Development of biocomposite superabsorbent nanomaterials: Effect of processing technique

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Abstract

Nanoclay particles have been usually introduced into protein-based bioplastics to obtain composite materials, showing enhanced mechanical properties. However, the addition of partially exfoliated nanoclay particles in these protein matrices may also involve an increase of others properties such as water absorption capacity, which may lead to the obtention of super absorbent biodegradable materials. Processing technologies exerted a remarkable influence on the techno-functional properties of the soy-based bioplastics studied in this research. On the one hand, extrusion technique led to bioplastics which showed enhanced mechanical properties. On the other hand, injection moulding technique yielded to non-exfoliated nanoclay particles within the protein matrix, which involved improvements of water absorption capacity. The development of superabsorbent protein-based biodegradable materials implied a deep knowledge of physicochemical properties of proteins and processing conditions of bioplastics. Extrusion or injection moulding techniques could be selected to obtain tailored protein-based bioplastics with enhanced properties.

Keywords: *Biopolymer processing; Mechanical properties; Montmorillonite; Proteins; Water absorption capacity*

Introduction

Society is highly interested in substituting petroleum-based plastics by other alternative materials to diminish human footprint [1]. These alternative materials should have suitable mechanical properties, and their use should reduce environmental damages caused by existing plastic materials [2]. In this sense, plastics made from renewable sources may be considered as an alternative to satisfy the above-mentioned social requirements [3, 4]. Bio-based materials are these ones derived, at least partially, from a renewable source (i.e. biomass). Proteins, polysaccharides and lipids, among others, have been postulated as excellent candidates for developing bio-based plastic materials which may exhibit suitable mechanical properties as well as consumer acceptation [5, 6]. Among these alternatives, soybean protein concentrates are co-products from the soybean-oil industry since they are obtained during the extraction of oil from soybean seeds. This could be the cause of being the cheapest in global markets. Interestingly, these protein concentrates exhibit excellent functional properties. For instance, they have been previously used for the development of emulsions and gels [7, 8]. In addition, they show hydrophilic amino acids which could lead to superabsorbent properties [9]. However, mechanical and techno-functional properties of these bio-based systems may not be enough to substitute petroleum-based polymers [10]. Not only chemical reagents have been used to improve these properties such as sodium sulphite or urea [11–13], but also they could be improved by the use of fillers [14–16]. For instance, sodium-montmorillonite (MMT-Na^+) is a natural clay which is made up by microcrystalline silicate aggregated in thousand of layers [17, 18]. This phyllosilicate has been one of the most studied nanofillers in plastic industry. Their particles may increase both, mechanical and techno-functional properties of bioplastic obtained since they exhibit a high surface area and they can interact with protein chains. In addition, they are cheap and readily accessible [19, 20]. However, interactions between synthetic polymer chains and nanoclay particles have been proved to be crucial. The exfoliation of nanoclay particles dominates further mechanical and techno-functional properties of bio-based nanocomposite materials [21, 22]. In this sense, the processing technique selected must ensure a homogenous dispersion of nanoclays

into biopolymer matrices. Among the different alternatives available in polymer industry, there are two of special industrial interest: injection moulding and extrusion. On the one hand, injection moulding is one of the most versatile and used technique for polymer processing [21], this technique is particularly indicated for polymers that exhibit a typical thermoplastic behaviour. On the other hand, extrusion is widely used to manufacture synthetic polymers on commercial scale. This technique is preferred by plastic industry since it can be operated in continuous mode [23].

This work is devoted to clarify the relationship between processing technique (either injection moulding or extrusion) of soy-based biocomposites materials and techno-functional properties of biocomposites obtained. To achieve this objective, the focus was on: i) nanoclay structure, analysed by means of X-Ray; ii) mechanical features, tested by rheological measurements and iii) techno-functional properties analysed by means of water uptake capacity.

Experimental

Materials

Soy Protein Isolated (SPI) Surpo500E was supplied by Protein Technologies International (Leper, Belgium). Dumas method was used to determine nitrogen content and protein content was expressed as %Nx6.25. Thus, the total protein content reach up to 910 ± 5 $g \cdot kg^{-1}$; ash and moisture content were 52 ± 1 $g \cdot kg^{-1}$ and 37 ± 5 $g \cdot kg^{-1}$, respectively. Glycerol (GL) was the only plasticizer used and it was purchased together with all other chemicals from Sigma-Aldrich (St. Louis, Missouri, USA). The clay (montmorillonite) introduced was Cloisite® Na^+ (MMT-Na^+), it was supplied by Southern Clay Products, Inc. (USA).

Sample preparation

Composites obtained by injection moulding (I-M) were formulated by adding 30 $g \cdot kg^{-1}$ nanoclay to blends containing 500 $g \cdot kg^{-1}$ SPI and 500 $g \cdot kg^{-1}$ glycerol. The injection moulding procedure was carried out in two separated stages. Firstly, blends were mixed at 25ºC and 50 rpm in a mixer which allows monitoring torque and temperature values (HaakePolylab QC; ThermoScientific, Germany). After the first mixing stage, bio-based composite materials were obtained using a MiniJet Piston Injection Moulding Systmem (ThermoHaake, Germany). Processing conditions

were fixed as follows: cylinder temperature (60 ºC), mould temperature (120 ºC), injection pressure (500 Pa for 20 s) and holding pressure (200 Pa for 300 s). Two different specimens were prepared by using different moulds: (1) 60×10×1 mm rectangular-shaped specimens used for dynamic mechanical analysis (DMA) and water absorption capacity and (2) dumb-bell-type specimens by ISO 527-1:2012 for analyzing tensile properties of samples.

As for extruded biocomposites (Ex), the protein/plasticizer ratio and the amount of nanoclay used for them were exactly the same that those used for the samples obtained by injection moulding. The twin-screw extruder used was the EuroLab 16 (ThermoScientific, Massachusetts, USA). The barrel diameter is 16 mm and the ratio length/diameter (L/D) is 40. All samples were processed at a constant rotational speed of 100 rpm and with a specific set barrel temperature profile (50-55-50-45-45-45-40-35-30-120ºC from hopper to die). An electrically heated sheet-shaped die was connected to the end of the extruder barrel to form the biocomposite as ribbon and sheets with thickness between 1.0 and 1.2 mm were obtained. The effective temperature of the dye was the same as the one used for the mould (120ºC).

Methods

Dynamic Mechanical Thermal Analysis (DMTA)

Rheology of solid probes was carried out at 30 ºC by means of a RSA3 rheometer (TA Instruments, New Castle, USA) using a dual cantilever tool. Frequency sweep tests were performed from 0.02 to 20 Hz. Strain sweep tests were carried out prior to frequency sweep tests to determine the linear viscoelastic region (LVR). All frequency test were run at a constant strain value of 0.08%.

Water uptake capacity

Water uptake capacity (WUC) of these biocomposite materials was measured following the standard method ASTM D570 indicated for determining water absorption in synthetic polymers. Rectangular probes (60×10×1 mm) were used. Specimens were dried into an oven at 50 ± 2 ºC over 5-6 h (conditioning) to determine their dry weights. Afterwards, they were introduced into a specific volume of distilled water and weighed after 2 and 48h water immersion. Finally, they

were subjected to drying (reconditioning) into an oven containing silica gel at 60 ºC over 24 h and subsequently they were weighed to determine the soluble material loss. Eq. 1 shows the mathematical expression followed to determine water uptake capacity:

$$WUC = \frac{Wet\ Weight - Initial\ DryWeight}{Initial\ DryWeight} \quad (1)$$

X-Ray measurements

The crystallinity of samples was studied using a D8 Discover device (BRUKE, Massachusetts, USA). The potential and intensity of the beam in these XRD studies were 40 kV, 30 mA, respectively, where Cu K_α radiation was used (λ=0.1516 nm). The step size selected for these experiments was 0.05º, whereas the scanning range (2θ) used was within 2 to 30°.

Fourier Transform Infra-Red (FTIR)

Fourier Transform Infra-Red (FTIR) measurements were performed using a Jasco FT4200 infrared spectrometer (JASCO Inc., Tokyo, Japan) equipped with an attenuated total reflectance (ATR) system. Biocomposite samples were loaded onto the ATR crystal area and the respective spectra obtained in the transmission mode over a scanning range of 550-4000 nm at a resolution of 4 nm.

Differential Scanning Calorimetry (DSC)

A calorimeter DSC Q20 equipped with an auto sampler unit (TA Instruments, USA) was used to perform DSC analysis. Samples were weight (5 - 10 mg) and they were placed into hermetic-sealed aluminium pans. The heating rate was 10 ºC/min, with a continuous flow of nitrogen (50 mL/min) was applied.

Statistical analysis

All measurements were carried out in representative triplicate. The average from the three replicates were plotted

Results and Discussion

The complex modulus (E*) and loss tangent (tan δ) as a function of frequency for biocomposites probes processed by injection moulding (I-M) or extrusion (Ex) were plotted in Figure 1.

As can be observed, complex modulus values range from $2 \cdot 10^6$ to $1 \cdot 10^8$ Pa. Moreover, they are not strongly frequency-dependent, supporting solid-like materials remains unaltered within the overall frequency interval studied. These values are in accordance with others obtained from other bio-based composite materials [11].

It is worth mentioning that G* values are affected by the processing technique used. Thus, values obtained by injection moulding are one order of magnitude lower than those obtained by extrusion processing. This different behaviour may be related to the fact that extrusion involves a higher shear in the initial dough-like material what would allow a higher protein crosslinking during the thermomechanical processing, as well as it would increase the exfoliation of nanoclay particles introduced [24].

As it is shown in Fig. 1, tan δ exhibit a low dependence on frequency and low values that is characteristic of solid materials. It may be also noticed that biocomposites processed by injection moulding show a soft minimum value for tan δ, related to the lower planarity of G" for this system. In this sense, the higher planarity found for biocomposites processed by extrusion suggests that these systems have higher structuration. Thus, this figure puts forward the improvements of mechanical properties of bioplastics obtained by extrusion compared to those obtained by I-M.

Results obtained from water uptake capacity tests for soy-based biocomposites materials processed by injection moulding (I-M) or by extrusion (Ex) are plotted in Figure 2. These results are expressed as grams of water absorbed per kg of bioplatic after immersion in water for 2 or 24 hours. Soluble matter loss values for all the samples under study were also plotted in this figure.

As may be observed, the WUC is remarkable high in all cases studied, regardless of the processing technique used. These results may be related to the presence of many hydrophilic groups in soy proteins [25]. However, the maximum value of WUC achieved strongly depends on the processing technique used. To understand the behaviour of these composites, we should describe three different assumptions for the nanoclay exfoliation, which depends on polymer/MMT-Na^+ interactions [26]:

- If interactions are very weak, tactoids remain unaltered inside of polymer matrix. As a result, mechanical properties of the final material are not markedly different to those of the original polymer, and nanoclay particles act as a filler.
- When there are moderate interactions, the clay interlayer expands its interstitial distance and protein chains can penetrate into the gaps between different layers. In this case, an intercalated structure is formed.
- If there are strong interactions, the initial structure of the nanoclay is lost and nanoclay particles have been exfoliated.

Among them, only the last assumption has been the one related to the overall improvements of mechanical properties of synthetic polymers [27].

According to mechanical properties showed in Figure 1, and the different relationship observed between soy protein and nanoclay particles, it could be concluded that when extrusion is used as processing technique a complete exfoliation of nanoclay particles take place, which may justify the remarkable increase in the complex modulus observed in Figure 1. The high values of water uptake capacity ~~of~~ obtained for composites processed by injection moulding, coupled with the fact that rheological properties showed in Figure 1 are not as high as those obtained from the extruded composites may suggest that nanoclay particles are not completely exfoliated in the biocomposites obtained by injection moulding technique (I-M). Thus, to elucidate whether or not nanoclay particles are completely exfoliated, X-Ray measurements were carried out to clarify the different crystalline phases present in these biocomposites.

XRD diagrams for soy protein concentrate, MMT-Na^+ dust, and probes obtained from injection moulding (I-M) or extrusion (Ex) processing were plotted in Figure 3.

As may be observed, the diffractogram obtained for MMT-Na^+ dust exhibits a strong peak at 7.24º, which corresponds to the interplanar spacing of MMT-Na^+ tactoids. Moreover, soy protein exhibits two notable peaks which corresponds to the 7S and 11S subunits [28].

First of all, note that the peak numbered as 1 is present only in the composite obtained by injection moulding (I-M). Its low intensity is related to the fact that there is only 30 $g \cdot kg^{-1}$ of nanoclay in

the sample. This peak indicates the presence of a crystalline compound, which is higher than the one found for the MMT-Na^+, according to the angle at which the interplanar spacing appears. This result suggests that when the injection moulding process is carried out MMT-Na^+ nanoparticles could not be completely exfoliated, and their interlayer expand, suggesting that they might ~~have~~ take place an intercalated structure.

On the contrary, this peak cannot be observed in the diffractogram obtained from the system processed by extrusion (Ex), which indicates that the structure of this system may correspond to an exfoliated structure. These results are consistent with the higher mechanical properties obtained for Ex systems, and the higher water uptake capacity found for the system processed by I-M technique.

In addition, it is also noticeable that the peaks which correspond to the 7S and 11S structures (peaks numbered as 2 and 3) are more intense for the systems processed by extrusion. This difference may be attributed to the protein matrix that seems to enhance its structure under the processing conditions corresponding to Injection Moulding. Such enhancement might be associated to the higher residence time over which the I-M sample is subjected to high temperature (which is above the glass transition temperature, where the mobility of protein chains is higher). Additionally, the high value for holding pressure may also contribute to this enhancement. On the other hand, the mixing stage of the I-M process, that provides lower shear forces than Ex processing, does not seem to be efficient enough to completely exfoliate MMT-Na^+ clay. In any case, the effect of processing on the protein matrix does not seem to be as relevant as the effect on the exfoliation of MMT-Na^+ clay.

Fourier transform infrared spectroscopy (FTIR)

Figure 4 shows FTIR spectra obtained from biocomposite probes processed by injection moulding (I-M) or extrusion (Ex) techniques. As can be observed, these biocomposite materials exhibit different absorbance regions which corresponds with several groups such as C-N, C=O, N-H. This agrees with others authors [29–31] and it can be expected since proteins contain a wide variety of functional groups. In any case, the broader peak was obtained in the range of 3000 –

3700 nm, which has been previously related overlapping contributions of the stretching vibrations of O-H and N-H groups [32] . On the other hand, the peaks observed around 1600 and 1500 nm are characteristic for soy protein, being related to amide groups [33, 34]. Thus, the former corresponds to de CO stretching vibration (80%) and minor C-N stretching vibrations, whereas the latter corresponds to N-H bonding (60%) and C-N stretching vibration (40%) [34, 35]. Under these premises, results from FTIR suggest the processing technique selected causes changes in O-H and N-H vibrations. Thus, these vibrations seem to be lower in case of Ex probes. According to the MMT-Na^+ exfoliation above-mentioned, the nanoparticles released may difficult the mobility of these groups. At this point, it could be worth mentioning that both groups are related to the hydrophilic character of proteins, thus a reduction of its mobility may cause as well a reduction of this character, which in turn involves a reduction of the water uptake capacity observed.

Differential Scanning Calorimetry (DSC)

Figure 5 shows DSC measurements for biocomposite materials prepared by I-M or Ex processes in order to compare the thermal stability of them. As can be observed from these measurements, the materials obtained show similar profiles, which agrees with the fact that both systems have the same matrix (soy protein). On the other hand, glass transition temperature (T_g) can be calculated from these plots. In this case, these results indicate that the T_g value was 59 ºC for the systems obtained by means of I-M, whereas it increased up to 65 ºC for the system obtained by means of Ex process. Since T_g values have been previously related to the mobility of protein chains [36], the higher value obtained for the Ex systems suggest that the protein mobility for this system is lower, due to the intercalation of nanoclay particles. Moreover, these results are in accordance with the lower molecular vibration obtained for the Ex system by means of FTIR measurements.

Concluding remarks

Techno-functional properties of soy-based biocomposite materials can be improved by nanofillers such as MMT-Na^+. However, its effect strongly depends on the processing technique used. Thus,

when biocomposites are obtained by extrusion, MMT-Na^+ nanoclay particles are completely exfoliated, and consequently rheological properties are high. By contrast, when biocomposite materials are obtained by injection moulding, nanoclay particles seem to have an exfoliated and intercalated structures, which yield bio-based nanocomposite materials with higher water uptake capacity. As may be observed, techno-functional properties of these soy-based bioplastics are dominated by the relationship between the nanofiller and protein chains, which can be modulated by the processing technique selected.

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Figure captions

Figure 1. E* and tan δ for composites materials processed by injection moulding (I-M) or by extrusion (Ex) as a function of frequency

Figure 2. Water uptake capacity and loss of soluble matter of samples, immersed in water at room temperature, after 2 and 48h

Figure 3. XRD diagrams for soy protein concentrate, MMT-Na^+ dust, and probes processed by injection moulding (I-M) or extrusion (Ex)

Figure 4. FTIR spectra for probes processed by injection moulding (I-M) or extrusion (Ex)

Figure 1

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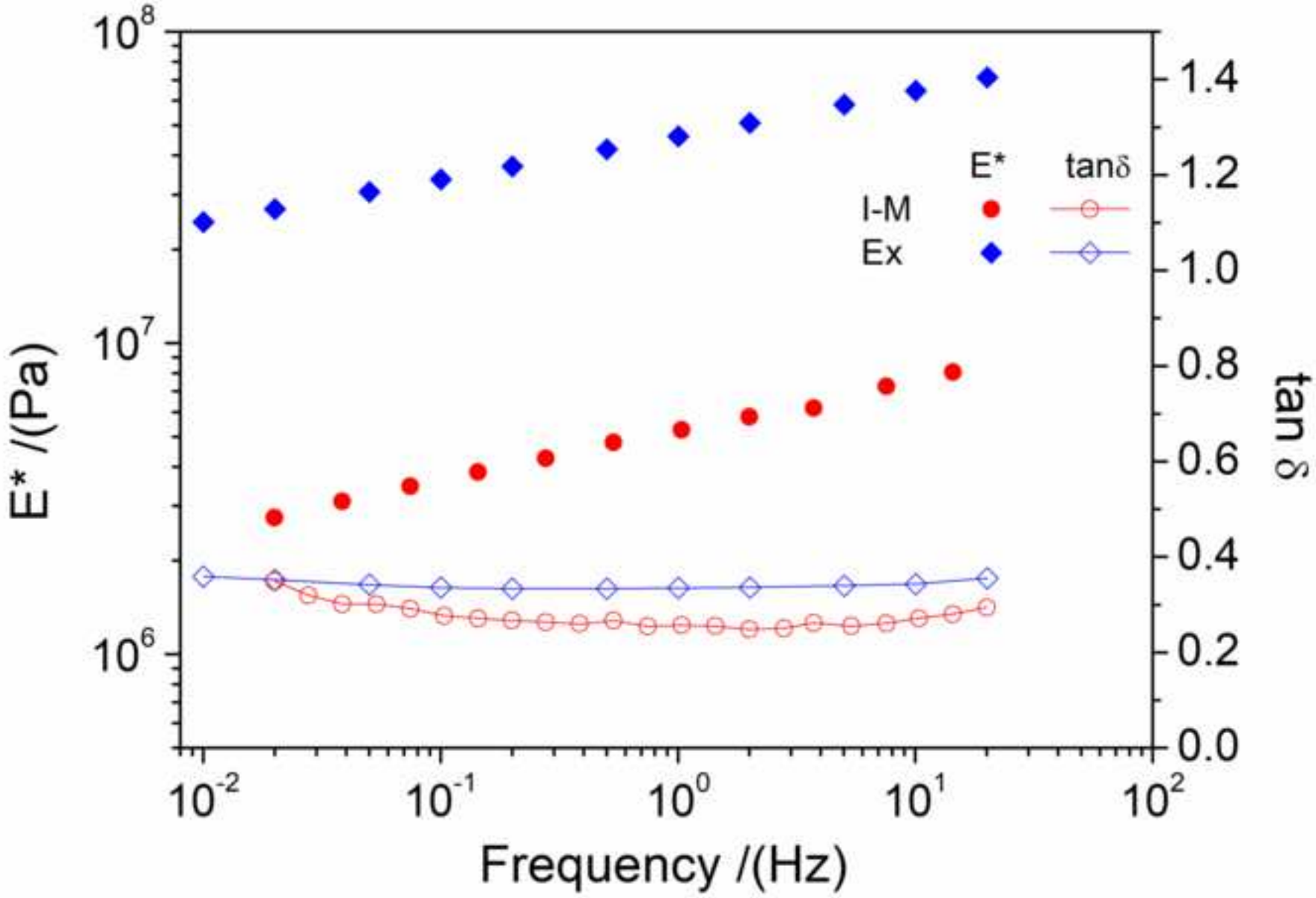

Figure 2

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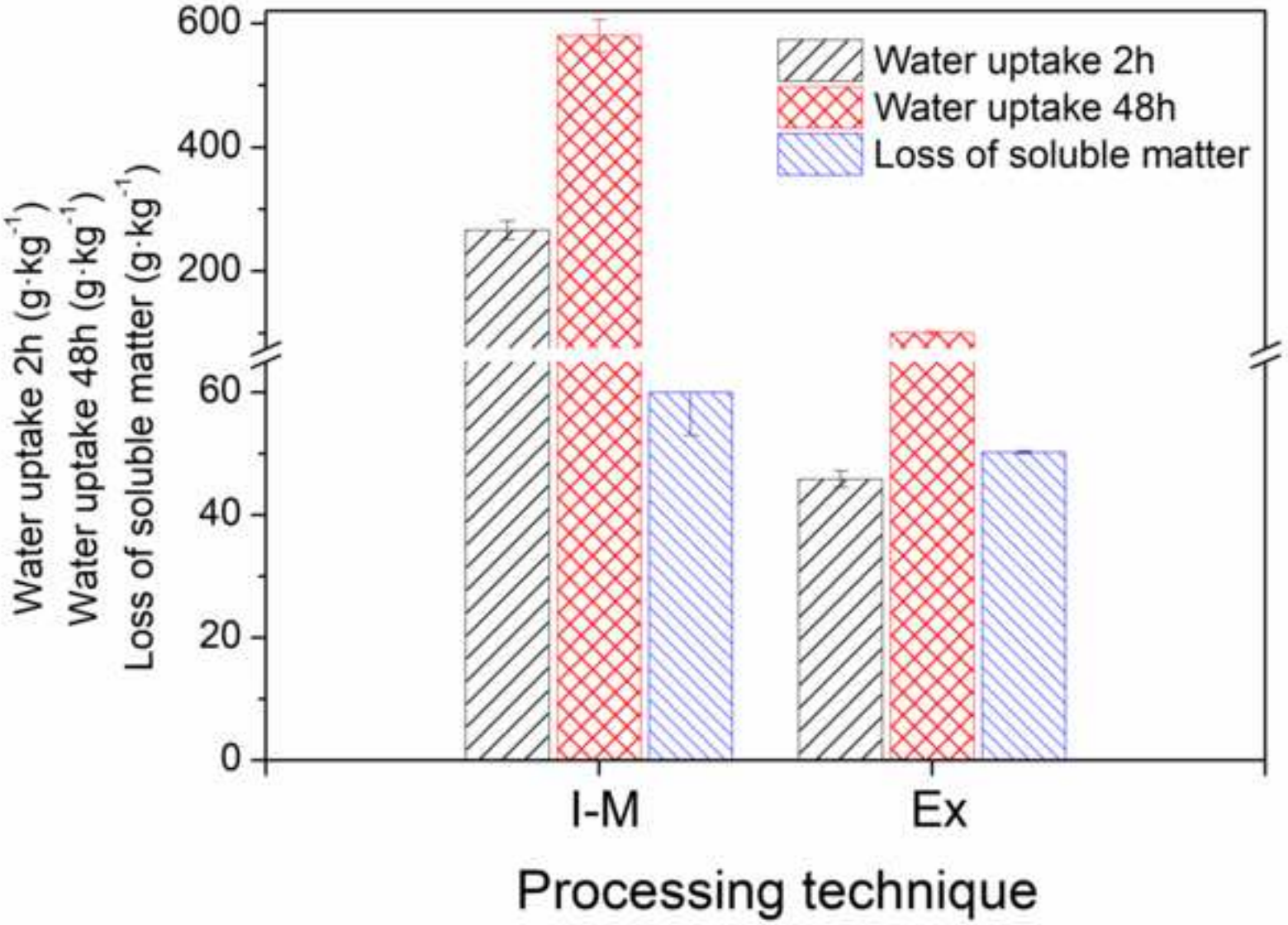

Figure 3

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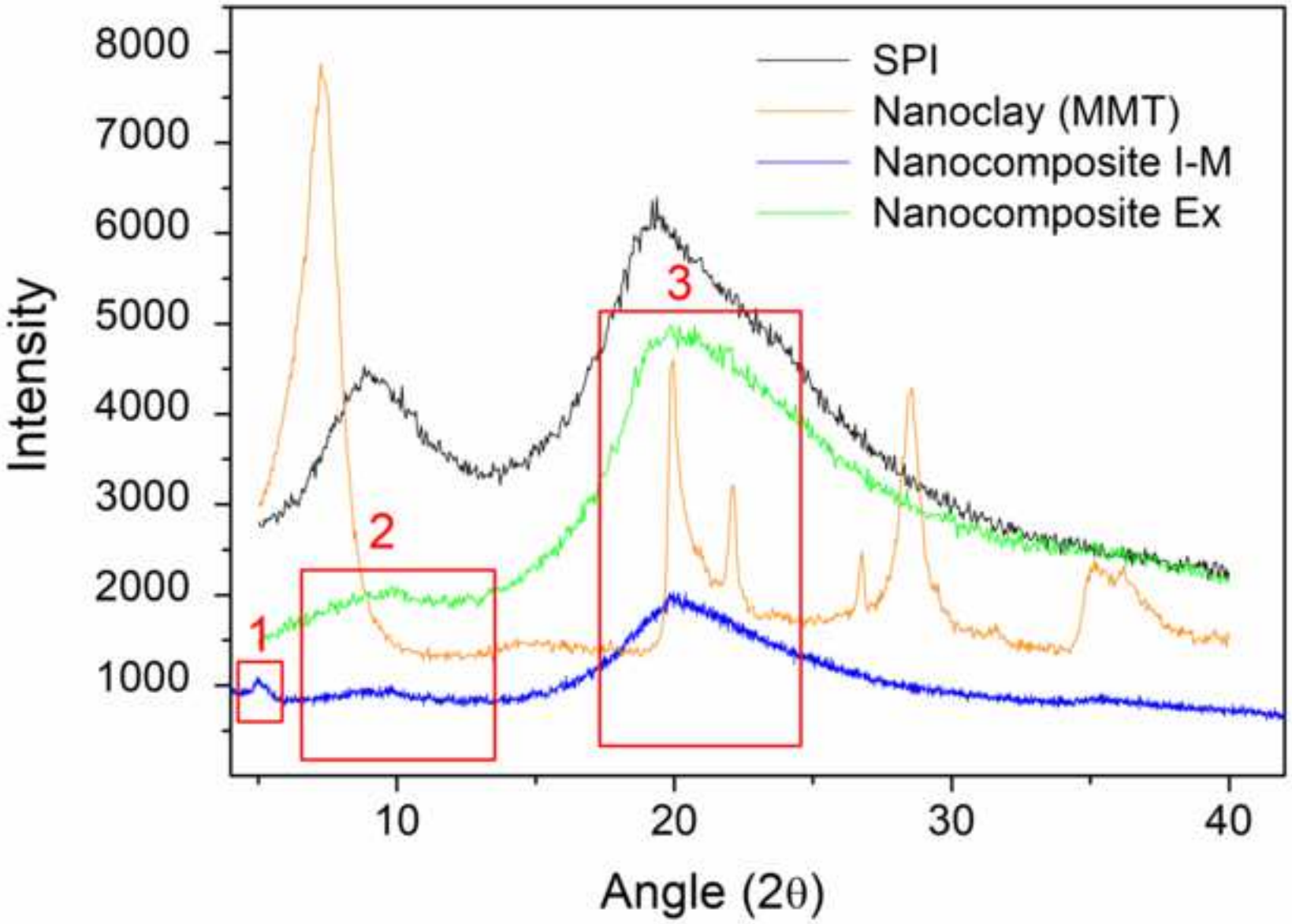

Figure 4

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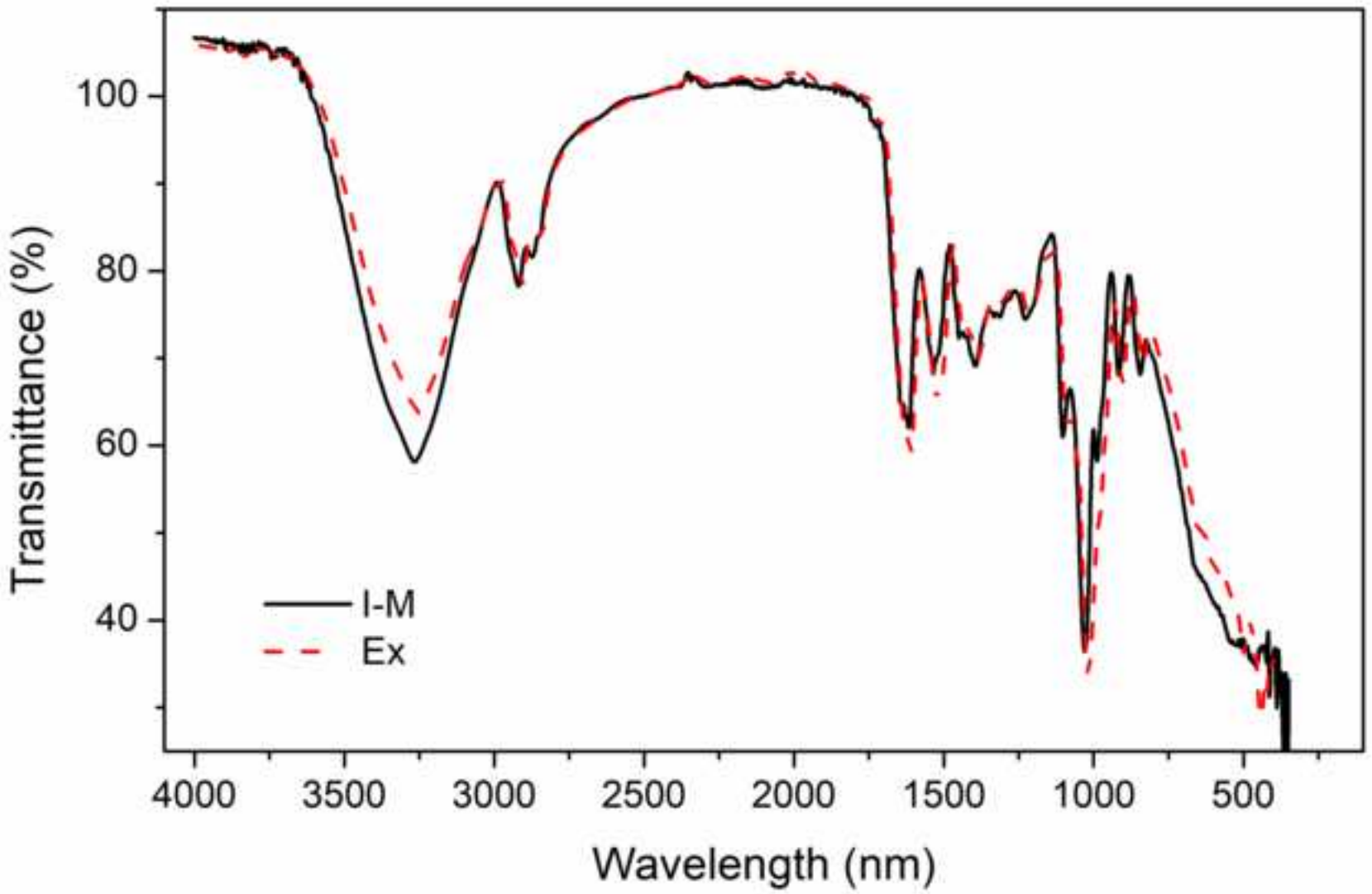

Figure 5

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