers have been thoroughly reviewed elsewhere [17,18].

Martin and Avérous [19] were the first to report on the properties of TPS/PLA blends. Three TPS with very different glycerol contents were first produced. The glycerol content controls the TPS viscosity in the melt phase and its rigidity in the solid form. The least plasticized TPS was rigid and brittle (modulus = 1 GPa, EB = 3%) while the most plasticized was flexible and ductile (modulus = 0.020 GPa, EB = 110%). Nonetheless, the TPS/PLA families were all extremely brittle with elongation at break below 6% as soon as the TPS concentration was increased over 10 wt%. The authors concluded that the lack of affinity between the TPS and PLA was a severe limitation and emphasized the need for some compatibilization strategy.

Interfacial modification in thermoplastic blends is slightly different from that in starch composites since the plasticized starch macromolecules in the former case are free to move to or to move away from the blend interface. In general, the compatibilization of immiscible polymer blends always involves the addition or the *in situ* formation of a block copolymer in which one block is miscible with one phase and another block is miscible with the other phase. The block copolymer acts as an emulsifier to reduce the blend segregation scale and if the block lengths are sufficient, they can entangle with the blend components at a molecular level and bring interfacial adhesion in the solid state. The block copolymer formed at the blend's interface can be a diblock if the reactive moiety is grafted on the chain end and that it reacts with the other polymer end groups. A textbook example of this is the reaction of maleated (end grafted) polypropylene with the amine end group of polyamides. This is rather an exception and the more general block copolymer will have a branched structure.

Surprisingly, there is very little literature examining the compatibilization of thermoplastic starch and other polymers. In particular, the compatibilization of PLA/TPS blends has not yet been explored. In this work, PLA-*g*-MA produced using a melt grafting technique similar to that reported by Carlson et al. [14] has been used to investigate the effect of compatibilization on the properties of PLA/TPS blends. Contrarily to blends with granular starch, the blending of the TPS and PLA can result in a wide variety of morphologies going from a dispersed starch/PLA matrix to a co-continuous starch/PLA structure or to phase inverted morphologies in which the starch is the matrix material. In this context, the interfacial modification plays a very important role controlling both the segregation scale and the solid-state adhesion between the components. The current study will focus on blends in which the PLA forms a continuous phase and will

investigate the effect of composition and preparation techniques on material properties. Ideally, the blending of TPS and PLA could enable tailoring the mechanical properties and biodegradability of the biomaterials according to application needs.

## 2. Experimental

### 2.1. Materials

The PLA was supplied by NatureWorks. The selected grade, PLA 2002D, is a semi-crystalline extrusion material. It was dried at 65 °C for a minimum of 8 h prior to use in a desiccating dryer. Wheat starch, Supergel 1203 from ADM-Ogilvy, was used as the standard starch grade but selected experiments were carried out with pea (Accugel supplied by Parrheim Food) and rice starch (Remy Fg supplied by Quadrachemicals) for comparison. The starch plasticizers were glycerol and water. The reactive modification of PLA was performed using 95% pure maleic anhydride (MA) and a peroxide initiator 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)-hexane (Luperox 101<sup>®</sup> or L101) obtained from Aldrich Chemical Company, Inc. The peroxide initiator was adsorbed on a silica support at an effective content of 45%.

### 2.2. TPS/PLA blend fabrication

The preparation of blends was based on the technique described by Rodriguez et al. for polyethylene/plasticized starch blends [20]. The blends are made on a Leistritz 34 mm co-rotating twin-screw extruder with an *L/D* ratio of 42. The process and screw configuration are presented in Fig. 1a. The first half of the twin-screw extrusion line is used to prepare the plasticized starch. The extruder is fed with a starch suspension in a glycerol/water mixture. The starch is gelatinized in a first mixing zone under pressure and at 130 °C to form a destructured thermoplastic starch. The water was then removed from the thermoplastic starch by vacuum venting located before mid-extruder to get a glycerol-plasticized thermoplastic starch with minimum residual water. The glycerol content in the TPS was varied from 30 to 39 wt% on a dry basis but was typically set to 36 wt% as a standard concentration. Typically, the starch content in the initial suspension was 50% and the water/glycerol ratio was set to obtain the desired glycerol content in the final water-free TPS. The PLA was added at mid-extruder using a single-screw extruder as a side feeder to the twin-screw line. The PLA and TPS underwent mixing in a zone maintained at 180 °C and composed of kneading blocks before the blend was extruded using a strand die, water-cooled and pelletized. The resulting pellets were dried at 65 °C in a desiccant dryer and injection molded into standard dumbbell samples for tensile testing. The TPS concentration in the blends was varied between 27 and 60 wt%. In all cases, this insured that PLA remained as the blends matrix.

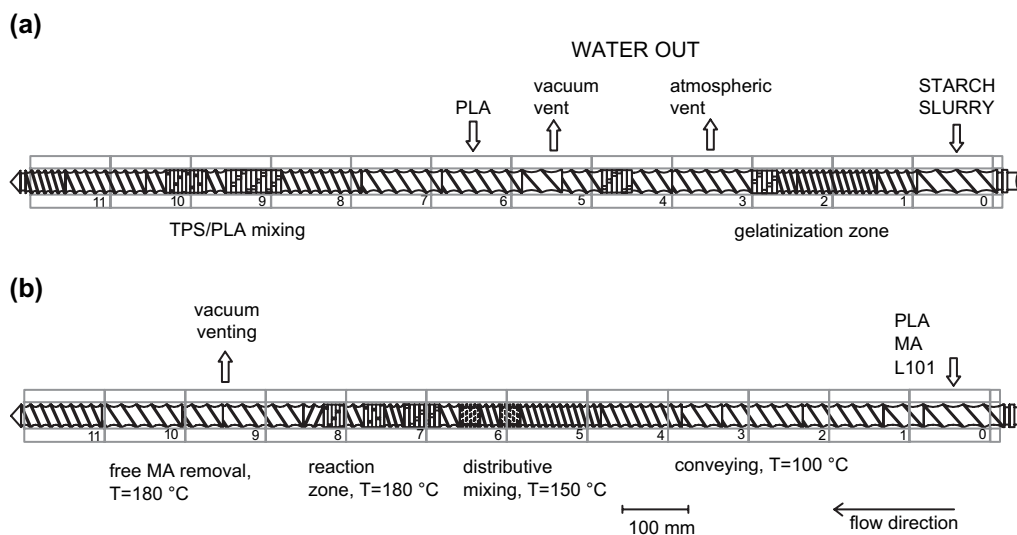


Fig. 1. Twin-screw process configuration for (a) TPS/PLA blending and (b) grafting of maleic anhydride unto PLA.

### 2.3. Interfacial modification

The interfacial modification is based on the use of maleated PLA. Two different approaches were taken to graft the MA group unto PLA. In the first variation, the PLA was first grafted using a dedicated reactive extrusion process design illustrated in Fig. 1b. It consists of a relatively gentle mixing section in which the grafting is expected to occur followed by a devolatilization section used to remove the unreacted MA. The first half of the extruder (sections 0–6) was kept at 100 °C to prevent free-radical initiation prior to MA melting and complete mixing of the ingredients. The subsequent section was kept at 180 °C to carry out the maleation reaction. The modified PLA was pelletized, dried and then in a second step, used in partial or total replacement of neat PLA in the PLA/TPS blending process described above. Because the PLA modification and TPS/PLA blending are made in separate operations, we will refer to this strategy as the two-step process. It is noteworthy that the PLA grafting was carried out using similar process conditions and reactant composition as those reported by Carlson et al. [14]. The modification was carried using a production rate of 10 kg/h and screw rotation speed of 100 rpm. The MA level was 2 wt% and the L101 concentration were 0.1, 0.25 and 0.5 wt%.

In the second variant of the interfacial modification strategy, the MA grafting unto PLA was carried out in the single-screw side extruder used in the TPS/PLA blending process. The reaction was carried out in similar conditions as above but the modified PLA did not undergo a pelletizing step prior to blending. Instead, it directly reacts with the TPS as it enters the twin-screw extrusion line. Since the MA grafting and TPS/PLA blending are carried in a single continuous operation, we will refer to this variant as the one-step process.

### 2.4. Rheological characterization

The viscosity of PLA and modified PLA was measured at 180 °C using a rotational plate–plate rheometer used in

dynamic mode. Care was taken to keep the samples dry during testing and it was verified that the viscosity and complex moduli were stable over time up to 30 min. The TPS viscosity is more difficult to measure since the residual moisture and glycerol can evaporate out of the sample during regular rotational rheometry testing resulting in dramatic viscosity increase over time. A different approach was therefore taken to assess the rheological response of the TPS. The viscosity was measured with a commercial on-line rheometer, Process Control Rheometer PCR-620 Series from Rheometric Scientific. The instrument is mounted in such a manner that a stream of the melt is drawn continuously from the process and brought to a slit die. The pressure gradient is measured with three pressure transducers while the volumetric throughput is controlled through metering pumps. This allowed the determination of the melt viscosity over a range of shear rates. For the TPS rheological measurements, only the first half of the screw length depicted in Fig. 1a was used in order to simulate the exact state in which the TPS meets with PLA at mid-extruder.

### 2.5. Morphological characterization

The blend morphology was assessed by observation of microtomed surfaces using scanning electron microscopy (SEM). The microtoming was carried out at room temperature using a diamond knife and the surfaces were subsequently treated with hydrochloric acid (HCl, 1 N) for 3 h to selectively dissolve the TPS phase.

### 2.6. Tensile characterization

The tensile testing was carried out at a rate of 5 mm/min according to ASTM D638. The samples were injection molded Standard type I dumbbell-shaped samples with a thickness of 3.1 mm. These were conditioned at room temperature for a period of four weeks prior to testing.

### 3. Results and discussion

The rheology of polymers is very sensitive to changes in the macromolecular chain structure and is therefore of practical and fundamental interest in the current study. Fig. 2 presents the viscosity of PLA, TPS and TPS/PLA blends with and without MA grafting at a temperature of 180 °C. The virgin PLA data are obtained from oscillatory measurement carried out on the non-extruded pellets. It exhibits a clear Newtonian Plateau with a zero-shear viscosity around 6 kPa s. As a control, PLA was extruded on the reactive extrusion configuration (Fig. 1b) to evaluate the molecular weight changes in the absence of reactants. The extruded PLA viscosity is relatively close to the non-extruded one and therefore, it can be inferred that the process configuration used here was adequate in terms of preserving the PLA molecular structure. The viscosity of the PLA grafted with 2% MA and 0.25% L101 in the one-step process is significantly lower from that of the virgin PLA. It also exhibits a clearly defined Newtonian region but the zero-shear viscosity is decreased to 800 Pa s, a 6-fold decrease when compared to the extruded PLA control. Similar shaped viscosity curves were found for the PLA grafted with the different peroxide levels but obviously the zero-shear viscosity values decreased with peroxide usage (not shown in figure). Zero-shear viscosity for the PLA grafted using 0.1, 0.25 and 0.50 wt% peroxide L101 (and 2 wt% MA) were found to be, respectively, 2.2, 0.81 and 0.26 kPa s. The polymer viscosity in the presence of a free-radical initiator does not always decrease. It is well known for example that peroxide initiated grafting in polyethylene increases viscosity as well as shear thinning. This is associated to a side reaction, the grafting of a PE side chain (instead of the MA) unto the reactive site created by the free-radical initiator. By opposition, peroxide initiated grafting in polypropylene always results in lower viscosity. In this case, the PP chain is first broken by the free-radical initiator and the free monomer can be grafted onto

activated chain ends. It seems from the presented results that PLA grafting falls in this second category but further direct analytical evidence would be necessary to confirm this. Similar viscosity was found for the PLA grafted using the one-step procedure indicating that similar grafting levels have been achieved in the two process variants, which was further supported by the morphological and mechanical results to be presented below.

Fig. 2 also presents the viscosity of the pure TPS containing 30% and 36% glycerol obtained using on-line rheometry. It is noteworthy that oscillatory shear measurements which are typically made at atmospheric pressure are useless for TPS at elevated temperature (e.g. 180 °C) because the glycerol tends to evaporate during the measurement. By opposition, the pressurized on-line rheometer used in for the TPS enables measurements in conditions that are representative of those found at mid-extruder when the PLA and TPS are put into contact. The TPS viscous behavior is clearly very different from that of PLA. The TPS does not exhibit any viscosity plateau in the investigated shear rate range and is highly shear thinning. This is typical of branched or highly entangled polymer melts. The increase in glycerol concentration from 30% to 36% decreases the viscosity by half (at constant shear rate) but does not change the general features described above.

The viscosity of TPS/PLA blends is presented in oscillatory shear only for the 27% TPS/PLA blends and the measurement was limited to the 1–100 s<sup>-1</sup> frequency range to limit the duration of the measurement. At this concentration, the PLA clearly encapsulates the TPS and thus retards glycerol evaporation. Oscillatory shear viscosity for higher TPS contents or at lower frequency evolved over the measurement time frame and was discarded. The non-modified TPS/PLA blend has a well-established Newtonian plateau just as the different PLA and its zero-shear viscosity is around 2 kPa s, significantly lower than the extruded PLA zero-shear viscosity. The lower blend viscosity compared to the extruded PLA may be explained by some PLA hydrolysis promoted by starch residual humidity. Nonetheless, the final material viscosity remains in an acceptable range. The same blend with the added reactants has a viscosity that is slightly below that of the grafted PLA and is relatively less affected by the blending process than the unmodified blend.

As discussed in Section 1, the use of maleated polymers in dry-starch/polymer composites improves interfacial adhesion through reaction of maleic anhydride grafts with hydroxyl groups present at the surface of starch particles. In the case of the TPS/PLA blends, the situation is more complex. First of all, the starch is in a plasticized form and therefore the amylose and amylopectin macromolecules are free to move to or away from the blend's interface. Secondly, the presence of a plasticizer, namely glycerol, could interfere with the starch MA reaction as MA grafts could potentially react preferably with the hydroxyl groups of the glycerol. Thirdly, residual humidity in the TPS phase may cause the opening of the MA cycle and thus reduce its reactivity. It is therefore not *a priori* evident that compatibilization effects observed in dry-starch composites can be totally reproduced in thermoplastic starch blends. To assess the potential of the current compatibilization

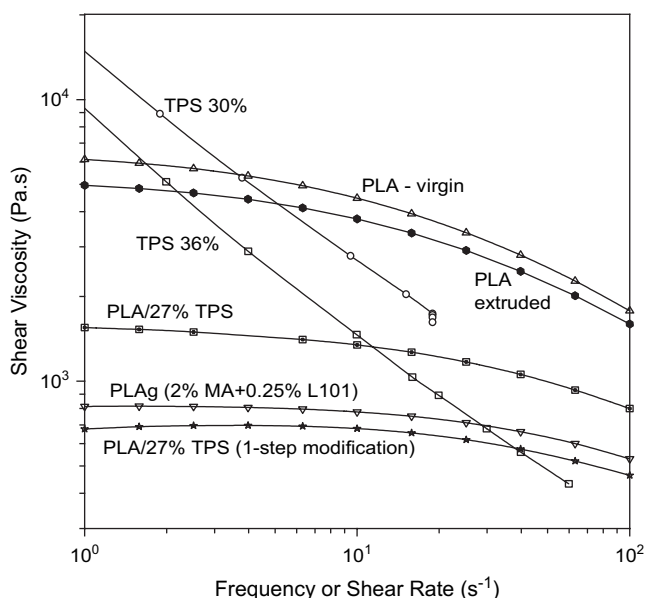


Fig. 2. Viscosity of PLA, modified PLA, TPS and 27% TPS/PLA blends.

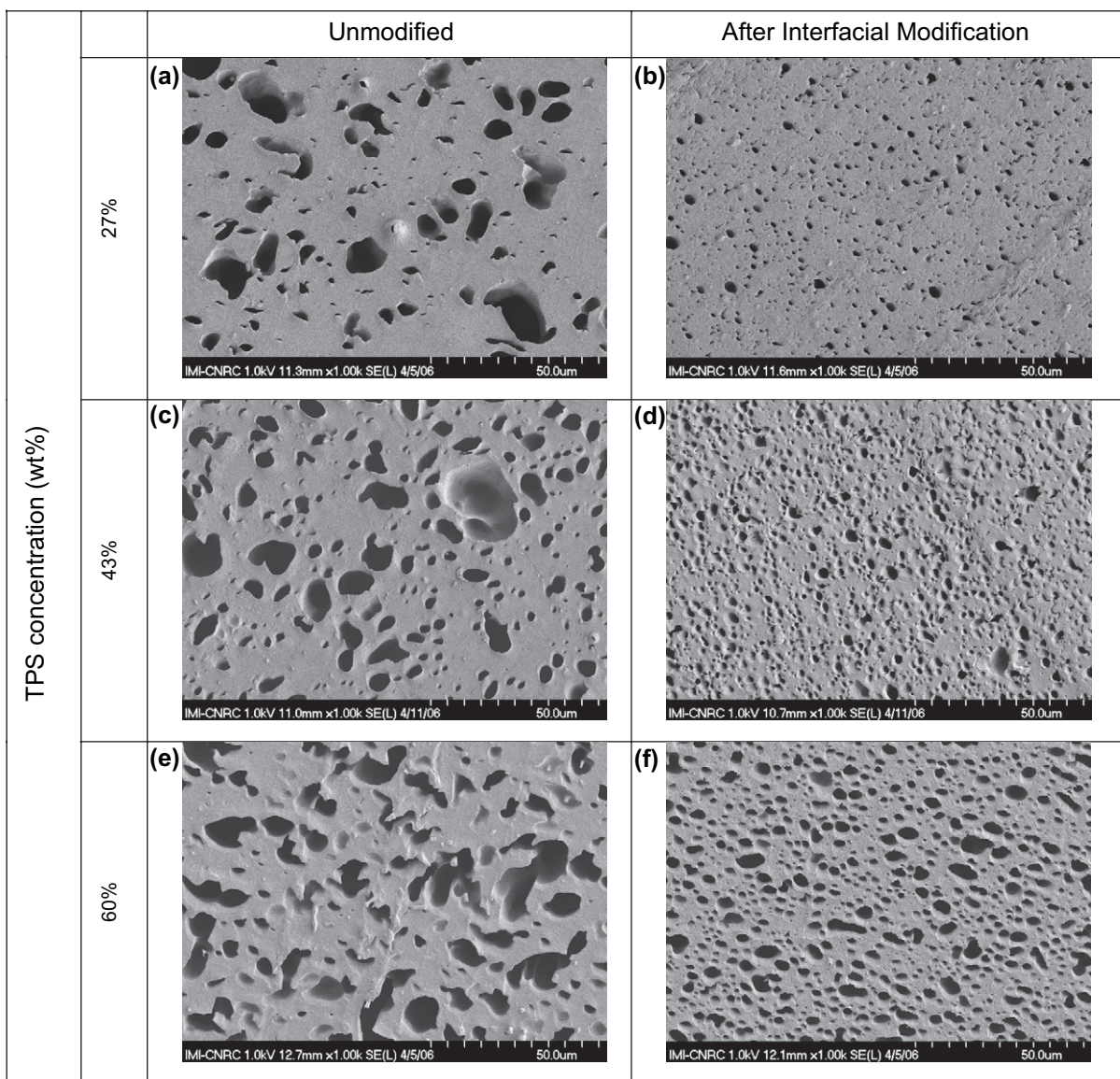


Fig. 3. Comparison of unmodified TPS/PLA blends and of interface-modified ones using the one-step process. The initial MA and L101 concentration are, respectively, 2 and 0.25 wt% based on total PLA content.

strategy, the blends morphologies for blends with and without the addition of the MA/L101 mixture using the one-step process are presented in Fig. 3. The blends comprise 27, 43 and 60 wt% of TPS and the TPS phase has been extracted to improve the micrograph contrast. For the unmodified blends, the morphology is very coarse as reported previously on fracture surface by Martin and Avérous [19]. The TPS particle size ranges from 5 to 30  $\mu\text{m}$ . The volume-averaged equivalent diameter,  $D_v$ , determined by image analysis is around 14  $\mu\text{m}$  for the 27% and 43% TPS blends. For the 60 wt% blend, the particles are larger and have irregular shapes as we approach the co-continuous concentration range. By contrast, the TPS particles in the modified blends are nearly spherical and relatively homogeneous. The average diameters for the 27, 43 and 60 wt% TPS blends fall respectively to 2.2, 2.6 and 4.2  $\mu\text{m}$ . The MA-grafted PLA is therefore decreasing the TPS phase size significantly providing indirect evidence that interfacial

reactions are decreasing the blend's interfacial tension. To the authors' knowledge, this is the first successful report on the potential of MA-grafted PLA as an emulsifying or compatibilizing agent for fully plasticized TPS/PLA blends.

The micrographs presented in Fig. 3 were obtained with the one-step process in which the MA and the peroxide initiator are introduced with the PLA at mid-extruder through a single-screw extruder side feed. The two-step variant of this process consists in first producing the grafted PLA using a dedicated twin-screw process and then substitute in part or in full the virgin PLA by the modified PLA in the TPS/PLA blending step. Fig. 4 presents SEM micrographs of 27% TPS/PLA blends prepared using the two-step method. The first three micrographs (a–c) were obtained for blends in which 20% of the PLA was replaced by three different MA-grafted PLA prepared with different peroxide levels. Fig. 4a–c corresponds to peroxide initiator levels of 0.1, 0.25 and 0.5 wt%,

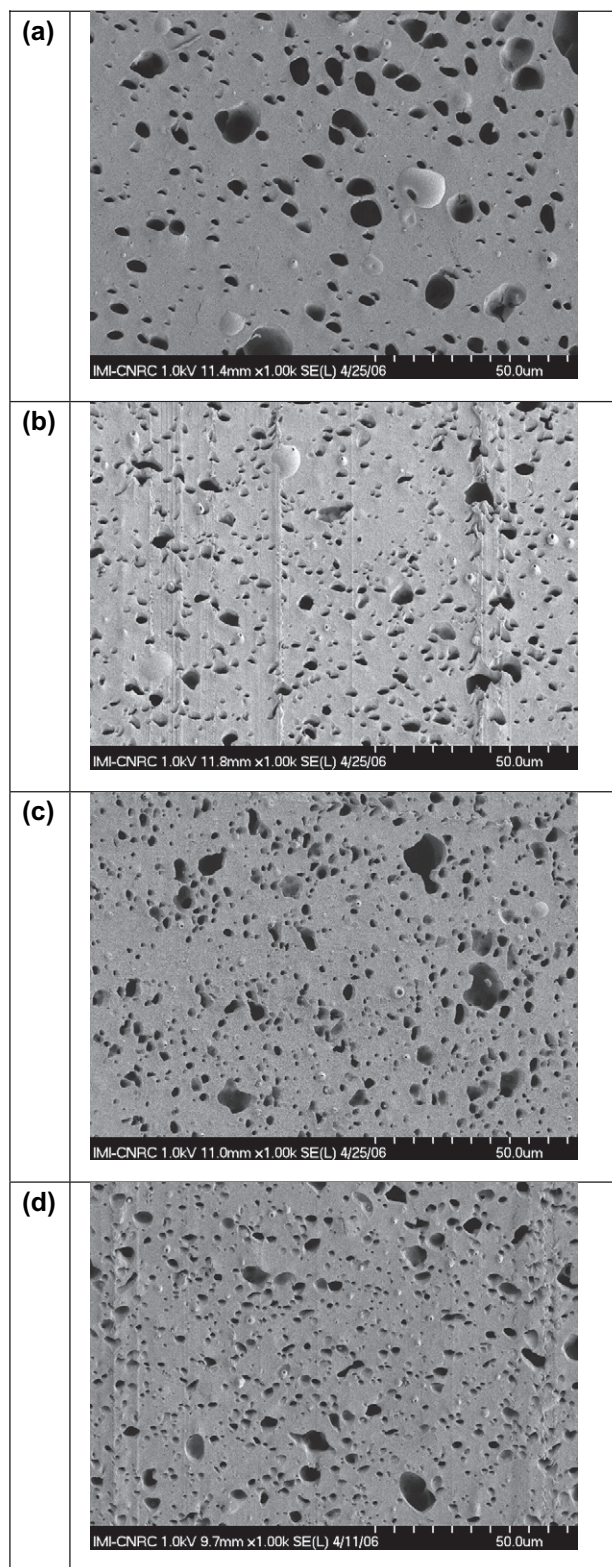


Fig. 4. Scanning electron micrographs for the two-step 27% TPS/PLA blends. In (a)–(c) 20% of the pure PLA has been replaced by PLA grafted using 2 wt% MA and (a) 0.10, (b) 0.25 and (c) 0.50 wt% L101. In (d) PLA has been fully substituted with the same grafted PLA as in (b).

respectively. In previous work, the grafting level obtained by reverse titration with these composition yielded MA grafting level of 0.23, 0.48 and 0.65 wt%, respectively [14]. In the

current work, the grafting level was measured only for sample produced with 0.25 wt% of peroxide initiator using the same analytical technique. A slightly higher grafting level (0.8 wt%) was found compared to prior report [14]. In all cases, the TPS phase size is reduced compared to the unmodified control presented in Fig. 3a but are not as finely dispersed as the blend prepared using the one-step compatibilization scheme (Fig. 3b). The smallest and most uniform TPS phase size is observed in Fig. 4b when using the 0.25 wt% peroxide level. The reason why higher peroxide level and thus higher grafting degree may not further reduce the TPS phase size is that it comes at the expense of increased PLA chain scission and viscosity reduction. The decreased ability to deform and disperse the TPS phase and the reduction in chain entanglement density between PLA and PLA-g-MA may therefore outweigh the benefit of a slightly higher grafting level. Fig. 4d presents the morphology for a blend where the PLA is entirely substituted by the PLA grafted using 0.25 wt% peroxide. No significant improvement is noticed when compared to the previous blends where only 20% of the PLA was substituted. It is noteworthy that the blend presented in Fig. 4d has exactly the same overall MA and peroxide content as the one presented in Fig. 3b obtained using the one-step process. In the current study, the one-step scheme leads to a slightly more effective emulsification. One potential reason for this is the partial loss of reactivity due to a higher level of residual water in the two-step process where the grafted PLA must be water-cooled and then dried in a desiccant dryer prior to PLA/TPS blending.

Interface modification in polymer blends is expected to decrease interfacial tension in the melt phase leading to a smaller segregation scale and to improve interfacial adhesion in the solid state. In order to investigate the effect of interface modification on the mechanical performance of the PLA/TPS blends, the tensile stress–strain behavior was characterized. Fig. 5 presents the tensile modulus, tensile strength and elongation at break for the modified and unmodified blends as a function of TPS concentration. In all cases, the TPS comprises 36 wt% glycerol. The tensile modulus decreases progressively with the addition of the TPS which intrinsically has a much lower modulus at the glycerol concentration used here (36%). The modulus is nearly unaffected by the interfacial modification. This is expected because the modulus is measured at low strain before any interfacial de-bonding may occur. Because of the very high PLA modulus, the material rigidity could be tuned in a very large range depending on application needs. In terms of tensile strength (i.e. maximum stress), a similar decrease with increasing TPS content is observed and again interfacial effects are modest. The maximum stress is recorded at strains around 5% independently from composition and is only slightly increased by interfacial modification. By contrast in dry-starch/PLA composites, the use of MA-grafted PLA matrix to the dry-starch particulates can lead to a 2-fold increase in tensile strength [16]. In the current case, since the TPS has a low tensile strength, improving the stress transfer between the PLA and TPS phase will not provide a similar increase. The interface-modified samples do show slightly improved strength but the dominant effect in the

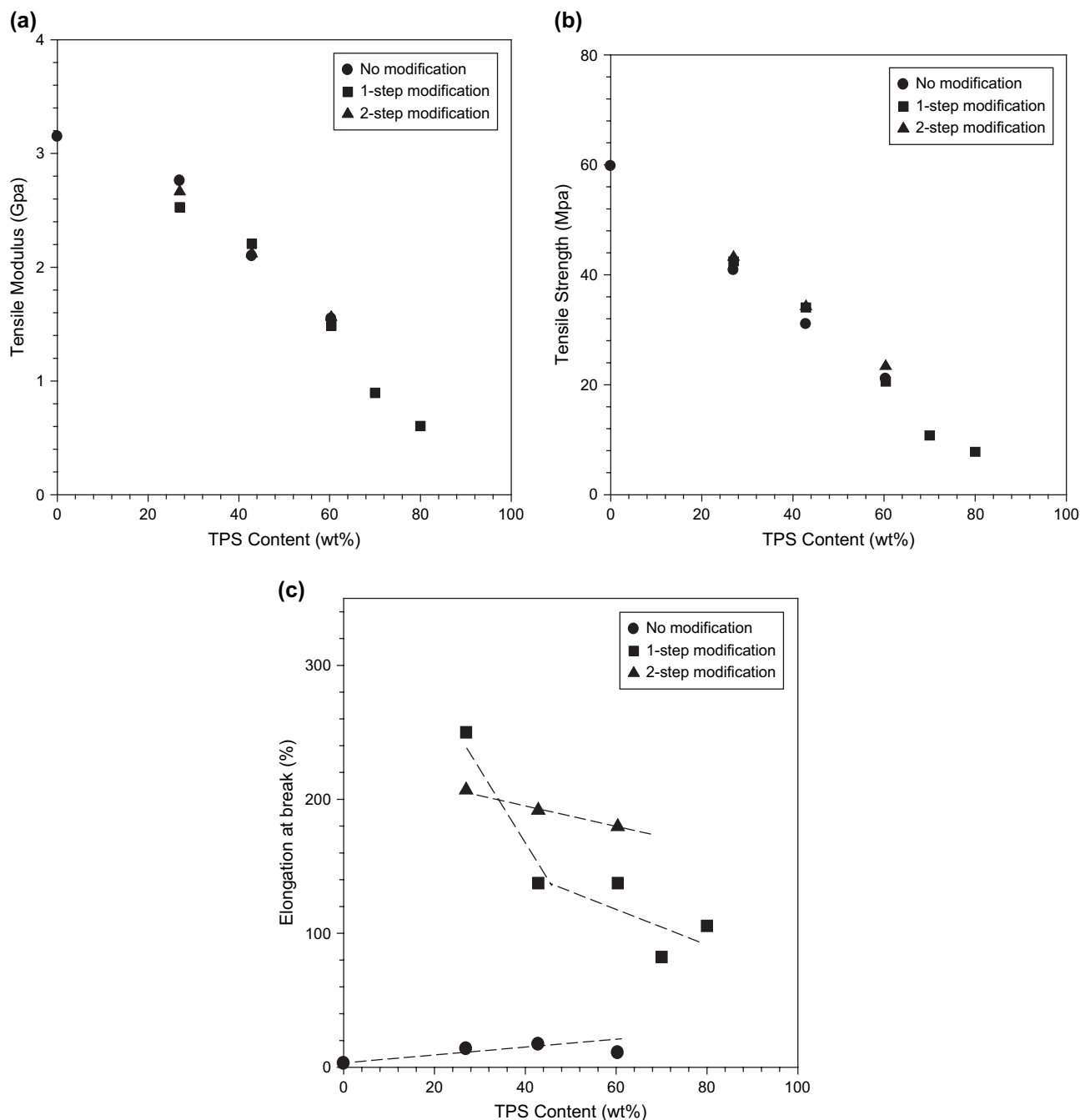


Fig. 5. Tensile properties of PLA/TPS blends. (a) Young's modulus, (b) tensile strength and (c) elongation at break.

system is the steady tensile strength decrease with the TPS content. It is at high strains that we see the most striking interfacial modification effect. For unmodified blend, the samples do not extend much after the maximum stress is attained and elongation at break occurs in the 10–20% range. This is only slightly higher than the measured values for pure PLA. On the other hand, the blends prepared using the one-step and two-step strategies exhibit a long plastic deformation plateau leading to elongation at break in excess of 150%. The stress value for these plastic deformation plateaus are 26, 21 and 14 MPa for the 27%, 43% and 60% TPS blends, respectively. It is expected that coarse blend dispersions will

lead to premature failure because the larger dispersed particles act as defects that initiate cracks in the material. The improved dispersion in the compatibilized blends is therefore expected to enhance the material ductility but the magnitude of this improvement points to a change in fracture behavior similar to that observed in rubber-toughened materials. Improvement in solid-state adhesion between the TPS and PLA is another factor that may improve the elongation at break. Direct adhesion measurements would be needed to confirm this effect. Even though the TPS is the most ductile component of the blend, the elongation at break decreases with TPS content. This is further indication that the presence of the TPS phase is



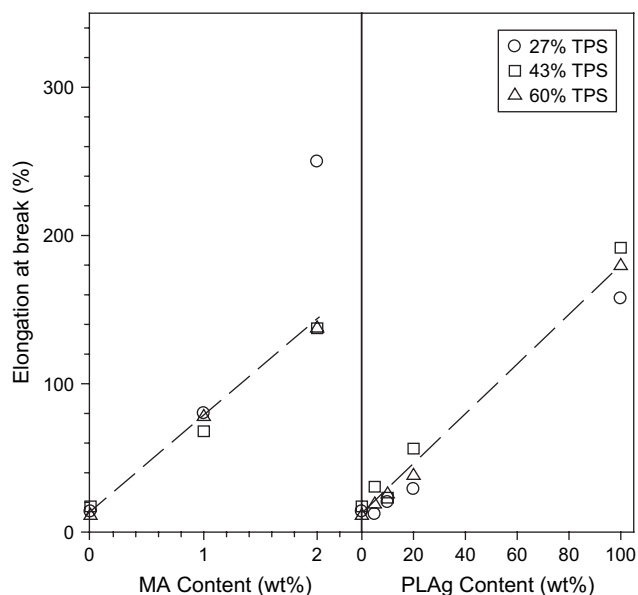


Fig. 6. Elongation at break as a function of MA content and PLAG content in PLA phase.

changing the fracture mechanics of the material leading to a synergistic effect. The one-step process leads to slightly lower values except for the 27% TPS blend but these differences are within the  $\pm 20\%$  uncertainty range associated with ultimate property measurements.

The interfacial modification results presented above were obtained using 2% MA. From a practical point of view it is important to investigate the mechanical properties and blend morphology of materials made with lesser amount of MA. Fig. 6 presents elongation at break results obtained using intermediate MA concentration. Using the one-step approach, reducing the MA and peroxide initiators will necessarily involve a reduction of the MA and peroxide used in the grafting step. This will lead to a decrease in the grafting efficiency since less active sites will be created and less MA will be available for grafting. In the case of the two-step approach, the global MA content in the blend can be decreased by using a mixture of neat and grafted PLA. Fig. 6 presents the elongation at break as a function of MA content in the one-step process or as a function of PLA-g-MA content in the PLA in the two-step process. In terms of total MA concentration on a PLA basis, the 0–100% scale for the two-step process correspond to the 0–2% scale in the one step and thus the two approaches can be compared on the basis of similar MA and peroxide usage. For the two approaches, we see that the elongation at break increases with the overall MA content. In the one-step approach, using 1% MA and the corresponding peroxide level leads to intermediate elongation values between those of the non-modified and the ones presented previously using 2% MA. For the two-step method, the elongation at break obtained when using 5–20 wt% PLA-g-MA does increase with concentration but is much lower than that obtained when using only the grafted PLA. In theory, complete blend emulsification can be obtained when the blend's interface is entirely covered by emulsifier, e.g. the *in situ* formed PLA–amylose copolymer.

This represents a fairly low concentration and in practice, compatibilizers such as MA-grafted polyolefins are used in the 5–10% range based on the polyolefin content. Therefore, future improvements in grafting levels, graft structure and interfacial reaction dynamics can be expected to improve properties at low grafted PLA concentration.

All results above were obtained using a glycerol content of 36 wt% in the water-free TPS phase. We will now discuss the effectiveness of the compatibilization approach using other plasticizer content. The glycerol plays an important role on the TPS properties especially in this study where it is the sole plasticizer (i.e. water-free TPS). Fig. 7 presents SEM

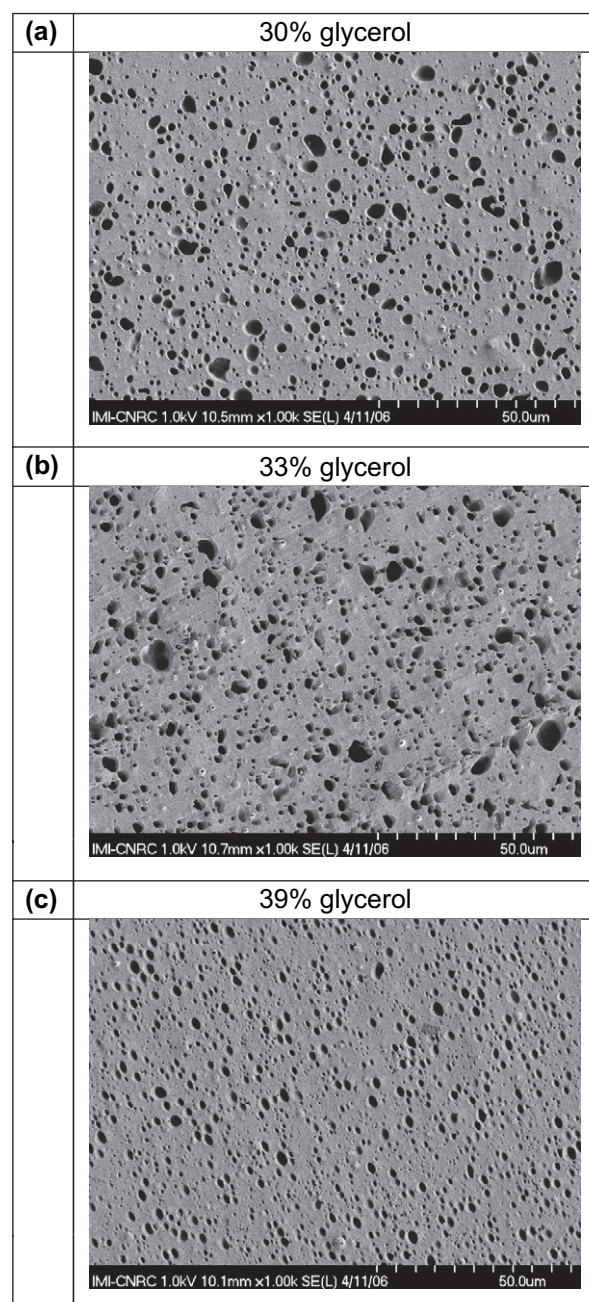


Fig. 7. Effect of glycerol content on the blend morphology of 27% TPS/PLA-g-MA blends produced with the one-step process. The glycerol content in the TPS phase is (a) 30%, (b) 33% and (c) 39%.

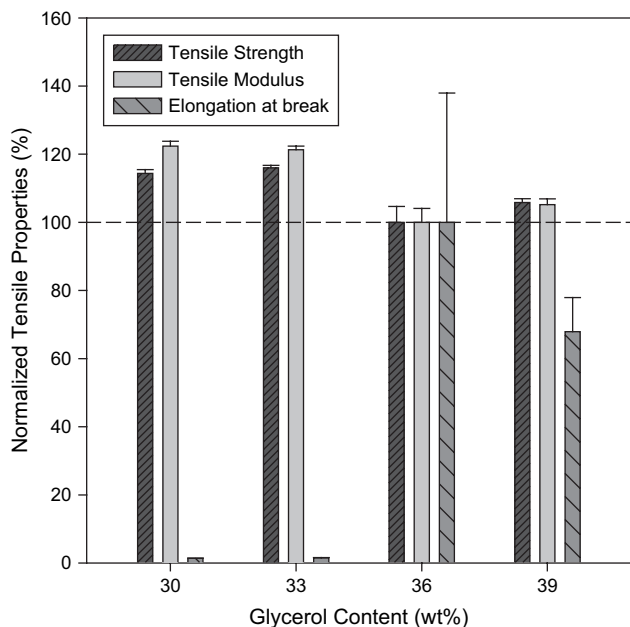


Fig. 8. Normalized tensile strength, tensile modulus, and elongation at break as a function for PLA/TPS blends in one-step modification as a function of glycerol content. Reference properties are those of the blends with 36% glycerol in TPS phase (dry basis).

micrographs of 27% TPS/PLA-*g*-MA blends in which the TPS phase contains 30, 33 and 39 wt% glycerol. This is to be compared with the reference 27% TPS/PLA blends already presented in Fig. 3. The 30 and 33 wt% glycerol TPS phase (Fig. 7a and b) is clearly much coarser than the 36 or 39 wt% glycerol TPS (Figs. 3b and 7c) but are still better dispersed and more uniform than the unmodified control (Fig. 3a). The increase in TPS phase size at low plasticizer content can be directly associated with the higher viscosity of TPS as discussed previously. The TPS comprising 30 wt% glycerol is approximately two times more viscous than the one comprising 36 wt% glycerol. This limits the deformability of the TPS phase during the mixing step and thus leads to a larger dispersed phase size. The effect of the glycerol plasticizer content on the tensile properties of the 27% TPS/PLA-*g*-MA blend is presented in Fig. 8. The data have been normalized using the properties of the blends with the 36 wt% glycerol TPS as the reference. As expected, the decrease in plasticizer content increases the modulus and tensile strength by stiffening the TPS phase. Increases between 15% and 20% are observed for the 30% and 33% glycerol levels. A much more dramatic effect is seen in the elongation at break which falls by a factor of 50. Elongation at break is expected to decrease when blend morphology coarsens but the observed effect is most probably related to the properties of the TPS phase itself when the plasticizer level is dropped below a critical threshold. Reliable mechanical data on the pure TPS were not obtained in this study because of difficulties in pelletizing and molding these highly plasticized TPS. However, data from Martin and Avérous [19] on TPS plasticized with a mixture of water/glycerol show for example elongations dropping from 100% to 3% and tensile moduli increasing by an order of

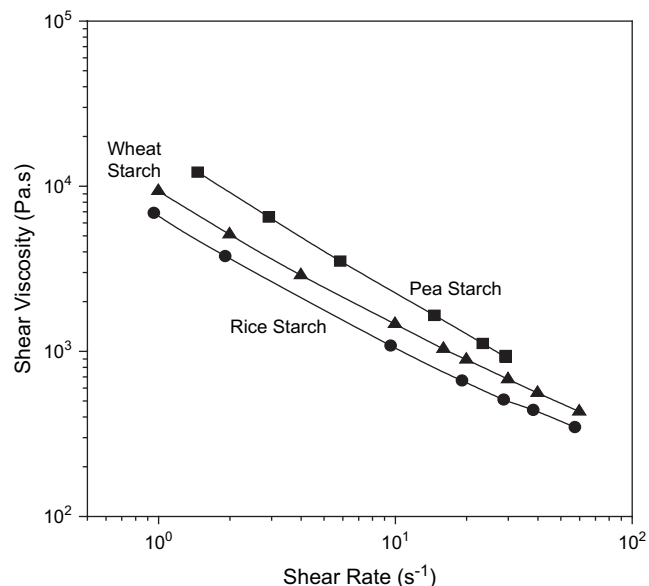


Fig. 9. Viscosity of TPS made of rice, wheat and pea starch as a function of shear rate. The measurements were carried out at 180 °C using the on-line rheometer.

magnitude when the total nominal plasticizer content is decreased from 30% to 26%. It is conceivable that below a certain plasticization level, the TPS particles become too stiff to deform thus reducing the ability of the material to dissipate energy during the tensile deformation process. The tensile properties obtained with the TPS containing 39% glycerol are not significantly different from the reference blend.

All results presented above were obtained using wheat as the starch source. Similar experiments using the 27% TPS/PLA blend composition were made using two alternative starch sources: rice and pea. Fig. 9 presents the viscosity of the water-free TPS based on rice, wheat and pea starch and comprising 36% glycerol. Interestingly, the TPS viscosity varies significantly with the starch source; the rice TPS being the most fluid and the pea TPS being the most viscous. This translate in Fig. 10 into blend morphologies that are much finer for the rice TPS and much coarser for the pea TPS. The wheat TPS morphologies presented earlier (Fig. 3a and b) are intermediate between the rice and pea TPS. For the already well-dispersed rice TPS, the phase size is further reduced when using the MA compatibilization strategy. The interface modification effect is more apparent for the pea TPS. These experiments show that the interfacial modification strategy is not dependent on the starch source and that it can be applied to a variety of starch sources and of blend compositions.

#### 4. Conclusion

The grafting of maleic anhydride unto PLA and subsequent blending of the grafted PLA with thermoplastic starch leads to blends with greatly improved ductility. Elongation at break of modified blends was in the 100–200% range compared to 5–20% for non-modified control and for the pure PLA. This

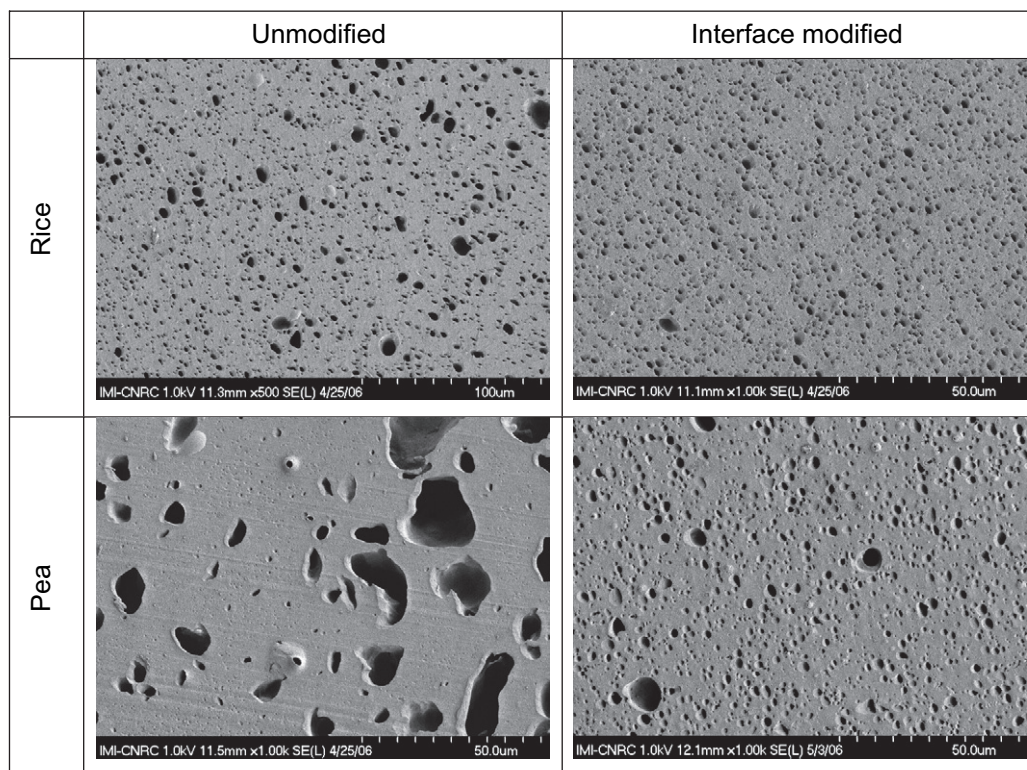


Fig. 10. SEM micrographs of unmodified and interface-modified 27% TPS/PLA blends where the TPS is based on rice or pea starch (instead of wheat in previous figures). The MA and L101 concentration are, respectively, 2 and 0.25 wt% based on total PLA content.

improvement is due to a more homogeneous blend and smaller TPS particle sizes and possibly due to improved interfacial adhesion between the TPS and PLA phases. Phase size reduction due to MA grafting was observed for different glycerol plasticizer levels but high elongation at break was observed only when the TPS phases comprised 36% and more glycerol. This was associated to insufficient ductility/too high rigidity of the TPS phase at lower plasticizer levels.

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