Chapter

Micro and Nano Structuring as Method to Enhance the Functional Properties of Starch-Based Polymeric Materials

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Abstract

The use of starch, the second most abundant natural resource in the word, as polymer is unprofitable and limited by certain functional properties. The structuring of multiphase polymeric materials represents the process of diminishing the dispersed phases till micro-and/or nano-dimensions and the positioning of the resulted fields in an order through which the properties of interest are achieved as far as possible. The structuring is reached by controlling the interface properties for achieving physical, chemical, biological or rheological compatibilization, mainly by melt compounding procedure. The chapter proves that the structuring of starch-based multiphases polymeric systems by reactive compatibilization is a good possibility to guarantee the functional properties, required by sustainable applications, of interest even in 2050 perspective. The chapter underlines also that the structuring by reactive compatibilization is connected with the formulation designing and choosing of the melt-compounding conditions in such a manner for the chemical bonding of the minority phases with the main polymeric matrix and therefore increasing the component miscibility and the functional properties of the resulted materials till the requirements of the sustainable applications.

Keywords: starch, multiphase polymeric systems, interface, reactive compatibilization, reactive extrusion

1. Introduction

After cellulose, starch is the second most abundantly available natural polymer in the world. Because of its biodegradability and non-toxicity to the natural environment, it becomes a raw material very attractive for the food and non-food application. Starch is a homo-polysaccharide made up of glucose units, linked together via glycosidic linkages, with a renewable-botanic origin (seeds and plant tubers), lowest price and highest industrialization potential for the next decade [1–13]. Starch has a biphasic composition because consists in two polysaccharides, amylose with linear macromolecules and low molecular weight and amylopectin with branched, clustered chains which belong simultaneously to several clusteres and high molecular weight. Depending on its origin, the diameter of the starch granules varies between 1 and 2 μm to 100 μm. The starch granules are different shaped: round (corn), oval (potato), rounded and truncated at one end (tapioca), flat, elliptical (wheat) [4–9]. Because each starch is different in composition the obtained films could exhibit different properties [10].

The ratio between the two constituent polymers of starch conditions the subsequent use of starch as thermoplastic polymer, as during the melted state flowing, the amylose macromolecules align in the flow direction and because its chemical strongly branched macromolecules, those of amylopectin cannot be aligned. The ratio between amylose and amylopectin depends on the starch origin and the growing climatic conditions. Starch is a semi-crystalline polymer that does not melt in the traditional sense to form a liquid. Starch melting occurs in the presence of a moderate (10–30%·w/w) water content. Starch crystals contain about 9–10%·w/w of bound water, which does not freeze at cooling below 0°C. Additional water or plasticizers is required for melting of starch at convenient temperatures below the water boiling temperature and the starch degradation temperature [11]. Starch has multiple glass transitions under which physical aging occurs. Due to the high hydroxyl content, the starch properties are strongly dependent on the moisture.

Currently, on the market, there are varieties of commercially starch available (potato, corn, wheat, topioca, etc)and numbers of un-explored and under-utilization sources of starch (fruits processing waste, different agro-industrial residues, etc.) [12, 13].

Starch is an important source of raw materials both as organic compounds and polymer used for plastic industry. It can be converted readily into a variety of useful monomeric and polymeric products by chemical and biochemical routs. Fermentation of starch to industrial-grade ethyl alcohols becoming more economically competitive with the synthetic methods due, largely, to the increasing cost of ethylene. Other biological conversions yield a variety of alcohols, ketones, and organic acids, and these too will become increasingly important as the petroleum situation worsens. Enzymatic conversion of starch to glucose, a useful starting compound for a variety of alcohols, acids, and polyols, proceeds readily and in near quantitative yield. Glycol glucosides, cyclic polyols derived by glycolysis of starch, are excellent replacements for petroleum-derived polyols in the production of rigid urethane foams, and can replace up to 85% of petroleum-based polyols in alkyd resins with no loss in quality of the resin [14].

However, its use as a polymer is unprofitable and limited by certain functional properties. Its hydrophilicity, thermal, and mechanical properties limitations, low physical properties (brittle, poor moisture resistance, low permeability to lower gases, high density) rapid degradability, and strong intra and intermolecular hydrogen bonding of the polymer chains hinder its melt processability and limit its widespread commercial application as a renewable biopolymer [3, 15]. Starch also is easy degradable under flowing in the melted state. Moreover there are many difficulties in controlling the functional properties during its service life because of frequently occurred phenomena as exudation of plasticizers (anti-plasticization), re-crystallization (retrogradation) [7].

The perspective for polymeric materials based on renewable resources will be constantly increasing as far as 2050. Due to the failure in solving the issue of environment infestation with secondary polymeric materials, the development policies in designing and achieving polymers and materials based on them are mainly oriented towards sustainable applications.

In order to reach functional properties of practical interest including the sustainable applications, the multiphase starch-based systems are structured mainly by reactive compatibilization at melt processing (reactive extrusion) which has proven to be the most effective method. That is why the chapter presents the possibilities to get new starch-base, multiphase materials proving that structuring based on reactive compatibilization are adequate and practical solutions to ensure functional properties for durable applications. The chapter presents the main possibilities of structuring multiphase systems based on starch and details certain aspects related to the compounds of starch with polyvinyl alcohol.

2. Structuring the multiphase polymeric materials

Multiphase polymeric materials are homogeneous or non-homogeneous systems which contain solid, liquid or gaseous phases and include categories as: composites, blends, gels, interpenetrated polymer networks, mono or layered structure, cellular solids (foams), including biological type (hydrogels) etc. [16, 17]. The dispersed phases into the polymeric matrix can be functionalized, microencapsulated, oriented, continuous or discontinuous, etc. [16–19].

The structuring of multiphase materials represents the process of diminishing the dispersed phases till micro-and/or nano-metric scale and the positioning of the resulted mico and/or nano fields in an order in which, the properties of interest are achieved as far as possible. The structuring consists in enhancing by controlling the interface properties the physical-chemical-biological-rheological compatibility of the blend components considering methods connected with mobility of the segments/macromolecules/morphological elements, or with reactivity of the components or/and with ordering of the flowing elements at melt compounding [16–18].

The structure-properties relationship has a crucial significance in the structuring of the multiphase polymeric materials for developing grades satisfying varied engineering requirements [18, 19]. With the help of modern technologies, the circumstances in which the phases of the heterogeneous polymeric materials can be so arranged to give the desired properties in correlation with the intended applications, is possible to be identify.

The interfaces adhesion between the dispersed phases and polymeric matrix are maintained by intermolecular physical or chemical forces and/or by chain entanglements [20]. In the absence of these interactions, the interface becomes the place where the brittle fracture takes place. The interface can be seen as a resistance between materials in contact and is characterized by interfacial tension (controlable by changing of the Gibbs potential per unit area). The interfacial tension depends on factors such as: phases geometry (shape, average size, particle size distribution, porosity, etc.), the characteristics of macromolecular chains (molecular structure, molecular architecture, tacticity, crystallinity, ramifications and/or, defects, impurities, ash), the size of thermo-mechanical stress, the melt flow features (the size of mechanical stress, temperature) [16, 21–25]. Most thermodynamic studies of multiphase polymer systems are based on Flory-Huggins' theory [26].

Changing the interface properties have the effect the modification of the material properties. The least common possibilities encountered in the practice of polymer blends achieving are those in which the compound properties are synergistic, i.e. the blend properties are greater than the additive properties of the individual polymers. The properties are synergistic for polymers showing high interface adhesion denoting that they are thermodynamically compatible [17, 27, 28]. The most common dependence blends properties - composition is the additive those, when the blend properties represent the average of the component properties in their pure state, without minimum or maximum. If the interfacial adhesion is very weak and the polymers are thermodynamically incompatible, this dependence does not follow the law of additivity, but shows a variation with a minimum, which means that the blend properties are lower than those of each individual components [17, 28].

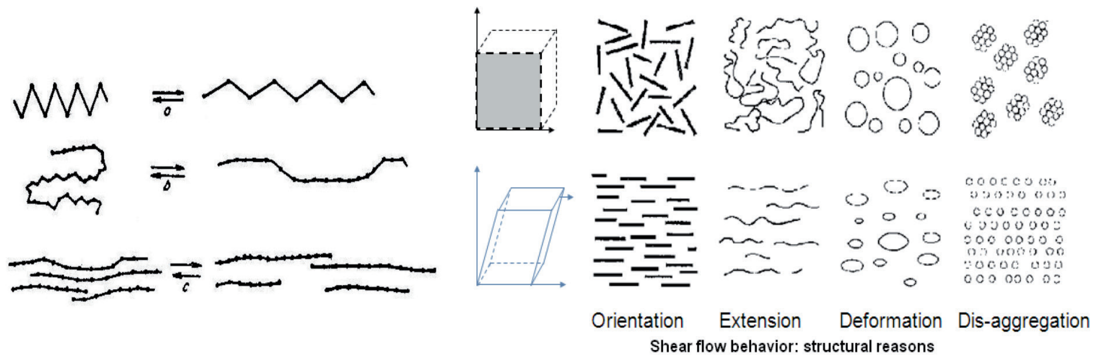
Compatibilization is the process of modifying the properties of the interfaces in immiscible polymeric systems which results in the creation of the interphase region in which a gradient of material composition is created [20]. By compatibilization the morphology of the new material is stabilized at macroscopic level and therefore, the functional properties are constant over lifetime. The degree of compatibility is estimated by the thickness of the interface, the size of the dispersed phases, the mechanical performances generally by all functional properties. Unlike the compatibility, the miscibility is related to the blending of components at the molecular level; in the whole mass, which means that in the case of miscible blends it is no longer about dispersed phases [20, 29].

In order to improve the compatibility, the problem of minority components dispersing into the majority polymeric matrix is solved by reducing the interfacial tensions using one of the following techniques: entanglement of the macromolecules, interpenetration of interfaces, development of chemical (covalent linkages) or physical (e.g.van der Waaals, hydrogen bonds, ionic interactions, etc.) bonds [22]. The entangled interfaces are found in miscible blends or composites with good interfacial adhesion. The interfacial tension can be controlled by using polymeric emulsifiers (grafted or block copolymers, others) which create secondary bonds or by using compatibilizers, which generate chemical bonds between phases, after reactions possible between several functional groups (anhydride-amine, epoxy-anhydride, oxazoline-carboxylic acid, isocyanate-carboxylic acid, lactic acid-amine, carbodiimides-carboxylic acid, ion exchange reactions, free radical grafting reactions at the phase interface [17]. By using a controlled method to improve the compatibility even miscibility between the components of a new multiphase polymeric materials is possible to achieve materials, with own functional properties correlated with requirements of various applications.

In case of multiphase polymeric materials with target fillers, the improving of compatibility is based also on the creating of physical and/or chemical bonds. If the cohesive energy thus developed is below a critical value, then morphological defects are created, between the filler and matrix, representing space filled with air, usually found as micro-voids, voids, macro-voids, cracks, fractures. The characteristics of the empty space depend on the shape of the filler. The cohesive energy may be below a critical value, situation in which the miscibility between the components is weak and/or when the distribution of the filler into the matrix is inadequate. In the engineering practice, there are no free-defects multiphase materials such as the mentioned those it was found that if the content of these defects is higher than 5%, then the material functional properties decrease with approx. 30%. The structural defects presence is dangerous because, under stress, it accelerates the mechanical destruction by cracking and breaking [30, 31]. A filler can act also as compatibilizer when the radius of the particle has the same order of size as the radius of gyration [32].

Changing the interface properties has as effect the adjusting of the polymeric system properties. The least common possibilities encountered in the preparation of polymer blends are those in which the dependence of compound property-composition is “synergistic”, i.e. the blend properties are greater than the additive values of the properties of individual polymers. The properties are synergistic only in case of the polymers showing high interface adhesion which means they are thermodynamically compatible [17, 27, 28]. The most common dependence blends properties—composition is the “additive” those, when the properties of the blend represent the average of the properties of its components in their pure state, without minimum or maximum. If the interfacial adhesion is very weak and the polymers are thermodynamically “incompatible”, this dependence does not follow the law of additivity, but shows a variation with a minimum, denoting that the blend properties are lower than those of each individual components [17, 28].

The quality of items obtained by melt processing techniques, expressed as morphological uniformity, anisotropy of properties, appearance of surfaces, etc. depends on the structuring under stress of the flow entities in the field of mechanical and thermal



(a) (b)

Figure 1.
Structuring melts by flowing in elongational (a) or shear stress field (b) [17, 33].

stresses. Structuring under stress is the result of the molecular disaggregation, deformation, orientation, extension of macromolecular chains developed when the melts in passing through the nozzle of the nozzle of the molder device (**Figure 1**) [3, 33].

The flow resistance of the polymeric melts, a parameter which control the structuring during the melt compounding flowing, depends both on the shear rates and the molecular parameters describing the chemical structure of the polymeric blends components [34]. As an effect of the order degree gained during the melts flow through the nozzles is the crystallization under stress [33].

In order to deepen the structuring phenomena, the elucidation of the correlation between the molecular parameters (degree of polymerization, Flory-Huggins interaction parameters, etc.) and macroscopic phase separation phenomena is necessary to be done by investigating the heterogeneous structure from submicron scale to nanometer those [35].

3. Structuring of starch based materials

To get functional properties of wide applicability, starch can be converted into multiphase polymeric compounds, by physical and / or physical-chemical and/or chemical modification with other polymers and/or non-polymeric materials [36] considering un-reactive and/or reactive melt compounding [25, 37–40]. Generally speaking, starch has low compatibility with other polymers or biopolymers and therefore the degree of compatibility varies depending on the specific used grades. The success of the starch converting into such multiphase polymeric systems is conditioned by the achievement of the molecular miscibility or, at least, by the creation of an advanced dispersion of minority components into the main polymeric matrix, via lowering the interfacial tensions considering the described compatibilization techniques [24, 41–43].

The convertion of starch into multiphases polymeric compounds of practical interest must consider both the starch origin, the ratio between the amylose and amylopectin, the constancy of this ration (especially for scaled up procedures), the correlation of the modification method with all the starch structural characteristics and the requirements of the considered application. The structuring possibilities are related equally to the way of designing the formulation and choosing of the melt compounding conditions the chapter presenting examples regarding the starch-polyvinyl alcohol compounds. An overview of the reactive compatibilization as method to get structured multiphase materials based on starch with other polymers is also given. A special attention is paid to the possibilities of avoiding the melt degradability of the multiphase systems based on starch. The chapter details also the structuring methods to achieve starch - PVOH nanocomposites with layer silicate content and presents a silicate treatment method which leads to the formation of exfoliated nanocomposites. The structuring through incorporation of a gaseous phase into the starch-starch matrix is also shortly described.

4. Structuring through melt compounding

Starch can be compounded with renewable polymers from *algal origin* (alginates); *microbial origin* (polysaccharides: chitosan, curdlan, gellan, pullulan, xanthan, bacterial cellulose; polyesters and copolyesters: polyhydroxyalcanoates (PHA), poly (butylene adipate-Co-terephthalate) (PBAT)); *plant origin* (polysaccharides: cellulose, pectin; proteins: soy proteins, zein, gluten: polyesters (polylactic acid PLA)); *animal origin* (polysaccharides: chitin, chitosan) [44, 45]. On the market there are also of interest starch compounds biodegradable or water- soluble oil-based polymers as: polycaprolactones (PCL), polybutylene succinate (PBS), polybutylene succinate adipate (PBSA) or polyvinyl alcohol (PVOH) [46].

Starch compounds with PVOH are designed for replacement of LDPE films in application where barrier properties are not critical, water-soluble laundry bags, biomedical and clinical fields, replacement of polystyrene foams as loose fill packaging materials, packaging applications. Blending of starch with other biodegradable polymers such as biodegradable polyesters; polylactic acid (PLA) and polycaprolactone (PCL), was recognized as a successful strategy to provide a renewable, fully biodegradable and cost-effective materials [47]. The compounds of starch with PLA are conceived for applications as food packaging, electronic devices, membrane materials (chemical and automotive industries), medical applications, packaging materials. The compounds of starch with PBSA are useful as antimicrobial packaging materials and those with PHB as biomaterial in medical applications. PBAT starch compounds have controllable mechanical properties and are therefore are designed for multiple types of packaging [48]. The use of starch in achieving of polyurethane (PU) multiphase materials not only yields PUs with outstanding mechanical properties but also makes the final PU products biodegradable. The hydrophilic nature of starch limits its dispersion in hydrophobic PU polymers [49] and therefore these compounds must be reactively compatibilized.

Renewable fillers play a valuable role in the development, of new multiphase polymer materials based on starch considering melt compounding techniques. It should be noted that the degree of compatibility between starch and other biopolymers extensively varies depending on the specific biopolymer, generally starch having as has been said low compatibility with other polymers [43, 50].

4.1 Melt compounding conditions

Starch can be melt compounded considering various conventional processing techniques, similar to those widely used for typical synthetic thermoplastics, such as extrusion, injection, compression molding, casting and foaming, as well as some new techniques as melt reactive melt compounding. Various starch-based products which have been developed and commercialized as extruded films/sheets, foams, shaped articles, etc. [51] using internal mixer, mono (**Figure 2**) or twin-screw extruders, injection devices, others can be obtain [52]. Formulations often require inlets for plasticizers, filler or other additives. Escape of volatiles such as steam will be required, without loss of other materials. High shear is required to disrupt the native starch structure and produce a uniform composition with other components. The extrudate must be a uniform continuous stream with rheology suitable for shaping [11].

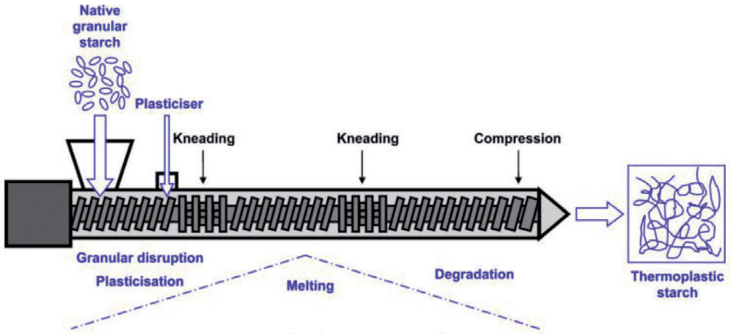


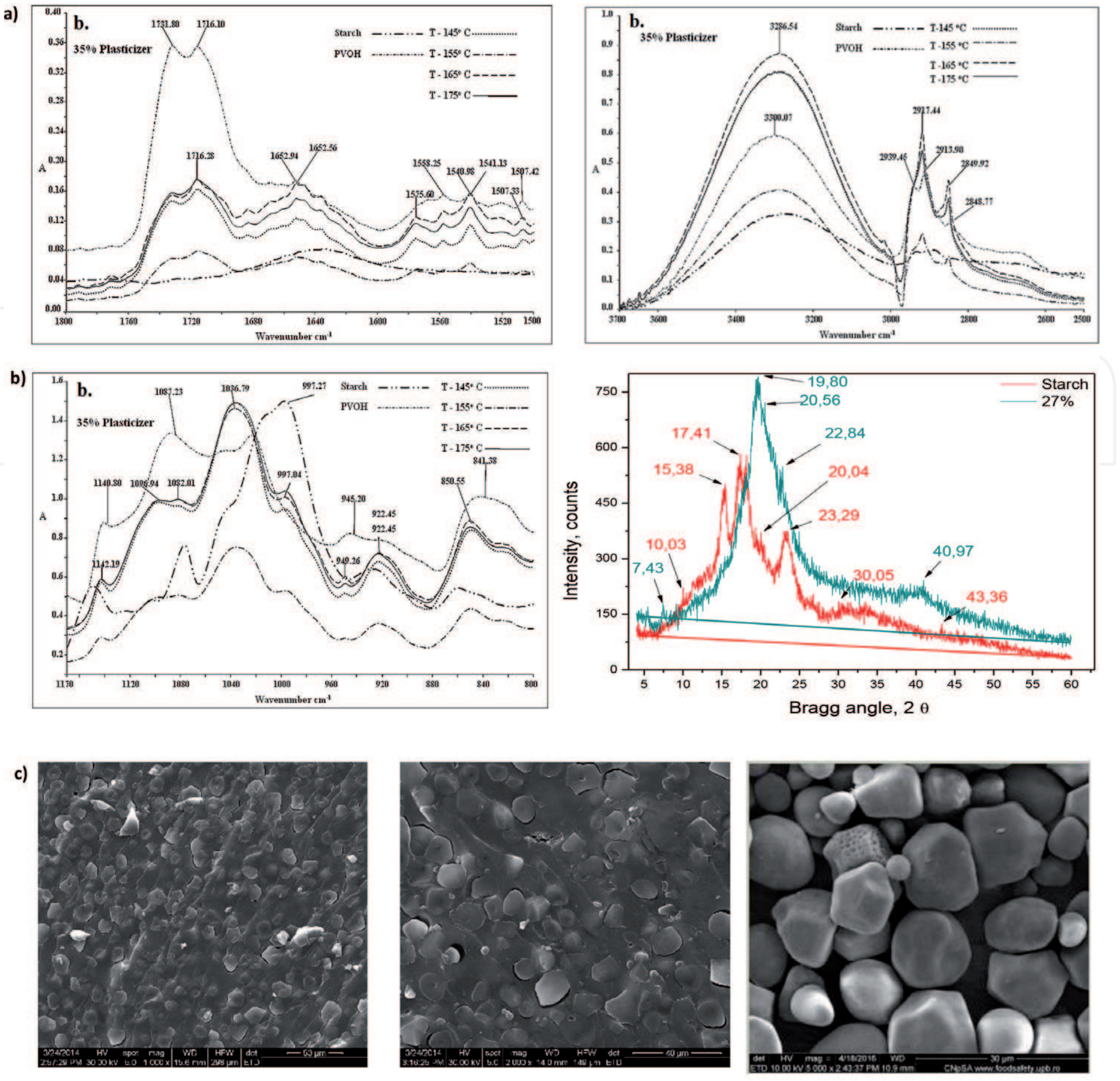
Figure 2.
Schematic representation of starch processing by extrusion [52].

A twin-screw extruder has a large operational flexibility (individual barrel zone temperature control, multiple feeding/injection, and screw configuration for different degree of mixing/kneading) and is useful for intensive mixing and compounding of components into starch plastics. In a twin-screw extruder the custom combinations of rheological elements can be assembled along the screw. Zone of high shear will assist with disruption of granules while uncoiling of molecules can take place in less shear intensive zones. Another advantage of the twin-screw extruder is to allow the decoupling of die flow and mechanical treatment. During extrusion of starch-based multiphase materials, residence times and specific mechanical energy inputs must be controlled, and high efficiency production can be achieved [52]. The temperature conditions for preparation and processing of these materials must be chosen to minimize possible degradation of the organic modifier and the matrix [53–55]. The shear experienced during compounding may have caused fragmentation of starch and destroyed its crystalline structure [56]. Shearing of the molten granules destroys their organized structure, and crystalline, granular starch is converted to a dispersed, essentially amorphous material [57]. It was found that if the extrusion is performed at high rotational speed and high stationary times the single helix crystallites are formed [58, 59]. Also during extrusion the shear stress may enhance starch separation, whereby amylose may be partly leached out of the amylopectin [60, 61].

Because the melt compounding conditions control the melt rheological properties they have a great impact on the properties of the resulted compounds [42, 52]. In [42] it has been shown that for the polymeric compounds sensitive to the melt processing parameters, such as those based on starch, the boundary between miscible and less miscible is very small and therefore each compounding ratio requires its own formulation and its own melt flow conditions. It was shown that the miscibility of starch-based compounds increases if, for each formulation is found the melt processing conditions which ensure the better improving of miscibility because the melt resistance to flow allows a suitable homogenizing without degradation of the macromolecules (**Figure 3**).

The starch-PVOH compounds designed for short life application which had enhanced miscibility achieved by controlling the melt resistance to flow via melt compounding conditions have a better surface appearance (**Figure 4**) and no longer presents the anti-plasticization and retrogradation phenomena [42].

It was observed that the starch polymer melts exhibit strong elastic properties and therefore phenomena as nozzle swelling, shark skin and wall slip [62] can be controlled. The experimental results have shown that these phenomena can be avoided by controlling the elastic component of the melt vasco-elastic properties considering the formulation and the selection of optimal compounding conditions. In this way the PVOH-starch compounds can be melt processed into items without defects and degradation, with natural color, smooth surface (**Figure 5**) and functional properties of interest for short-life applications [17, 63].

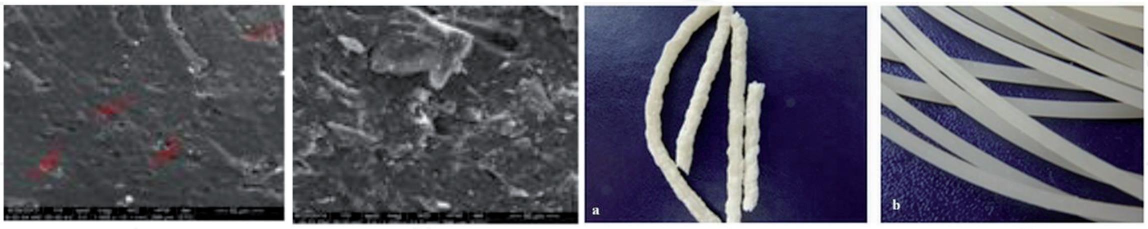


1000 X

2000 X

5000 X

Figure 3.
Dependence of the shape of the FTIR spectra (a) and of the XRD diffractograms (b) and the SEM micrographs aspect (fracture) of some starch-PVOH compounds (c) on the melt compounding conditions [42].



a)

b)

c)

d)

Figure 4.
Morphology (fracture, 1000×) (a, b) and surface appearance (c, d) before (c) and after (d) improving the miscibility via controlling the melt resistance to flow of some starch-PVOH compounds [42].

Figure 5.
Granules (20–70% starch content) and items achieved from PVOH-starch compounds after elimination of defects via structuring by controlling the melt resistance to flow [17, 63].

5. Solid state properties conditioning the structuring efficiency

5.1 The polymers particles shape and size influence

In [64] was found, that the turning of corn starch via melt compounding with PVOH can be achieved by providing similar melting behavior of the starch and of PVOH powder and by controlling the process sensitivity of the new compounds. The corn starch and PVOH particles had their own size distribution and shape. If the starch particles were rectangular, those of PVOH were spherical [64]. The PVOH particles shape depends on the manufacturing technology and can be spherical only if the polymer was obtained by reverse suspension hydrolysis of poly (vinyl acetate) (PVA) [65]. It has been shown that the particles of the two polymers cannot be melt compounded than after the selection of fractions with particle size variable the same range. If the particle size distribution of the two polymers is wide, then the obtained compounds include defects, either rough surfaces or un-melted inclusions. Variable sized particles have distinct melting times, longer for those with larger diameter and smaller for those with smaller diameter. The rough surface results due to the degradation of small particles and solid inclusions represent un-melted particles because they had large diameter and have no time to melt. Due to the variation of the particle sizes of the two polymers even the morphologies of the achieved compounds and their dynamo-mechanical properties are affected (**Figures 6** and 7). If the particles of the two polymers have approximately the same size then they melt in approximate identical time and the two type of defects are avoided.

In addition, if the blends obtained through melt compounding of starch with PVOH contains un-melted particles, then morphological defects such as voids, cracks fractures, may appear around them (**Figure 6**), The new compounds always will contain, near un-melted particles because of their size, parts from the starch grains, representing the branched macromolecules of amylopectin, very well visible on the SEM micrographs.

Considering the word "compatibility" describing the partial miscibility of the compounds components which result in macro-metric scale time stability of the obtained compounds, appropriate for the life-time, the term "miscibility" reflects the interpenetration of the components at the molecular level and so stability for an unlimited period for the new materials [64]. It can be appreciated that the

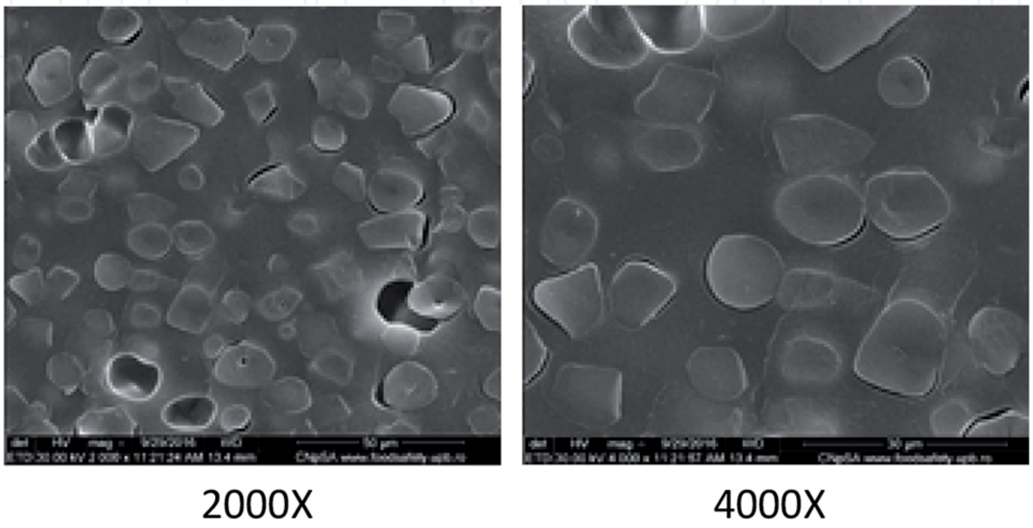


Figure 6.
Morphological defects of the compound achieved from starch with 40–63 µm sized particles and PVOH with particles of 80–100 µm (1/1 blending ratio) [64].

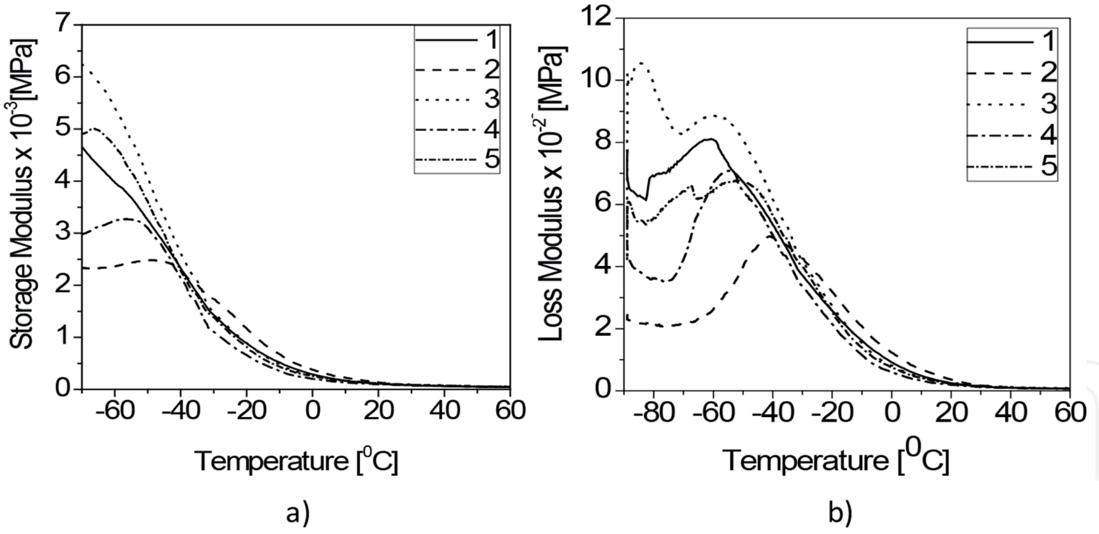


Figure 7.
The dependence of the dynamo-mechanical properties of the starch-PVOH compounds (storage modulus (a), loss modulus (b)) on the temperature and the particle size (1—P1 (80–100 μm)/P2 (80–100 μm); 2—P1 (80–100 μm)/P2 (100–200 μm); 3—P1 (80–100 μm)/P2 (200–300 μm); 4—P1 (63–80 μm)/P2 (80–100 μm); 5—P1 (63–80 μm)/P2 (80–100 μm)) [64].

polymeric particles, through their size, make the differences even between compatible and miscible compounds. In analyzing the compatibility/miscibility between starch and PVOH compounds (claimed compatible by some authors and opposite by others) the influence of the particles size and of the amylopectin content should be equally considered. In accordance with [64] the starch-PVOH compounds obtained from small sized particles are close to be totally miscible, presenting a single glass transition without shoulders, totally different as those of starch and PVOH beeing almost a continuous phase, only with few defects as voids etc. In the last period, on the commercial market, can be found grades of thermoplastic starches which represent plasticized starch powder melt processed into granules.

6. Structuration through reactive compounding (*in situ* compatibilization)

The experimental practice has shown that only physical compatibilization which establishes only secondary bonds between the dispersed phases and the matrix does not generate functional properties of practical interest. As it has been pointed out, because of poor interactions, starch is generally thermodynamically immiscible with all renewable polymers showing a dispersed structure (ex. ternary blends based on PCL/starch/PLA, starch-PBAT [66]. Structuration through reactive compounding (*in situ* compatibilization or chemical compatibilization) involves the development, in the melted state, during compounding, of chemical reaction between the functional groups of the compatibilizer and those of the starch and the second polymer from the compounds. The process involves the *in-situ* formation of amphiphilic structures, and thus covalently bonding the phases in the melt state. Reactive melt compounding is a convenient and cost-effective technique for the esterification of polysaccharides using anhydride reagents In this way the interface tension decreases, the size of the dispersed phases decreases and the functional properties can be controlled [67, 68]. The chemical compatibilization is relevant when morphology present regions with fully continuity or presents a co-continuous aspect.

To understand the lack of affinity between the different phases, interface adhesion can be investigated by contact angle measurements. The compound morphology can be better observed using microscopy techniques (e.g. SEM, etc.) The rheological investigations in solid (DMA) and melted state helps to understand better the blend structure formation during the process [69]. Currently, nanofillers are used to improve both mechanical properties and the phase morphologies of immiscible blends. The main advantage of using nanofillers, when compared to copolymers, is that the former can simultaneously act as nano-reinforcements and compatibilizers [67]. There are situations when the reactive compatibilizers can fulfill other functions such as antibacterial agent [70].

Twin-screw extruders are typically used for reactive compounding due to their excellent control of mixing, temperature, and residence time distribution, with highly accurate feeders, systems for removal of reaction heat, etc. [71–75].

Because of interest for industrial quantities of compatibilized multiphase renewable polymeric materials and the possibility to ensure functional properties of practical interest for desired applications, the chemical compatibilization strategy is usually implemented in reactive melt processing procedure (reactive extrusion) [71]. The concrete reactive compatibilization solution depends on the nature of the renewable multiphase polymeric system which must be structured [76–78].

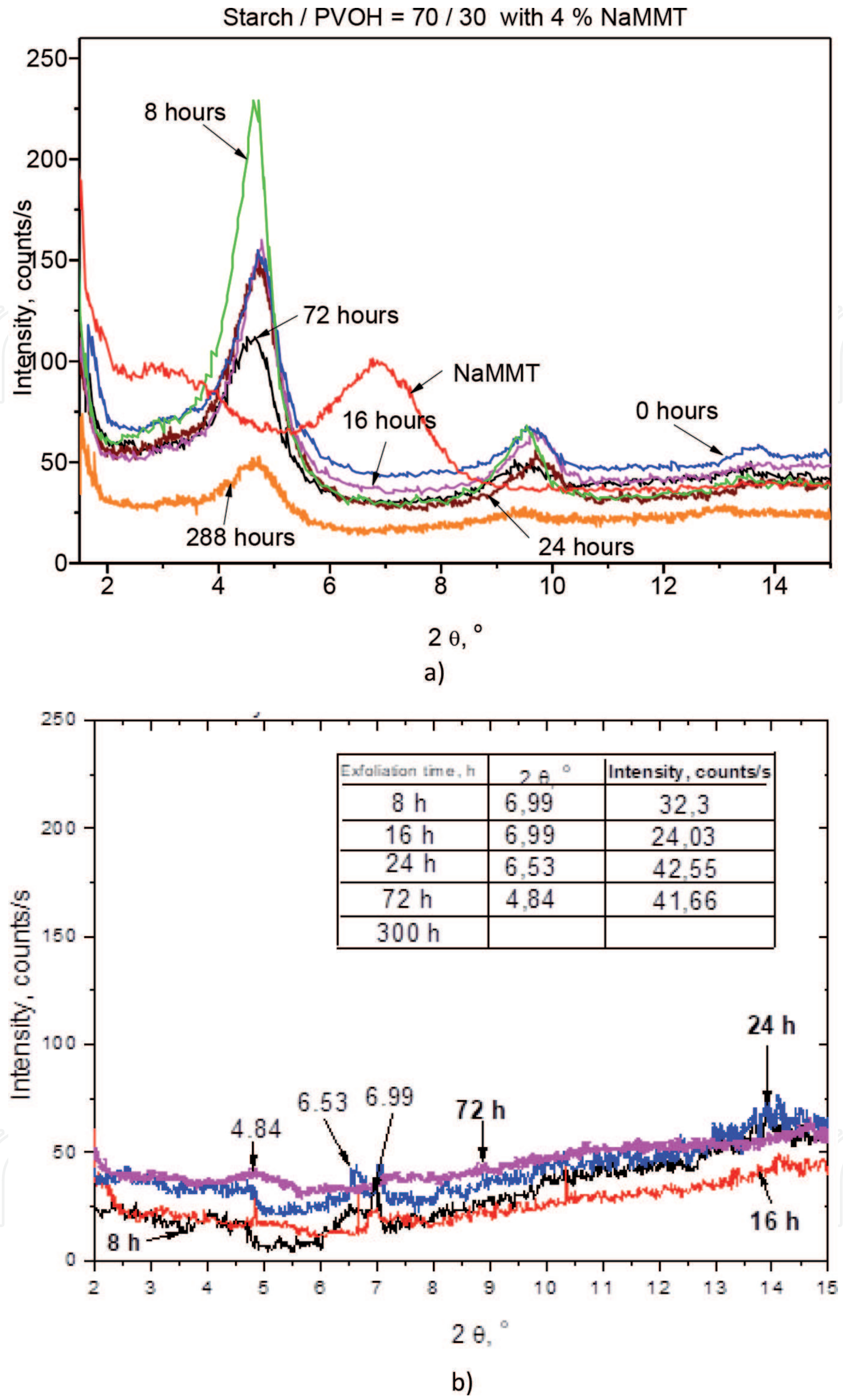
7. Structuring by incorporating layered silicates

Polymeric nanocomposites have achieved much more attention due to their enhanced physic-chemical and mechanical properties, improved moisture sensitivity in comparison to the pure polymers. Due to its chemical and physical properties, starch is highly valuable to be structured through converting into nano-composites considering melt compounding procedures (twin screw extruder) including the reactive melt processing [79, 80].

Various types of nano-fillers that have been used with plasticized starch can be used such as montmorillonite, cellulose nano whiskers, cellulose nano-fiber, and starch nano-particles (obtained by acidic hydrolysis of waxy maize starch granules as reinforcement [81]). The starch-based nano-composites with different nanofillers for reaching a optimal dispersion and properties need particular preparation strategy [82–85]. The incorporation of various fillers in a starch-based polymer matrix generates specific structuring process because in this situation they control the specific orientation and/or crystallization processes.

For getting starch-based nano-composites, blends of starch with bio-polyesters or other renewable- or synthetic-based polymers can be used, e.g. which can be considering various obtaining procedures [86].

Regarding the achieving of the starch-PVOH nano-composites structured with layered silicates in a melt compounding procedure were studied aspects as: the dependence of miscibility, morphology and other functional properties on the layered silicate nature, the functionalization strategy of the galleries [87, 88] the target filler content [89], the incorporating method of the layered silicate into the starch matrix [90–92], the correlation between miscibility and the surface defects [31, 93]. At first sight, the dispersion of the layered silicate with the help of shear stress at melt compounding should favor the exfoliation process. In reality, this method is limited both by the low thermo-stability of the polymers and those of the used modifiers but also due to the loss of hydration water of the layered silicate consequence of long maintenance at high temperature in the compounding device. It was also found that, at the same target filler content, the size of the dispersed phase and the number of dispersed phases per unit area (drops) depend on the type of filler, nature of the surface treatment and particle size. It was concluded that the degree of intercalation of the layered silicate with the PVOH-starch matrix increases if purified layered silicate (NaMMT)



Exfoliation time, h	2 θ, °	Intensity, counts/s
8 h	6,99	32,3
16 h	6,99	24,03
24 h	6,53	42,55
72 h	4,84	41,66
300 h		

Figure 8.
The swelling and exfoliation of NaMMT during a thermo-mechanical procedure applied before melt compounding (a—stirring without temperature; b—stirring with temperature) incorporation into a starch-PVOH matrix [91].

or ammonium ion functionalized layered silicate (Nanocor I 28) are used to strengthen the STARCH-PVOH matrix. If, on a macroscopic scale (100 μ) the starch-PVOH-layered silicate compounds seem to be compact materials, at microscopic level (10 μ), defects as gaps, cracks, fracture etc. appear. These morphological defects seem to illustrate a disordered microstructure, due to the poor distribution of swollen silicate tectoids into the continuous polymeric phase, possibly due to inadequate compounding conditions. It has been shown that the PVOH-starch-treated layered silicate blends which, according to X-ray diffractograms, appear to be of exfoliated type and which have an improved thermal behavior, including in terms of uniformity of the melting process, have homogeneous surfaces and low material imperfections as gaps, cracks. SEM micrographs show that the surface of the compositions which, according to X-ray diffraction, are exfoliated intercalated nano-composites. Are characterized by small contact angle, are nano-structured, show advanced miscibility (demonstrated by FTIR analysis), have smaller number of defects as gaps, cracks, fractures [31, 87–93]. Compounds that, according to XRD diffractograms, are micro-structured, have frequent surface defects and irregular fracture areas, which are the starting points for cracking, crack propagation and stress rupture [31, 87–93].

In order to achieve a good swelling of the layered silicate and a homogeneous dispersion of the obtained lamellae into a starch-PVOH compound, it has been shown that, the layered silicate needs to be swelled, better in a pre-compounding procedure [91]. The layered silicate (NaMMT) was treated, before compounding in water, an effective starch and PVOH plasticizer. It was shown that the degree of exfoliation of the multilayer silicate and the properties of the achieved micro- and nano-composites depend on the way the silicate was treated (stirring of layered silicate at 1500 rpm, in water, at room temperature or at 50°C, for (8, 16, 24, 76, 288 h) (**Figure 8**). A small degree of silicate exfoliation reveals that the layered silicate was not sufficiently hydrated and therefore did not disperse well in water. If the silicate was treated an optimal time at room temperature or better at 50°C, a much shorter time, then the

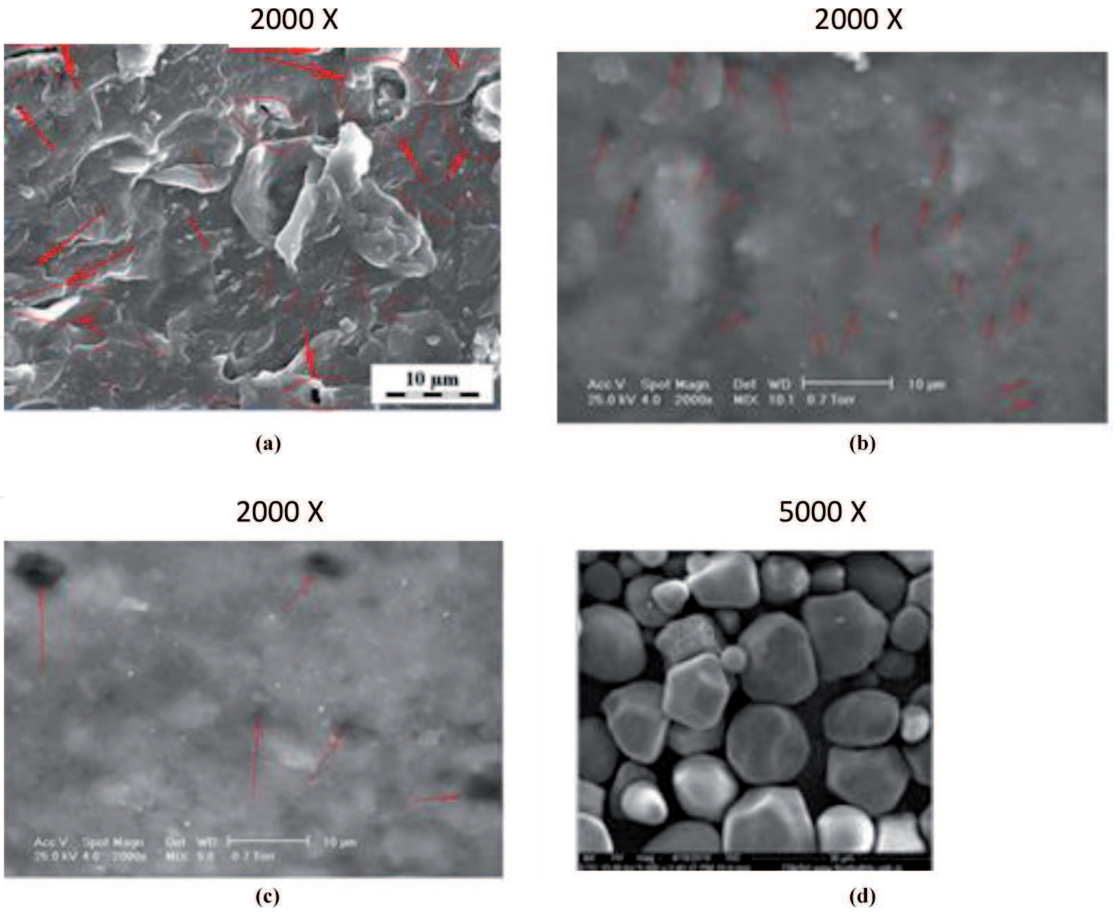


Figure 9.
Influence of silicate treatment on the surface appearance of a multiphase compound with 70% starch and 4% NaMMT (untreated (a), treated at 50°C, for 8 h (b) and treated for 24 h (c); starch particles (d) (SEM micrographs).

XRD diffractograms show the swelling of the NaMMT lamellae and even their exfoliation [91]. The obtained results show that even for starch-PVOH compounds the target fillers, well selected and properly embedded, function as efficient interface agents.

If the surface appearance of the PVOH-starch composites containing untreated NaMMT is compared with that which enclosed pretreated silicate at 50°C for 72 h, reveals that for the latter, the surface defects and the included spherical shapes with well-defined interfaces are almost disappeared (see SEM micrographs from (**Figure 9**).

As consequence of the layered silicate de-lamination the storage modulus increases from 2 to 6 MPa, for the starch-PVOH compound without silicate, to 35–40 MPa, if the blend contains NaMMT stirred with water at 50°C, for 72 h. Depending on the characteristics of the applied treatment, starch-PVOH based micro- and/or nano-structured, intercalated and/or exfoliated nano-composites were obtained [91].

8. Structuring by incorporating gaseous phase

Depending on the dynamo-mechanical modules and the glass transitions, starch-PVOH formulations were selected for obtaining biodegradable structured foams of practical interest, with a compressive strength of 5–25 MPa and which supports compressions of 80–90%.

Biodegradable foams with variable starch content were made, with open pores of 2–3 mm, storage modulus 2–40 MPa, loss modulus of 2–8 MPa and which supports

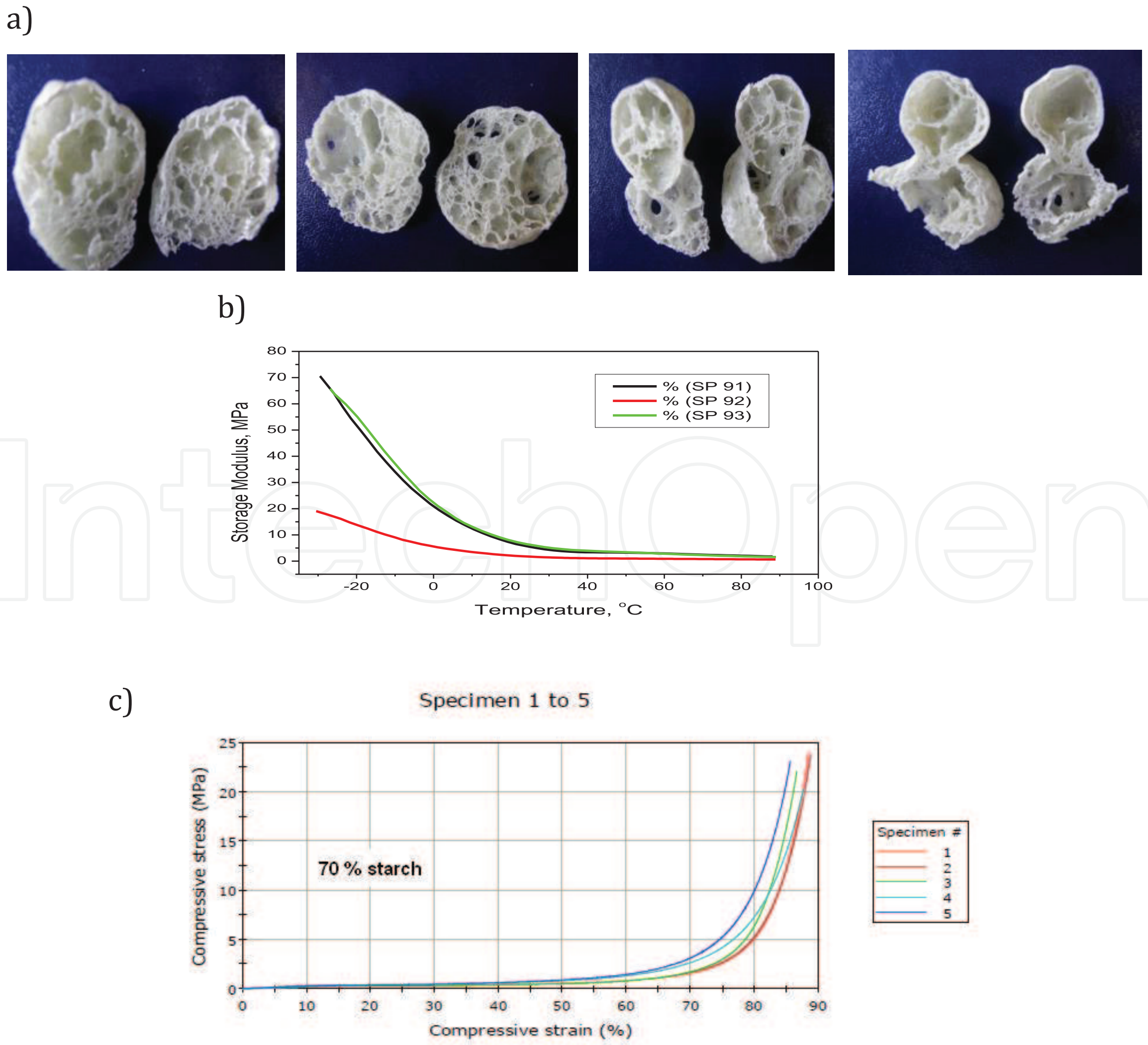


Figure 10.
Starch-PVOH-based foams (a) and their properties; (b) storage modulus; (c) compressive stress [17].

Property	**Starch content, %**			
	10	**20**	**30**	**40**
Storage modus, T = −30°C, MPa	4.5	3.5	2.5	2
Loss modulus, T = −30°C, MPa	6	7	5	4.4

Table 1.
Dependence of the storage and loss modulus on the starch content of the basic blend [17].

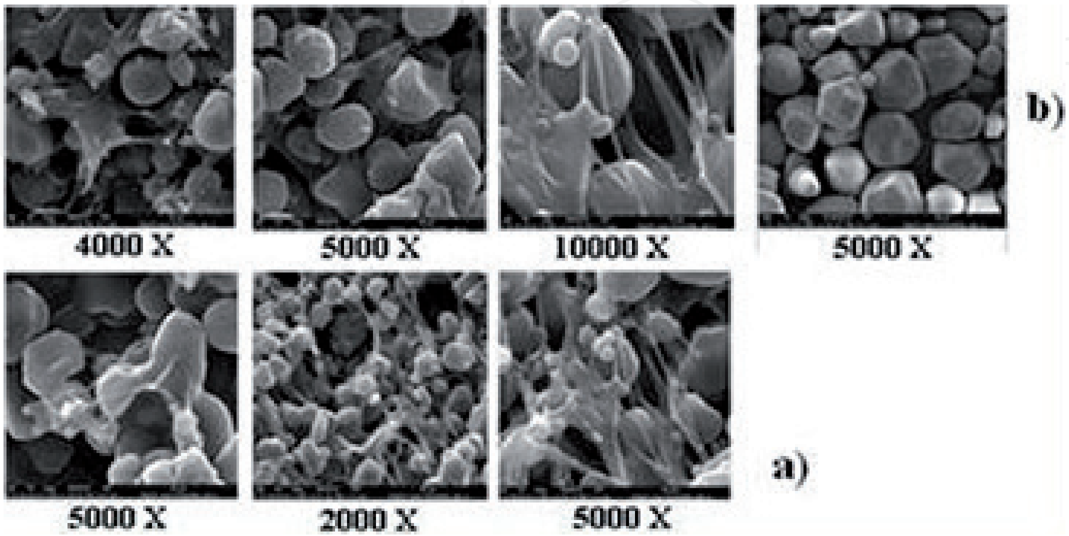


Figure 11.
Morphology of starch-PVOH based foams (a); shape and size of the starch particles (SEM micrographs) (b) [17].

a compression deformation of 60–85% (**Figure 10** and **Table 1**) [17]. By using a proper foaming agent the density of the foam was reduced to 0.219–0.458 g/cm^3. The original composition was patented [17].

Depending on the amount of foaming gas appeared, the process involves, in its first phases, only the rupture of the continuous matrix in which the dispersed gas phase is placed (**Figure 11**) [94].

9. Conclusions

1. The structuring of multiphase polymeric materials is the process of arranging the material components in an order in which, the properties of interest are achieved as far as possible. The structuring is achieved by controlling the interface properties so that to be possible the physical-chemical-biological-rheological compatibility of the components considering mainly the melt compounding.

2. To guarantee functional properties of wide application interest, the starch, which as polymer is unprofitable and limited by certain properties, can be converted into multiphase polymeric systems considering melt compounding technique which offers the possibility to dispose the minority components into the majority polymeric matrix in variants with improved compatibility and desired functional properties.

3. The multiphase polymeric systems based on starch can be structured by any method by which the phenomena of the interface are controlled such as: formulations, melt compounding parameters, the flow in the melted state to

avoid phenomena as nozzle swelling, shark skin and wall slip, incorporation of target fillers and nano-fillers, incorporation of gaseous phase, the nature and intensity of the homogenization in the melted state, etc. Some possibilities to structure some starch-PVOH compounds are deepened.

4. Structuring of multiphase systems based on starch by reactive compatibilization is connected with designing of the formulation and choosing of the melt compounding conditions which make possible the chemical bonding of dispersed phases and the base polymeric matrix and, in this way, the increasing of miscibility and the level of functional properties so that to be possible the application in sustainable fields of the new obtained starch-based materials.

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Conflict of interest

The authors declare no conflict of interest.

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