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Whey based binary bioplastics

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ABSTRACT

We fabricated and characterized whey protein bioplastics obtained via blending the protein with two abundant biopolymers: natural latex and egg white albumin. Natural latex and albumin contain amino acids with reactive groups that make the materials potentially compatible with whey protein. The bioplastics were obtained by compression molding where water was added as plasticizer. Thermal transitions, tensile stress, percent strain at break, and Young's modulus were measured for the materials. It is demonstrated that addition of about 10% of the latex and albumin to the whey based bioplastics improves the toughness characteristics of whey based materials without compromising their strength and stiffness.

1. Introduction

Films and coatings from biopolymers such as proteins, starches and lipids have been studied extensively due to their environmental benefits and sustainability (Cuq et al., 1998; Redl et al., 1999; Hong and Krochta, 2003; Ramos et al., 2012). Among the biopolymers, polypeptide (protein) macromolecules have the highest versatility of chemical compositions and properties due to the numerous possible arrangements of amino-acid monomers in the polymer chain. Thermoplastic processing such as compression molding and extrusion can be the most efficient methods from economies of scale to produce edible and/or biodegradable polymer films/sheets (Hernandez-Izquierdo and Krochta, 2008). However, only abundant in nature proteins can be used for fabrication of economically feasible bioplastics (Pommet et al., 2003). One of those abundant proteins is whey protein, which is a mixture of globular proteins isolated from milk as a by-product of the manufacture of cheese or casein (Morr and Ha, 1993).

Whey protein has been already explored in packaging applications because of its excellent oxygen barrier properties and abundant availability (50 million tonnes of annual unprocessed whey) (Markus Schmid et al., 2012). However, it is necessary to decrease the intrinsic stiffness/brittleness of whey bioplastics for their perceived benefits in packaging and other plastic applications. To this end, the objective of this research is to fabricate and characterize whey protein bioplastics obtained via blending whey protein with two abundant biopolymers: natural latex and egg white albumin. For the blending we selected materials that contain proteins, since presence of aminoacids with complementary reactive groups (e.g. amino, carboxyl, and hydroxyl) in the polypeptide chains make protein containing blends potentially compatible. The uniqueness of this research study was to utilize the complementary potential of two or more proteins as well as abundantly available natural rubber to develop desired tensile toughness. Moreover, the thermoprocessing capability of whey-based biopolymer blends would allow food and packaging industries for large-scale production of food-contact films and other shaped products.

In general, protein-based bioplastics pose following challenges: thermal and water stability; consistency and reliability in the mechanical performance; and cost competitiveness. Some of these concerns can be overcome or minimized by blending in which two or more polymers are combined in one polymeric material. For a polyblend, a weakness in one component can, to a certain extent, be camouflaged by the strength in the remaining parts (Koning et al., 1998). In a homogeneous (one-phase) blend, the components of the blend lose part of their identity. The final properties of a miscible blend usually follow the so-called "mixing rule". In a phase-separated blend, the properties of all blend components are present, and the final performance of the blend is dependent upon the size of structural elements and their adhesion at the interface (Koning et al., 1998). As a general rule, majority of blends are immiscible/incompatible and demonstrate negative deviation from the "mixing rule" because of gross phase morphology and low

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interfacial adhesion. These blends are in many ways futile if they are not compatibilized. In a few exceptional cases, some properties of a compatible blend may be better than those of the individual components: a synergistic effect, which is sometimes difficult to predict, is observed.

To date several studies have been undertaken to develop biocomposites and/or bioplastics from blends of protein, starch, rubber latex, biodegradable polymers to address mechanical performance and water resistance properties (Wu et al., 2007; Salmoral et al., 2000). For instance, blends of synthetic and natural polymers (e.g., polysaccharide, proteins) as well as blends of natural polymers and/or their derivatives (e.g., starch, protein, methyl cellulose) have been used to produce totally and partially degradable blends with varying mechanical properties (Arvanitoyannis, 1999) (Yoo and Krochta, 2012). In one study, the blends of soy protein and synthetic biodegradable polycaprolactone, along with methylene diphenyl diisocyanate (MDI) as a compatibilizer, were used to prepare plastics with improved mechanical and water resistance properties (Zhong and Sun, 2001). Moreover, they used another synthetic polymer, poly(ethylene-ethyl-acrylate) along with MDI, to produce plastic with better properties than those demonstrated by the blends of soy protein and polycaprolactone (Zhong and Sun, 2003). In another study, biocomposites having mechanical properties similar to commercial thermoplastics such as polystyrene were developed from the blends of soybean and synthetic biodegradable polymer poly(hydroxyl ester ether) as well as wheat gluten and poly(hydroxyl ester ether) (Wang et al., 2002). In addition, injection-molded biodegradable plastics from the blends of corn gluten meal (a byproduct of ethanol industries) and polycaprolactone were developed for packaging applications (Aithani and Mohanty, 2006). Similarly, bioplastics from the blends of soy protein and biodegradable polyester, along with polyvinylpyrolidone as a compatibilizer, were developed, exhibiting reduced moisture sensitivity—resulting in a good shelf life and stability under ambient conditions (Mungara et al., 2002).

Protein–protein blends have also been studied for developing glues, fibers, and plastics. For example, Zhang et al. extruded zein-soy protein to develop wet-spun fibers (Zhang et al., 1997). The tenacity of these fibers was greater than that of soy protein fibers at 11% relative humidity. Kumar et al., in a review, stated that soybean protein was mixed with animal blood to produce adhesive glue and found to be ideal for wood product assembly (Kumar et al., 2002). In addition, soluble dried chicken blood blended with soy protein in a 1:1 ratio, crosslinked with dialdehyde starch, has been used for manufacturing interior-type plywood. Soybean-casein glues had also demonstrated composite performance for developing panels and flush door assemblies (Kramárová et al., 2007).

2. Materials and methods

2.1. Materials

The whey protein isolate (BiPro, Davisco Foods Intl.) and albumin from chicken egg whites (A5253, Sigma–Aldrich) contained 91% and at least 90% proteins, respectively. According to the supplier, the egg white protein was composed of 77% ovalbumin and 16% beta-Globulin. Ovalbumin has a molecular weight of 43 kD, including 385 amino acid residues; beta globulin has a molecular weight of 76 kD, including 686 amino acid residues (http://www.rcsb.org). Whey protein is composed of 50–55% Beta lactoglobulin (18 kD with 185 amino acid residues) and 20–25% alphalactalbumin (14 kD with 123 amino acid residues). Natural rubber latex (70% solid plus 30% water; pH: 10.8) samples were supplied by Chemionics Corp.

2.2. Specimen preparation

Whey and albumin proteins were dry-blended by using a mechanical stirrer; water was then added to the mixture drop by drop (up to 25% on dry weight of proteins), based on previous study (Sharma and Luzinov, 2012). The mixture was kept overnight for equilibration with water. Type I specimens (ASTM standard D638-03) and flexbars (for Dynamic Mechanical Analysis, DMA) were molded from these mixtures at 150 °C and a pressure of 20 MPa for 5 min in a hot press (Carver 60 Ton Economy Motorized Press), followed by ambient cooling and subsequent annealing overnight in an oven at 50 °C. The picture frame mold used was at room temperature during material filling.

It was observed that at more than 20% of natural rubber content it was difficult to mix and extrude the blend due to the increased viscosity—rubber has a molecular weight in excess of one million (Hart et al., 2007). Whey and the natural rubber latex were mixed and stirred manually. Water was added until it reached 105% per protein weight to obtain smooth processability during blending. This mixture was then blended in a DSM microblender with a co-rotating twin screw extruder at an rpm of 100. It was observed that plastic samples were not possible to prepare using molding conditions of whey-albumin blend bioplastics described above. In addition, higher water content (more than 25%) results in a foam-like material. Therefore, samples were prepared using the modified molding conditions—temperature of 120 °C, pressure of 20 MPa, holding time of 5 min—followed by ambient cooling and subsequent drying in an oven at 70 °C for 3 days. The dried sample contained residual moisture content of approximately 6%.

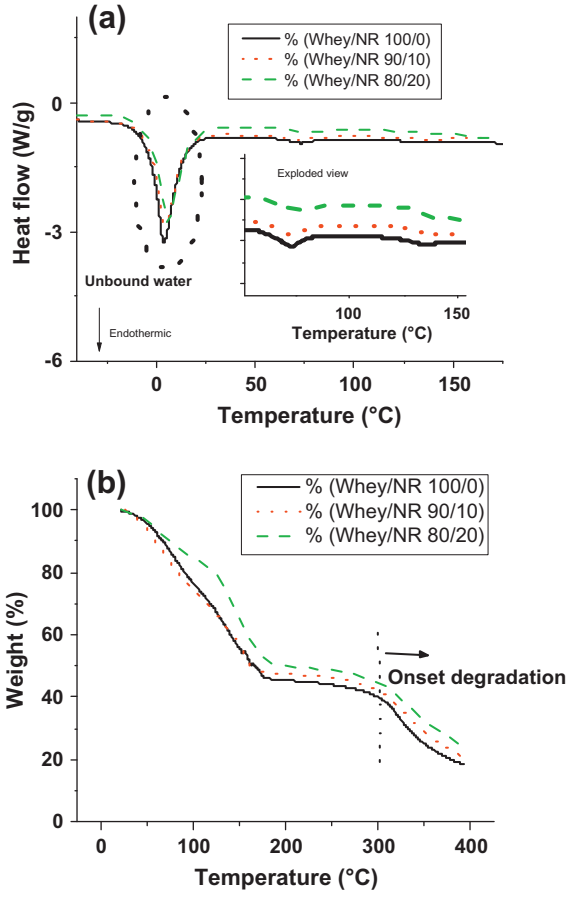

Fig. 1. Thermal analysis of whey/NR blends before molding at the elevated temperature: (a) DSC; and (b) TGA.

2.3. Mechanical properties

Tensile stress, percent strain at break, and Young's modulus were measured using the Instron testing system (Model 1125) interfaced with computer operating Blue Hill software. The test was performed under controlled environment (20 °C, 65% RH), according to the standard test method for tensile properties of plastics (ASTM D638-86) at 5 mm min^{-1} crosshead speed with a static load cell of 100 kN.

2.4. Thermal analysis

DSC (Differential Scanning Calorimetry) (Model 2920 TA instruments) was carried out in order to determine the denaturing temperature (*T*d) and the safe processing temperature window of the protein materials at a heating rate of 20 °C min^{-1}. TGA (Thermogravimetric Analysis) was carried out under N_2 purge (40 ml min^{-1}) at a heating rate of 20 °C min^{-1} with a TA instruments' Hi-Res TGA 2950 in order to study the thermal stability.

2.5. Moisture testing

A Sartorius MA50 moisture analyzer was used to analyze the moisture. For moisture testing, the samples were ground using liquid N_2. Moisture Content (MC) was determined by

$$MC = [(W_0 - W_{0d})/W_0] \times 100 \quad (1)$$

where W_0 = initial weight of specimen; W_{0d} = weight of specimen after drying.

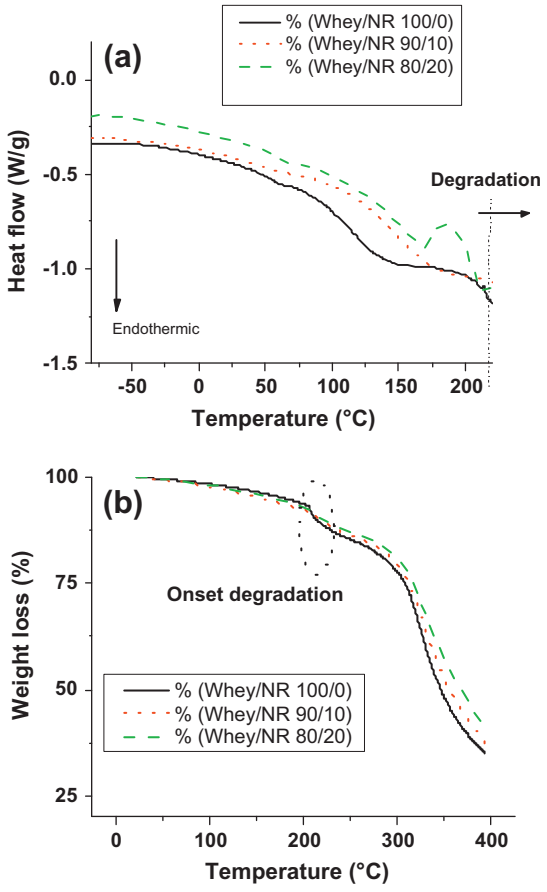

Fig. 2. Thermal analysis of plastic samples from the whey/NR blends: (a) DSC; and (b) TGA.

2.6. Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was performed using a DMS 210 Tensile Module (Seiko Instruments Inc., Japan) with specimen dimension of 40 mm × 10 mm and an effective gauge length of 20 mm. Samples were analyzed over a temperature range of 50–225 °C at a heating rate of 2 °C min^{-1}, a frequency of 1 Hz and a deformation amplitude of 10 μm. Data was analyzed using EXSTAR6000 version 5.5 software.

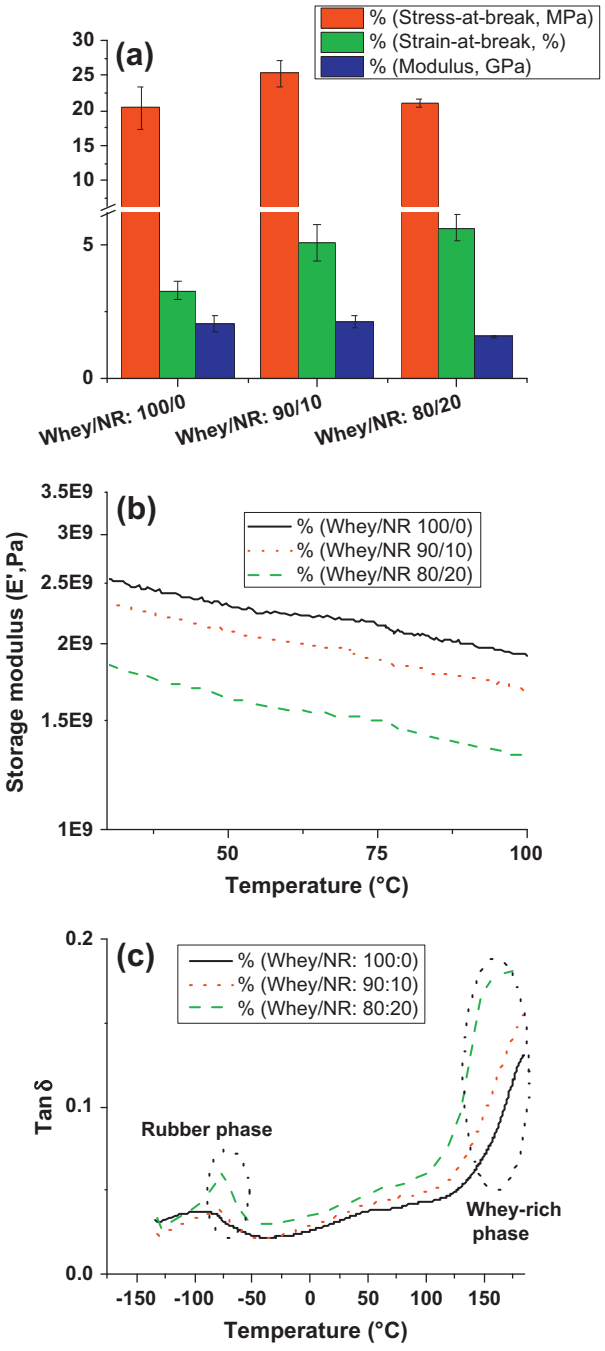

Fig. 3. Mechanical and thermo-mechanical performance of whey/NR bioplastics: (a) Static mechanical properties; (b) DMA-storage or elastic modulus; (c) DMA-Tan δ or loss factor of the plastics, molded at a temperature of 120 °C and a pressure of 20 MPa for 5 min, followed by ambient cooling and subsequently annealing in an oven at 70 °C for 3 days.

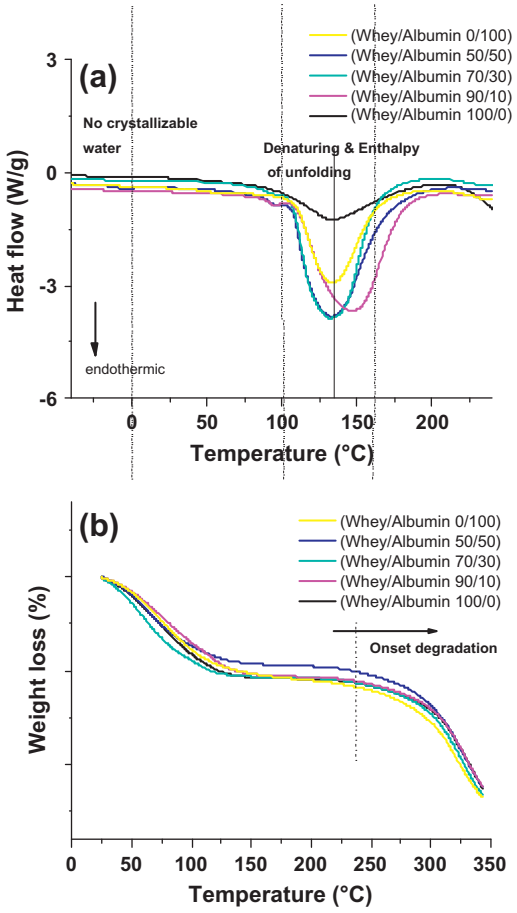

Fig. 4. Thermal analysis of whey protein blends: (a) DSC thermograms; and (b) TGA thermograms.

3. Results and discussion

3.1. Whey protein/natural rubber blend

The natural rubber (NR) is biobased and biodegradable natural polymer and has been used for improving the elongation and toughness properties of various polymeric materials (Ezoe, 1996; Hart et al., 2007; Kramárová et al., 2007). The natural rubber latex is essentially a dispersion or emulsion of *cis*-1,4-polyisoprene in water, having the particle size between 0.15 and 3.0 μm. Other components of the rubber latex are 1–2% protein and phosphoproteins, 2% resins, 1% fatty acids, 1% carbohydrates, and approximately 0.5% inorganic salt. For our purpose it is important that the rubber particles are surrounded by protein anions, which hinder the coagulation of the latex (Greeve, xxxx; Cuq et al., 1997; Zhang et al., 1997; Rouilly et al., 2001; Carvalho et al., 2003). The aminoacids of polypeptide macromolecules are able to react with aminoacids located in the whey protein chains during the blend fabrication at the elevated temperatures. The reaction can provide for the strong adhesion between rubber particles and whey protein matrix. Therefore, blends of whey protein and rubber latex might be compatible and demonstrate improved mechanical properties.

Fig. 1 shows thermal analysis of the whey/NR blends before molding at the elevated temperature using DSC and TGA. The DSC thermograms in Fig. 1a did not demonstrate prominent endothermic peaks due to denaturing of the whey protein, indicating the over-plasticizing effect of water. However, an endotherm at 0 °C due to unbound (free, crystallizable) water can be observed. Previous research has shown that to produce a plastic with acceptable performance from proteins, plasticizers such as water or other low molecular weight molecules are required to improve the processability and thermoplasticity/polymerization of proteins during molding (Cuq et al., 1997; Cunningham et al., 2000; Matveev et al., 2000; Ogale et al., 2000; Rouilly et al., 2001; Zhang et al., 2001). Although amount of plasticizers may vary between 20% and 25% by weight to produce required polymer mobility for processing and plastic fabrication (Sharma and Luzinov, 2012), whey/NR blends demand more water for homogenous blending.

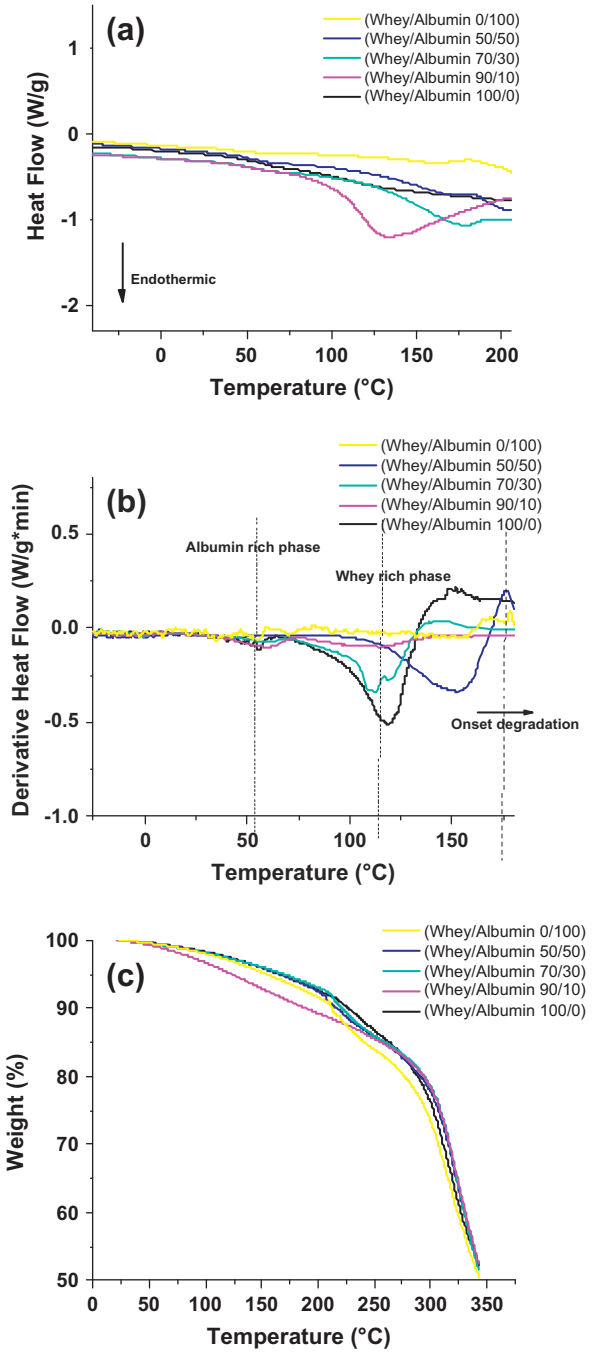

Fig. 5. Thermal analysis of whey bioplastics by using egg white protein as a modifier, produced at a temperature of 150 °C and a pressure of 20 MPa, followed by ambient cooling and annealing overnight at 50 °C. (a) DSC of whey/albumin bioplastics; (b) derivative heat flow of whey/albumin bioplsatics; and (c) TGA of whey/albumin bioplastics.

Figs. 2 and 3 show the results of thermal and thermo-mechanical analysis of whey/NR blend plastics obtained by the compression molding. The DSC thermograph shown in Fig. 2a did not clearly indicate the presence of two distinct phases: natural latex and whey protein. However, the Dynamic Mechanical Analysis (DMA), Fig. 3c, confirmed the presence of two phases with different mechanical properties. This difference can be attributed to the higher sensitivity of DMA over DSC. TGA results in Fig. 2b point to a different weight-loss pattern for the plastic samples in comparison with the blend material before molding: the first weight loss (bound water and/or low molecular-weight volatiles) occurred over a more extended temperature range—from room temperature to below 220 °C. The slowdown of the water loss can be attributed to the denser structure of the plastic sample due to more polymer–polymer (protein–protein and protein-NR) interactions.

The static and dynamic mechanical properties of the whey bioplastics at different blend ratios are presented in Fig. 3. The tensile toughness properties, i.e., both tensile strength and elongation in Fig. 3a, show improvement compared to the neat whey plastic. This improvement in toughness can be attributed to strong interfacial adhesion between the protein and the natural rubber particles. Fig. 3b demonstrates an overall depression in the storage modulus especially as the amount of rubber component increased to 20%. This phenomenon is typical for the blends made of synthetic

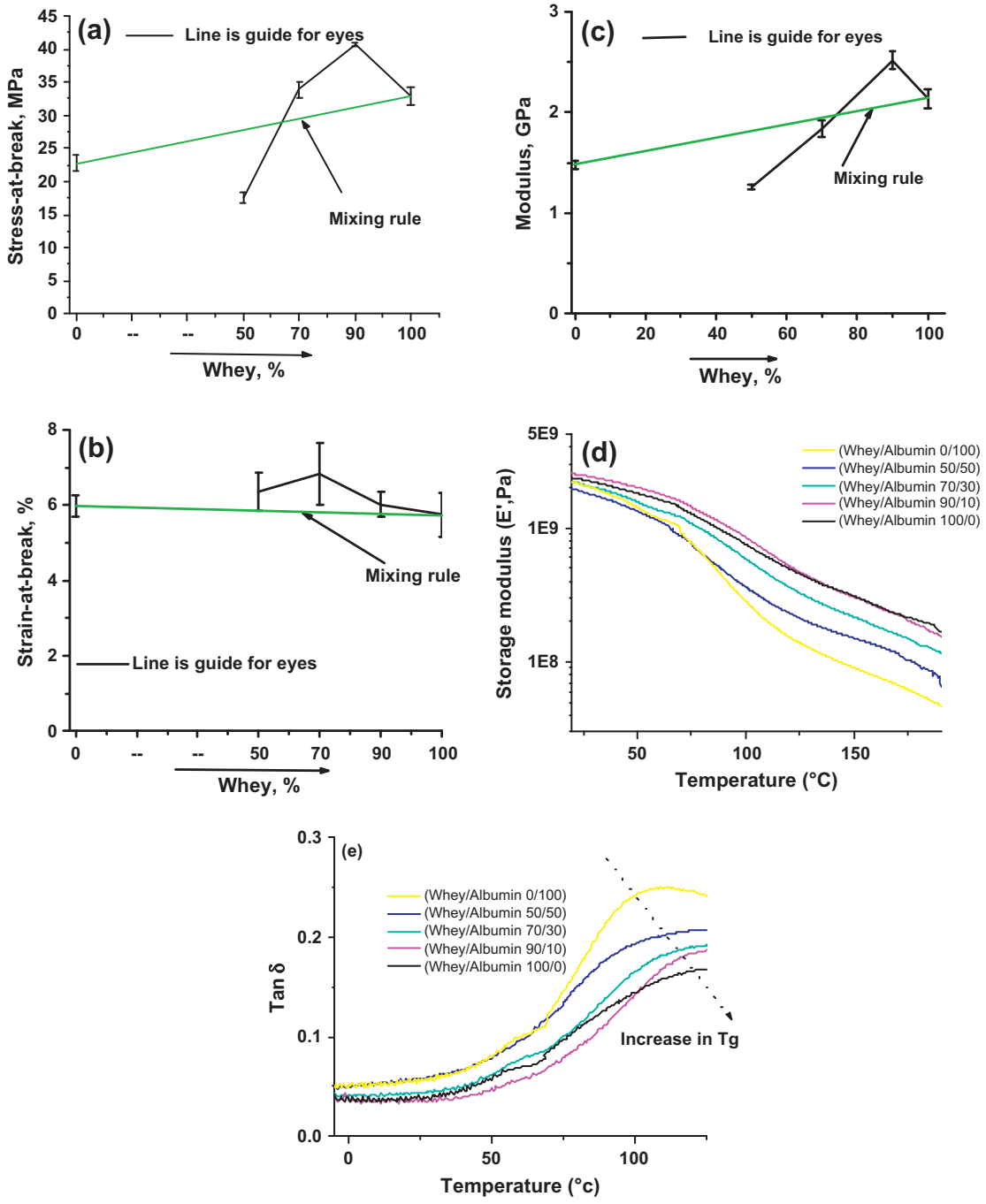

Fig. 6. Static and dynamic mechanical properties of whey bioplastics by using egg white as a modifier, produced from protein blends molded at a temperature of 150 °C and a pressure of 20 MPa, followed by ambient cooling and annealing overnight at 50 °C: (a) strength; (b) elongation; (c) modulus, (d) storage modulus; and (e) internal friction (Tan δ).

polymers. For example, past study dealing with the blends of rigid polystyrene and synthetic rubber (styrene–butadiene-styrene block polymers) has demonstrated that, by incorporating the rubber particles, the modulus of composite reduces and can be predicted by certain theoretical models (Nielsen, 1974). The height of Tan δ or loss factor peaks in Fig. 3c increased with rubber content, confirming the improvement in toughness properties with NR addition. Tan δ (ratio of the loss to the storage modulus) is the measurement of the damping whereby the material loses energy to molecular rearrangements and internal friction (Menard, 1999). In addition, the lower transition at approximately – 75 °C can be attributed to the rubber phase, and the one around 175 °C to whey-rich phase. Overall, our results show that NR demonstrates definite potential as a blend component to improve the toughness characteristics of whey bioplastics.

3.2. Whey/egg white albumin blend

Blends of whey and albumin at various w/w ratios were prepared by "dry-blending", water addition, and compression molding to study the effect of albumin addition on the properties of the whey bioplastics. The protein–protein blend is assumed to be compatible because the proteins contain complementary reactive functional groups. Because of the reactions between the functionalities at the phase boundary, strong interfacial adhesion could be readily achieved during the molding at an elevated temperature (~150 °C).

A DSC study of the protein mixture showed no crystallizable (unbound) water in the samples (Fig. 4a), suggesting the water molecules in the mixture were bound to the protein macromolecules through hydrogen bonding. Denaturing peak temperatures of blends were practically unchanged on mixing; these peaks were approximately at 132 °C. However, enthalpy of protein unfolding was found to be higher in blends than in individual protein components. This interesting effect needs further investigation; however, the formation of contacts between whey and albumin proteins might be responsible for this behavior. The TGA analysis (Fig. 4b) shows the weight-loss of the protein blends samples before the compression molding. The first weight-loss occurred from room temperature to approximately 100 °C, a loss that was primarily caused due to the water evaporation. The second weight-loss, suggesting significant degradation of the protein, was initiated at 225 °C.

Fig. 5 shows the thermal characteristics of the whey/albumin plastic produced by compression molding at various blend ratios. Phase separation is not clearly visible in the DSC thermograph of Fig. 5a. However, Fig. 5b shows the derivative heat flow, the peaks of which correspond to transitions such as glass-transition (*Tg*). *Tg* of approximately 60 °C is due to albumin-rich phase. *Tg* of approximately 120 °C is due to whey-rich phase. The temperature of degradation, as shown in Fig. 5c, however, is not influenced by the blending: the loss in weight below 200 °C can be attributed to residual, bound water and low-molecular weight volatiles; the proteins begin degrading around 225 °C.

Fig. 6 shows static and dynamic mechanical properties of these bioplastics of varying blend ratios. Below 30% of egg white albumin protein, both strength and modulus followed the mixing rule or showed synergistic effect, as can be seen in Fig. 6a and c. The additive mixing rule described for the tensile properties of the blends is shown by following equation:

$$T_{\text{blend}} = \sum W_i T_i$$

where T_{blend} is the tensile properties (e.g., modulus, stress-at-break, or strain-at-break) of the blend without considering interaction whereas W_i is the mass fraction and T_i the tensile properties of individual components.

When the whey component was more than 70%, the plastic demonstrated a much higher strength and modulus—typical high stiffness associated with 100% whey protein bioplastic. This result may be attributed to the higher effective concentration of complimentary reactive groups (COOH, OH, NH_2) in whey protein (9.6×10^{20} reactive groups per gram) than in albumin protein (6.2×10^{20} reactive groups per gram), leading to more crosslinks and resulting in a stronger network structure. However, elongation properties in Fig. 6b demonstrated the opposite behavior, which is common. At 50% of each component, there was a significant drop in strength and modulus. We suggest that co-continuous morphology formed at these ratio is resulting in a mismatch of mechanical properties and leading to failure, due to the component having a lower strength (albumin in this case).

In general, protein based bioplastics suffer with low tensile toughness characteristics (high modulus or stiffness and low extension). However, because of functionalization potential, they can be modified to be compatible with their synthetic counterparts. It is worth to note that these protein based resins cannot completely replace synthetic plastics because of lack of control on the molecular weight and its distribution. Nevertheless, they can substitute/replace the synthetic resins to certain extent without compromising the desired performance properties. Therefore, there is a need to alter the properties of standalone protein resins to keep them competitive with traditional synthetic resins by utilizing their renewability and environmentally friendliness. Table 1 compares some of the best tensile properties of whey based binary bioplastics to the one obtained from other natural protein biomass (both from animals and plants) in the literatures. Protein–protein and protein-natural rubber blends show the characteristics of miscible blends. These bioplastics behave similar to or better than Zein (expensive than whey protein) bioplastics while not requiring glycerol as a plasticizer, which may create problem of leaching.

Fig. 6d shows the storage modulus obtained from dynamic mechanical testing. As this figure indicates, the storage modulus—measured over a range of room temperature to 150 °C—increases as the whey content in the blend increased. We attribute this phenomenon to increased crosslinks between polypeptide chains involved. The Tan δ curves, the ratio of loss modulus to storage modulus shown in Fig. 6e, peak at secondary transition or glass transition temperature (*Tg*). Increasing the whey component in blends leads to a shift in Tan δ peaks towards higher temperature values, which indicates higher *Tg*, a decrease in the height of Tan δ peaks, implying an increase in stiffness (more elastic or storage component). It appears that egg white albumin disrupts the interactions among whey protein macromolecules plasticizing the

Table 1
Comparison of mechanical properties of whey based binary bioplastics to other bioplastics and/or blends.

Comparative whey based binary bioplastics to other bioplastic materials		
Bioplastic type	Percent extension	Stress-(MPa)
Plasticized wheat gluten/starch (Song et al., 2010)	169	1.7
Plasticized wheat gluten (Song and Zheng 2008)	132.8	1.7
Zein (Sessa et al., 2008)	8.5	25.3
Plasticized egg white albumen/corn starch (González-Gutiérrez et al., 2011)	50	5
Plasticized egg white albumen/potato starch (González-Gutiérrez et al., 2011)	35	4.25
Soy protein isolate (Mo et al., 1999)	1.2	13.0
Egg white albumin (Sharma and Luzinov 2012)	2.8	16.7
Whey/NR (80/20) (this study)	5.6	21
Whey/albumin (70/30) (this study)	6.8	34

material. Overall, adding egg white albumin improves the flexibility of whey based binary bioplastics.

4. Conclusions

Whey protein bioplastics obtained via blending the protein with two abundant biopolymers: natural latex and egg white albumin can be fabricated by compression molding where water is added as plasticizer. It is demonstrated that addition of about 10% of the latex and albumin to the whey based bioplastics improves the toughness characteristics of whey based materials without compromising their strength and stiffness.

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