Development and Characterization of a Gelatin-Based Coating with Unique Sealing Properties

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ABSTRACT: The experimental results on the development of thin ($\sim$ 1.5 μm) gelatin-based coatings and the investigation on their sealing attribute when applied onto oriented polypropylene (OPP) are reported. The sealing performance, expressed as the strain energy required to separate the sealed joints, was studied as a function of three different influencing factors. pH of the hydrogel solution was varied between 5 and 11. The highest seal strength values were obtained for pH values beyond the isoelectric point (IEP) of the gelatin molecule. The effect of the plasticizer (glycerol) was studied by changing its concentration from 2.5 wt % to 7.5 wt % to the total weight of the hydrogel solution. Glycerol concentration = 7.5 wt % was found to be the best for achieving adequate strain energy values. The influence of a hydrophobic component on the capability of the coating to act as a sealant has also been assessed. The hydrophobic component had a positive effect only up to a certain level (1 wt %, weight percent), whereas beyond this value, it affected the seal strength attribute. According to the best setting conditions, seal strength values for the OPP biocoated films of $\sim$ 61 $N \times$ mm were attained, with a corresponding maximum force required to break the joints of 2.4 N. These results are discussed by taking into consideration the modality of seals opening. Interestingly, the heat-seal (temperature: 90°C; dwell time: 1 s; pressure: 4 bar) failed in both peeling and tearing mode failure, as confirmed by microscopy, spectrophotometric, and particle size analyzes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2969–2975, 2010

Key words: DSC; failure; heat-seal strength; poly(propylene); SEM

INTRODUCTION

The use of thin polymeric coatings encompasses different fields like automotive, medical/pharmaceutical, marine, photography, packaging, textile, army, and architecture, where they find application as adhesives, protective barriers, slip/anti-slip agents, conductors, decorations, inks, and paints.[1] The packaging sector, accounting for several branches like food, pharmaceutical, biomedical, health-care, etc., is a major field of application of coatings, either to improve bulk properties of their substrates like barrier,[2] optical,[3] mechanical,[4] thermal,[5] anticorrosion,[6] sealing,[7] or to add new features such the antimicrobial activity.[8] To this purpose, polymers of synthetic origin have predominantly been used so far, being the most practical, economical, and useful solution for packaging applications, principally due to their low cost and ready availability.

Only recently it has been expressed an increasing interest towards new formulations originating from natural and renewable resources,[9] not only due to the increase in the price of crude oil but also because of other established advantages mostly related to their versatile nature and chemical structure. In addition, biobased coatings have been indicated as a promising way to face the waste disposal issue.[10] Biobased coatings made of whey protein isolate (WPI) have been credited of both excellent transparency[11] and barrier properties against oxygen[12]; it has also been outlined the great potential of coatings made of soy protein isolate (SPI) as an efficient carrier of bioactive compounds (e.g., antimicrobials)[13]; polyolefins coated with a natural slip agent (acetic acid esters) added to a protein matrix showed improved frictional properties[14]; chitosan has been proved to be effective as a coating material on paper and paperboard[15] and for producing biopolymer coated polypropylene films with biocidal activity.[16] Among biopolymers, gelatin has been widely used due to its multifaceted nature. Filmogenic and foam behavior, good barrier properties against oxygen, and transparency, besides abundance and relatively low cost, justified its use for many different purposes. Indeed, gelatin found application to produce new high-performance biodegradable laminates,[17] for manufacturing antimicrobial edible films,[18] to fabricate wound dressing,[19] and as soft capsules.[20] Of late, gelatin-based coatings have been formulated in the attempt of exploiting its ancient feature, i.e., the adhesive property, which allowed obtaining
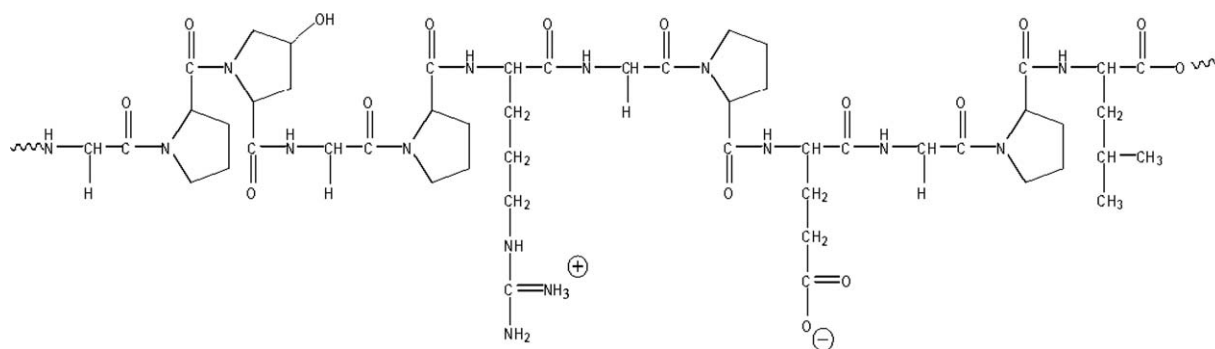

Figure 1 Schematic exemplification of a gelatin molecule segment.

the earliest glues in the New Stone Age.[21] The adhesive properties of gelatin, credited to be responsible for the adhesion properties of such a biopolymer, can be ascribed to its inherent chemical structure, accounting for polar and/or chargeable functional groups such as hydroxyl (OH), carboxylic acid (COOH), and aminic (NH$_2$) along its molecular backbone,[22] as shown in Figure 1. The functionality of these groups, and thereby of the whole macromolecule, is strongly influenced by external factors such as pH and ionic strength. In our previous work,[23] we studied the influence of the most relevant process variables (i.e., the temperature of the sealing bars, the pressure exerted by the bars during the seal process, and the dwell time) on the seal strength of a heat-sealed gelatin-based coating coupled to a plastic substrate. We demonstrated that, unlike the conventional heat sealant thermoplastic films, the factor influencing the seal strength the most is the bars pressure rather than temperature and time. Nevertheless, the effect relying on the key-formulation factors has not been quantified so far. Therefore, also in the attempt to provide further information on the development of bio-based functional coatings, this work aimed at: (1) understanding the effect of the components used in the coating formulation as well as the influence of the pH of the hydrogel solution on the seal strength of coated polypropylene strips; (2) pinpointing adequate sealing performance that can profitably used in practical applications, such as the sealing of plastic surfaces; (3) providing an exhaustive explanation towards the mode of failure underlying the physics of the heat-seal separation.

EXPERIMENTAL

Coating preparation

Type A, 133 Bloom, pharmaceutical and food grade pigskin gelatin powder (Weishardt International, Graulhet/France), acetic acid esters produced from monoglycerides (Grindsted Acetem 70-00 P,Danisco A/S, Langebrogade/Denmark), glycerol (Giomavaro,

Brugherio/Italy), and milli-Q water (18.3 $M\Omega$) were used as received for the hydrogel solutions preparation. The bio-coated plastic films were prepared according to the procedure protected by international patent WO 2008/075396 A1.[24] Briefly, the gelatin-glycerol mix was first heated to 60°C to obtain a complete solubilization and denaturation of the protein. When necessary, the pH was adjusted using sodium hydroxide (Fluka Sigma-Aldrich, Milano/Italy) $1M$. At this point, the lipid component was added and mixed for 2 min with a homogenizer (IKA-Werke, Staufen/Germany), at the speed of 24,000 rpm. The different hydrogel solutions were obtained by varying the pH between 5 and 11. The glycerol content was varied between 2.5 wt % and 7.5 wt % on the total weight of the water hydrogel solution. The lipid concentration was varied between 1 wt % and 3 wt %. The amount of gelatin in the final slurry was kept constant at 10 wt %, which has been previously suggested for a proper deposition of the coating on the plastic substrate.[14] The gelatin-based solutions so obtained were poured on the corona-treated side (24 × 18 cm) of oriented polypropylene films (Radici Film, S. Giorgio di Nogaro/Italy) 20 ± 0.5 μm thick, with an automatic applicator (Ref. 1137, Sheen Instruments, Kingston/UK) equipped with a steel horizontal rod to obtain a wet coating thickness of ∼ 10 μm (data provided by the factory). Coating deposition was performed according to ASTM D823-07—Practice C,[25] at a constant speed of 150 mm min^{-1}. Coated films were dried using a constant and perpendicular flux of mild air (25 ± 0.3°C for 2 min) at distance of 40 cm from the applicator, and then stored under controlled conditions (23 ± 0.5°C, 40 ± 2.0% RH) for 24 h. At least five replicates for each sample were used for the analyzes.

Characterization techniques

Thickness determination

The thickness of the uncoated plastic films was measured with a micrometer (Dialmatic DDI030M, Bowers Metrology, Bradford/UK) to the nearest

0.001 mm at 10 different random locations. For the determination of the thickness of the biodegradable layers coated on the plastic films, a 10 × 10 cm sample was cut and weighed (M_1). The coating was mechanically removed using hot water (80°C) and the resulting base film weighed (M_2). The apparent thickness of the coating was obtained using the following equation:[26]

$$l = [(M_1 - M_2/\rho)] \times 100 \qquad (1)$$

where M_1 is the unit total mass (plastic film and coating), M_2 is the unit mass of the plastic film (g dm^{-2}), ρ is the density of the aqueos solution (g cm^{-3}), l is the thickness (μm), being known $M_1 - M_2$ and ρ.

Seal strength determination

Strips of 2.54 cm wide and 15 cm long were obtained using a precision sample cutter (mod.MMT, Thwing-Albert, West Berlin/NJ). Two strips at a time, were placed on top of one another, and an area of 2.54 × 1.5 cm was heat sealed using a thermal heat sealer Polikrimper TX/08 (Alipack, Pontecurone/Italy) provided by smooth bars. Temperature, pressure, and dwell time of the sealing bars were kept constant respectively at 90°C, 4 bar and 1 s, which were proved to be the best experimental setting conditions.[23] Sealed samples were kept for 24 h at 23 ± 0.5°C and 50 ± 2.0% RH in a climatic chamber to achieve chemical stabilization before testing. Seal strength expressed as strain energy (N × mm) was measured through the so-called T-peel test according to the standard method as described by ASTM F 88M-09[27] by means of a dynamometer (mod. Z005, Zwick Roell, Ulm/Germany) fitted with a 100 N load cell and connected to two clamps placed at a distance of 10 cm one from the other. Each run was performed at a crosshead speed of 300 mm min^{-1}.

SEM analysis

Morphological investigation of the surface of the coated plastic films after joints breakage was performed to achieve more detailed information on the mode of failure of the seal. Strips of dry film were immersed in liquid Nitrogen for 5 min and then cross fractured manually using cold tweezers. The dried fragments were glued to specimen stubs, sputter-coated with a thin layer of gold, and examined with a Phenom^{TM} scanning electron microscope (FEI Co., Hillsboro/OR). At least 10 images were collected for each sample.

Particle size measurement

The mean particle size of the biopolymer systems was determined using a commercial dynamic light scattering instrument (Zetasizer NanoZS, Malvern Instruments, Worcestershire/United Kingdom). Based on measurements of the Brownian motion of the particles in the solution, the z-average diameters (s) of the particles were determined using the Stokes–Einstein equation. All measurements were made on at least two freshly prepared undiluted samples at 40°C, i.e., the temperature at which the coating hydrogel solution is spread on the plastic substrate.

Thermal analysis

Differential scanning calorimetry analysis was performed using a DSC 823 (Mettler Toledo, Columbus/OH) supplied by a quench-cooling accessory. Biocoating samples were first placed in desiccators containing $CaCl_2$ for two weeks. Approximately 10 mg biocoating samples were then put in a hermetic sealed aluminum pan. With the objective of determining only the melting temperature (T_m) of the dry coating, a unique scan from 5°C to 110°C in an inert environment (100 mL min^{-1} N_2) at 10°C min^{-1} was run. The temperature of the endothermic peak was taken as the melting temperature, T_m. It was calculated by the software Star^e version 9.0 (Mettler Toledo, Columbus, OH).

Transparency measurement

Transparency was determined according to ASTM D 1746-88[28] using an UV-Vis spectrophotometer (Lambda 650, PerkinElmer, Waltham/MA) for measurements between 200 and 800 nm. In particular, the transparency of both uncoated and coated films was measured in terms of specular transmittance, i.e., the transmittance value obtained when the transmitted radiant flux includes only the light transmitted in the same direction as that of the incident flux in the range 540–560 nm. Then, the correspondent transparency value was obtained according to the equation:

$$(T_s) = 100 \, I_s/I_0 \qquad (2)$$

where T_s is the specular transmittance at 550 nm; I_s is the light intensity with the specimen in the beam; I_0 is the light intensity with no specimen in the beam.

RESULTS AND DISCUSSION

Influence of the pH

The influence of the pH on the seal strength attribute of the coating was studied by keeping the
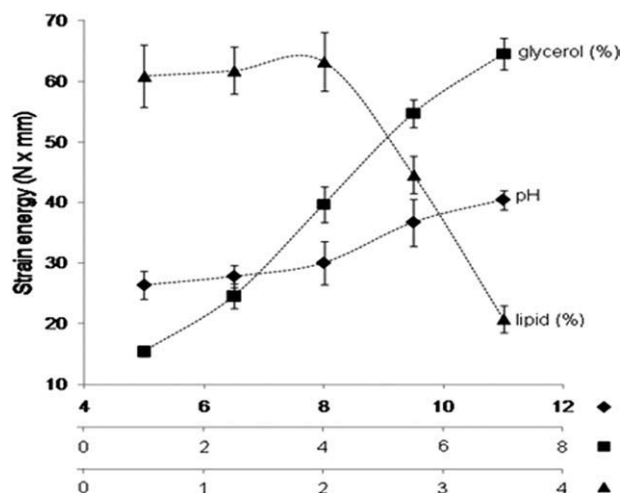
Figure 2 Strain energy evolution as a function of the different setting conditions of pH, glycerol (%), and lipid (%).

glycerol and lipid concentrations at 5 wt % and 2 wt %, respectively. The pH value was varied from 5 to 11. It has been observed (Fig. 2) that as the pH increases, the seal strength, expressed as strain energy, increases from $26.37 \pm 2.3 \, N \times$ mm to $40.41 \pm 1.56 \, N \times$ mm. The positive influence of the pH on the seal strength is likely ascribable to charge distribution reasons. Supposedly, since the isoelectric point (IEP) of the gelatin used in this work ranges from 8.5 to 9.0, at pH = 11 most carboxylic groups, which account for the majority of the charged groups along the gelatin backbone,[29] are de-protonated (i.e., carboxylates). It seems to be beneficial to the seal strength attribute of the gelatin-based coating, due to the established contribute of the —COO⁻ groups to the adhesive properties of gelatin.[21] In addition, beyond the IEP electrostatic repulsion exists between gelatin molecules, allowing the unfolding of the triple-helix chains. As a consequence, a higher reactivity of the charged groups underlying the seal formation is expected under this pH value. Therefore, to achieve the best sealing performance, the pH value was fixed at 11.

Influence of glycerol concentration

The effect of glycerol concentration was assessed by varying its concentration from 2.5 wt % (17.24 wt % on dry basis) to 7.5 wt % (38.46 wt % on dry basis) and keeping the pH of the solution at 11 and the lipid content at 2 wt %. From Figure 2, it is clearly seen that an increase in the glycerol content promotes a proportional increase in the seal strength attribute. More specifically, the strain energy values range from $15.42 \pm 0.74 \, N \times$ mm to $64.53 \pm 2.68 \, N \times$ mm as the glycerol concentration moved from the minimum to the maximum values. As known, the effect of glycerol can be explained in terms of free

volume theory.[30] Indeed, such a small molecule acts as a plasticizer, thus filling the gaps especially at intermolecular level. It gives rise to a reduction of the T_g of the thermoplastic biopolymer (i.e., gelatin), due to a marked increase in the mobility of the polymeric chains, which in turn is provoked by a reduction of the molecular interactions (e.g., hydrogen bonds) between adjacent chains. As a consequence, a deeper interaction (entanglement) between melted molecules is promoted, being constant the setting of the sealing process variables (bars temperature, sealing time, and bars pressure). Thus, glycerol = 7.5 wt % (wet basis) was used for further experiments.

Influence of lipid concentration

To determine the influence of the hydrophobic component used within the coating formulation, the hydrogel solutions were prepared by fixing the pH and the glycerol concentration at 11 and 7.5 wt %, respectively. The acetic acid esters concentration was varied from 1 wt % (5.40 wt % on dry basis) to 3 wt % (14.63 wt % on dry basis). As shown in Figure 2, a double behavior can be observed as the concentration of the lipid component is varied. In particular, from 1 wt % up to 2 wt % there is a slight increase in the strain energy values (from $60.89 \pm 5.16 \, N \times$ mm to $63.28 \pm 4.78 \, N \times$ mm), though not statistically significant. The scenario changes completely beyond 2 wt %: the strain energy values drop quickly up to a minimum of $20.79 \pm 2.16 \, N \times$ mm at 3 wt % concentration. It can be probably explained in terms of dilution effect. As the concentration of the lipid is increased beyond a certain boundary value (i.e., 2 wt %) the strain energy is straightaway suppressed, due to the additive effect of the lipid that, together with the glycerol and the water added for adjusting the pH, acts synergistically as a plasticizer, thus reducing the cohesive energy density of the protein network with a detrimental increase in free volume.[14] This finding emphasize the importance of the "glycerol-lipid" interaction, which can be indicated as driving force governing the seal strength performance of the bio-based coating.

According to the results obtained in this first step, the best heat-sealing bio-coatings in terms of seal strength have been obtained for pH of the hydrogel solution equal to 11, glycerol concentration = 7.5 wt %, hydrophobic component amount = 1 wt %, and gelatin concentration = 10 wt %. According to this formulation, a strain energy value of $61.12 \, N \times$ mm (± 5.85) was recorded for OPP-biocoated strips, to which corresponded a seal strength of 2.39 N (± 0.21), expressed as the peak load required to break the joints (maximum force). These values are
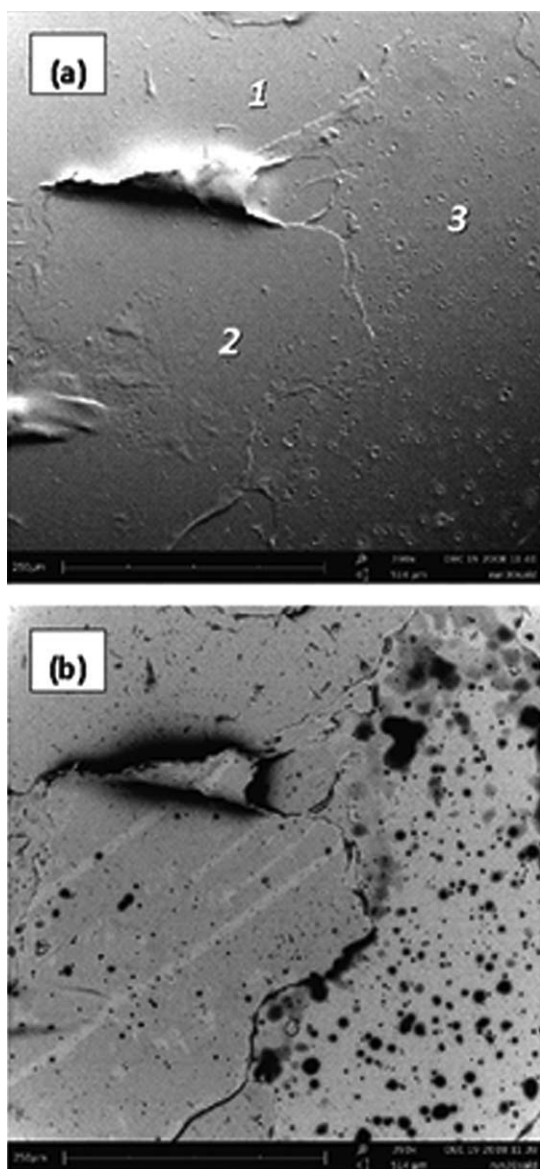
Figure 3 SEM images of the heat-sealed interface of OPP strips after rupture: (a) topographical mode; (b) compositional mode. Coating formulation: pH = 11; gelatin 54.05 wt %; glycerol 40.55 wt %; lipid 5.40 wt %.

deemed acceptable for those packaging applications requiring good peelable seals.

Characterization of the optimized sealing coating

Once the contribution of each individual factor to the selected response was estimated; specific analyzes were carried out to get more detailed information on the physical phenomenon at the base of the adhesion between the two coated side of the OPP film after heat-sealing. To this purpose, coatings of a dry thickness average of 1.51 μm ± 0.08 were obtained. Figure 3 shows SEM images collected after rupture of sealed (temperature: 90°C; dwell time:

1 s; pressure: 4 bar) OPP strips coated according to the selected formulation. Three different zones were clearly visualized, as displayed in Figure 3(a), which was captured in topographical mode: (1) the substrate (OPP); (2) the coating initially lied on the upper OPP strip, de-bound from the substrate after rupture; (3) the coating initially lied on the lower OPP strip, still bound to the substrate. This configuration allows the mode of failure of the heat-sealed joints after rupture to be elucidated. It is likely that two different modes took place during joints separation. Region 3 suggests that the heat-seal failed in peeling mode failure. As it has been pointed out by Yuan et al.,[31] under this failure mode, disentangles and extricates chain ends from the opposite surface occurred, in which the heat-seal bond was peeled apart. In our case, this happened for strength of the seal lower than the adhesion forces at the OPP/coating interface. Conversely, Regions 1 and 2 may be explained in terms of tearing mode failure, which is typical of strength of the seal higher than the strength at the substrate/coating interface.

This double behavior has been already cited for polyethylene-based seals done at a temperature range few degrees below the melting point of the thermoplastic molecule, namely at the transition region in which the failure mode turns from peeling to tearing mode failure.[31] Although in our knowledge, this behavior has never been described before for seals originating from biopolymers like gelatin, it is reasonable to think that a combination of both failure modes involved also our coating. This is because also the sealing temperature adopted in this work (90°C) was slightly lower than the melting temperature of the coating, as supported by the DSC analysis performed on the dried coating (Fig. 4), which exhibited a melting temperature of approximately 94°C. The coexistence of both tearing and peeling modes of failure can be thus explained considering that, at this boundary thermal region, it is unlikely that the thermoplastic macromolecule (i.e., gelatin) undergoes only one discrete physical transition. Indeed, it is fairly probable that some domains, in which the amorphous phase prevails, would completely melt (leading to the tearing mode), whereas for other domains (those with a partial crystalline feature) the transition would be only at the beginning (leading to the peeling mode). Neither the effect arising from the corona treatment performed before coating deposition should be underestimated at this juncture. Due to the heterogeneity of the electrical discharge onto the plastic surface, it is plausible that some areas of OPP resulted more suited to bind the biobased coating than those regions where the treatment was less effective.

Finally, the role played by the lipid component is worth to be mentioned. Hydrophobic substances,
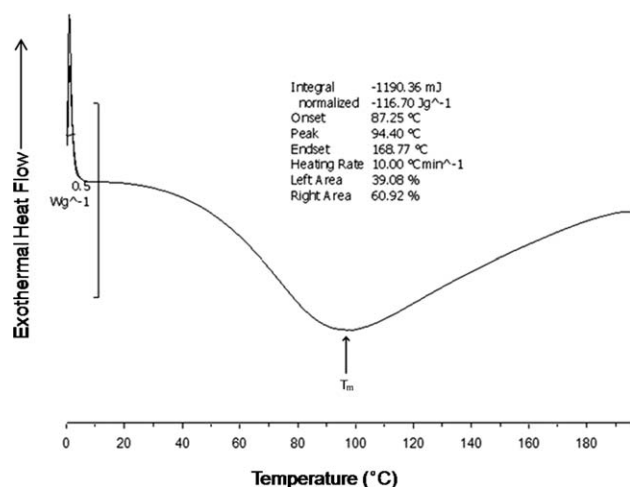
Figure 4 DSC heating scan of dried coating. Coating formulation: pH = 11; gelatin 54.05 wt %; glycerol 40.55 wt %; lipid 5.40 wt %.

like paraffin and waxes, are generally used for applications where high bond strengths and heat resistance are not required, but remarkable seal continuity is aimed. Indeed, the addition of such a component makes easier filling any voids that might have appeared onto the substrate, to the detriment of the seal strength, which turns into peelable.[32] These considerations are in agreement with our observations. Figure 3(a) provides an overview on the coating surface, showing that Region 2 was smooth and regular, whereas Region 3 had a 'moon-like' surface, being clearly visible depressions similar to craters. At first glance, they might be due to the presence of air bubbles formed during the emulsification process that moved from the bulk to the solid-air interface. A deeper investigation suggested the blooming of the phase-separated glycerol and lipid upon the coating deposition. It seems to be confirmed by Figure 3(b), where the darker regions are normally attributed to the lower molecular weight components within a formulation, according to the compositional mode images acquisition.
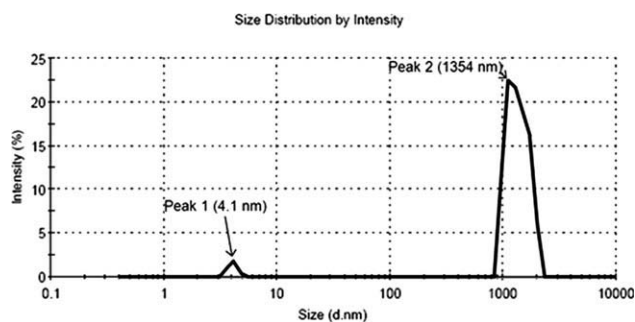

Figure 5 Size distribution by intensity of the gelatin-based hydrogel solution. Hydrogel solution formulation: pH = 11; gelatin 10 wt %; glycerol 7.5 wt %; lipid 1 wt %.
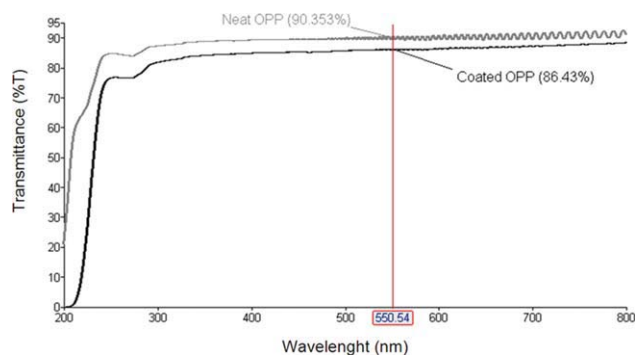

Figure 6 UV-Vis mean spectra of neat and coated OPP. The transmittance values at 550 nm are displayed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The presence of particles dispersed within the hydrogel solution is further confirmed by the particle size analysis shown in Figure 5. The coating sample showed two peaks centered at 4.1 nm and 1354 nm, the latter supposedly due to small drops of phase-separated lipid and glycerol after the emulsification process. The scattering phenomenon of visible light through the film is somehow confirmed by UV-Vis spectra of both uncoated and coated polypropylene films (Fig. 6). Transparency of the coated films (86.43% ± 1.7) was inferior to that of the neat films (90.35% ± 0.5), although the 'see-through' property of the original films was not affected significantly, as also confirmed by visual inspection. As already pointed out, such 'hazy' effect seem to be due to the morphological inhomogeneity of the coating thickness across the width, since the lipid component in the final formulation is in the form of tiny drops entrapped in the gelatin network (especially after mechanical homogenization).[14]

CONCLUSIONS

Based on these present results and those in our previous study,[23] biomacromolecules such as gelatin, acetylated monoglycerides, and a proper plasticizer (e.g., glycerol) show the potential as a sealable coating for many packaging applications. Further, our findings suggest that a new class of coatings may be accurately designed to originate tailored seals, i.e., ranging from weak peelable to hermetic. However, for such a new class of biocoatings to work efficiently, a proper setting of the main parameters (both process and formulation variables) is of utmost importance. At the same time, to implement the scale-up process, further issues should be faced. Among them, quantification of cling of the bioseal surface to the release surface claims particular attention, since rolls of coated plastic films must unwind smoothly on the packaging equipment. Finally, it

must be kept in mind that the potential linked to these coatings relies also on the possibility of exploiting them as multifunctional devices. Ongoing works in our team seem to confirm that, for instance, these coatings can be simultaneously used as both sealing layers and natural reservoir of active compounds (e.g., antimicrobials) to be released in the package in a controlled manner under the effect of a selected trigger (e.g., temperature, humidity, etc.).

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