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Bio-adhesives from soy protein concentrate and montmorillonite: rheological and thermal behaviour

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Abstract

The incorporation of different amounts of montmorillonite (MMT) to soy protein concentrate (SPC) was used to improve the performance of the bio-nano-adhesive obtained. X-Ray diffraction, rheology, thermogravimetric analysis and scanning electronic microscopy were carried out to characterize the adhesives, and dry and wet strength was used to determine the adhesion strength. In the rheological measurement, the incorporation of up to 3 wt.% of MMT did not modify the consistency index values of the SPC, while an increase in the flow consistency index for higher concentrations can be observed due to a strong interaction between MMT and the protein. Besides, the flow point values increase four times with respect to the value obtained for SPC alone. The decomposition temperature of SPC increases with the addition of MMT, which provides a tortuous pathway that obstructs the diffusion of volatile products out of the bio-nano-adhesive. Further addition beyond 5 wt.% led to the formation of agglomerates, as verified by SEM. Moreover, the roughness of the fractured surface of the matrix can explain the decrease of the net adhesion of the nano-particles to the SPC suspensions.

1. Introduction

Formaldehyde based resins like urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-formaldehyde (MF) are widely used in wood industry where they have replaced protein-based adhesives due to their higher bonding properties and lower cost [1]. However, there is a growing concern, both in the scientific and industrial communities, about developing renewable, non-toxic and environmentally-friendly materials [2,3,4,5]. A potential solution to this problem is the use of soy-based products as raw materials for the production of bio-adhesives.

High-protein-content raw materials, like soybean, are commonly grown in the South American region as a result of favorable weather conditions. Moreover, Argentina is one of the largest producers of soybean and by-products. Therefore, they become relatively inexpensive and attractive as raw materials for the development of value-added products [6]. Soy protein concentrate (SPC) is obtained by processing soybean meal, reaching 60 % of protein. Nishinari and collaborators studied the main components of soybean proteins [7]. The main ingredients are four protein categories differentiated from each other by their Svedberg sedimentation coefficients: conglycinin (2S), β-conglycinin (7S), glycinin (11S) and dimer globulins (15S). Furthermore, 7S and 11S represent 80 wt. % of soy protein content and the ratio between them depends on the varieties used [8].

Soybean adhesives possess lower dry bonding strength than formaldehyde-based synthetic resins and almost no tensile strength in wet conditions. Therefore, many attempts were made to enhance dry and wet bonding properties. The strategy is to expose the protein´s reactive groups, which makes them available for interaction and reaction [9,10,11,12]. Chemical modification of protein adhesives can be complemented with other techniques in order to improve wet bonding strength of soybean adhesives and reach adhesion values similar to synthetic latex-based wood adhesives [13,14].

Various nano-particles, such as cellulose nanofibers, calcium carbonate nano-crystals and layered silicates, have been used to improve the performance of wood adhesives [15,16,17,18]. In particular, the addition of clay minerals, such as montmorillonite (MMT), could lead to an improvement in the added value of a renewable raw material [19,20].

Clay minerals are hydrous aluminum phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations found on or near some planetary surfaces. Additionally, MMT can be classified as a three-layered silicate with a 2:1 type structure and it is a member of the smectite clay family [21]. The layered structure consists of an aluminum or magnesium hydroxide octahedral sheet between two silicon oxide tetrahedral sheets. Different composite materials can be obtained by mixing layered particles into a polymer matrix [22]. Conventional composites are formed when there is no intercalation between the polymer and the clay platelets. On the other hand, intercalated or exfoliated nano-composites are obtained when good interaction occurs between both components. The improvement of several properties depends on the type of material: nano-composites show better performance than microcomposites [23].

Layered silicates have been used to enhance different properties of polymer composites due to their high aspect ratio, which promotes good interaction with the polymer at low clay concentrations [24]. Moreover, organo-clays improve the mechanical and thermal properties of synthetic wood adhesives like polyvinyl acetate and urea-formaldehyde [25,26,27,28].

The mechanical properties of protein adhesives strongly depend on the application conditions and the penetration of the adhesive into the rough substrate. For this reason, rheology is useful to understand the behavior of complex fluids and to characterize rheological parameters such as viscosity (η), storage modulus (G ') and loss modulus (G "). Rheology also provides information about the internal structure of the adhesive and the interactions that occur between the protein chains caused by chemical phenomena (weak chemical bonds) and physical phenomena (entanglements and coiling of protein long chains) [29, 30]. Furthermore, the incorporation of nano-particles affects the rheology of the material; therefore, rheological properties become important to study mixing and application conditions and to analyze the interactions between polymer chains and nano-particles [31].

The main goal of this work was to study the rheological properties of an SPC adhesive reinforced with sodium MMT and, simultaneously, to explore the improvement of thermal and mechanical properties by the incorporation of nano-particles. This work is part of a wider research plan aimed at the modification of vegetable proteins by means of additives to enhance their water resistance, in order to obtain high performance adhesives of a semistructural type.

2. Experimental

2.1. Materials

Soy protein concentrate (SPC; Alpha DK) was kindly donated by Tecnoalimenti S.A. The protein content of SPC, as measured by the Kjeldahl method, was 63 ± 2 % (w/w, dry weight; N x 6.25). Sodium hydroxide (NaOH) was purchased from Merck. TEGO Foamex 1488 was used as antifoam, provided by Clariant Argentina S.A. Sodium MMT (supplied by Southern Clay Products, USA) has a cation-exchange capacity of 0.93 meq/g clay, a typical interlayer distance of 1.17 nm, a bulk density of 2.86 g cc^{-1}, and a typical particle-size distribution between 2 and 13 μm.

2.2. Preparation of SPC-MMT adhesives

Figure 1 summarizes the procedure for adhesive preparation and characterization. Briefly, slurries were made by mixing SPC with deionized water (13% w/w) in an industrial stirrer at 300 RPM for 2 hours. Different amounts of MMT (from 0 to 9 % w/w) were dispersed in water and then incorporated into the SPC suspension. The samples obtained were denoted: MMT-1 for sample containing 1 wt. % of MMT, MMT-3 for that sample containing 3 wt. % of MMT, and so on, and the sample without MMT was denoted as MMT-0. The pH was adjusted to 12 by using a NaOH solution. A few drops of a diluted antifoam solution were added and then a vacuum was applied to eliminate air before rheological analysis or application. Before XRD and TGA/DTA analysis, the samples were freeze dried in a Virtis sp Scientific lyophilizer at -60 °C and 13 mT.

2.3. Characterization

X-ray diffraction (XRD) patterns of MMT and protein-based adhesives were recorded on a Philips PW 1710 diffractometer using a Cu K$_\alpha$ radiation (wavelength $\lambda = 0.154$ nm) at a generator voltage of 40 kV and a current of 40 mA. The analyses were carried out in the range $3 ° \leq 2\theta \leq 10 °$, with a scan rate of 1 °/min and counting time of 10 s/step.

Viscosity was measured at 25 °C, over a shear rate range of 10-250 s^{-1} using a rotational test on an oscillatory Rheometer (Physica MCR301; Anton Paar, Austria) equipped with a concentric-cone geometry (CC27). Viscoelastic properties were evaluated through amplitude sweep test at 10 s^{-1}

over a strain range of 0.01-100 % using an oscillatory test equipped with a cone-plate geometry (CP50) at 25 ℃. The viscosity of each suspension was measured 6 h after preparation. In order to obtain a representative value, the test was replicated five times for each sample and the average values were reported.

Thermogravimetric analyses were performed using a thermogravimetric analyzer (Netzsch STA 409 PC/PG; Germany) with alumina as a reference (simultaneous DTA/TGA). Samples (10.0 mg in a platinum pan) were heated to 900 °C at a rate of 10 °C/min in an air atmosphere.

The morphology of the fracture surfaces (cross-sectional surface) of the bio-nano-composite films were analyzed under a scanning electron microscope (Quanta 250 FEG; FEI Inc., OR, USA). Films were frozen in liquid nitrogen, cut using a sharp razor blade, and mounted on specimen stubs with 2-sided carbon tape. The fracture surfaces of the films were sputtered with a thin layer of gold–palladium (Au–Pd).

Dry bonding strength was measured following the procedure depicted in ASTM D2339-98 standard [32] (ASTM Standard, 2002). A Universal Testing Machine (Model 4467; Instron, Canton, MA, USA) with a cross-head speed of 2.54 mm/min was used to evaluate the dry bonding strength. The test was replicated ten times for each sample. The adhesive was manually applied, with a spread rate of 1 kg/m^2, on two pieces of hardwood (Balfourodendron riedelianum) over an area of 5.0 cm x 5.0 cm. Then samples were heat pressed together at 0.27 MPa for 20 min at 70 ℃. After that, the samples were left to stabilize for 48 h at room temperature. Prior to testing, the samples were soaked in water for 3 h and dried for one week at room temperature for wet adhesion measurement.

Results were expressed as the mean standard deviation, and the data were compared by analysis of variance (ANOVA). Means were tested with the Tukey Test for paired comparisons, at a significance level $P < 0.05$, through the use of the OriginPro 8 SR0 v8.0724 software (OriginLab Corporation, USA).

3. Results and discussion

3.1. Structure of nano-composites

The exchange of inorganic interlayer cations by organic molecules generates the interlayer or basal space modification, which can be followed by the shift of the XRD reflection peak d001 [33]. **Figure 2** shows the XRD patterns of SPC (as received) and the MMT used to prepare the bioadhesives. The MMT spectra present a peak centered at 7.5°, which is related to the interlaminar distance within galleries. This peak shift is expected to lower the values when the protein enters the galleries. SPC and MMT-0 show no significant peaks in the 2θ range from 1 to 10°, showing that the soy protein has no ordered structure in this dimension range. In the case of bio-nano-composites, no significant peaks are observed, which implies that soy proteins of low molecular weight penetrated the basal space and separated the clay platelets reaching a high degree of exfoliation / intercalation of clay in the matrix [34]. Therefore, the crystalline order of the MMT was destroyed by the intercalation with the protein and it became exfoliated. The basal spacing of MMT has been calculated to be 1.15 nm using Bragg function:

$$\lambda = 2d \, \sin \theta \tag{1}$$

SPC, MMT-0 and all bio-nano-composites showed no significant peaks in the 2θ range from 1 to 10°. indicating the disordered structure of the soy protein in this dimension range. The

disappearance or shift to low angles (< 2°) of MMT basal space could involve a reasonable degree of exfoliation / intercalation of clay in the matrix. This could mean that the soy proteins of low molecular weight entered into the basal space and separated the clay platelets by more than 4.0 nm.

Rheology can be applied to study the dispersion of montmorillonite within a matrix [35]. **Figure 3** presents the viscosity values as a function of the shear rate. The viscosity of all samples decreases as a consequence of the breaking of Van der Waals forces between the proteins' chains due to applied deformation. Lin and Gunasekaran studied the rheological behavior of protein adhesives; the relatively low viscosity at high shear rates makes the adhesive mix and pour easily, and high viscosity values at low shear rates provides good suspension properties [36]. Furthermore, a rise in the viscosity values is observed when the amount of MMT is higher than 3%, maintaining the pseudoplastic behavior. This can also be analyzed by fitting the viscosity curves to the Ostwald I method (power-law):

$$\tau = c \cdot \dot{\gamma}^p \tag{2}$$

Where τ is the shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), c is the flow consistency index (Pa.s) and p is the flow behavior index (dimensionless). **Table 1** presents c and p values for all samples. The index values for MMT-0, MMT-1 and MMT-3 are 53.98, 37.96 and 52.76 respectively. A further incorporation of MMT (higher than 3 wt. %) increases the flow consistency index, at 188.69, 205.97 and 204.48 for MMT-5, MMT-7 and MMT-9 respectively. This increment of the index reveals a strong interaction between clay and the protein chains.

Viscoelastic properties allow us to analyze the internal structure of the adhesive, which is affected by both chemical (such as interactions due to weak intermolecular forces) and physical phenomena (such as entanglement and coiling of the polymer chains). Amplitude sweeps are mostly carried out to determine the limit of the linear-viscous behavior (LVE). While G´ maintains a constant value (plateau), the sample will keep the 3D structure. When the amplitude exceeds the limit of the LVE range, i.e. G' decreases, the structure of the sample will change irreversibly.

Table 2 summarizes the results of the amplitude sweep test of all systems. It is interesting to note that rigidity enhanced from 25% to 857% when the content of MMT rose from 1 wt. % to 9 wt. %. Furthermore, ductility decreased drastically, i.e. the LVE range was exceeded at lower shear strain percentages. In agreement with data from the XRD analysis, this analysis could indicate the intercalation of the protein into the basal space of the clay platelets.

Damping Factor is known as the quotient of the lost and the stored deformation energy. It therefore reveals the ratio of the viscous and the elastic portion of the viscoelastic deformation behavior:

$$\tan \delta = \frac{G''}{G'} \tag{3}$$

At the cross-over point, i.e. tan δ = 1, the gel character (G' > G'') changes to a liquid character with (G'' > G'). The shear stress value at which the cross-over occurs is often known as the Flow Point, and it represents the amount of energy given to the system to start to flow. **Figure 4** shows tan δ values as a dependence of the shear stress. The Flow Point values of MMT-5, MMT-7 and MMT-9 were four times higher than the value of MMT-0, which could obstruct the application process by spray. Moreover, these samples may also obstruct the wetting process on the wood surface.

Figure 5 displays SEM micrographs of soybean adhesives with and without MMT. The fractured surface of MMT-0 (**Fig. 5A**) seems homogeneous and smooth. MMT-1 and MMT-3 (**Fig. 5B and 5C**) exhibit similar surface roughness in comparison with the unreinforced adhesive. However, a significant change was observed for samples containing a higher amount of MMT (5, 7 and 9 wt. %). Moreover, MMT-9 exhibits blisters in the matrix due to increased viscosity, hindering degassing. Changes in the surface roughness could be attributed to the change of direction of the tip crack due to the presence of high content of MMT, which corresponds to an energy absorption mechanism [37, 38].

3.2. Thermogravimetric analysis

Thermal analysis can be useful to determine further process conditions such as the hot press temperature of the adhesives. Protein degradation was studied by TGA/DTA. **Figure 6** shows weight loss curves as a function of temperature. Three stages can be distinguished in the degradation process of protein adhesives: In the first stage, from 35 °C to 120 °C, weight loss is assigned to evaporation of free and bonded water. The protein degradation has two more stages: from 250 °C to 360 °C and from 430 °C to 630 °C) [39].

Table 3 summarizes the decomposition temperature (T_d), which was determined by DTA. The addition of MMT led to a higher T_d, indicating a slight improvement of the thermal stability of the adhesive, which would be beneficial for industrial applications at high operational temperatures [40]. In particular, Kumar et al. studied the mechanism to improve the thermal stability of biocomposites with the addition of clays. They stated that the presence of MMT platelets reduces the diffusion rate of volatile decomposition products out of the matrix. Moreover, MMT platelets create a tortuous pathway for volatile decomposition products to diffuse out of the bio-nano-adhesive [41].

3.3. Bonding performance

Theories explaining the adhesion between bioadhesives and wood substrates indicate a combination of mechanical interaction, physical adsorption and chemical bonding. [42]. This means that, in order to achieve adequate adhesion, the adhesive must have flowability, must wet and penetrate the roughened surface of the substrate, and must work as an anchor.

Penetration of adhesives is generally believed to have a strong influence on bonding mechanical performance. Adequate penetration provides a substantial interphase that promotes interaction, perhaps reaction, and also mechanical interlocking. On the other hand, excessive penetration could lead to a "starved" bond-line that has a poor performance.

In order to use globular soy proteins in wood adhesives, the weak bonds and interactions that shape their structure must be broken, leading to a change in the viscosity [43]. In a previous work, it was concluded that the pH adjustment 12 generated desirable rheological properties and thus the best bonding performance [44]. **Table 4** shows values of dry and wet adhesion for samples with and without MMT. Dry bond strength does not change significantly with the addition of MMT in comparison with that obtained with MMT0. On the other hand, the addition of 1 wt. % and 3 wt. % of MMT produces an increase in the wet bond strength with respect to MMT-0, which could be related to the improvement of the barrier properties of the bioadhesive. Zhang and collaborators explained that the incorporation of a low concentration of ionic groups, such as Na^+ cations present

in the interlaminar space of montmorillonite, can improve the mechanical properties of polymer materials through the formation of ionomers [45]. Furthermore, the exchangeable cations act like ionic nanodomains that are covalently attached to the polymer backbone and affect the rheological and bonding properties of the adhesive. On the contrary, wet bond strength values for MMT-5, MMT-7 and MMT-9 exhibit similar values to MMT-0, which could be explained by the high viscosity values obtained for the MMT-based systems resulting in difficult interaction between the adhesive and the wood.

4. Conclusions

Bio-nano-adhesives were obtained by dispersing MMT clay into a SPC matrix. XRD, SEM and rheological analyses demonstrated a good intercalation degree of the reinforcement in those samples with lower MMT content. In these samples, wet bonding performance was improved due to the enhanced barrier properties. The interaction of the MMT platelets with the cationic groups of the side chains of the protein provides a tortuous pathway for water molecules during the wet test. Thermogravimetric analysis confirmed that the presence of MMT enhanced the decomposition temperature by creating a tortuous pathway for volatile decomposition products to diffuse out of the bio-nano-adhesive. Finally, the incorporation of a higher amount of MMT leads to an increase in viscosity, which can diminish the ability of the adhesive to wet the wood surface. This behavior decreased the wet adhesion of the nano-composites to similar values of the adhesive without nano-particles.
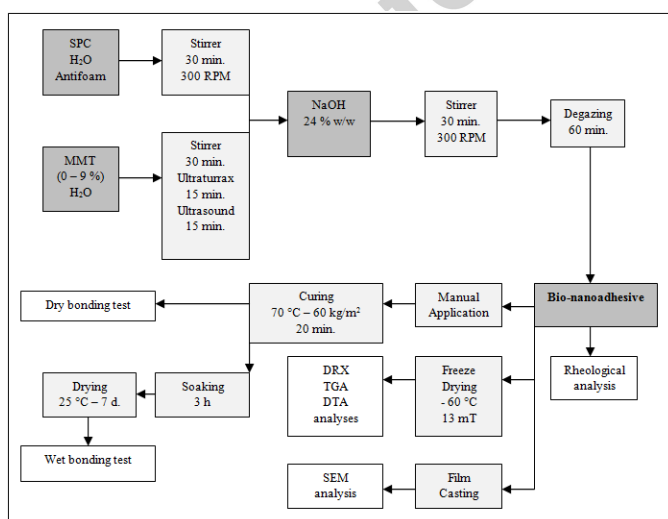
Acknowledgments

Figure 1. Flow diagram process for the preparation and characterization of SPI-MMT bio-nano-adhesives.
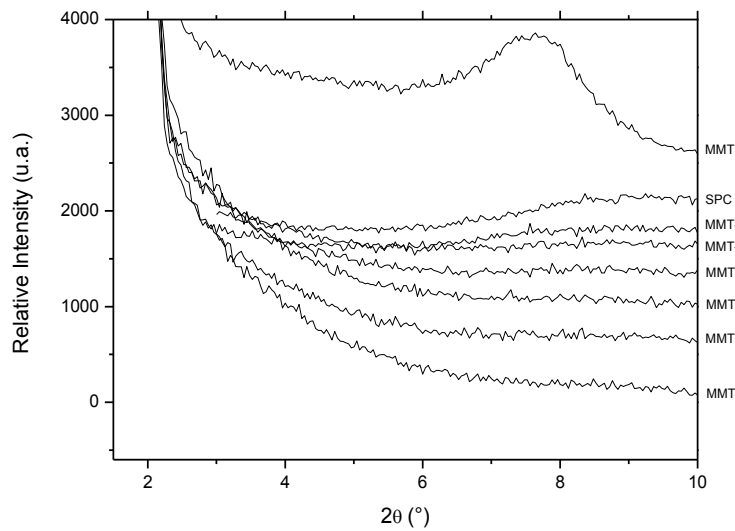
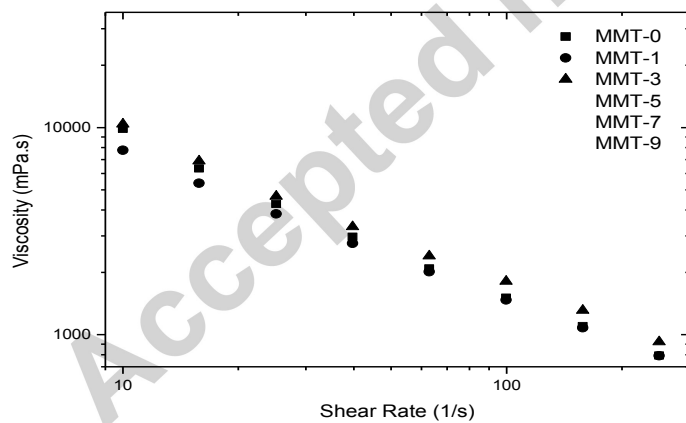**Figure 2.** X-ray diffraction patterns of MMT and bio-nano-adhesives.

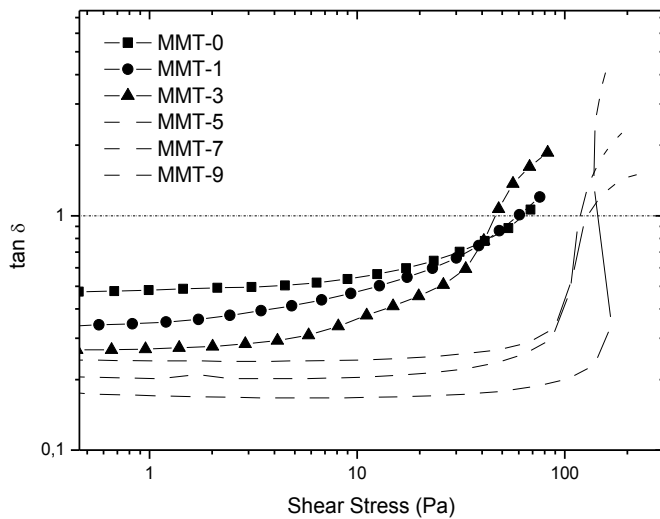**Figure 3.** Viscosity curves for bioadhesives with different MMT contents.

Figure 4. Effect of shear stress on tan δ of SPC adhesives with different amounts of MMT.
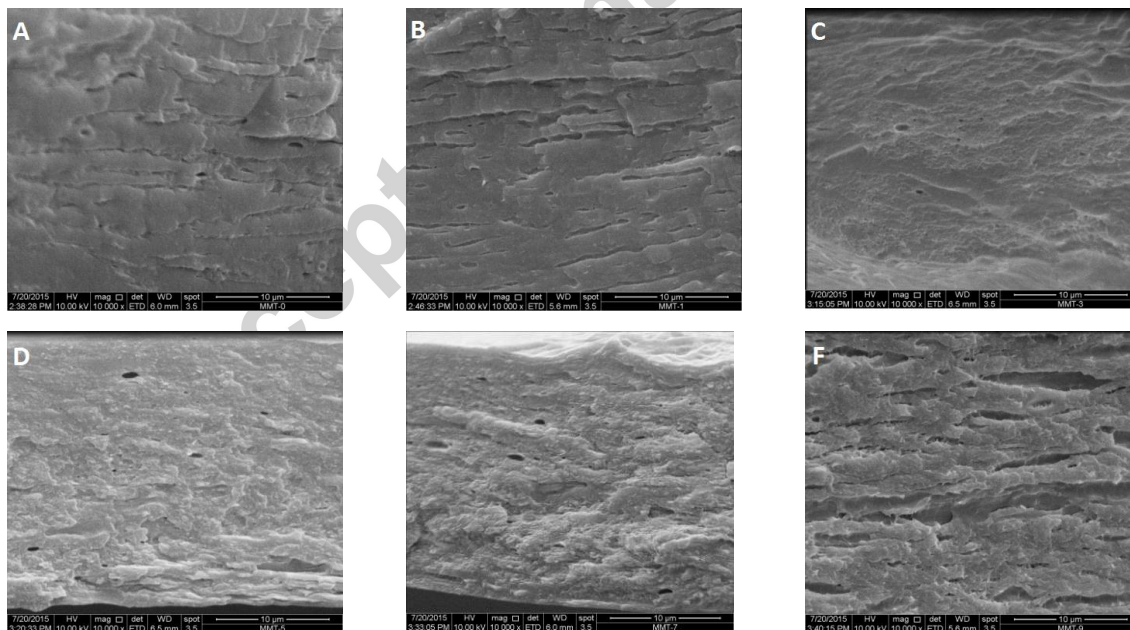

Figure 5. SEM micrographs of the fractured surface of the bio-nano-adhesives. (A) MMT-0, (B) MMT-1, (C) MMT-3, (D) MMT-5, (E) MMT-7 and (F) MMT-9.
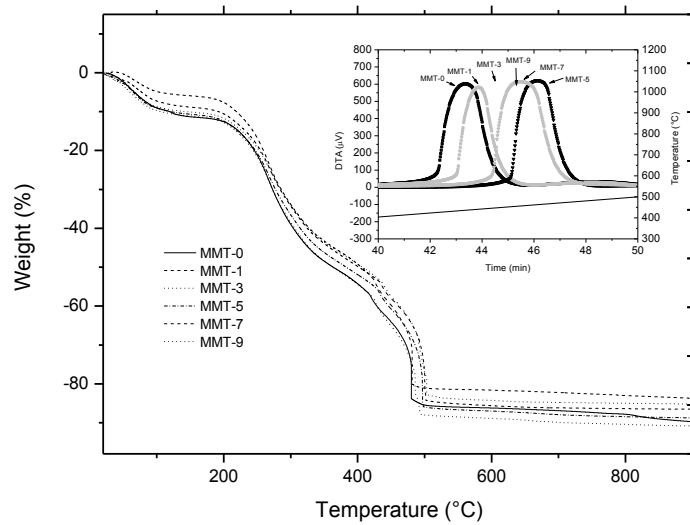
Figure. 6. TGA and DTA curves of SPC/MMT bio-nano-adhesives.

Table 1. Power-law index values of all adhesives.

Sample	c	p	R^2
MMT-0	53.98	0.23	0.971
MMT-1	37.96	0.29	0.996
MMT-3	52.76	0.26	0.984
MMT-5	188.69	0.12	0.993
MMT-7	205.97	0.19	0.804
MMT-9	204.48	0.18	0.979

Table 2. Amplitude sweep test. The values of shear strain, flow point and G' are the limit values of the LVE range.

Sample	LVE (%)	G' (Pa)	G'/G'_{MMT0} (%)
MMT-0	88.37	50.55	0.00
MMT-1	66.37	63.50	25.62
MMT-3	29.03	112.20	121.96

MMT-5	33.29	271.30	436.70
MMT-7	23.33	357.80	607.81
MMT-9	19.84	478.70	846.98

Table 3. Effect of MMT on the decomposition temperature determined by differential thermal analysis.

Adhesive	T_d (°C)
MMT-0	436.3
MMT-1	441.0
MMT-3	447.9
MMT-5	462.8
MMT-7	456.8
MMT-9	455.8

Table 4. Effect of content of MMT on bond strength of SPC adhesive.

Adhesive	Dry strength (MPa)	Wet strength (MPa)
MMT-0	3.827 ± 0.376 a	2.933 ± 0.415 a
MMT-1	3.738 ± 0.612 a	3.621 ± 0.182 b
MMT-3	3.667 ± 0.367 a	3.404 ± 0.263 b
MMT-5	3.529 ± 0.481 ab	2.838 ± 0.221 a
MMT-7	3.165 ± 0.439 ab	2.855 ± 0.473 a
MMT-9	2.827 ± 0.421 b	2.845 ± 0.325 a

Mean values ± standard deviations. Means in the same column followed by the same letter are not significantly different (P > 0.05, Tukey test).

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