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EFFECT OF SODIUM DODECYL SULFATE ON THE PHYSICAL PROPERTIES OF GELATIN/MULTI-WALLED CARBON NANOTUBES SOLUTIONS AND FILMS

EFFECTO DEL DODECIL SULFATO DE SODIO EN LAS PROPIEDADES FÍSICAS DE SOLUCIONES Y PELÍCULAS DE GELATINA/NANOTUBOS DE CARBONO

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Abstract

The effect of sodium dodecyl sulfate (SDS) on multi-walled carbon nanotubes (MWCNT) dispersion, was studied. Four gelatin film forming solutions (GFFS) with SDS concentrations of 0, 0.1, 0.6 and 1.1g/100g gelatin, containing 0.1g of MWCNT /100g gelatin, were subjected to dynamic rheology. These GFFS were used for film obtainment, to which mechanical, optical, structural (diffractometry) and thermal (thermogravimetry) analysis were determined. The surfactant effect of SDS, was better at the critical micelle concentration of 1.1g/100g gelatin, causing the best MWCNT dispersion and highest elastic modulus (G') in GFFS. Both the control and sample 0.1GFFS, at frequencies lower than 5 rad/s, behaved as mainly dilute solutions (G" > G') at 25°C, while samples 0.6GFFS and 1.1GFFS, displayed physical gel properties (G' > G") at the same temperature. At 10°C, all GFFS showed typical viscoelastic gel-like behavior. Thermogravimetry and diffractometry showed re-ordering on gelatin triple helix, when the MWCNT dispersion increased. The SDS critical micellar concentration increased 60.66% the elongation at break of films. The optical photomicrographs showed an improved homogeneous distribution of the MWCNT, as the SDS concentration increased.

Keywords: sodium dodecyl sulfate, multi-walled carbon nanotubes, dynamic rheology, dispersion, gelatin films.

Resumen

Se estudió el efecto de dodecil sulfato de sodio (SDS) en la dispersión de nanotubos de carbono de pared múltiple (MWCNT), de soluciones formadoras de película de gelatina (GFFS). Cuatro GFFS con concentraciones de 0, 0.1, 0.6 y 1.1g SDS/100g de gelatina y con una concentración de MWCNT (0.1g/100g de gelatina), se sometieron a reología dinámica. Las GFFS fueron utilizadas para la obtención de las películas, determinando sus propiedades mecánicas, ópticas, difractométricas y termogravimétricas. El efecto tensoactivo del SDS fue mejor a la concentración micelar crítica de 1.1g/100g de gelatina, produciendo la mejor dispersión de los MWCNT y el mayor módulo elástico (G') de las GFFS. El control y 0.1GFFS a frecuencias inferiores a 5rad/s, se comportaron como soluciones diluidas (G' > G'), mientras que 0.6GFFS y 1.1GFFS mostraron propiedades físicas de un gel (G' > G") a 25°C. A 10°C, todas las GFFS mostraron un comportamiento típico de gel viscoelástico. La termogravimetría y difractometría mostraron un re-ordenamiento tipo triple hélice en la película, al aumentar la concentración de SDS. La concentración micelar crítica del SDS aumentó el porcentaje de elongación en las películas (60.66%). Las fotomicrografías ópticas mostraron una distribución homogénea de los MWCNT conforme la concentración de SDS incrementó.

Palabras clave: dodecil sulfato de sodio, nanotubos de carbono de pared múltiple, reología dinámica, dispersión, películas de gelatina.

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1   Introduction

Undegradable plastic residues accumulation, have caused environmental pollution problems, giving place to research on new biodegradable materials, with functional properties similar to synthetic plastics. Several studies on production of films or coatings, using different biopolymers, such as polysaccharides, lipids and proteins have been undertaken successfully (Martucci and Ruseckaite, 2010; Ramírez-Hernández *et al*., 2015). Natural biopolymers have the advantage of being biodegradable, renewable and in many cases, edible. However, films made from biopolymers have shown poor mechanical and barrier properties compared to traditional polymeric films, limiting its commercial use (Herrera-Franco *et al*., 2016).

Bovine gelatin is a biopolymer known from ancient times, being one of the materials used initially to manufacture films, which is still used for this purpose, because it is an abundant raw material, with low production costs, world-wide accessible and easily handled during film formation (Morães *et al*., 2009). This biopolymer is a water-soluble protein, obtained by either acid or basic hydrolysis of collagen. Gelatin is used in a lot of applications, such as jellying agent, dispersant, pharmaceutical capsules and potentially, in the formulation of new biodegradable packages (Andreuccetti *et al*., 2009)

Gelatin films are very susceptible to the environmental conditions, especially to the relative humidity (RH), so that when this factor varies, both the mechanical and barrier properties deteriorate drastically (Andreuccetti *et al*., 2009). Several attempts have been made to overcome these limitations, such as the combination with other components, as the poly vinylalcohol (Morães *et al*., 2009), glutaraldheydes (Bigi *et al*., 2001), cross-linking with transglutaminases (Lim *et al*., 1999), use of plasticizers as glycerol (Rivero *et al*., 2010), tributyl citrate, acetyl-tributyl citrate, triethyl citrate and acetyl-triethyl citrate (Andreuccetti *et al*., 2009).

Over the last years, a great interest in the research of the use of nanoparticles in polymers has risen, due to its cross-linking capacity that improves remarkably the polymers properties, when used either alone or with macro-particles. The potential improvements involve a higher mechanical strength, increase heat treatment resistance, better barrier properties and weight reduction (Sinha Ray and Okamoto, 2003).

Multi-walled carbon nanotubes are comprised from 2 to 30 concentric graphitic layers, whose diameters range from 10 to 50 nm and lengths that can reach up to more than 10 μm (Yumura, 1999). One single perfect carbon nanotube is from 10 to 100 times stronger than steel, but six times lighter (Demczyk *et al*., 2002). Due to its high hydrophobicity, MWCNT tend to agglomerate (Rausch *et al*., 2010), on this status, they do not cause any effect, since they need to be homogeneously dispersed to be able to give a continuous support to materials (Huang and Terentjev, 2008). Several dispersion methods of MWCNT in polymeric solutions can be found in the literature, such as; chemical surface modification (Shieh *et al*., 2010), use of ultrasonication (Park *et al*., 2002) and use of solvents (Yu *et al*., 2007).

In a previous work, the effect of MWCNT on gelatin films without considering the effect of differing sodium dodecyl sulfate concentration, on carbon nanoparticles dispersion was studied (Ortiz-Zarama *et al*., 2014). Thus, the aim of this work was to manufacture films from the biopolymer gelatin, assessing the effect of MWCNT dispersion, by the addition of various SDS concentrations, on its filmogenic solutions rheology and films physical properties.

2   Materials and methods

2.1   Materials

Commercial type "B" bovine gelatin with 290 °Bloom (Duche, México); analytical grade glycerol (Fermont, Mexico); multi-walled carbon nanotubes (MWCNT) (China) and analytical grade sodium dodecyl sulfate (SDS) (Reasol, Mexico) were used. To maintain the films moisture, analytical grade sodium bromide (NaBr, Fermont, Mexico), was employed.

2.2   Obtainment of filmogenic solutions

A previous work (Sifuentes-Nieves *et al*., 2015), used three different concentrations of MWCNT and SDS (0.1, 0.2 and 0.4 g/100g gelatin), with no optimum combination MWCNT-SDS for an adequate MWCNT dispersion found within the above concentration range; that is why it was decided for this work, to use the lowest MWCNT concentration, but increasing the amount of SDS, seeking for the effect on its film properties. For surface tension tests, about six lots of eight GFFS containing SDS at different concentrations (0, 0.01, 0.1, 0.2, 0.3, 0.6, 1.1 and 2.2 g/100g gelatin) and one concentration of MWCNT (0.1 g/100g gelatin) were prepared using distilled water. These were put into an ultrasonic water bath at

60°C for 4 h. Besides, solutions with 9 g gelatin/100 g water, containing 33.3 g glycerol/100g gelatin were prepared at 60°C with distilled water, subjected to continuous agitation using a magnetic stirrer. The gelatin-glycerol solutions were mixed with each of the above eight mentioned solutions containing SDS and MWCNT, and put into the ultrasonic water bath at 60°C for 1h to obtain the GFFS. From the surface tension results, four GFFS were selected and prepared with 0.0, 0.1, 0.6 and 1.1 g SDS/100g gelatin, for the rheological tests, which will be named throughout the text as control, 0.1GFFS, 0.6GFFS and 1.1GFFS respectively.

2.3 Manufacture of films from gelatin

Four SDS concentrations were used: 0.0 or control, 0.1, 0.6 and 1.1 g/100g gelatin. The above selected GFFS were poured on squared Petri dishes with an area of 529 cm^2 (23 x 23 cm), and dried in an oven at about 45°C during 24 h. Then, the films were detached from the plates and stored in a desiccator for 7 days at room temperature with an RH of about 57%, provided by a saturated solution of NaBr (Mali and Grossmann, 2003). Throughout the text, the mentioned gelatin films (GF) will be named respectively as control, 0.1GF, 0.6GF and 1.1GF. Film thicknesses were measured with a micrometer (Mitutoyo Corp., Tokyo, Japan), 10 times along the GF, over a length of 10 cm.

2.4 Surface tension

A Du Noüy interphase tensiometer (CSC, Fairfax, Va.-USA) equipped with a 1.9 cm Du Noüy platinum ring was used to measure all GFFS surface tension (n=15). The critical micellar concentration (CMC) was calculated by linearizing the data.

2.5 Dynamic viscoelastic tests

Rheological oscillatory or dynamic tests were undertaken at two stages (25 and 10°C), using a stress controlled Rheometer TA Instruments, Model AR1000, on its strain mode, with a cone and plate system, diameter of 60 mm, angle of 2°, and a gap of 0.64 mm. These tests were used to measure the viscoelastic profiles of control, 0.1GFFS, 0.6GFFS and 1.1GFFS. To define the linear viscoelastic region (LVR), strain amplitude sweeps were carried out within the range 0.1 to 15%, at a constant frequency of 6.28 rad/s, setting at 25 and 10°C.

Frequency (ω) sweeps were run from 0.628 to 62.8 rad/s, at a constant strain of 10%, which was within the LVR. All measurements were done in triplicate. All oscillatory tests were done isothermally; starting at about 25°C and then at 10°C, by cooling down the samples at 5°C/min. All samples were let in rest at each temperature for about 5 minutes, before starting any test, to dissipate any previous strain. To avoid any moisture losses during tests, the solvent trap of the geometry was filled with distilled water. The storage or elastic modulus (G'), the loss or viscous modulus (G") and the loss tangent or tanδ (G"/G'), were evaluated using the software from the equipment. To evaluate the type of gel formed by the gelatin, the Eq. (1) was used; where *n* and *K* are constants, *n* is the degree of frequency dependence (Egelandsdal *et al.*, 1986; Tunick, 2011).

$$\log G' = n\log\omega + K \qquad (1)$$

2.6 Thermogravimetric analysis (TGA)

A thermogravimetric analyzer linked to a computer for control and data analysis was used. The method suggested by Hoque *et al.* (2011) was followed, where a platinum pan was taken previously to constant weight to do all measurements. Samples of pure MWCNT, control, 0.1GF, 0.6GF and 1.1GF were analyzed. All measurements were done by triplicate. About 4 to 10 mg of sample were weighed, the heating sweeps were done from room temperature till 600°C, at a heating rate of 5°C/min to achieve a total sample calcination. Pure nitrogen at a rate (flux) of 20 ml/min was circulated through the oven, to maintain an inert atmosphere. Two plots were obtained; one using the film weight change versus temperature and the other one, that of the corresponding to the first derivative of thermogravimetric analysis (DTGA). Data were gathered and analyzed with the program TA Instruments Universal Analysis 2000.

2.7 X-ray Diffraction (XRD)

To obtain the X-ray diffraction patterns of control, 0.1GF, 0.6GF and 1.1GF, samples were cut into pieces of 1.5 x 2 cm. A diffractometer Panalytical, model XPERT MRD equipped with a Pixel detector was used, in the reflection geometry within the angular range 3-400 (2θ), with Cu radiation operated at a voltage of 45 kV and 40 mA, with an angular step of 0.02° in a registering time by an angular step of 298 s. Chart speed with a constant rate of 2q/min was used.

2.8 Mechanical tests

The tensile strength (TS, MPa) and the elongation at break (EB, %), were measured following the standard method of the American Society for Testing and Material (ASTM D882 - 12, 2012) in a universal texture analyzer (TA model XT2i, Stable Micro Systems, Ltd., Godalming, Surrey UK.), using a cell calibrated at a maximum load of 25 Kg. Samples of control, 0.1GF, 0.6GF, and 1.1GF that were previously cut and shaped following the American Society for Testing and Material (ASTM D638 - 10, 2010), were maintained at an RH of about 57 %, for seven days. The distance between the griping plates of the texture meter was of 6 cm. A deformation rate of 0.3 mm/s was used. The TS was evaluated at the point of maximum force, and the EB was taken as the maximum distance the sample was deformed before breaking. A total of 60 samples were tested for each type of film.

2.9 Photon optical microscopy

Micrographs were taken for each type of film, in areas selected randomly. These were captured with a stereoscopic microscope (NIKON model SMZ 1500, Japan), assembled to a digital camera (MTI model 3CCD, Dage-MTI Inc., Michigan, USA), using a diascopic illumination, an objective of 1.5X and a zoom of 0.75.

2.10 Statistical analysis

In all cases, the experimental data plots were obtained using OriginPro, v8 (Origin Lab Corporation, Northampton, MA, USA). To identify differences between the degree of frequency dependence (*n*) at 25°C and 10°C, the tensile strength (TS) and the elongation at break (EB); an analysis of variance (ANOVA) was applied using the program SigmaPlot version 11.0, followed by a Tukey multiple comparisons test when differences were found. The significance level (P) was 0.01 in all cases (Montgomery, 2006).

3 Results and discussion

3.1 Surface tension

Fig. 1 shows that the increase in the SDS concentration, decreased the surface tension from 56 to 46 (mN/m), it was also found a critical micellar
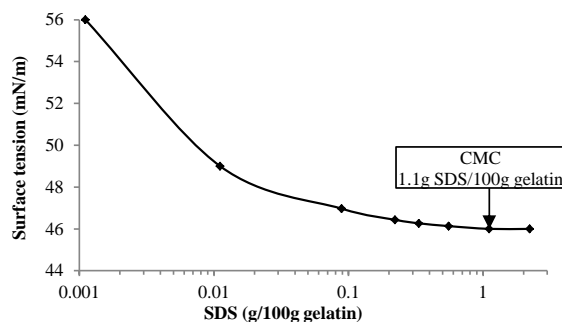

Fig. 1. Surface tension of gelatin filmogenic solution with eight different SDS concentrations, showing the critical micellar concentration (CMC) at 28 ºC.

concentration (CMC) of about 1.1 g SDS/100g gelatin with 0.1g MWCNT/100g gelatin. A higher amount than 2.2 g SDS/100g gelatin, did not allow an adequate gelatin film formation, because SDS at high concentrations denature proteins completely, due to its link to the protein chain, interfering with any link among protein chains. Since both gelation and film formation depend on bonds re-formation (renaturation) of protein chains, these events were noticeably affected (Srinivasan, 1996).

According to Jiang *et al*. (2003), when SDS concentration is very low, its adsorption is very poor, and thus, there are not enough electrostatic repulsion forces, which may counteract the van der Waals forces that keep the MWCNT agglomerated. But, if the SDS concentration is high, two events might be observed; on the one hand, the MWCNT clusters become big and dense, which might probably be attributed to a decrease in the electrostatic repulsion forces among the MWCNT, due to an increase in the size of SDS micelles in the aqueous solution, which could no longer be inserted among the MWCNT clusters. Thus, no MWCNT dispersion was attained. On the other hand, the osmotic pressure of the system increases, promoting an attraction among the MWCNT (i.e., depletion attraction) which tends to agglomerate again.

Yu *et al*. (2007), studied the optimum conditions to disperse highly concentrated MWCNT dispersions in SDS solutions, finding that the highest concentration (g/100g solution) to disperse 1.4 g MWCNT /100 g, was about 2.1 g SDS /100 g. Jiang *et al*. (2003) obtained stable colloidal dispersions, reporting as optimum concentrations (g/100g solution), 2.0 g SDS/100 g with 0.5g MWCNT/100g in distilled water. This apparent inconsistency in the reported data is because the MWCNT dispersion might be affected by the surface chemistry and length of MWCNT.
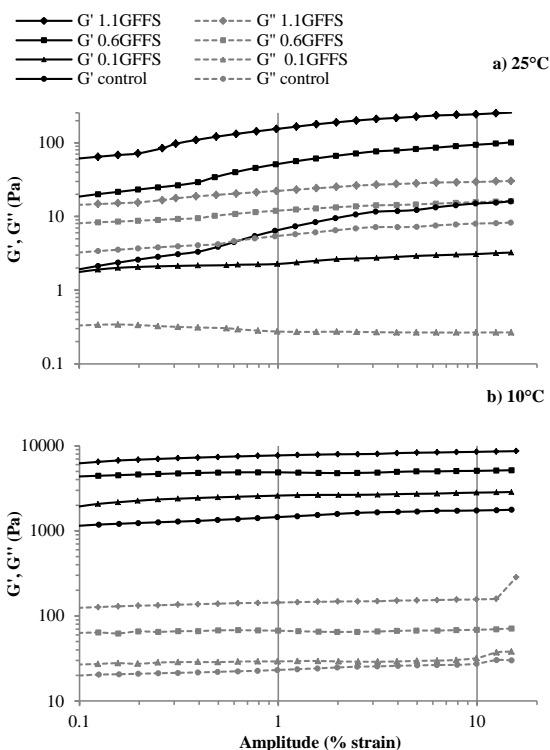
Fig. 2. Strain amplitude sweep at 6.28 rad/s, of gelatin film forming solutions prepared with 0.1g MWCNT/100g gelatin and 0.0, 0.1, 0.6 and 1.1g SDS/100 g gelatin named as control, 0.1GFFS, 0.6GFFS and 1.1GFFS respectively a) at 25°C and b) at 10°C.

3.2 Dynamic viscoelastic tests

The storage and loss moduli (G', G") profiles of the strain amplitude sweep undertaken to the GFFS, at the two previously mentioned temperatures (25 and 10°C), showed generally flat plots (Fig. 2a-b), with the values of the moduli independent of the applied strain over the range 2 to 15%, which might well be considered within the LVR, taking then, the value of 10% strain for all frequency tests.

Except for Control at 25°C, predominance of G' is observed at both temperatures, although the profiles at 25°C are more widespread than those at 10°C, the higher the SDS addition, the higher the elastic character values, being this trend more notorious at 25°C (Fig. 2a), where a "stabilization" period is observed from nil to 2 % strain, an event not seen at 10°C (Fig. 2b), suggesting a more homogeneous or stable structure at this last temperature.
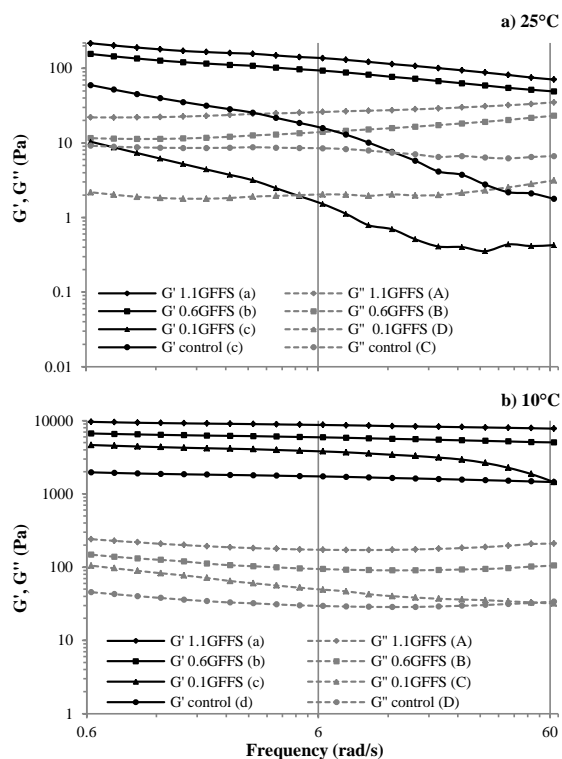

Fig. 3. Frequency sweep profiles of the storage and loss moduli (G' and G"), of gelatin filmogenic solutions, with 0.1g MWCNT/100g gelatin and 0.0, 0.1, 0.6 and 1.1g SDS/100 g gelatin named as control, 0.1GFFS, 0.6GFFS and 1.1GFFS respectively a) at 25°C and b) at 10°C.

Fig. 3a shows the results of the frequency sweep at 25°C, at this stage, except for 0.1GFFS, all plots are approximately linear with some frequency dependence, but no evidence of sudden changes in moduli, which could indicate a breakdown in the structure of the materials under test. The control and 0.1GFFS showing a cross-over at about 12 and 8 rad/s respectively, behaved as entangled networks, these were soft gels with strong G' versus ω profiles dependence and a G'-G" crossover, meaning that they were liquid-like at low frequencies and solid-like at higher frequencies (Tunick, 2011).

For 0.6GFFS and 1.1GFFS, the elastic modulus predominated (G' > G"), all over the frequency range applied, this behavior is consistent with that of physical gels, which are intermediate between strong and weak gels, having some frequency dependence and no G'-G" crossover (Tunick, 2011). Overall, an improvement of the moduli profiles was seen in samples with more than 0.1g SDS/100g gelatin, being however, in essence the same shaped curves as the

control, suggesting that the dispersed MWCNT, had induced some strengthening of the original structures.

The value of frequency dependence degree (*n*) for control and 0.1GFFS showed no statistically significant difference (P > 0.01). Thus, no effect of SDS on MWCNT at the lowest SDS concentration (0.1 g SDS/100g gelatin) was found, because of a low nanomaterial dispersion. The *n* values for 1.1GFFS and 0.6GFFS also showed no statistically significant difference (P > 0.01), i.e., no difference between the concentrations of SDS used was detected. On the contrary, the *n* values for Control/0.1GFFS and 1.1GFFS/0.6GFFS showed statistically significant differences (P ≤ 0.05). Control/0.1GFFS presented *n* values close to -0.8, and 1.1GFFS/0.6GFFS presented *n* values around -0.2 (Table 1). A perfectly cross-linked (covalent) gel has a *n* value of about zero. Therefore, 1.1GFFS/0.6GFFS systems approached a covalent gel-like behavior (Tunick, 2011).

When all GFFS were cooled down to 10 °C (Fig. 3b), the G' profiles were nearly ten times as much as those of G", showing all systems a behavior between cross-linked gels and physical gels (G' > G"), as found by Yang *et al*. (2015) at 20°C. According to the *n* value (Table 1), the behavior of 1.1GFFS was closer to that of a cross-linked gel, followed by 0.6GFFS and the control. Cross-linked gels are strong systems with permanent covalent networks and low frequency dependence. While the behavior of 0.1GFFS was closer to that of a physical gel, which is intermediate between strong and weak gels, with some frequency dependence and no G'- G" crossover (Tunick, 2011).

It could be expected that gelatin coils assembled into triple helices links, forming a network that resulted in a gel. This trend is probably related to the network conformation of the samples structure,

giving place to more elastic than viscous systems. Overall, both moduli (G', G") had quite flat frequency profiles. At 10°C, there is an explicit dependence of the moduli values with the SDS concentration added, with a general G' and G" increase as SDS increased, indicating the already mentioned strengthening of the existing structures. As known, systems that provide true gels usually show these frequency profiles, suggesting that the applied strain on the network structure is entirely reversible. Besides, from the molecular viewpoint, it has been proved that the elastic character is a function of the number of chains enabled to take part in a network structure (Gómez-Guillén *et al*., 2007).

Moniruzzaman and Winey (2006) found that for MWCNT and polymer solutions, the linear viscoelastic response, may give an indirect measurement of the dispersion status of MWCNT in composite materials, where an adequate MWCNT dispersion, could be related to high values of G', or to a lower slope of the frequency sweep plots. On this basis, in this work it was found the highest G' values for 1.1GFFS, being consistent with the surface tension results, and also agreeing with the theory that the optimum SDS concentration to disperse MWCNT, is achieved when this is similar or slightly lower than that of the critical micellar concentration (Jiang *et al*., 2003).

Respect to the $\tan \delta$ data (Fig. 4a-b), which is the ratio of the energy lost to energy stored in a deformation cycle, reflecting the phase changes taking place in the material, it can be seen in Fig. 4a, that the control and especially 0.1GFFS showed frequency related behavior, since at frequencies lower

Table 1. Degree of frequency dependence (*n*) at 25°C and 10°C from gelatin film forming solutions (GFFS). Tensile strength (TS), and elongation at break (EB) from gelatin films (GF), prepared with 0.1g MWCNT/100g gelatin and 0.0, 0.1, 0.6 and 1.1g SDS/100 g gelatin named as control, 0.1GFFS or 0.1GF, 0.6GFFS or 0.6GF and 1.1GFFS or 1.1GF respectively.

Sample	*n*	*n*	TS	EB
	25°C	10°C	MPa	%
Control	-0.789 ± 0.039[b]	-0.0445 ± 0.0036[a]	14.759 ± 1.747[a]	33.361 ± 4.579[d]
1.1 GFFS - 1.1GF	-0.859 ± 0.055[b]	-0.0519 ± 0.0071[b]	12.900 ± 1.833[b]	60.665 ± 5.291[a]
0.6GFFS - 0.6GF	-0.276 ± 0.123[a]	-0.2161 ± 0.0014[d]	12.532 ± 1.093[b]	49.304 ± 5.287[b]
0.1GFFS - 0.1GF	-0.238 ± 0.059[a]	-0.0633 ± 0.059[c]	12.759 ± 2.135[b]	44.536 ± 6.259[c]

Mean values ± standard deviation, degree of frequency dependence (n=3), tensile strength (n=60), elongation at break (n=60). Figures within each column with the same letter are not significantly different (P > 0.05).

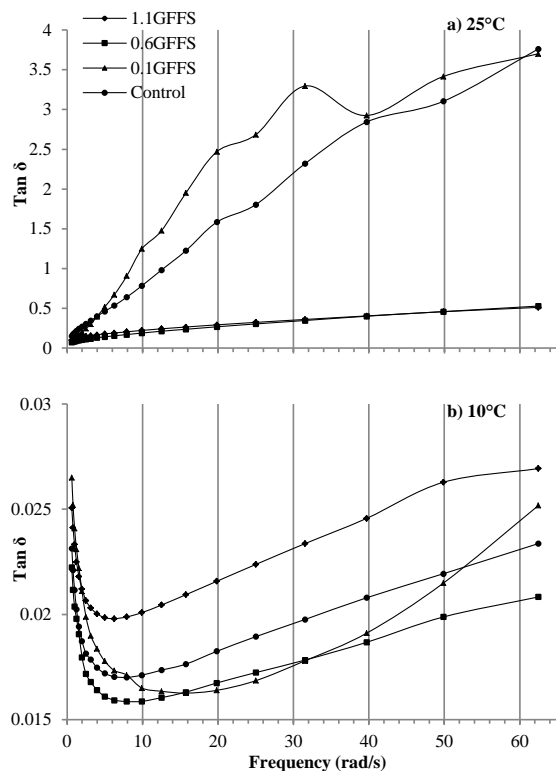Fig. 4. tan δ profiles of gelatin filmogenic solutions with 0.1g MWCNT/100g gelatin and 0.0, 0.1, 0.6 and 1.1g SDS/100 g gelatin, named as control, 0.1GFFS, 0.6GFFS and 1.1GFFS respectively a) at 25°C and b) at 10°C.

than 8 rad/s, they showed tan δ values less than unity (G' > G"), which is similar to what has already been described as that of a gel-like material, increasing substantially its tan δ values as the frequency increased, starting a change in its behavior to that of viscous-like materials (G" > G') at frequencies higher than 12 rad/s. In contrast, samples 0.6GFFS and 1.1GFFS displayed tan δ values lower than unity (G' > G") all over the applied frequency range, being consistent with the moduli (G', G") behavior previously mentioned.

It is also notorious that tan δ values of 0.1GFFS were higher (i.e., more diluted) than those of the control, suggesting that at this SDS concentration, no real surfactant effect was achieved, but the MWCNT were agglomerated instead, producing a dispersion rather than a real solution. All this suggests that except for the first level of SDS, the increase in SDS concentration added, produced a more homogeneous GFFS, making the MWCNT favor the formation of gelatin network structure, giving place to an increase

in its connectivity. It is also seen that at 10°C (Fig. 4b), differences in tan δ are seen especially at frequencies
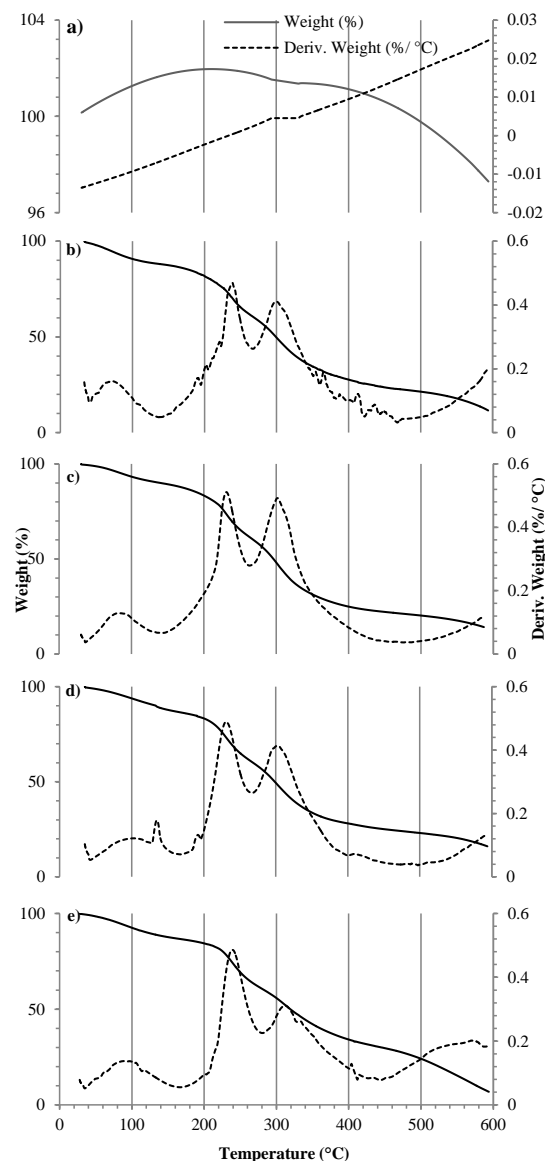

Fig. 5. TGA and DTGA profiles from a) MWCNT, b) control gelatin film, c) film with 0.1g SDS/100 g gelatin and 0.1g MWCNT/100g gelatin, d) film with 0.6g SDS/100 g gelatin and 0.1g MWCNT/100g gelatin, e) film with 1.1g SDS/100 g gelatin and 0.1g MWCNT/100g gelatin.

higher than 5 rad/s, and beyond this point, although the GFFS presented the highest profiles, all tan δ values are within a narrow range (0.017-0.025), suggesting that irrespective of the amount of SDS added to the GFFS, all conform a viscoelastic gel system, and also that the effect of the temperature, surpass that of the

GFFS treatment.

3.3   Thermogravimetric analysis (TGA)

The plots from the TGA and DTGA for the MWCNT are shown in Fig. 5a, where a weight loss of about 4.66 % was detected, due to leaking out of the CO2 produced during the MWCNT oxidation (Adhikari *et al*., 2006). It is worth mentioning that it has previously noticed that the lower the weight reductions, the higher the MWCNT purity (Carson *et al*., 2009), so that on this basis, the MWCNT used in this work were of high purity. Fig. 5b-e show the TGA and DTGA results of GF control and manufactured with the different concentration of SDS. It is observed that all films presented four main stages of weight loss. The first stage took place between 35 and 150°C, such a loss of weight is probably related to the loss of adsorbed free water.

The second stage of weight loss happened between 160 and 260°C, being associated with the loss of glycerol and structural water. The third stage which was observed between 260 and 440°C, is attributed to the gelatin chain degradation and breaking of peptide bonds. And finally the fourth stage, seen from 440°C onwards, is associated to the decomposition of thermally more stable structures, due to cross-linking reactions taking place during the heating of the sample (Mu *et al*., 2012).

In relation to the profiles of the DTGA, in the first stage, a slight displacement of the first peak was observed as the SDS concentration increased respect to the control, this could be because the SDS made water be strongly bound to the protein matrix (Haider *et al*., 2007), requiring a certain amount of energy to achieve its evaporation. In the second stage, no perceptible change is observed in any GF-peak, neither for SDS nor for MWCNT addition. In the third stage, again a slight displacement of the peak was observed respect to the control, possibly because of the MWCNT addition and the increase in its dispersion, besides; for the 1.1GF the peak size has been reduced, but the peak belonging to the fourth stage is the largest of all films, probably due to a more stable structure formation between the MWCNT, SDS and the protein α chains. This behavior is closely related to the material thermal stability, since a higher amount of energy needs to be applied to achieve the film decomposition as suggested by Mu *et al*. (2012). Also, the increase of 1.1GF thermal stability may well be related to the rheological behavior of its original material (1.1GFFS), because this system behavior was close to that of a cross-linked gel at 10°C, having a permanent covalent network that caused a more stable structure.

Similar profiles of both TGA and DTGA results have been reported for biodegradable bovine GF prepared in three layers (Martucci and Ruseckaite, 2010); also for GF from *Sepia pharaonis* with various glycerol contents (Hoque *et al*., 2011); and for edible GF cross-linked with carboxymethyl cellulose aldehyde (Mu *et al*., 2012), where the same thermal decomposition stages were found. In the three above mentioned works, the main stage was seen at 332°C, related to breaking of peptide bonds, which is consistent with the results found in this study.

3.4   X ray Diffraction (XRD)

The diffractograms of all materials (MWCNT and gelatin films) involved in this work are shown in Fig. 6. The XRD of the MWCNT (Fig. 6a) displayed a typical highly crystalline material pattern, presenting a single high intensity domain, with a narrow base and a maximum of intensity lying at 2θ equals to 26.5°, observed in the diffraction of MWNT can be attributed to the hexagonal graphite structure. Li *et al*. (2003) and (Shanmugharaj *et al*. (2007)) reported for MWCNT, the presence of a peak at $2\theta = 26.5°$, similar to that obtained in this work.

The XRD patterns of the gelatin films are shown in Fig. 6b-e; all film diffractograms showed two peaks, the first one lying between $2\theta = 4$ and 10.6° (peak I), which is related to the diameter and amount of re-natured triple helix structures. The second peak is observed between $2\theta = 10.4$ and 20.3 (peak II), which corresponds to the distance between the aminoacid residues all along the single chain (random coil) of gelatin (Bigi *et al*., 2004).

A change in the maximum intensity position respect to 2Θ for peak I is observed, this behavior might be the result of a change in the ordering of the triple helix, since for film samples with SDS concentrations of 0.6 and 1.1g SDS/100g gelatin, there was a better MWCNT dispersion, and so, a molecular re-ordering as a result of the re-naturation degree of the triple helix structure (Bigi *et al*., 2004).

3.5   Mechanical properties

The films mean thickness was 0.318 mm, with a standard deviation of 0.0508 mm, with no significant differences ($P > 0.01$) among the various kinds of films. This result indicated that the films had a

homogeneous thickness over its entire surface. The EB and TS data from the GF are shown in Table 1. An increase in the EB was observed when the MWCNT dispersion increased, as an effect of SDS concentration, presenting 1.1GF the highest values, being consistent with results from dynamic tests, where G' is highest for the same above concentration (1.1). This behavior could be due because at low SDS concentrations, there is an increase in MWCNT agglomeration, which leads to a decrease on its

mechanical properties, since it interferes with the polymeric matrix continuity and as a consequence, it reduces the interaction numbers.

Also, the change in diffractograms of all materials might be the result of a decrease of rigid bonds and an increase of elastic junctions, giving as a result a more elastic film, without losing its strength. A uniform MWCNT distribution is one of the most important features during the manufacture of MWCNT-polymer composites, due to the common aggregation nature of the MWCNT (Yun *et al.*, 2008). The MWCNT dispersion increase with the SDS concentration, improving in consequence, the EB of the GFs. This might due to the MWCNT interaction with hydrophobic residues of gelatin α chains, which in turn, increased the films flexibility (Haider *et al.*, 2007).

It has been reported in the literature that at low MWCNT concentrations, the gelatin/MWCNT composites had a slightly higher hydrophilic nature than the control one, increasing the films plasticity, but decreasing, in turn, the TS (Haider *et al.*, 2007). This is consistent with this work, since the control film had a higher TS value than 0.1GF, 0.6GF and 1.1GF respectively. Thus, it can be asserted that films should not only exhibit good TS, but also have an adequate EB, because it has been found that films with a high TS are extremely crumbly and fragile, especially under low RH and temperatures (Lim *et al.*, 1999).

3.6 Photon optical microscopy

Fig. 7 shows the optical photomicrographs of the surface of the different gelatin films. Overall, it was observed an improved homogeneous distribution of the MWCNT as the SDS concentration increased (Fig. 7a-c); as expected, the control sample (Fig. 7d), did not present such a distribution. Yang *et al.* (2015) found the presence of micron-scale MWCNT agglomerates (5-30 μm) in optical microscope images, which tended to be bigger at higher MWCNT concentrations. In contrast, in this investigation, the concentration was constant (0.1g MWCNT/100g gelatin), and the better distribution was due to SDS addition. The 0.1GF had the biggest agglomerates and could cause a poor rheological behavior (G' and G'' values lower than control GFFS moduli values, with bigger frequency dependence), because agglomerates interfered with the crosslinked network formation (Moniruzzaman and Winey, 2006).
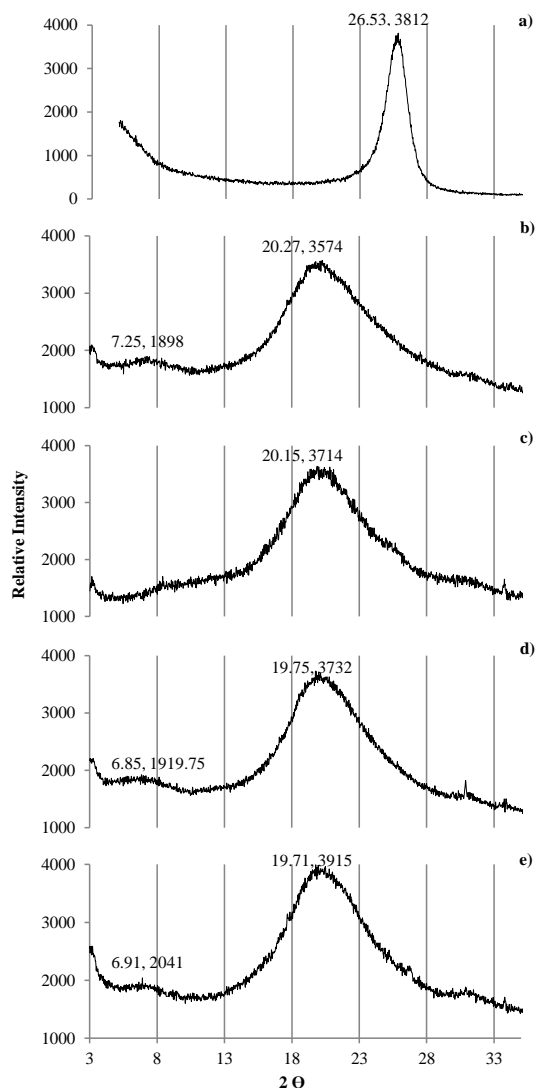

Fig. 6. X ray diffractograms from a) MWCNT, b) control gelatin film, c) Gelatin film with 0.1g SDS /100g gelatin and 0.1g MWCNT/100g, d) Gelatin film with 0.6g SDS/100g gelatin and 0.1g MWCNT/100g, and e) Gelatin film with 1.1g SDS/100g gelatin and 0.1g MWCNT/100g.
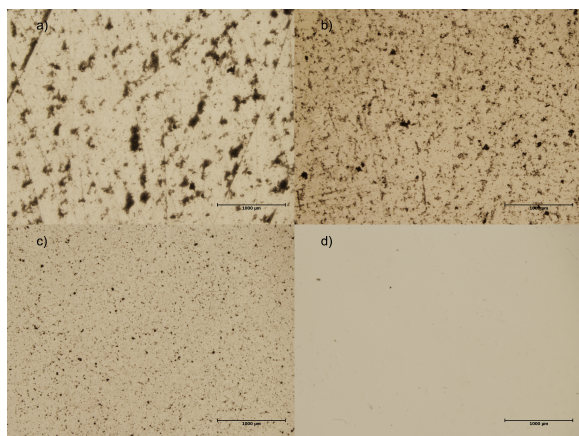
Fig. 7. Optical photonic micrographs from the surface of gelatin films with 0.1g MWCNT/100g gelatin and with (a) 0.1g SDS/100 g gelatin, (b) 0.6g SDS/100 g gelatin, (c)1.1g SDS/100 g gelatin and (d) control film. Scale bars represent 1000 micrometers.

Conclusions

The SDS decreased the surface tension of the GFFS, and also, increased noticeably the MWCNT dispersion. Within the range involved, there was a close relationship between the storage and loss moduli and the SDS concentration added, obtaining the highest values for 1.1GFFS, being consistent with its effect on the MWCNT dispersion. Control and 0.1GFFS behaved as an entangled network (soft gels) at 25°C, while 0.6GFFS and 1.1GFFS, displayed physical gel properties at the same temperature. Four stages of thermal degradation were detected within the temperature range from 35°C to 600°C, finding that the higher the MWCNT dispersion, the higher the thermal stability. Diffractometry showed re-ordering on gelatin triple helix when the MWCNT dispersion increased, and the 1.1GF were more elastic than the control at the RH of 57%, this could be caused by the change in the GF crystalline structure, giving; as a result, a decrease of rigid bonds (crystalline structure) and an increase of elastic junctions (amorphous material), resulting in a more elastic film, without losing its strength. Optical photomicrographs showed an improved homogeneous distribution of the MWCNT as the SDS concentration increased, being consistent with XRD data. A better MWCNT distribution increased gelatin interaction with such compound, thus resulting in a stronger system, raising the elastic film behavior. The MWCNT agglomeration, lead to a decrease in GF

mechanical properties and a poor rheological behavior, since it interrupted the polymeric matrix continuity and as a consequence, it reduced the number of interactions.

Acknowledgments

Nomenclature

0.1GF	gelatin films with 0.1 g SDS/100g gelatin
0.1GFFS	gelatin film forming solutions with 0.1 g SDS/100g gelatin
0.6GF	gelatin films with 0.6 g SDS/100g gelatin
0.6GFFS	gelatin film forming solutions with 0.6 g SDS/100g gelatin
1.1GF	gelatin films with 1.1 g SDS/100g gelatin
1.1GFFS	gelatin film forming solutions with 1.1 g SDS/100g gelatin
CMC	critical micellar concentration
DTGA	first derivative of thermogravimetric analysis
EB	elongation at break
F	F from the Fisher test
G'	storage or elastic modulus
G"	loss or viscous modulus
GF	gelatin films
GFFS	gelatin film forming solutions
LVR	linear viscoelastic region
MWCNT	multi-walled carbon nanotubes
n	number of samples
NS	non-significant value
P	probability
RH	relative humidity
S	significant value
SDS	sodium dodecyl sulfate
$\tan\delta$	loss tangent
TGA	thermogravimetric analysis
TS	tensile strength
XRD	X-ray diffraction

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