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Design of rigid wheat gluten materials

Improved mechanical properties by blending with polyamides

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I dedicate my work to my mother Şeyma and my father Hamit, above all who first taught me to believe.

Leuven, May 2014 Alican GENÇER

Abstract

There is an increasing attention for the development of bio-based materials in recent years because of the diminishing stocks of petrochemicals and environmental problems caused by petroleum based polymers. Hence biopolymers are potentially good alternatives to synthetic polymers since most of them are sustainable and environmentally friendly. Aim of this research is the development of rigid wheat gluten based materials with improved mechanical properties. Wheat gluten has a high stiffness when molded, but it is brittle. A proper strategy is required to produce high performance materials with reasonable toughness. One of the options to improve the mechanical properties of polymers is to blend them with suitable other polymers. Thus, wheat gluten was mixed with aliphatic polyamides in a mutual solvent at different compositions. Very often, compatibilizing the phases of immiscible polymer blends is mandatory for achieving desired polymer blend mechanical properties. Therefore, studies on improving the compatibility between the blend phases were included and involved blending with a third reactive component. Samples obtained by high temperature compression molding of freeze-dried and powdered blends were thoroughly characterized using thermal, mechanical and morphological methodologies. Three point bending tests were used to measure the stiffness, flexural strength, elongation at break and toughness. DMA and DSC studies revealed the thermal transitions of the blends. The morphology of cryo-fractured sample surfaces was investigated by SEM, for binary as well as ternary blends. X-ray scattering was used to elucidate aspect related to the crystallinity of the added nylon.

Contents

1. Introduction

People use a lot of different materials in their daily life. Those are mostly made of wood, metal, agricultural products, petroleum and similar. Polymers are one of the important classes of materials. There are mainly two groups of polymers which are either petroleum-based or bio-based. Each year vast quantities of petroleum based polymeric materials are produced and used. However in most cases petroleum based plastics are not biodegradable and so waste disposal of products that have reached their end of life has been identified as a serious problem which must be addressed. In addition, petroleum oil is not a sustainable source and therefore there is a dependency on the limited amount of petrochemicals. In this respect alternative materials based on biopolymers can be considered advantageous, since many are biodegradable, sustainable and renewable[1]. In addition, a shift to bio-based polymers decreases our dependency on petroleum oil and may increase cost efficiency. A wide range of naturally occurring polymers obtained from renewable resources can be exploited for material applications. However, mechanical properties of most bio-based polymers are currently outperformed by synthetic polymers and must be improved to be considered as a viable commercial alternative.

1.1. Polymers

Polymers are large molecules which consist of repeating chemical units that are called monomers[2]. Examples of some common polymers are polyethylene, polystyrene and polyvinyl chloride. The term “polymers” is commonly used to describe a broad range of materials, from synthetic materials, such as plastics, rubbers, fibers, coatings, filtration membranes, adsorption resins and adhesives; to natural materials, such as natural rubbers, silks, hairs, and chitins; and bio-macromolecules, such as DNA, cellulose, proteins[3]. It is important to distinguish between these polymers. Scientists classify polymers in order to have clear understanding. Classification can be based on a variety of criteria including origin, structure or applications. For example in terms of their origin; natural polymers, artificial polymers and synthetic polymers can be distinguished[4]. Natural polymers already exist in nature and are obtained from vegetable and animal sources. Artificial polymers are obtained via chemical modification of natural polymers. Inspired by nature, scientists mimic natural polymers to obtain synthetic polymers via polymerization. A large variety of petroleum based synthetic polymers are commercially available on the market today (Table 1).

Table 1 Some of Commercial Polymers (invention year) [5]

Polymer	Year	Company
Bakelite	1909	General Bakelite Corp.
Rayon	1910	American Viscose Company
Poly(vinyl chloride)	1927	Goodrich
Styrene–butadiene copolymer	1929	I.G. Farben
Polystyrene	1929/1930	I.G. Farben and Dow
Neoprene	1931	DuPont
Poly(methyl methacrylate)	1936	Rhom & Haas
Nylon-6,6	1939/1940	DuPont
Polyethylene (LDPE)	1939	ICI
Poly(dimethyl siolxane)	1943	Dow Corning
Acrylic fiber	1950	DuPont
Poly(ethylene terephthalate)	1953/1954	DuPont/ICI
Polyurethane block copolymers (Spandex)	1959	DuPont
Poly(phenylene terephthalamide)	1960	DuPont

However, petroleum oil which is not renewable is getting more expensive and insufficient for the demand. Measures also should be taken to avoid CO_2 emissions and reduce carbon footprints. A zero material carbon footprint is required to control and reduce CO_2 emissions. A zero material carbon footprint means that the rate of CO_2 release to the environment at the end-of-life equals the rate of photosynthetic CO_2 fixation by the next generation of crops planted. This can be achieved via replacing the petro-fossil carbon with biobased carbon in plastics and other polymer materials[6]. Petrochemical based products are disadvantageous in terms of their carbon footprint because plant biomass is fossilized over geological time frames (>10^6 years) in order to provide petroleum, natural gas and coal. These fossil feedstocks are converted to polymers, chemicals and fuel, which then release the carbon back into atmosphere as CO_2 in a short time frame of 1-10 years (Fig. 1). Biomass is an advantageous alternative to fossil fuel in this respect as its carbon source is agricultural feedstock which can be renewed much faster[7]. As a result, polymers from renewable agricultural products, plant biomass and forestry crops are termed biobased polymers and allow sustainable development with minimal environmental impact. It is also preferred that those biobased polymers are biodegradable. Some of the most common biobased polymers are polylactic acid (PLA), polyhydroxybutyrate (PHB), soy based plastics, cellulose polyesters, starch based bioplastics, vegetable oil derived bioplastics, poly (trimethylene terephthalate), biopolyethylene etc. [8].

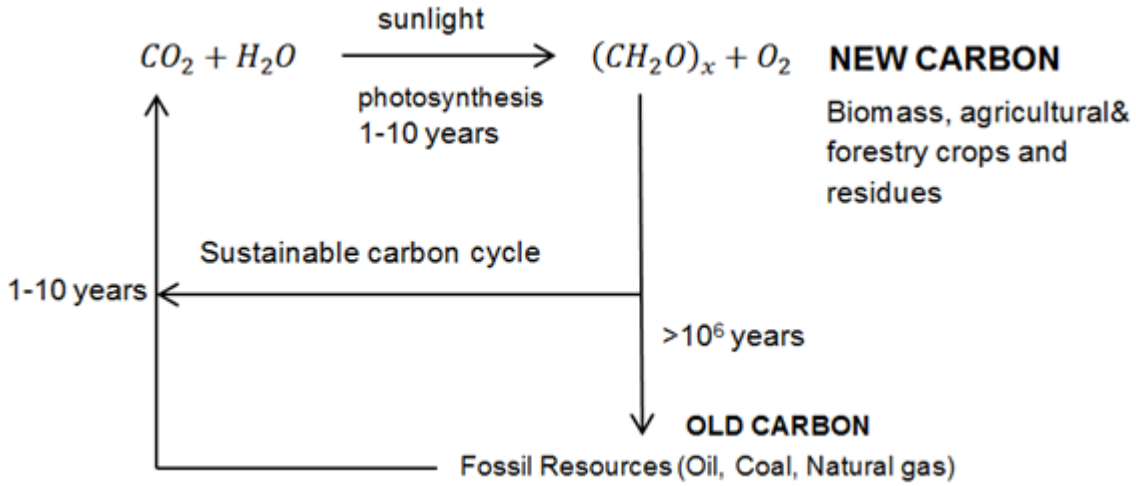

Figure 1 Biological carbon cycle – value proposition for using biobased feedstocks instead of petro-fossil carbon feedstock [6]

In certain cases researchers still make use of polymerization reactions to produce biobased polymers. The synthesis of polylactic acid is a well-known example in which the lactic acid monomers are obtained from a renewable feedstock and are subsequently polymerized to produce polylactic acid[9]. It is also significant to differentiate between already existing natural polymers and artificial polymers which are obtained via modification of natural polymers (Table 2). For example, cellulose is a natural polymer produced by nature whereas cellulose acetate is an artificial polymer obtained by the reaction of cellulose (natural polymer) with acetic anhydride[10].

Table 2 List of some natural polymers [11]

Polysaccharides	from plant/algal: starch, cellulose, pectin, konjac, alginate, caragreenan from animal: hyluronic acid from fungal: pulluan, elsinan, scleroglucan from bacterial: chitin, chitosan, levan, xanthan, curdlan, gellan,dextran
Protein	**wheat gluten,** soy, zein, casein, serum, albumin, collagen/gelatine silks, resilin, polylysine, polyamino acids, poly(Ɣ-glutamic acid), elastin
Lipids	acetoglycerides, waxes, emulsan

1.2. Polymer Blends

In order to optimize the mechanical performance of bio-based materials, the polymer architecture is carefully considered and many routes such as the use of fibers, nanoparticles and blending with other polymers have been explored. Multicomponent polymer blends and polymer composites are widely studied and utilized in industry to fabricate polymeric materials with superior properties[12]. Mixing polymers sometimes can be a difficult task. It is important to take into account the miscibility and compatibility of the different polymer components. It is possible to obtain miscible, partially miscible or immiscible blends. The miscibility depends on several factors such as the nature of the polymers composing the blend and the amount of each component in the blend. Miscibility can also be described as a thermodynamic concept. In order to achieve mixing, the Gibbs free energy of mixing must be negative. Thus, immiscibility can be explained by a low entropy of mixing in conjuction with an endothermic enthalpy of mixing (Eqn. 1) [4].

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

Equation 1 Gibbs free energy of mixing

Miscibility can sometimes be obtained by varying the temperature or by introducing specific interactions between the polymers. The Flory–Huggins theory of mixing describes the polymer blend miscibility (Eqn. 2) [4].

$$\Delta G_{\text{mix}} = RT(N_1 \ln \Phi_1 + N_2 \ln \Phi_2 + \chi_{\text{mix}} N_1 \Phi_2)$$

Equation 2 Gibbs free energy of mixing according to Flory-Huggins Theory

where N_1 and N_2 are the number of moles of polymers, ϕ_1 and ϕ_2 are for volume fractions of the polymers and χ_{mix} is the polymer–polymer interaction parameter and equal to;

$$\chi_{\text{mix}} = \Phi_1 \chi_{13} + \Phi_2 \chi_{23} - \chi_{12} \Phi_1 \Phi_2$$

Equation 3 Polymer- polymer interaction parameter

The interaction of polymers via dipole-dipole forces, hydrogen bonds or donor-acceptor interactions increase the chance of obtaining miscible polymer blends. In the case of immiscible blends, compatibilization is often required to control the surface tension and interfacial adhesion between the two phases. Two-phase blends can have different types of morphologies such as drop matrix (one phase is dispersed in another) or co-continuous. Compatibilization can control the size and morphology of the dispersed phase and its stability to coalescence[13]. Thus optimization of interfacial tension, stabilizing morphology and improving adhesion between phases can improve the mechanical properties of polymer

blends. Compatibilization is done either by addition of a compatibilizer or by reactive blending[14]. For example, a third component which is miscible with both phases or a block copolymer whose one part is miscible with one phase and the other with another phase can be chosen as a compatibilizer. Reactive blending can occur in certain cases when the blended components contain functional groups which can react during mixing to generate trans-reactions and copolymers such as graft and block copolymers.

Polymers can adopt a wide array of molecular structures depending on features such as side chains, cross-link density and degree of crystallinity which can be collectively referred to as the polymer architecture (Fig. 2). All these features can have an effect on the mechanical properties of polymers and must be considered in material design. In the case of polymer blends, blend composition, blend morphology, viscoelastic properties of the components and interfacial adhesion are among the parameters to control mechanical properties. Hence, there is a possibility to improve mechanical properties and performance of natural polymers via controlling the nature of the components, blend composition and morphology.

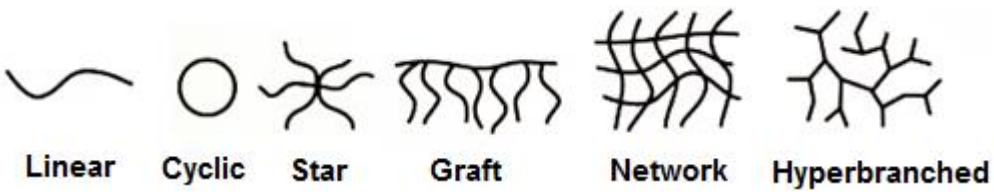

Figure 2 Topology of polymers [15]

High-impact polystyrene (HIPS) is a good example of where smart design was used to produce a high performance engineering plastic from a polymer with relatively poor properties. HIPS is obtained by mixing polystyrene and polybutadiene to give an immiscible two phase structure of spherical polybutadiene rubber particles incorporated in a matrix of polystyrene. Polystyrene homopolymer is itself stiff but brittle. However, a tough material with a satisfactory stiffness is obtained via blending with rubbers[16] (Fig. 3). Samples of polystyrene break after the first observation of a craze and thus exhibit brittleness. When a stress is applied to HIPS, a large number of crazes are generated at the surfaces of the rubber inclusions which produce many stress concentrations. Rubber inclusions induce plastic deformation to the matrix which absorbs energy via crazing (each craze only runs to an adjacent rubber particle where it terminates). It is also noted that crazing occurs more difficult in smaller sized inclusions as voiding at small particles is more difficult than in large inclusions [17]. On the other hand, in pseudoductile polymers, such as polycarbonate (PC), polyvinyl chloride (PVC) and polyamides, shear yielding is usually the major energy absorbing mechanism [18].

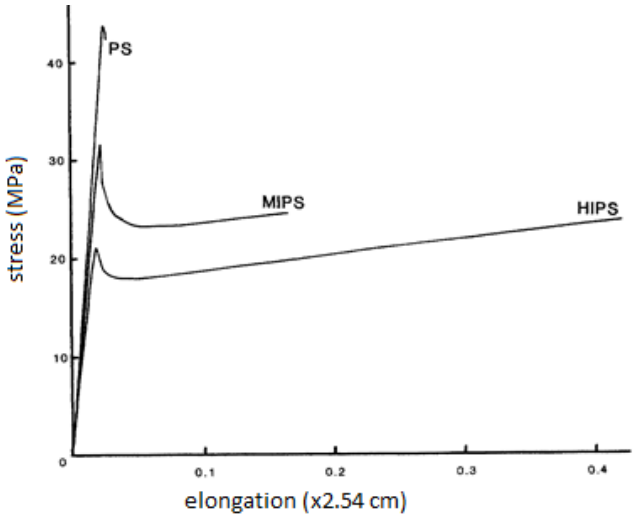

Figure 3 Tensile stress-strain curves of PS (polystyrene), MIPS (Medium Impact PS) and HIPS (High Impact PS) obtained at a displacement rate of 12, 7x10^{-7} cm/min [19]

In order to address the previously discussed concerns associated with synthetic (petroleum based) polymers, it could be beneficial to investigate bio-alternatives to high-impact polystyrene. Thus, bioplastic obtained via renewable agricultural resources can create opportunities to have equivalent high performance materials. Wheat gluten protein could be a candidate resource to obtain bioplastics as its inherent stiff but brittle nature is similar to that of polystyrene. Wheat gluten is easily available as a co-product of the wheat starch industry at low cost, it is biodegradable and renewable [20]. In addition, wheat gluten offers a better environmental performance compared to PLA and LDPE without any toxic effect on the microorganisms during the degradation process[21] [22].

1.3. Wheat Gluten Proteins

Wheat gluten proteins are the storage proteins of the wheat grain [23]. They are mostly found in bakery products such as bread, pasta, cookie etc. Gluten proteins can be categorized into two groups according to their solubility in aqueous alcohols, the soluble gliadins and the insoluble glutenins. Both groups of proteins have similar protein components consisting of high glutamine and proline contents[24]. Gliadins are monomeric (single-chained) proteins with molecular masses around 30,000–80,000 whereas glutenin consists of aggregated proteins linked by interchain disulfide bonds; having molar masses ranging from about 80,000 to 20 million[25]. Glutenin polymers consist of subunits which are called high-molecular-weight glutenin subunits (HMW-GS) and low-molecular-weight glutenin subunits (LMW-GS). They can be obtained after treatment of glutenin with a disulfide reducing agent such as β-mercapto-ethanol or dithiothreitol [26]. After reduction of disulfide bonds, the resulting glutenin subunits dissolve in aqueous alcohols similar to gliadins. Non-covalent bonds such as hydrogen bonds, ionic bonds and hydrophobic bonds are vital for the aggregation of

gliadins [24]. Cysteine residues play an important role in the structure of both gliadins and glutenin subunits. These cysteine residues are either involved in disulfide bonds within the same polypeptide (intra-chain disulfide bonds) or in disulfide bonds between different polypeptides (inter-chain disulfide bonds) [26]. Gluten is versatile for further modification and processing because of its structural and functional properties. Presence of sulfhydryl (SH) and disulfide (SS) groups have effects on physical and chemical properties of gluten. It has also some unique characteristics such as its viscoelastic properties and ability to cross-link[20].

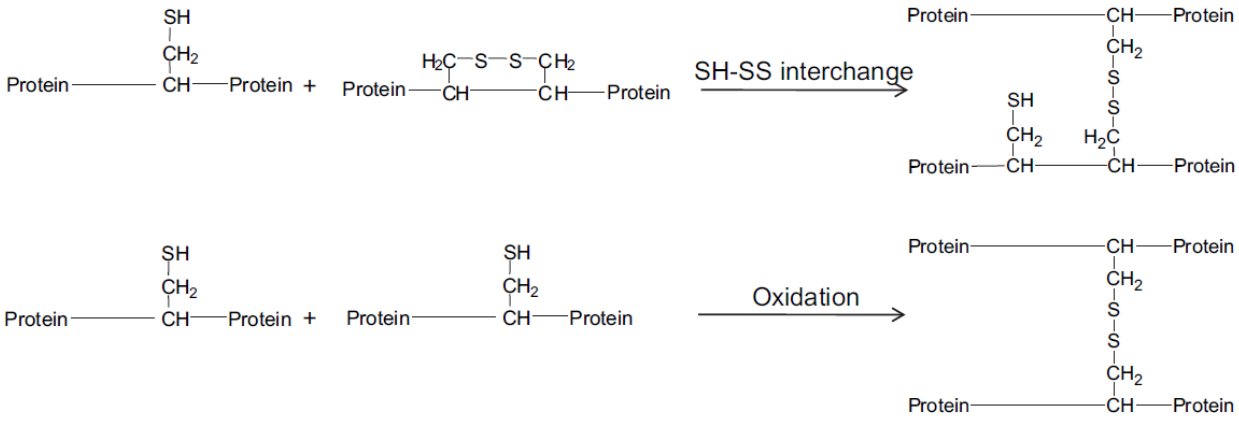

Figure 4 Reactions involving cyst(e)ine residues [27 28]

Gluten has a high stiffness when molded into plastic in the range of epoxy ($E \sim 1$ - 4 GPa) and reasonable strength (35 - 50 MPa) in comparison with other bioplastics [29]. However, wheat gluten is brittle like polystyrene [30]. To tackle this problem, it is necessary to control structural characteristics of wheat gluten proteins. Network formation and cross-linking play a significant role in determining the mechanical characteristics of wheat gluten proteins. Structural modifications can be achieved via physical (temperature or pressure treatment), enzymatic (hydrolysis, transamidation, attachment of amines and deamidation) or chemical (cross-link) methods [29 31]. In addition, transamidation reactions are significant since they would exchange the constituents of two different amide groups between phases [32 33]. Transamidation reactions are generally reported to occur at high temperatures (300 °C) which are not suitable for reactions on proteins since there is a risk to degrade the protein [34 35]. Alternatively, study of transamidation held at lower temperatures with the help of metal catalysts was reported [32]. However, metal catalysts are not preferred since they are not environmentally friendly. Deamidation, the conversion of amide groups of asparagine and glutamine to carboxylic acids, has been shown to decrease the surface tension and remarkably increase the surface hydrophobicity of gluten in proportion to the degree of deamidation[36]. Deamidation might induce conformational changes of wheat gluten protein by increasing the electrostatic repulsion and decreasing the hydrogen bonding.

1.4. Previous Research on Wheat Gluten

Research has already been done to study changes of rubbery and rigid wheat gluten properties by changing the physical treatments [37] [38] or blending with other polymers, additives or plasticizers[39] [40]. Homogeneous blends of wheat gluten and glycerol were thermally treated to investigate the effect of thermal treatments on the mechanical properties of the ensuing rubbery material and solubility of the wheat gluten-based network [37]. It was reported that an increase in treatment temperatures (from 80 to 135 °C) induces an increase in mechanical resistance of the gluten network (tensile strength increases from 0.26 to 2.04 MPa) and a decrease in deformability (elongation decreases from 468 to 236%). Temperature changes affect the wheat gluten network formation due to intra and intermolecular interactions such as cross-linking and reactions between cyst(e)ine residues.

Studies were carried out to optimize the conditions for processing wheat gluten protein into a rigid material, i.e. wheat gluten in absence of plasticizers or moderate amounts of it. Effects of molding temperature, molding time and moisture content on the mechanical properties of compression molded wheat gluten bioplastics were reported [41]. It was shown that higher gluten powder moisture contents increased the cross-linking degree for molding at 130 °C and 150°C. Another research has been held to study the influence of mixing and molding temperature of wheat gluten-based materials plasticized with moderate amounts of glycerol and water [39]. Plasticizers are used to improve the processability and the brittleness of the products. It is concluded that moderate molding temperature resulted in more ductile materials whereas higher mixing and molding temperatures led to bioplastics with higher elastic modulus.

Chemical modification of wheat gluten protein structure has also been investigated to enhance the material performance. Modifications are based on the formation of different chemical and network structures[42]. A graft copolymer of wheat gluten with epoxy-functionalized alkoxysilanes was synthesized and characterized. The epoxy groups were grafted to the amine groups of wheat gluten, and then the condensation reactions between alkoxysilane segments occurred during thermal processing to form wheat gluten−siloxane networks (Fig. 5)[43]. The amount and type of alkoxysilanes have an effect on mechanical properties and molecular motions of the networks. Strength improvement was achieved with the help of the flexible nature of the siloxane components.

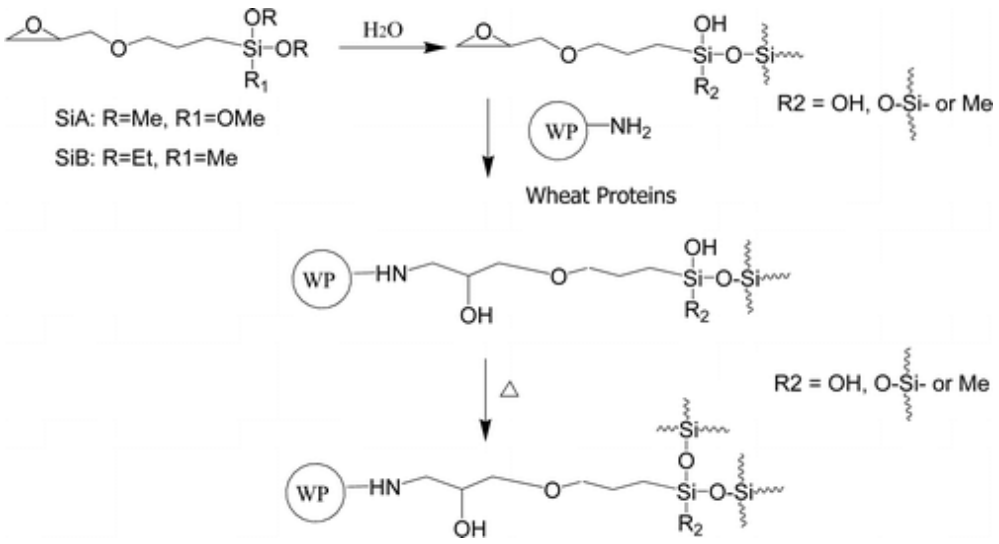

Figure 5 Chemical Structures of Alkoxysilanes SiA and SiB and Their Reactions with Wheat Proteins [43]

In a similar study, chemical modification was achieved via grafting and cross-linking reactions with poly (ethylene glycol) diglycidyl ether (PEGDE) and subsequent reaction with ethylene diamine (EDA) (Fig. 6)[44]. Different network structures were obtained via chemical reactions between wheat gluten protein, PEGDE and EDA. Samples were characterized by NMR to prove the formation of chemical networks and DMA was used to study the sample glass transition temperatures. The mole ratio of PEGDE to EDA was varied to obtain different blends with different mechanical properties. The study showed that different network structures alter the solubility, modify mechanical properties and improve the flexibility of wheat gluten based materials.

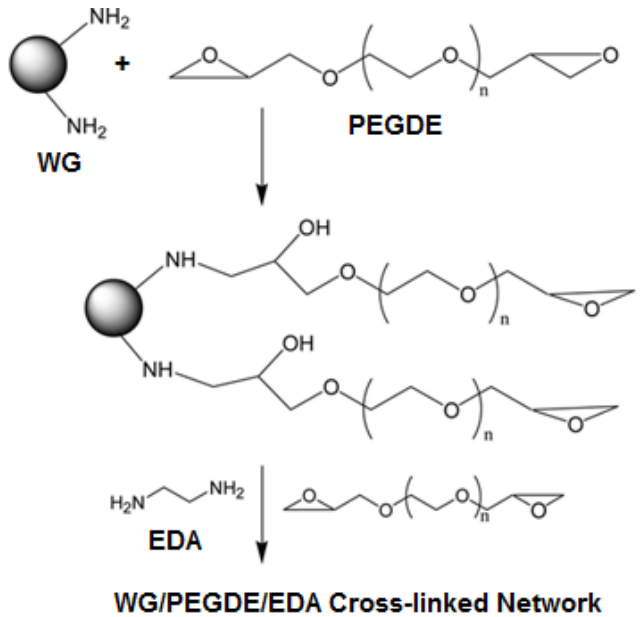

Figure 6 Formation of different networks via grafting PEGDE to wheat gluten proteins and cross-linking with EDA [44]

Blends of wheat gluten (WG) and thiolated poly (vinyl alcohol) (TPVA) were also studied to obtain improved mechanical properties [29]. It was reported that PVA/WG blends had similar or lower stress and strain to failure compared to wheat gluten. Additional thiol groups were subsequently grafted onto the PVA chains (leading to thiolated PVA, TPVA) in order to facilitate reactivity with the gluten protein. The TPVA/WG blends provided larger strain at break, flexure strength and a slightly higher modulus than pure WG and PVA/WG (Fig. 7).

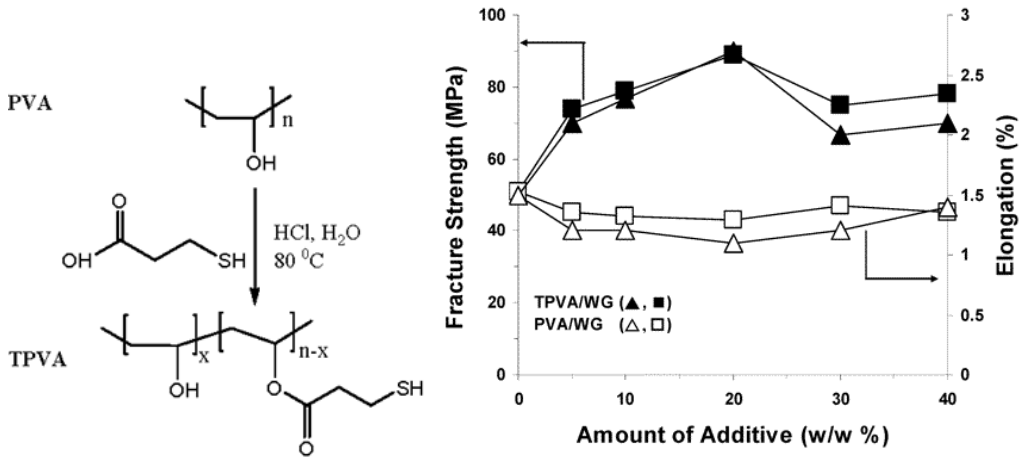

Figure 7 Study on mechanical properties of blend of Wheat Gluten and TPVA, PVA (fracture strength □, elongation △) [29]

Further work was done to determine whether TPVA and WG form protein conjugates or microphase-separated morphologies. The morphology of WG protein blends with PVA or TPVA were investigated by atomic force (AFM) and transmission electron microscopy (TEM) as well as by modulated differential scanning calorimetry (MDSC)[45]. Compatibility of TPVA to wheat gluten was compared to PVA/Wheat gluten blends. It was concluded that TPVA is much more compatible with wheat gluten and phase separates into much smaller domains than in the case of PVA. However there are still two kinds of phases in the blend, WG-rich phases and TPVA-rich phases.

These investigations show that the strategies used to convert PS into HIPS (making blend of polystyrene- polybutadiene to increase mechanical properties) can be used for modification of the mechanical properties of wheat gluten materials. Factors such as compatibility of phases, blend morphology, crystallinity and water absorption are very critical parameters to be controlled to obtain high performance materials.

1.5. Aim of Thesis Research

This research aims to obtain rigid wheat gluten based materials with improved mechanical properties. The desired material should have mechanical characteristics similar to HIPS (Fig. 3). It is targeted to enhance strength, strain to failure and toughness without compromising too much on the material stiffness. A blending strategy will be adopted to achieve this goal. Aliphatic polyamides will be used as the blended polymer as it is anticipated that the amide groups will induce compatibility with the analogous peptide links of the gluten protein. An investigation will be carried out to find optimal blending conditions. Changes in mechanical properties upon varying the amount of polyamide added to the blend system will be examined with several characterization methods. It is aimed to use a low energy blending route via lowering the melting temperature of polyamides with the use of solvent dissolution under pressure[46]. It is also expected that the addition of crystalline polyamide sections into the gluten network will affect mechanical properties such as increase the heat distortion temperature and the modulus. In addition, inclusion of aliphatic nylons to wheat gluten will lower the water uptake thus problems due to water absorption such as change in mechanical properties and susceptibility to microbial attack will be counteracted.

In order to obtain good dispersions of small particles of the nylon phase, extra compatibilization efforts may be mandatory. To this end, reactive compatibilization via the addition of a functional compatibiliser will be studied in order to modify the interface between the phases and increase adhesion[13]. Compatibilizers capable of reacting with both the amide groups of nylon and the amino acid residues of wheat gluten proteins will be selected for this purpose [47]. To fulfill this criteria, difunctional epoxides capable of reacting with both nylon and gluten phases will be focused on as compatibilizing agents.

2. Experimental Section

2.1. Materials

Wheat gluten with protein content ~78% and a moisture content of 6% was obtained from Tereos Syral (Aalst, Belgium). Elvamide® 8061 nylon multipolymer resin was obtained from DuPont® (Mechelen, Belgium). Elvamide is a ternary copolymer of nylon-6, -66 and -610 [48]. Poly(ethylene glycol) diglycidyl ether (average M_n 500) and Poly(propylene glycol) diglycidyl ether (average M_n 640) were obtained from Sigma-Aldrich® (Diegem, Belgium). Distilled water was used for each experiment together with Disinfectol ® as ethanol denaturated with up to 5% ether (Chem-Lab®, Zedelgem, Belgium) and ethanol absolute AnalaR NORMAPUR® (VWR®, Leuven, Belgium).

2.2. Gluten/Nylon Blend Preparation

Gluten and polyamide were mixed in ethanol/water (70% v/v - 500ml) in a Büchi Glas Uster® (Switzerland) pressurized reactor (Fig. 8). Mixing was carried out for 1 h at the desired temperature with a mixing speed of 100 rpm. The reactor was subsequently cooled to 25 °C during 30 min before mixtures were removed and collected in 1 l round bottom flasks. Ethanol was removed via distillation using Rotavapor R3000 (Büchi®, Switzerland). 100 ml of distilled water was then added and the samples were shaken to achieve a good dispersion before freezing in liquid nitrogen. Samples were freeze-dried (Martin Christ®, Osterode, Germany), and ground in a laboratory mill (IKA®, Staufen, Germany). A solid homogenized powder of wheat gluten and polyamide was obtained which was, sieved through a 250 µm sieve. The resulting powder was conditioned for 1 week at 50% RH and 20 °C in a moisture chamber. (Memmert®, UK)The moisture content of the powdered samples after conditioning was determined with the weight loss of a product during drying at standard conditions according to AACC Approved Method 44-19. Thus, around 2 g of each sample were dried in an oven at 130 °C, 2 h in aluminum moisture cups and then moisture content was calculated using equation 4.

$$MC = \frac{M_{cc} + m_i - M_f}{m_i} \times 100$$

Equation 4 Formula used to determine moisture content of powder blends

MC: moisture content of product (%), M_{cc}: mass of the cup+cover (g), m_i: initial mass of the sample (g), M_f: final mass of the cup+cover+dry sample (g)

It was found that the calculated moisture content for the powdered samples after conditioning (1 week, 50% RH, 20 °C) was in all cases around 8±1%.

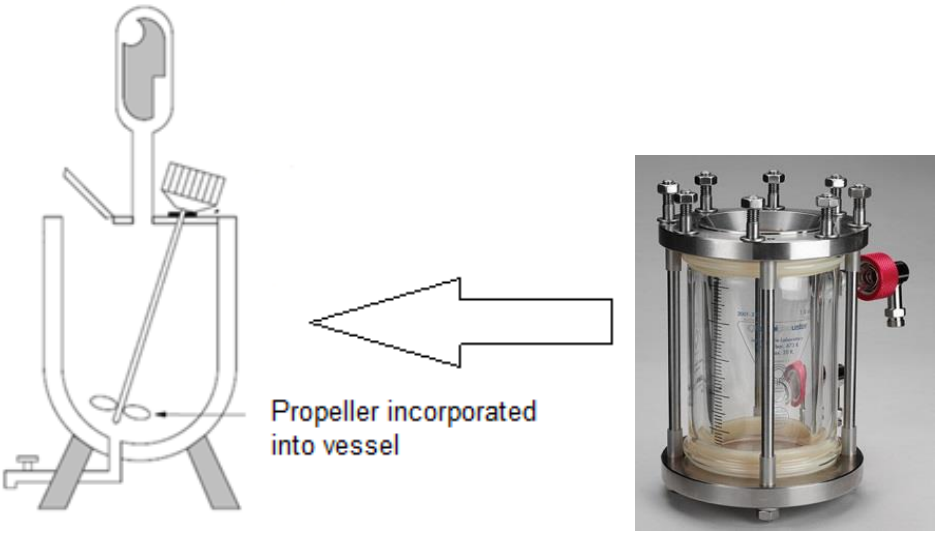

Figure 8 Pressure vessel made from metal and glass (Büchi Glas Uster®)

2.3. Preparation of Molded Specimens

Samples were compression molded in a preheated mold between two metal sheets with a Presse P 200 E (Collin®, Germany). High temperature compression molding was performed at 100 bar (10000 kPa), 5 min heating at 150 °C and then 5 min cooling to room temperature. Rigid brown homogenous plates were produced with rectangular shape. Then, six bars were obtained with averaged size approximately 53 x 13 x 1,90 mm^3 via cutting plates with an IsoMet® low speed graphite saw (Buehler®, Illinois, USA). Lastly, bars were conditioned for two days at 50% RH and 23 °C in a moisture chamber before any characterization test.

Water absorption test were also conducted on compression molded bars. The sample was submerged in deionized water (containing 20 mg/l sodium azide to avoid microbial growth) at 20 °C. At specified time intervals, samples were withdrawn and droplets were removed from the surface with paper tissue. The samples were then immediately weighed (m_1) and submerged again. The water absorption was monitored for 72 h. The samples were dried for 24 h at 130 °C and the dry mass was determined (m_2). The water absorption due to immersion was determined in duplicate expressed as the increase in sample mass divided by its dry weight after immersion for 72 h.

$$water\ absorption = \frac{m_1 - m_2}{m_2} \times 100$$

Equation 5 Formula used to determine water absorption of molded blends

Further work investigated the mechanical performance, the morphology and thermal transitions of polymer blends.

2.4. Dynamic Mechanical Analysis (DMA)

DMA is a technique used to characterize mechanical properties of polymers such as viscosity, modulus and glass transition temperature together with their dependence on temperature or time. The basic working principle of DMA is based on the application of an oscillating force to a sample and examining the response of the sample to that force. In other words, a sinusoidal stress is applied while the resultant sinusoidal strain is measured. Viscoelastic materials exhibit a phase difference between the stress and strain sine waves (Fig. 9). Using this phase difference, together with the amplitudes of the stress and strain waves, a complex modulus (E*), an elastic (storage) modulus (E'), and an imaginary (loss) modulus (E") are calculated from the material response to the sinusoidal stress. Characterization of the material includes examining the ratio of the material ability to return or store energy (E') to its ability to lose energy (E"), i.e. tan δ which is called the damping[49].

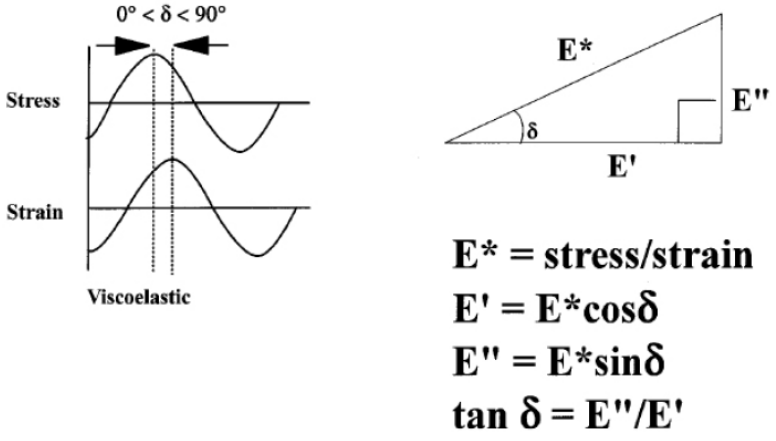

Figure 9 Complex modulus (E*), an elastic (storage) modulus (E'), an imaginary (loss) modulus (E") and tan δ

The T_g can be defined by either the peaks of tan δ, E" or the beginning of the drop in *E*'. The drop in the elastic modulus was determined from the intercept of the extrapolated glassy modulus and the extrapolation of the slope at the inflection point in the drop in *E*'. Pure wheat gluten shows the behavior of an amorphous polymer i.e. with increasing temperature, these amorphous proteins go through the glassy region, the transition region (tan δ peak and *E*' modulus drop), and a rubbery plateau. The size of the tan δ peak reflects the volume fraction of the material undergoing the transition[50]. DMA conveniently reveals transitions in materials via changes in the E' relating to temperature (Fig. 10).

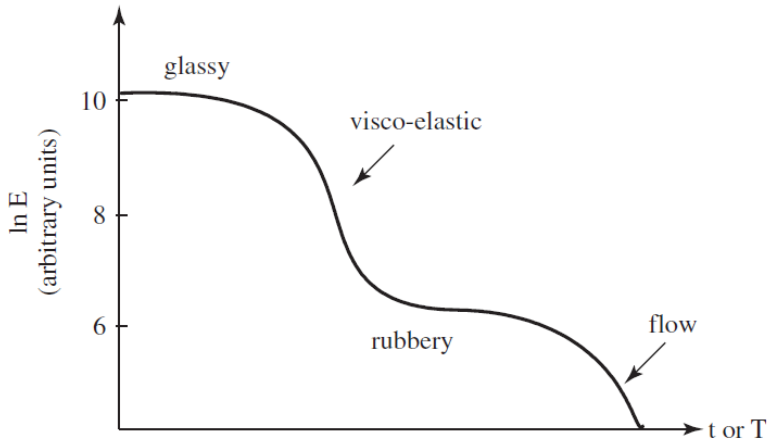

Figure 10 Modulus behavior with temperature [4]

2.4.1. Experimental Setup of DMA

The storage modulus, loss modulus and tan δ as a function of temperature were recorded using a DMA 2980 (TA Instruments, New Castle, USA). These tests were carried out using a single cantilever clamp (Fig. 11), with a heat rate of 3 °C / min from -30 °C to 175 °C, and amplitude of 20 µm with 1 Hz frequency. Cooling was achieved via liquid nitrogen. T_g was determined from the peak of the loss modulus (E") curve.

Figure 11 Single/Dual cantilever clamp

2.5. Differential Scanning Calorimetry (DSC)

DSC is a characterization technique which measures the change of the difference in the heat flow rate to the sample and to a reference sample as a function of time and temperature. Change of heat capacity with temperature and change of enthalpy with temperature can be acquired from DSC experiments. It is used to determine temperature of thermal transitions such as T_g; the glass transition temperature, T_c; the temperature of crystallization for polymers, and T_m; the melting temperature. Glass transition temperature can be determined comparatively to DMA. T_g was determined by loss modulus peaks in DMA whereas onset temperature of heat flow curve was used in DSC. DSC and DMA measure different processes thus there is a difference between values of T_g. However, it is reported that DMA is more sensitive to changes occurring at T_g than DSC. On the other hand, DSC is a better

method with respect to DMA for characterizing crystallinity[49]. In addition, studying crystalline behavior by DSC can be a complimentary technique to WAXD[51].

In heat-flux DSC, the sample and inert reference material are heated or cooled at a controlled rate in a single cell while recording simultaneously the temperature difference between them (Fig. 12).

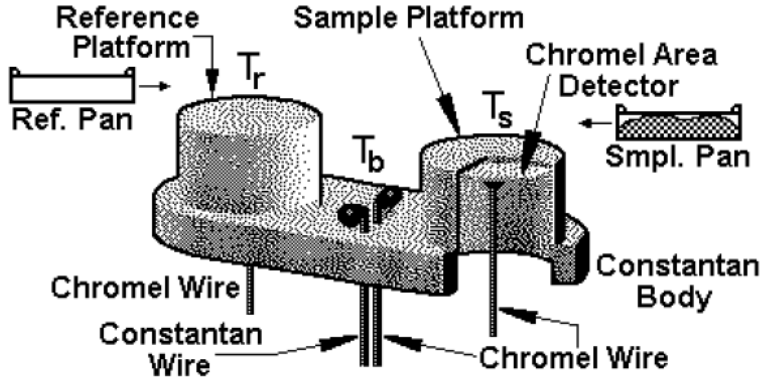

Figure 12 Modern Heat-Flux Differential calorimeter [52]

2.5.1. Experimental Setup of DSC

The glass transition temperature of samples was measured with DSC Q2000 (TA Instruments, New Castle, USA). Around 10 mg of sample was weighed into an aluminum pan (Tzero®) which was hermetically sealed to prevent loss of volatiles. An empty pan was used as a reference and the system was calibrated with indium. First, the sample was equilibrated at -30 °C. Then a heating ramp was applied at a rate of 10 °C/ min up to 120 °C. Then cooling was performed to -30 °C at a ramp rate of 10 °C/ min. Finally the sample was heated to 175 °C at 10 °C/ min. A nitrogen flow rate of 50 ml/min was used in every experiment and each pan was weighed subsequent to testing to confirm that there was no loss of volatiles.

T_g was established by scanning the sample twice since the first scan eliminates any structural (enthalpy) recovery, and secondly produces more easily interpretable data associated with the glass transition. Therefore, T_g values based on the second heating runs were reported by the onset temperature of the glass transition in heat flow curve (exotherm up) using TA Instruments Universal Analysis 2000 software.

2.5.2. Evaluation of glass transition temperature (T_g)

DMA is more suited compared to DSC for determining T_g for polymers which have a broad transition and small heat capacity jump at T_g. DMA is more sensitive to the changes in molecular motions and interactions occurring over the transition region[50]. In addition, the storage modulus can be acquired over large temperature range with DMA which can be compared to results of three point bending test. The DMA sensitivity is illustrated by the observation that for the blends two separate T_g were found in DMA whereas only one T_g is seen in DSC experiments. T_g values were shifted to higher temperatures in DMA experiments compared to in DSC. This also holds for T_g values based on tan δ peaks. The reasonable explanation for this phenomenon is that water evaporates while heating in the DMA so that T_g shifts to higher temperatures.

The glass transition temperature of polymer blends depends upon the phase behavior of the components. If the polymer blend is completely immiscible, it will exhibit two separate glass transition temperatures corresponding to the T_gs of the homopolymers; whereas if the polymer blend is miscible or partially miscible the glass transition temperature of a given phase can be related to the phase composition through e.g. the Fox equation [53] (w_1 and w_2 ; weight fractions of components).

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

Equation 6 Fox equation

Storage modulus graphs give an idea on the amount of cross-linking, entanglements and chain mobility (Fig. 13)[54].

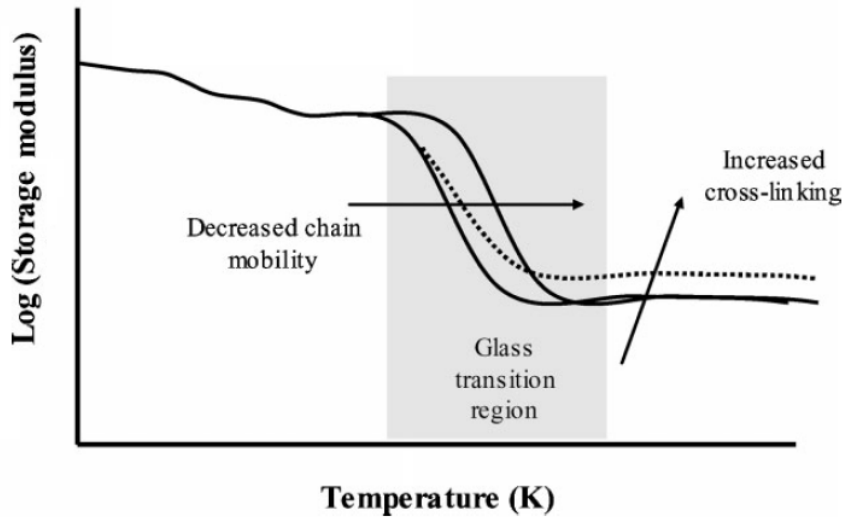

Figure 13 Change of properties in storage modulus with temperature

DSC is not suited to study crosslinking reactions that involve the breaking and formation (i.e. exchange) of similar bonds (disulfide bonds), since in that case no net heat flow is involved[55].

The measured value of T_g depends on the thermal history of the polymer, the measurement method and the rate of heating or cooling. It is found that a lower cooling rate results in the lower value of T_g[53]. It is also known that the physical characteristics of molecules such as molar mass, crystallinity, branching and cross-linking affect the glass transition temperature.

2.6. X-Ray Scattering and Scanning Electron Microscopy (SEM)

Determining polymer morphology is very significant to understand macromolecular self-organization, structure-property relationships and micromechanical mechanism[17]. Polymer morphology can be studied by different characterization methods such as microscopy and X-ray techniques. It is not convenient to use optical microscopy to study smaller scale morphology. Therefore higher resolution techniques such as SEM or X-ray scattering have to be employed since SEM allows better resolution and larger depth of focus than the light microscope [56](Fig. 14). Comparative studies can improve the understanding of polymer morphology, crystallinity and phase behavior.X-ray scattering techniques are complementary to microscopy and provide structure information in reciprocal space.

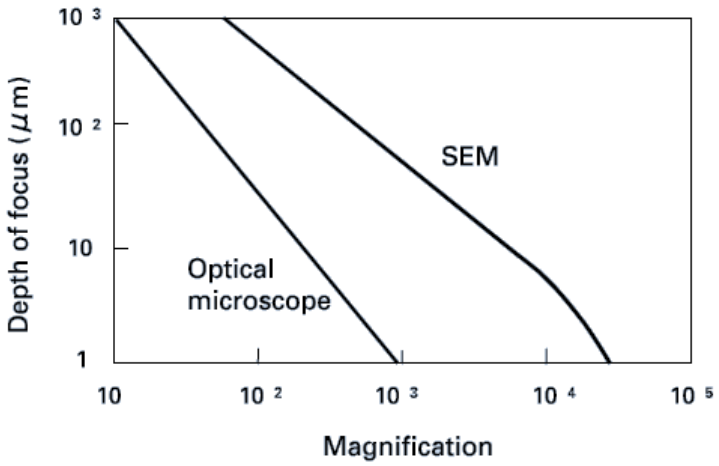

Figure 14 Difference of depth of focus between SEM and optical microscope

SEM is used for observation of specimen surfaces such as the ones obtained after cold fracture in liquid nitrogen. SEM gives information about the processes of crack initiation and crack propagation up to final fracture of samples. The influence of structural heterogeneities (defects) on the initiation, as well as on the propagation of cracks can be studied[57].

The working principle of SEM is based on detecting secondary electrons emitted from the sample which is irradiated with a fine electron beam[58]. The electron beam is produced with a system consisting of an electron gun, a condenser lens and an objective lens (Fig. 15).

X-ray scattering techniques have the advantage of being fast and non-destructive. SAXS (small angle X-ray scattering) and WAXS (wide angle X-ray scattering) are used to characterize morphology of polymer blends and the degree of crystallinity. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle.

Scattering from an amorphous material such as a melt or a glass gives intensity patterns that are broad and essentially featureless except for the so-called amorphous halo. The diffraction pattern obtainable from a good crystalline material, on the other hand, consists of a series of sharp Bragg peaks, which can be easily and clearly distinguished from the diffuse background. A semicrystalline polymer gives a scattering pattern consisting of a superposition of both of these features, their relative contributions reflecting the relative amounts of the noncrystalline and crystalline phases present. Scattering is actually the primary method by which the presence of any crystalline order in a material can be detected[59].

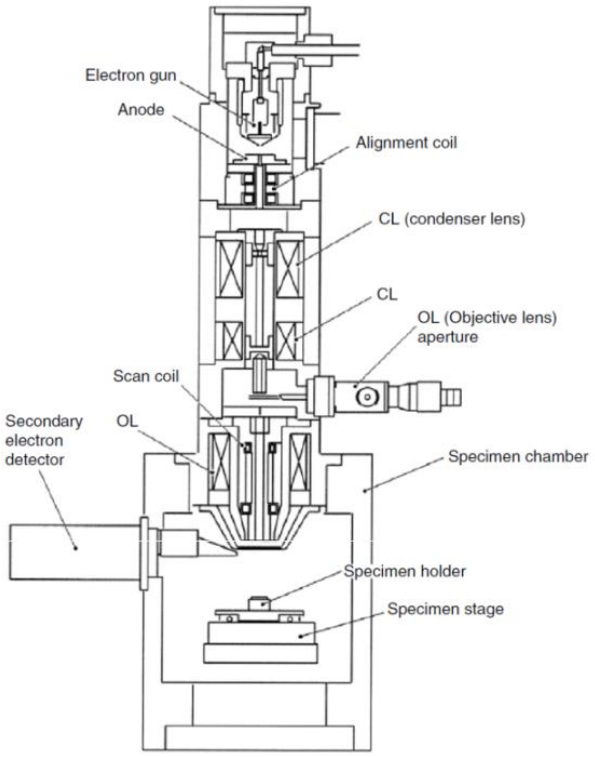

Figure 15 Schematic diagram of a scanning electron microscope (JSM—5410, JEOL, USA)

Figure 16 XeuSS setup for X-ray studies

2.6.1. Experimental Setup of X-ray Scattering

X-ray data were collected with a XeuSS setup (Xenocs®, Sassenage, France) equipped with a high brilliance, low divergence micro-focused GeniX 3D Molybdenum source at a power of 50 kV – 1mA and 2D plate detector (Fig. 16). It is possible to cover a large q-range, covering both SAXS and WAXS in a single shot with this instrument. Compression-molded samples were analyzed for polymer blends. Gluten and Elvamide references were also molded with obtained powders processed in same conditions with blends. A background correction was applied to all measurements. Conex, software was used for converting series of two-dimensional X-ray powder patterns measured on flat two-dimensional detectors into one-dimensional scattering patterns[60].

2.6.2. Experimental Setup of SEM

The surface morphology of compression molded gluten and nylon blend plates was studied with a scanning electron microscope (SEM; Philips XL30 field emission gun, Philips®, Eindhoven, Netherlands). SEM images of gold coated samples were obtained with an acceleration voltage of 10 kV and a high resolution secondary electron detector. Freeze fractured samples in liquid nitrogen were coated with gold to increase electron conductivity.

2.7. Flexural Properties via three point bending test

Three point bending tests were used to measure the flexural modulus (slope of stress-strain curve) flexural strength (ultimate stress) and strain at break (ultimate strain). The bending test is frequently easier to conduct on brittle materials than the traditional tensile test. The modulus was determined by fitting a straight line to the stress-strain curves in the early region at strains approximately 0.2%.Toughness values were also calculated for each sample by integrating the area under the stress-strain curves (Fig. 17). The three point flexural test produces its peak stress at the specimen mid-point with reduced stress elsewhere. This stress localization is ideal for testing for specific isolation of stress on a material.

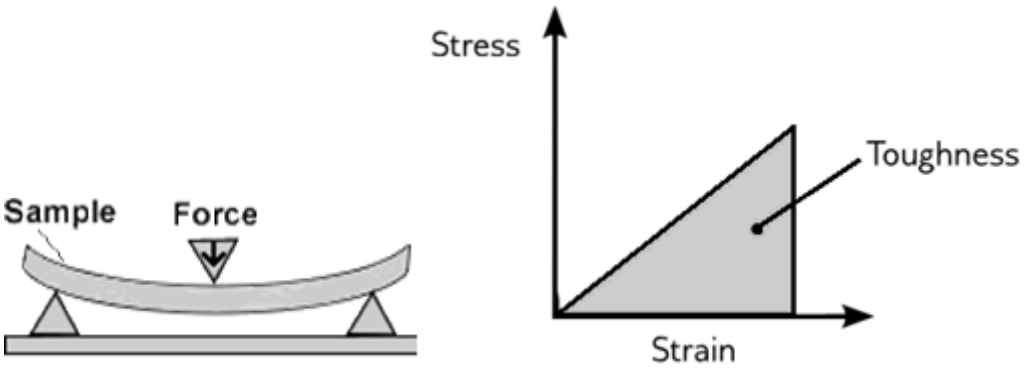

Figure 17 Three point bending test and evaluation of data

2.7.1. Experimental Setup of three point bending test

An INSTRON® 5567 instrument (Massachusetts, USA) was employed for three point bending test to measure the mechanical properties of the samples at room temperature after conditioning at 50% RH. The test was carried out according to ASTM standard D790-03 for flexural properties. The calibrated instrument was equipped with a 1 kN load cell using a crosshead speed of 1.0 mm/min and a 40 mm support span. The data analyses were completed using Blue Hill software. Five samples were conditioned for 2 days at RH=50% and their results were reported with mean standard deviation (±) to confirm the tests were carried out correctly.

3. Health, Safety and Environment

It is a must to be aware of possible risks of using chemicals to avoid health and environmental problems. Chemists learn handling chemicals and practicing experiments in a safe and environmentally friendly way in a lab. In order to conduct experiments securely, Prof. Eric Nies gave a seminar in division of polymer chemistry and materials in KU Leuven at 04/10/2013. Information was given about regulations followed by the department of chemistry. In addition, introductory safety guidelines which include information about emergency situations, risk assessments, proper usage of chemicals were provided by the department.

Further safety instructions are necessary since X-ray sources are used in our division. Thus, I followed series of lectures related to radiation protection training in UZ Leuven at 13/11/2013. The lectures consist of administrative procedures and good laboratory practice. Information was presented about radiation measuring equipment, radioactive waste and contamination. A dosimeter was used each time when an experiment was conducted in the related lab. Along with that, each experiment involved wearing lab coat, goggles and gloves. Information related to work safety was also provided in the chemical engineering department since compression molding was conducted at this department.

Material safety data sheet (MSDS) have to be read and understood before using each chemical. Wheat gluten was chosen as source which is environmentally friendly, biodegradable, recyclable and sustainable. Water was used as solvent which is environmentally friendly. Elvamide® is not known to contain Toxic Chemicals under Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR part 372. Ethanol absolute AnalaR NORMAPUR® analytical reagent was used carefully since it is flammable liquid. Poly(ethylene glycol) diglycidyl ether and Poly(propylene glycol) diglycidyl ether are non-hazardous substances according to Regulation (EC) No. 1272/2008. This substance is not classified as dangerous according to Directive 67/548/EEC. However, sodium azide which was used in water absorption test is very hazardous in case of skin contact (irritant), eye contact and highly toxic in case of ingestion and inhalation. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

4. Results and Discussion

4.1. Phase behavior of nylon

In order to facilitate efficient blending of gluten and nylon, the phase behavior of the components first needed to be understood. Mixing can occur most effectively if the components are both soluble in a mutual solvent and to realize nylon solubility, the polymer must be in the molten state. Elvamide, a ternary copolymer produced by DuPont was selected for this study because of its low melting temperature with respect to other polyamides. Melting points for Elvamide multipolymer resins range from 115 °C to 160 °C, compared with e.g. 265 °C for high temperature resistant nylon 6,6 homopolymer.

Thermal transitions such as glass transition, crystallization and melting of Elvamide were investigated using differential scanning calorimetry. Figure 18 shows the second heating curve after cooling the polymer at 10 °C/min from the melt. A step in the heat flow at 26 °C shows the onset of T_g. This is followed by an exothermic peak at 75 °C which is assigned to cold crystallization of the polymer. Finally an endothermic melting peak was observed at 154 °C.

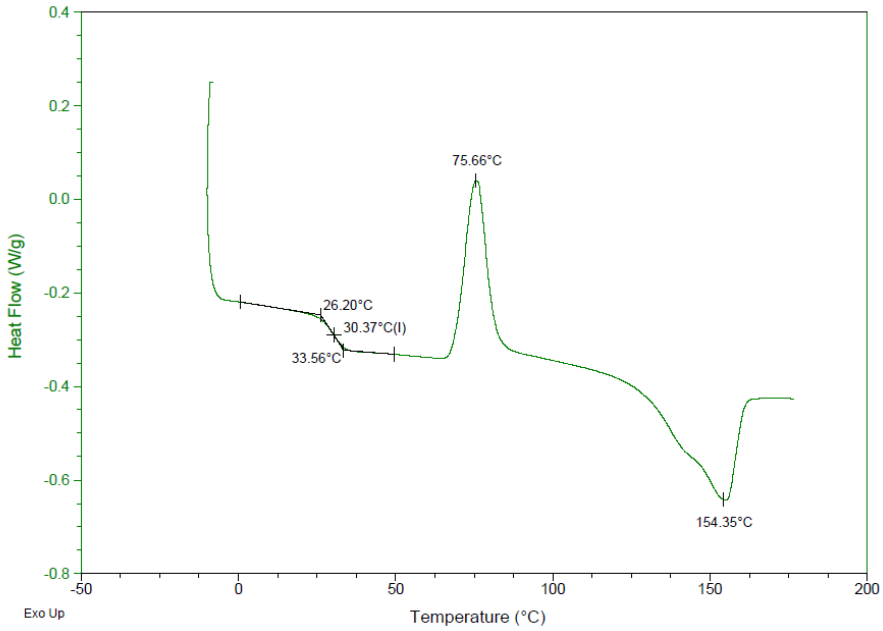

Figure 18 DSC analysis of Elvamide®

It has been reported that wheat gluten proteins are prone to thermal degradation upon prolonged heating above 150 °C and so the processing temperature should preferably be well below this temperature[35]. Melting point depressions of PA6 in water and PA4.6 in water and ethanol under pressure have previously been reported[61]. It was also mentioned that dissolution of polyamides under pressure significantly decreases their melting temperature [46].

To study the effect of solvent on the melting behavior of Elvamide, a second DSC experiment was carried out in ethanol. A granule of Elvamide resin was mixed with ethanol (50% w/w) within a steel high pressure DSC pan which was sealed at room temperature. The result obtained via the second heating curve exhibits a broad melting peak which has onset temperature of 36 °C and maxima of 66 °C (Fig. 19).

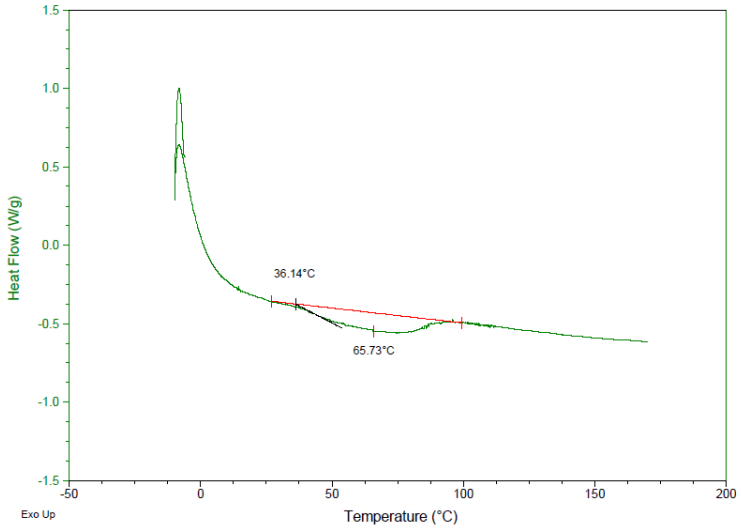

Figure 19 DSC analysis of Elvamide® with ethanol

The solubility of Elvamide in alcohol can be explained by the disorder brought by the mixture of nylon polymers and the alcohol molecules, leading to the absence of both homogeneous hydrogen bonding among the chains of the individual components and heterogeneous hydrogen bonding among unlike nylon chains.

There is already much reported in literature on the phase behavior of gluten. Particularly gliadins are known to be soluble in a solution of ethanol/water (70% v/v)[62]. Thus based on the solubility of the Elvamide and gluten it was decided to use a 70% ethanol/water system to blend the components.

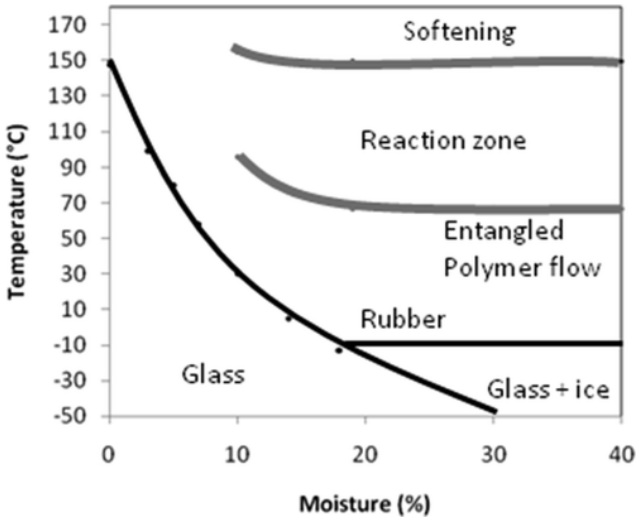

Figure 20 State diagram of glutenin [63] [20]

Gluten and its components, gliadin and glutenin show a broad range of glass transition temperatures from 120 °C to 180 °C [63] [64]. At temperatures above T_g gluten polymers obtain mobility necessary to react. DMA data can also be used to reveal this mobility. At increasing temperatures, chemical changes may be induced in the reaction zone (Fig. 20) [63]. Accordingly, different temperatures of mixing were studied for polymer blend systems.

4.2. Gluten/Nylon mixed at low temperature

After determining a suitable solvent system for blending gluten and Elvamide, the temperature of mixing was varied in order to study the effect of the mixing temperature on mechanical properties. Firstly, it was decided to mix at low temperature in order to avoid gluten degradation and limit gluten cross-linking. Different weight percentages of Elvamide were mixed with wheat gluten at 60 °C, 1 h in 500 ml ethanol/water (70% v/v). A reference sample was prepared by compression molding wheat gluten powder as received from the suppliers after conditioning (50% RH, 20 °C) but without any solvent treatment. Table 3 shows the mechanical properties obtained for the gluten reference sample in the 3 point bending test. Also included in table 3 is mechanical data for Elvamide copolymer (provided by DuPont® material datasheet).

Table 3 Mechanical properties of Wheat Gluten and Elvamide 8061 (*tensile test)

	ASTM method	Temperature °C	RH %	Modulus (GPa)	Strength (MPa)	Elongation (%)
Gluten	D790	23	50	**3,7**	**44,3**	**1,2**
Elvamide	D638*, D790	23	50	**0,9**	**51,4***	**320***

During the preparation of the blends at 60 °C, some problems were encountered. It was observed that some of the nylon had already separated from the gluten after freeze drying and thus some of the material could not be milled to a powder. As a result some material had to be discarded after the milling/sieving stage and it was suspected that this would alter the gluten/nylon ratio in the remaining sample. The mechanical properties (determined via three point bending tests) of processed bars obtained from the blends are reported in Table 4. The results were compared to reference sample properties. It was observed that the mechanical properties did not change significantly upon altering the blend composition. Flexural modulus was constant with increased amount of Elvamide added to the polymer blend. Also no significant change in terms of flexural strength, elongation at break and toughness was seen.

Table 4 Effect of different amounts of polyamide in polymer blend on mechanical properties

#	Gluten (g)	Elvamide (g)	Elvamide %	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
1	40	2,1	5	**3,2 ± 0,1**	**42,4 ± 2,4**	**1,3 ±0,1**	**0,28**
2	40	4,5	10	**3,1 ± 0,1**	**44,0 ± 3,0**	**1,5 ±0,1**	**0,33**
3	40	7,1	15	**3,1 ± 0,1**	**46,2 ± 2,9**	**1,6 ±0,1**	**0,37**
4	40	10	20	**3,3 ± 0,1**	**43,6 ± 0,4**	**1,4 ±0,0**	**0,31**
5	40	13,4	25	**3,1 ± 0,1**	**46,5 ± 1,2**	**1,6 ±0,1**	**0,37**

After analyzing the mechanical properties of the blends, it appears likely that the nylon possibly didn't melt completely in the solvent during the reactor blending, and so efficient mixing was not achieved during processing. In order to prove or disprove this hypothesis, the temperature of mixing was raised and the test results were compared with previous case in terms of mechanical properties.

4.3. Gluten/Nylon mixed at high temperature

Samples of wheat gluten and Elvamide were mixed at 110 °C, 1 h in 500 ml ethanol/water (70% v/v). The vapor pressure of the ethanol/water solution was calculated as 228 kPa using Raoult's law[65] (Eqn. 7). Antoine's equation was used to determine vapor pressure of the pure components ($p_a{}^*, p_b{}^*$) at 110 °C (*T)* where A, B and C are component-specific constants (constants are obtained from Dortmund Data Bank). It also had to be considered that ethanol/water solutions show greater positive deviation from Raoult's law and form a low-boiling azeotrope at a specific composition[65].

$$p = p_a{}^* x_a + p_b{}^* x_b \ , \ \log_{10} p_a{}^* = A - \frac{B}{C+T}$$

Equation 7 Raoult's law and Antoine equation

Gluten reference (sample 1) was also mixed at 110 °C, 1 h in 500 ml ethanol/water (70% v/v). Another reference (sample 2) was directly molded from unprocessed gluten powder as described in the previous case. The results obtained from three point bending tests are reported in Table 5. It was noticed that sample 1 processed at 110 °C had a lower flexural strength and toughness as compared with the unprocessed sample 2. This could be a result of partial degradation of the gluten proteins. There is also a clear decrease in the values of flexural modulus with increased nylon content. This sharp decrease wasn't observed when previously mixing at 60 °C.

Table 5 Mechanical Properties of Compression molded Gluten/Elvamide Blends

#	Gluten (g)	Elvamide (g)	Elvamide %	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
1	40	0	0	**3,7 ± 0,1**	**40,4 ± 2,9**	**1,1 ± 0,1**	**0,20**
2	40	0	0	**3,7 ± 0,1**	**44,3 ± 1,0**	**1,2 ± 0,1**	**0,31**
3	40	2,1	5	**3,3 ± 0,1**	**40,2 ± 2,1**	**1,2 ± 0,1**	**0,23**
4	40	4,5	10	**3,0 ± 0,1**	**45,7 ± 2,0**	**1,6 ± 0,1**	**0,37**
5	40	10	20	**2,6 ± 0,2**	**42,6 ± 2,4**	**1,7 ± 0,1**	**0,39**
6	40	13,4	25	**1,8 ± 0,1**	**31,6 ± 1,7**	**2,4 ± 0,2**	**0,40**
7	40	17,3	30	**2,1 ± 0,1**	**36,4 ± 0,9**	**2,0 ± 0,1**	**0,38**

The lowering of the modulus with increasing nylon content is to be expected considering the lower modulus of Elvamide and so it suggests that nylon is not lost during processing as was observed at 60 °C. This confirms the previous speculation that melting of components is not feasible at low temperature (60 °C) and that some nylon was lost during processing.

Changes of mechanical properties show that the mixing was achieved efficiently via increased temperatures of mixing as anticipated. Flexural strength also decreased with increasing nylon content which was accompanied by an increase in failure strain (Table 5). There is also a limit in terms of the amount of nylon added to polymer blend system. The flexural modulus was increased again between samples 6 and 7 which could also be attributed to the loss of nylon during processing of the blends. Evidence of losing nylon during process can also be obtained via DMA results since the size of the tan δ and loss modulus peaks reflect the volume fraction of the material undergoing the transition[50].

Figures 21-25 were obtained from DMA experiments held on molded samples. In Figure 21 there is only one T_g observed in the loss modulus which is due to gluten phase. On the other hand, figures 22-24 display two different loss modulus peaks which are due to glass transitions of nylon and gluten phases. In immiscible or partially miscible polymer blends a separate T_g for each phase is found. In gluten/nylon blends, a T_g appeared around 20 °C which is due to Elvamide. This T_g value was already observed in DSC experiments on pure Elvamide (Fig. 18). The blend containing 10 g nylon (20% w/w) had the lowest area in loss modulus curve (Fig. 22). As the temperature of mixing increases, the integral of loss modulus peaks of nylon phase also increases even though the blend contained less nylon which proves that the addition of nylon to the polymer blend is more efficient at higher temperatures (Fig.25).

In conclusion, efficient mixing of two phases was achieved at 110 °C rather than 60 °C. This was confirmed by comparing mechanical properties of processed polymer blends and evaluating dynamic mechanical analysis results.

Table 6 Tg values obtained by peaks of loss modulus for different polymer blends

	Gluten (g)	**Elvamide (g)**	**T_g gluten (DMA) °C**	**T_g Elvamide (DMA) °C**	**Temperature of mixing °C**
Fig 21	40	-	78,7	-	110
Fig 22	40	10	79,4	24,6	60
Fig 23	40	5	82,6	22,0	110
Fig 24	40	13,4	88,3	20,6	110

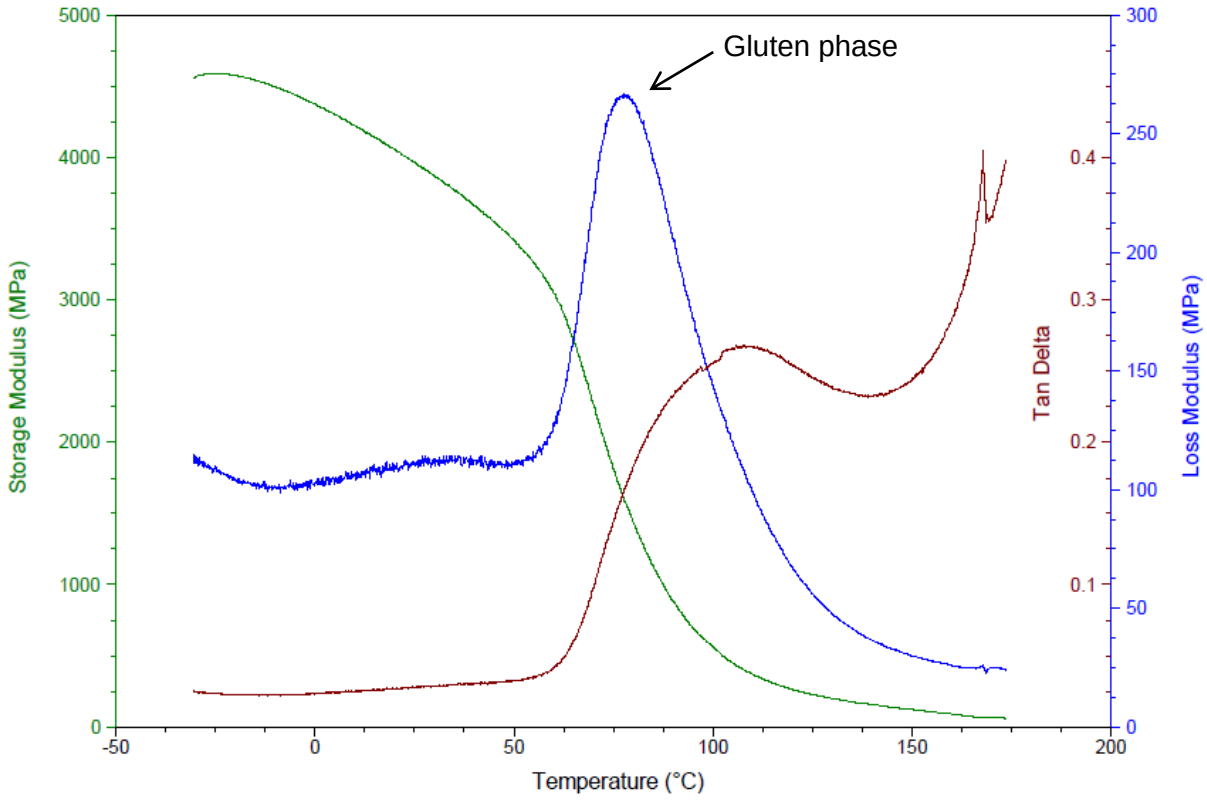

Figure 21 Gluten reference mixed at 110 °C in ethanol/water (70% v/v)

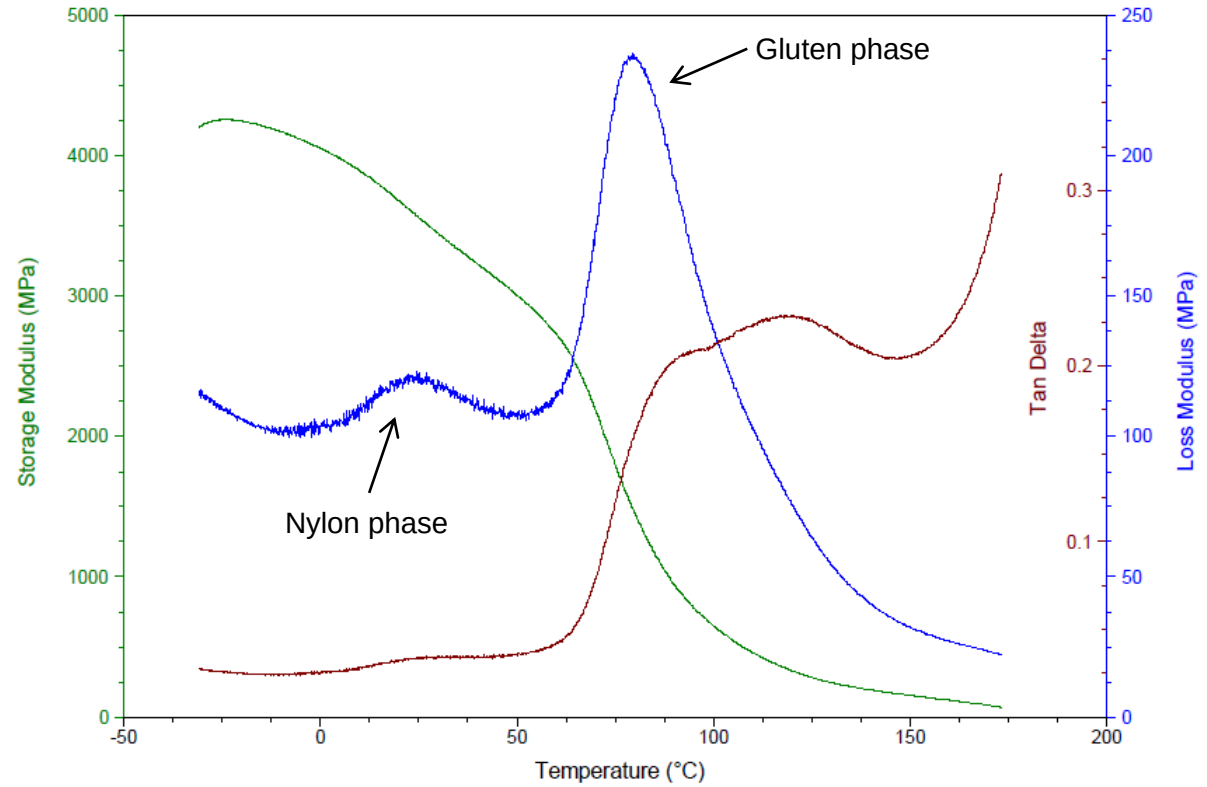

Figure 22 Elvamide (10 g-20% w/w) and gluten (40 g) mixed at 60 °C in ethanol/water (70% v/v)

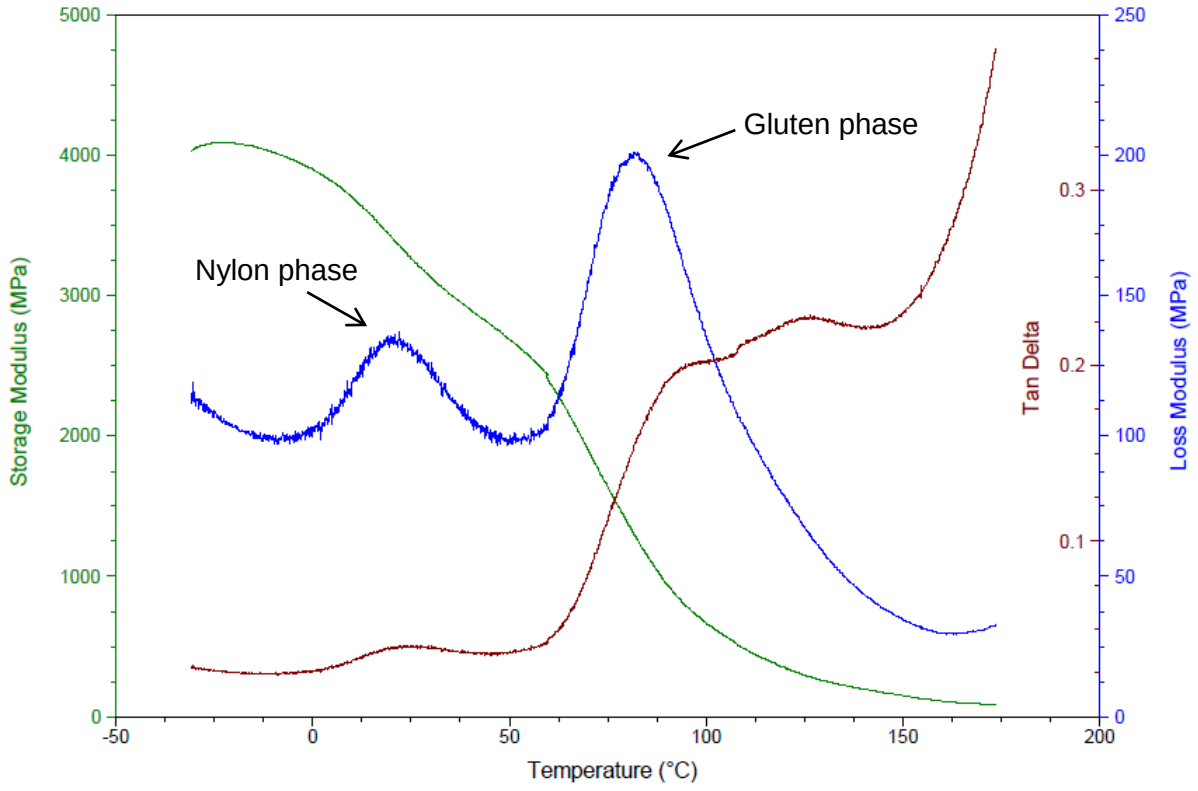

Figure 23 Elvamide (5 g-10% w/w) and gluten (40 g) mixed at 110 °C in ethanol/water (70% v/v)

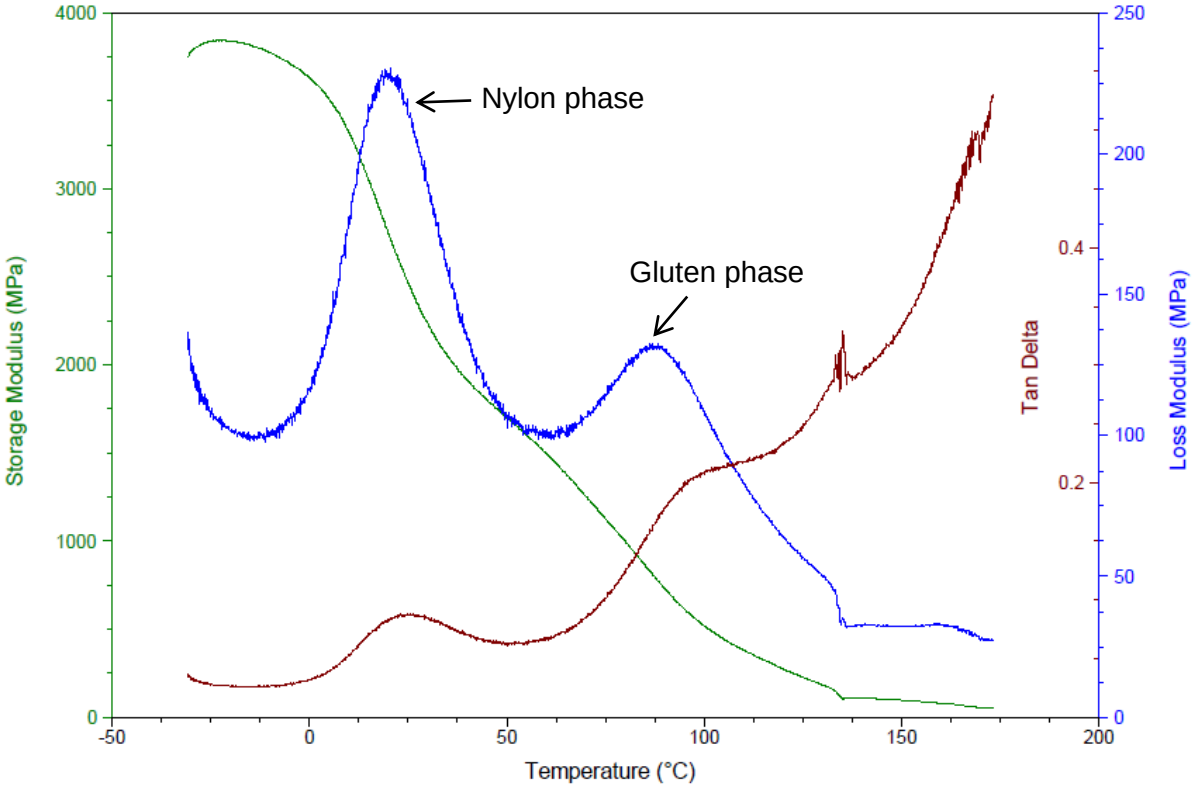

Figure 24 Elvamide (13,4 g-25% w/w) and gluten (40 g) mixed at 110 °C in ethanol/water

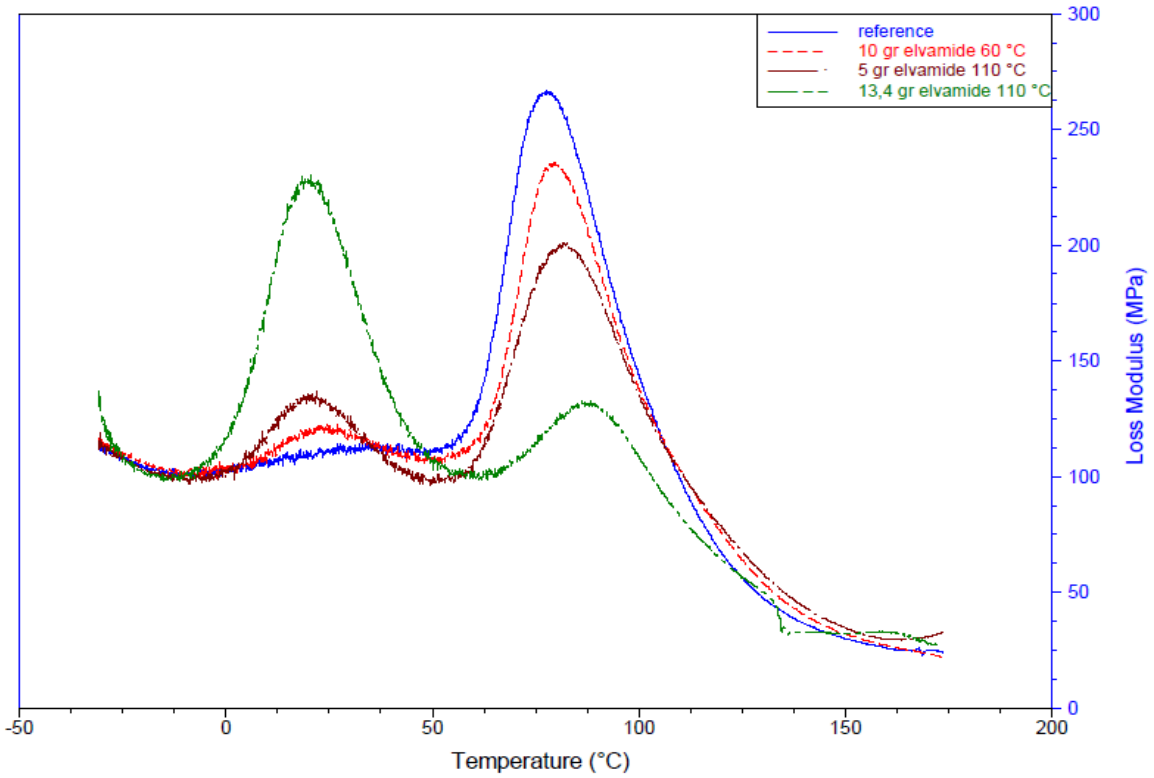

Figure 25 Comparison of figures 21-24 in terms of area of loss modulus

SEM studies were also held to study the relation between microstructure and mechanical properties of the gluten/nylon blends. Wheat gluten reference showed a smooth cold fracture surface with respect to nylon blended samples (Fig. 26). Some cracks were already observed in the reference which could reflect the brittle character of gluten. Particles that accumulated together and voids can be explained by the incomplete polymer flow during molding. It was difficult to obtain clear micrographs at smaller scales (<5μm) due to the resolution limits of the instrument.

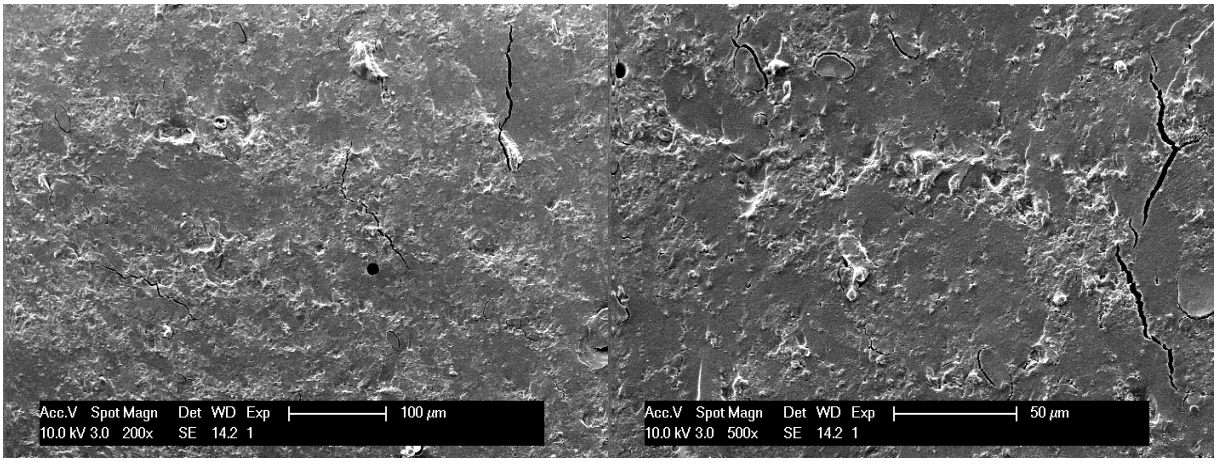

Figure 26 SEM micrographs for reference gluten mixed at 110 °C

The fracture surfaces of the nylon blended samples exhibited a more heterogeneous, rough appearance as the content of nylon was increased (Figures 27-30). This reflects the less brittle nature of nylon as compared with gluten. SEM micrographs of the blends with low nylon content (< 10%) showed a dispersion of small spherical particles in a matrix (Fig. 27, 28). It is believed that the particles are the nylon with the gluten forming the continuous matrix. Small cracks and non-embedded particles were seen which suggests evidence of poor adhesion. It must be noted that starch particles are also known to be present in the gluten material and so conclusively assigning the nylon particles is not always easy.

At higher nylon contents (> 25%) the 'particle in a matrix' morphology was no longer obvious (Figures 29-30). It becomes much more difficult in this case to differentiate between the nylon and the gluten phases. It is possible that nylon particles aggregate together with increased amount of nylon leading to a more co-continuous morphology.

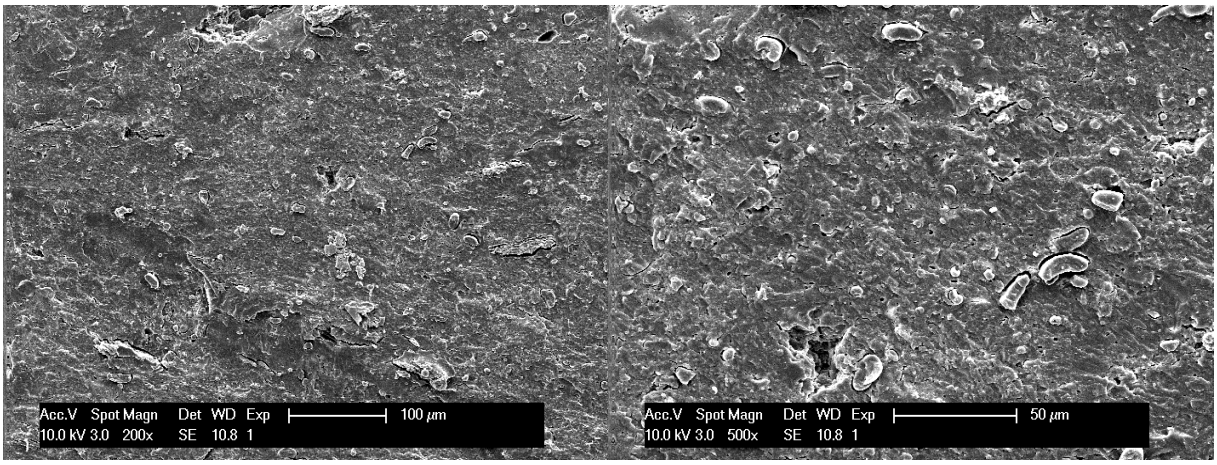

Figure 27 SEM images of Elvamide (2,1 g-5% w/w) and gluten (40 g) mixed at 110 °C in ethanol/water (70% v/v) at different scales

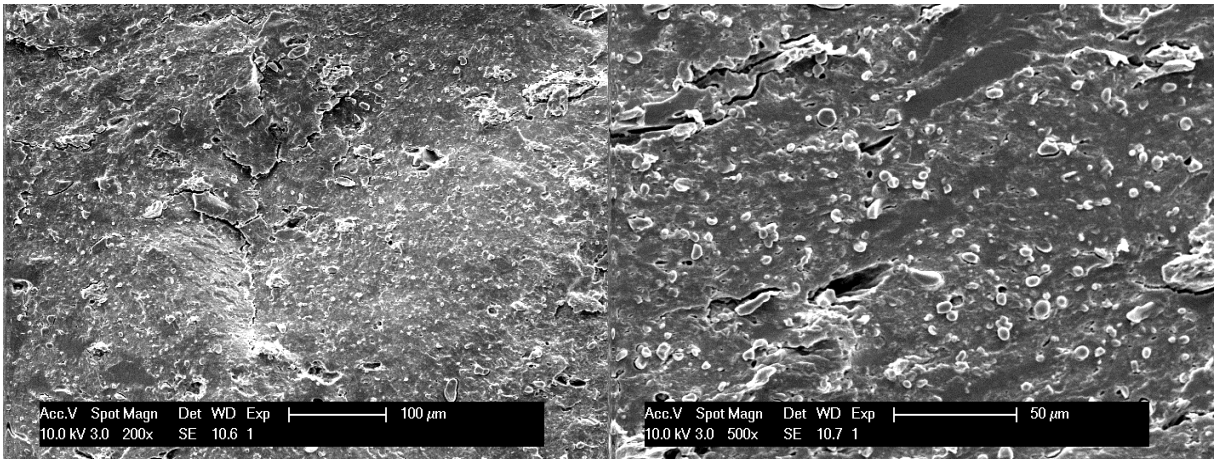

Figure 28 SEM images of Elvamide (5 g-10% w/w) and Gluten (40 g) mixed at 110 °C in ethanol/water (70% v/v) at different scales

A decrease in the number of voids was observed with addition of nylon. In general, voids and cracks may act as stress concentrators which induce fracture of samples. It is difficult to relate micrographs to the mechanical properties of samples. For example, although the number of cracks decreased as nylon was added to gluten, there were no important changes observed in flexural strength of samples. On the other hand, increasing the nylon content from 10% w/w to 25% w/w appeared to result in conversion of drop matrix morphology into co-continuous morphology (Fig.28, 29). This change was verified in terms of significant decrease in flexural modulus and strength demonstrated in Table 5. Thus, SEM gives an idea related to morphology of components and mechanical performance of blends. A better understanding of the relations between blend morphology and mechanical properties is crucial. It is generally known that the mechanical properties of blends depend on the morphology and interfacial adhesion between the phases.

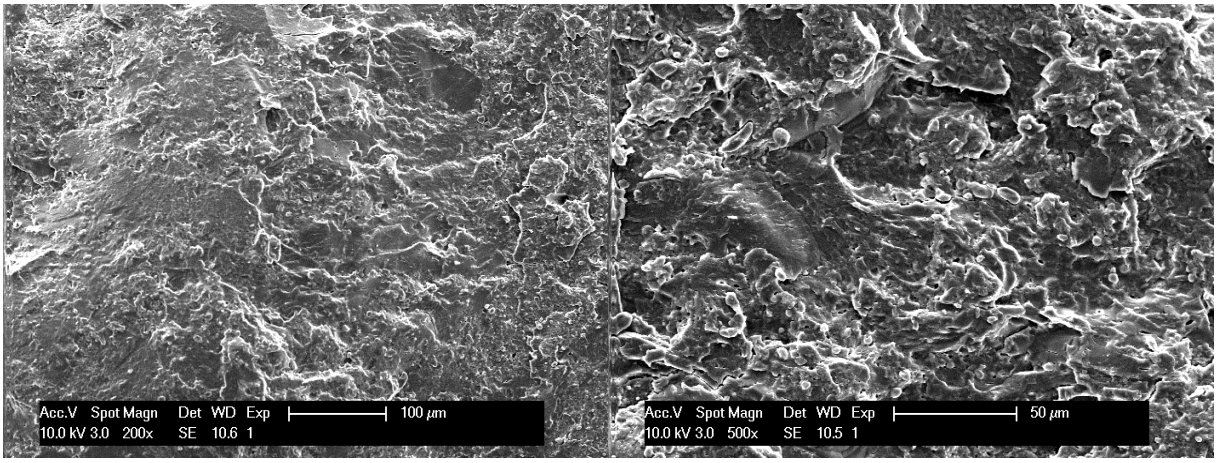

Figure 29 SEM images of Elvamide (13,4 g-25% w/w) and Gluten (40 g) mixed at 110 °C in ethanol/water (70% v/v) at different scales

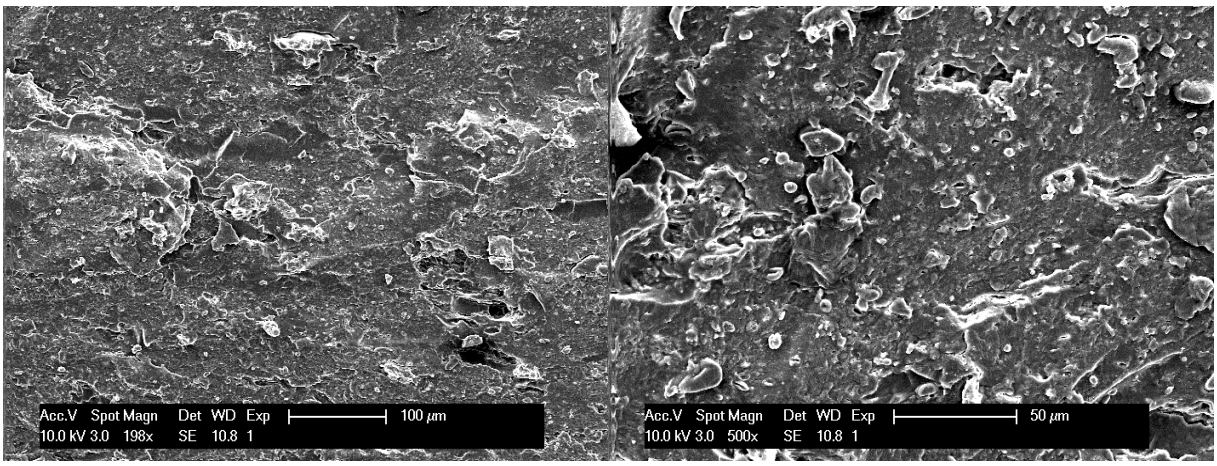

Figure 30 SEM images of Elvamide (17,3 g-30% w/w) and Gluten (40 g) mixed at 110 °C in ethanol/water (70% v/v) at different scales

DSC and DMA were used to characterize the T_g of the processed polymer blends. An increase in T_g was observed with the addition of nylon to the blended sample (Fig. 31). It is reported in literature that the glass transition temperature of gluten decreases with the increasing moisture contents (Fig. 32)[41, 66]. This is consistent with the significant plasticizing effect of water on gluten and the presence of aliphatic nylon reducing the water uptake.

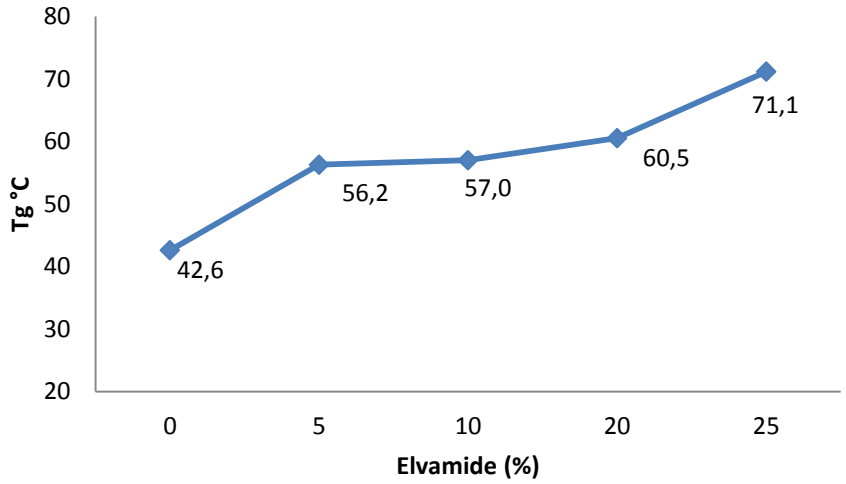

Figure 31 Tg values for Gluten/Elvamide blends obtained via DSC

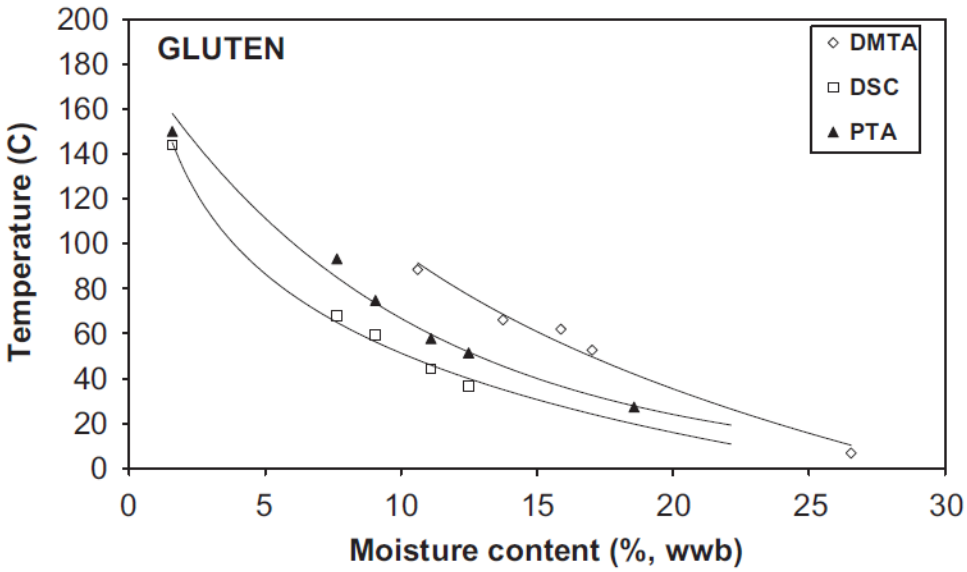

Figure 32 Comparison of the effect of the water content on T_g values of gluten measured using DSC, DMTA and PTA (pulse thermal analysis) [66]

In order to understand the observed increase in T_g, water absorption tests were also held on the molded samples of gluten/nylon blends. The results, which can be seen in Figure 33, showed that water absorption decreased for blends with increased nylon content. Therefore, T_g increase for increased nylon content can be related to decreased water uptake. A correction was made to the data in Figure 33 to account for the relative percentage of gluten

in each of the blends (Fig. 34). It was observed that curves demonstrating 5, 10 and 20% of nylon blend overlap each other which are also reflected in similar T_g values (Fig.31, 34). This behavior can possibly be related to the morphology of the blends since those samples which display similar water absorption properties also exhibit the same morphology i.e. drop matrix (Fig. 27, 28) whereas blends of 25% nylon and above appear to exhibit a co-continuous morphology (Fig. 29).

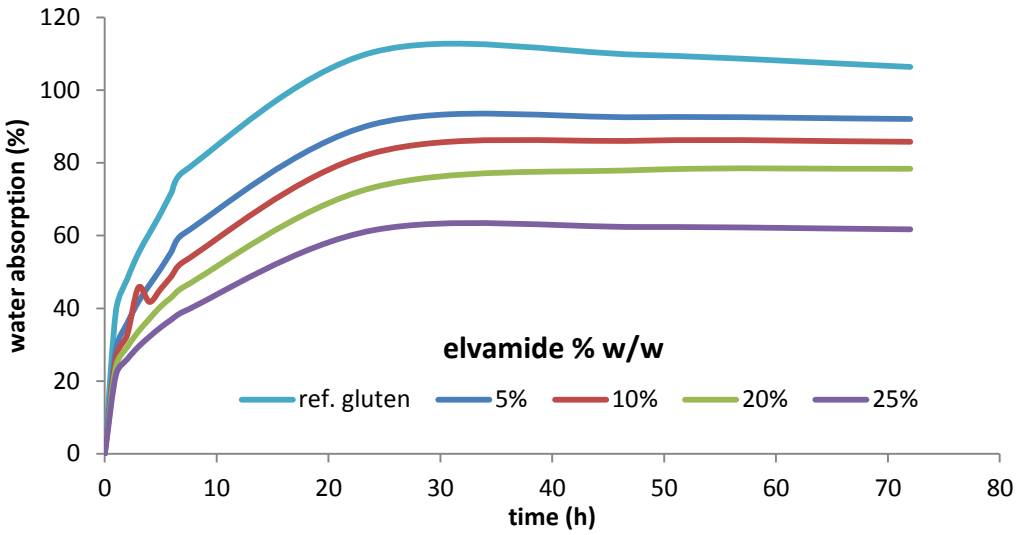

Figure 33 Absolute water absolution values determined as the increase in sample mass expressed as percentage of the dry weight after submersion

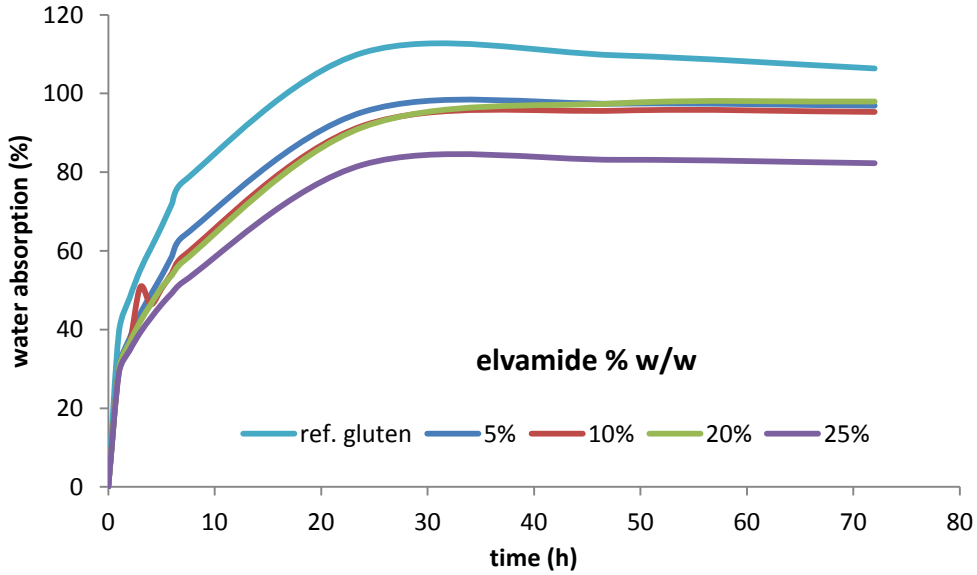

Figure 34 Corrected water absolution values with respect to water absorption of reference and added nylon content

Table 7 shows that increased amount of nylon increases T_g as the water uptake decreases. The values of T_g obtained from different methods can differ from each other which is also the case for gluten/Elvamide blends.

Table 7 Tg values for Gluten/Elvamide blends obtained via DMA and DSC

Gluten (g)	Elvamide (g)	T_g gluten (DMA) °C	T_g Elvamide (DMA) °C	T_g (DSC) °C
40	-	78,7	-	42,6
40	5	82,6	22,0	57,0
40	13,4	88,3	20,6	71,1

It should also be considered that water absorption causes problems in natural polymers since it can lead to swelling, low thermal resistance and change in mechanical properties [67].

4.4. Crystallinity

One of the initial aims of blending nylon with gluten was to introduce crystallinity into gluten based materials. X-ray scattering experiments were therefore held to determine the presence of crystallinity in the blended samples. First, the crystallinity of Elvamide reference was studied after processing in the same way as the obtained blends (reactor mixing followed by compression molding). The scattering pattern showed a very broad peak around q~1.5 (Fig. 35).The aliphatic ternary copolymer exhibited very low crystallinity behavior since it is composed of copolymer of different polyamides.

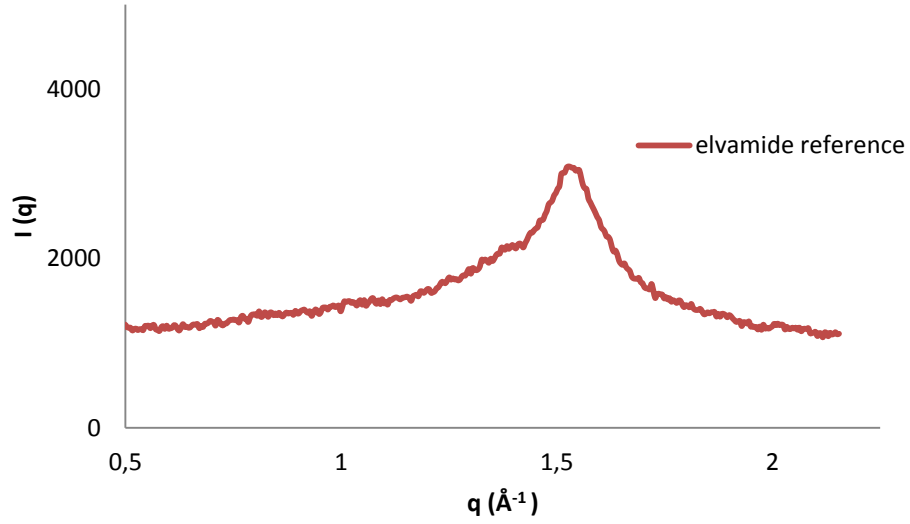

Figure 35 X-ray scattering data for processed reference Elvamide

Another study held on unprocessed gluten reference exhibits two amorphous peaks (Fig.36). On the other hand, thermal treatment of gluten caused generation of small sharp peaks around q~0.9 and q~1.3 which remain to be identified (Fig.37).

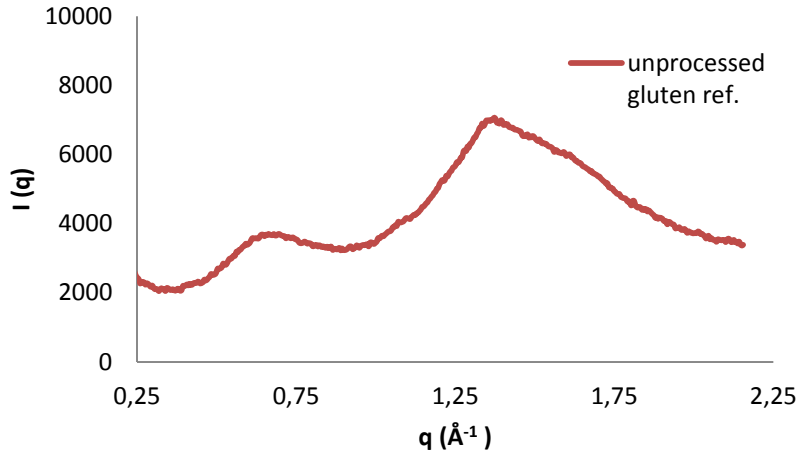

Figure 36 X-ray scattering data for unprocessed reference gluten

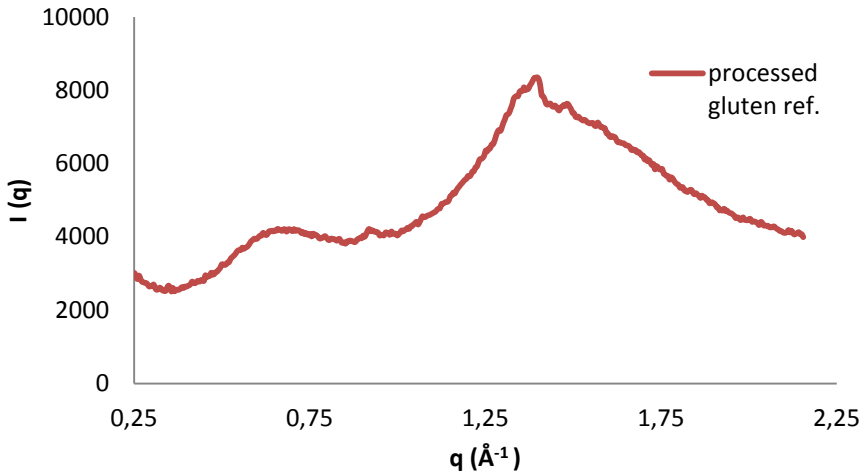

Figure 37 X-ray scattering data for processed reference gluten

Addition of 13,4 g (25% w/w) Elvamide to gluten generates another peak around q~1.5 which proves the addition of nylon phase (Fig. 38).

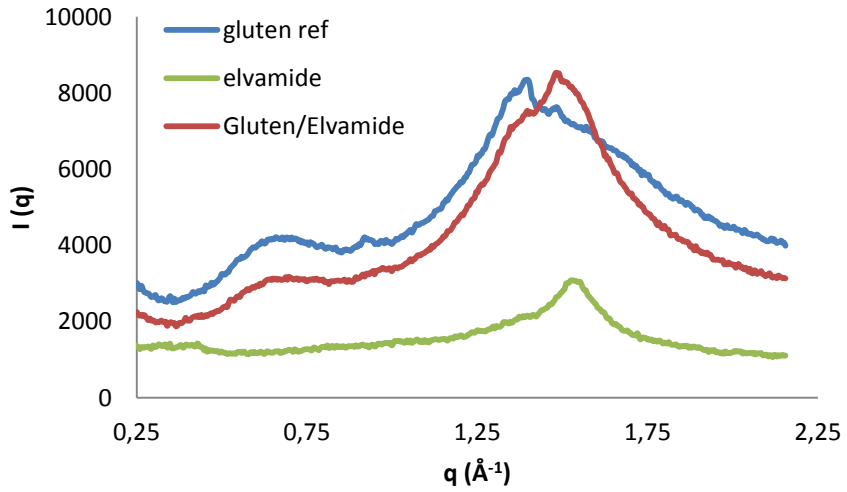

Figure 38 X-Ray scattering data for reference gluten, Elvamide and gluten/Elvamide blend

In Figure 39, this behavior is demonstrated clearly since increased amount of nylon creates another peak whereas the peak observed in reference gluten disappears.

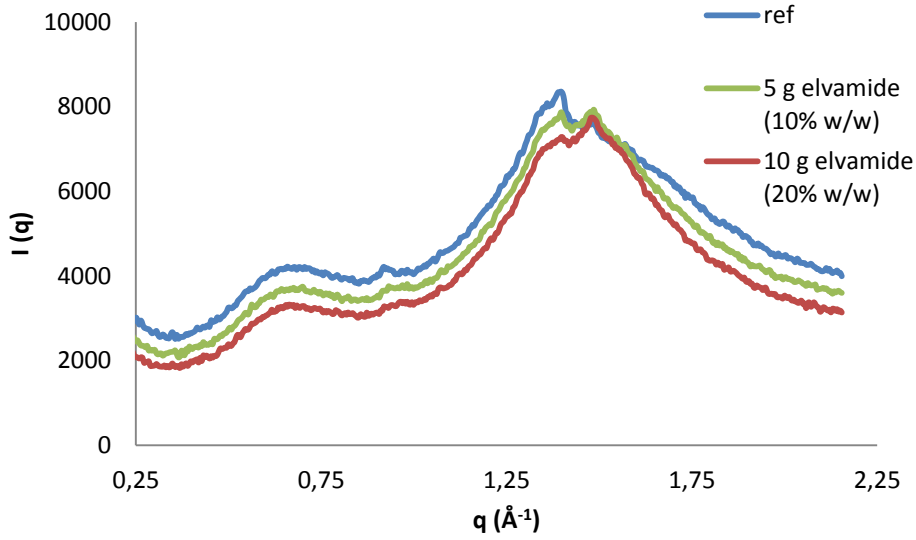

Figure 39 X-Ray scattering data for gluten/Elvamide blends

Annealing tests were held on samples that were already compression molded at 150 °C for five minutes heating and then five minutes cooling to room temperature. These plates were heated again to 80 °C (based on the crystallization peak position in Figure 18) and cooled to room temperature in five minutes to induce crystallinity in the samples. There was, however, no change in terms of scattering peaks, mechanical properties and T_g values for annealed samples (Table 8).

Table 8 Tg data for compression molded and annealed samples of Gluten/Elvamide blends

Sample	Gluten (g)	Elvamide (g)	Temperature of mixing °C	T_g gluten (DMA) °C	T_g Elvamide (DMA) °C	T_g (DSC) °C
1	40	10	60	79,4	24,6	55,1
2 annealed	40	10	60	80,3	23,5	52,7

It was concluded that little crystallinity is added to the blend samples. It is important though to be able to vary the crystallinity of blends since the degree of crystallinity of polymers affects the physical and mechanical properties of the materials. For example, the resistance against chemicals, the moisture absorption, and mechanical properties like abrasion resistance, stiffness, tensile properties and toughness are directly related to the crystallinity [68].

4.5. Addition of compatibilizer to blend system

A difunctional epoxide capable of reacting with both gluten and nylon was introduced as a potential compatibilizer. PEGDE (Fig. 40) is widely used as an additive for cross-linking polymers since it contains two epoxy groups that can react with amino, hydroxyl, and carboxyl groups [69] [70]. It is aimed to graft PEGDE to wheat gluten proteins and further cross-link with aliphatic polyamide mixtures.

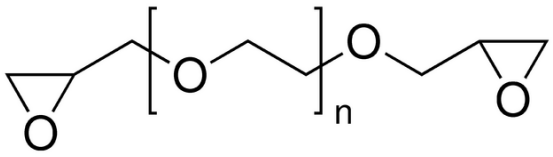

Figure 40 Chemical structure of poly (ethylene glycol) diglycidyl ether (PEGDE) average M_n 500

Wheat gluten and Elvamide were mixed with PEGDE at 110 °C for one hour in 500 ml ethanol/water (70% v/v). High temperature compression molded bars were used in three point bending test to measure the mechanical properties of the samples (Table 9).

Table 9 Mechanical properties of three components blend system

Gluten (g)	Elvamide (g)	PEGDE (g)	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
40	2,1	0	**3,3 ± 0,0**	**40,2 ± 2,1**	**1,2 ± 0,1**	**0,23**
40	2,1	0,5	**3,5 ± 0,1**	**59,1 ± 1,0**	**1,8 ± 0,0**	**0,57**
40	2,1	2,4	**3,2 ± 0,1**	**63,9 ± 1,8**	**2,2 ± 0,1**	**0,77**
40	2,1	5	**2,6 ± 0,2**	**60,1 ± 1,7**	**3,1 ± 0,1**	**1,13**
40	2,1	10	**2,6 ± 0,1**	**58,9 ± 2,4**	**2,7 ± 0,2**	**0,92**

In Figure 41, one representative stress-strain curve has been selected from five different test results for each sample. The change in mechanical properties was studied with respect to change of PEGDE since amount of gluten (40 g) and Elvamide (2,1 g- 5% w/w) was kept constant in the polymer blend. The mechanical properties were significantly increased by the addition of PEGDE. A maximum strength value was achieved with the addition of 2,4 g PEGDE, whereas maximum elongation at break was achieved with addition of 5 g PEGDE. Elongation at break increases gradually with addition of PEGDE, however it dropped with a content of 10 g PEGDE. Toughness values were also increased with increasing PEGDE however a penalty of decreased modulus occurred with the addition of >5 g. It is important to obtain polymer blends with increased strength without compromising the modulus. Therefore, the polymer blend with 2,4 g PEGDE is promising with respect to the other blend compositions.

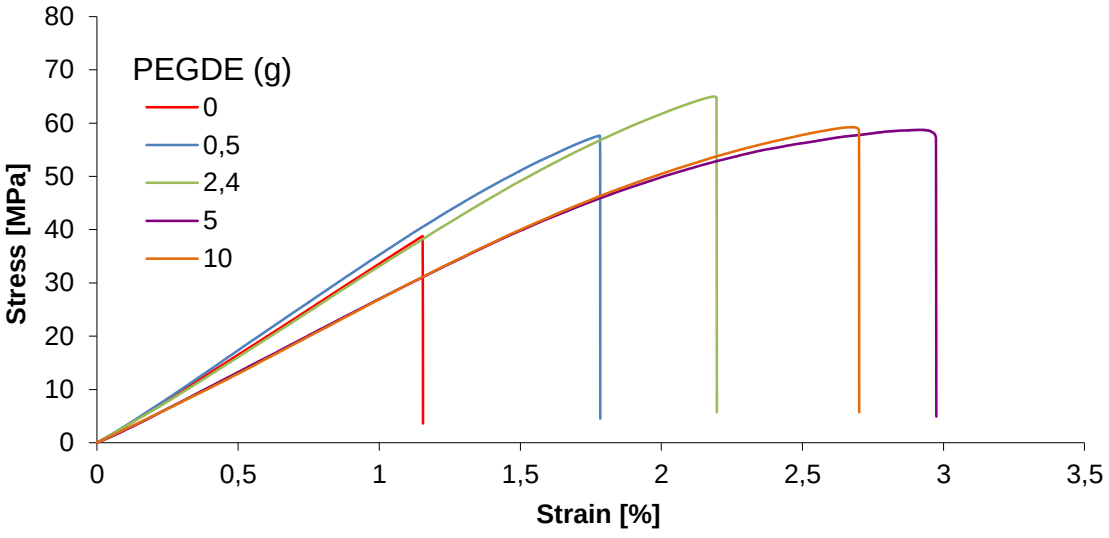

Figure 41 Stress vs. Strain values obtained by 3PB for polymer blend consisting of Gluten (40 g), Elvamide (2,1 g) and PEGDE

Similar tests were held with increased amount of Elvamide (5 g- 10% w/w) to study changes in mechanical properties with varied quantity of PEGDE (Table 10). Strength values were moderately similar among this set of samples; however elongation at break was increased with addition of PEGDE. An increase in toughness values were also achieved as elongation at break increased. The modulus clearly dropped with addition of 5 g PEGDE to the polymer blend (Fig. 42).

Table 10 Mechanical properties of three components blend system

Gluten (g)	Elvamide (g)	PEGDE (g)	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
40	5	0	**2,9 ± 0,1**	**44,2 ± 1,5**	**1,7 ± 0,1**	**0,39**
40	5	0,5	**3,0 ± 0,1**	**55,6 ± 2,6**	**2,1 ± 0,1**	**0,62**
40	5	1	**2,6 ± 0,0**	**50,3 ± 2,1**	**2,2 ± 0,1**	**0,64**
40	5	2,4	**2,7 ± 0,0**	**56,4 ± 2,5**	**2,6 ± 0,1**	**0,84**
40	5	5	**2,2 ± 0,1**	**49,6 ± 1,1**	**3,1 ± 0,1**	**0,94**

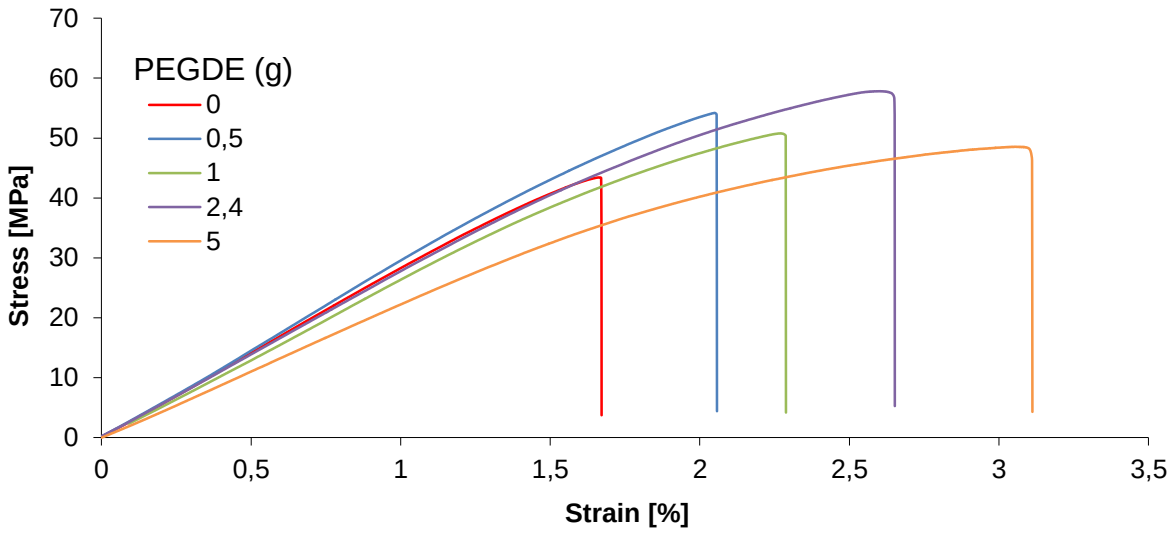

Figure 42 Stress vs. Strain values obtained by 3PB for polymer blend consisting of Gluten (40 g), Elvamide (5 g) and PEGDE

Table 11 Tg values of blends obtained by DMA

Gluten (g)	Elvamide (g)	PEGDE (g)	T_g gluten (DMA) °C	T_g Elvamide (DMA) °C
40	5	-	82,6	21,9
40	5	0,5	80,4	17,6
40	5	1	83,1	20,4
40	5	2,4	84,1	20,9
40	5	5	71,7	15,2

T_g values obtained by DMA for increased amount of PEGDE shows consistency, however there is a sharp decrease for the value of T_g containing 5 g (10% w/w) PEGDE (Table 11). The same trend was also observed within DSC studies (Fig.43).

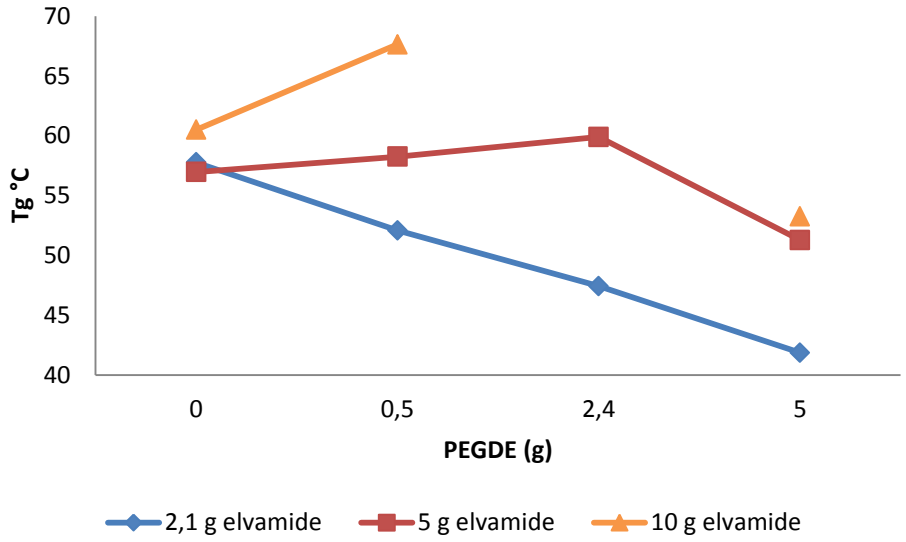

Figure 43 Tg values determined by DSC for polymer blend consisting of Gluten (40g), Elvamide (2,1 g, 5 g and 10 g) and PEGDE

Increased amount of Elvamide resulted in the decrease of modulus and strength (Table 9, 10) and the increase of T_g values for ternary blend systems (Fig. 44). The higher T_g can be explained as previously stated by the lower level of water absorption. Alternatively it should be considered that the presence of crystalline phases constrains amorphous chain motions in a non-uniform manner thus T_g increases in amorphous regions of semi-crystalline polymers than in purely amorphous polymers [71] [72]. However, crystalline domains in a semi crystalline polymer can occupy a very large fraction of the total volume of the specimen, and often have transition into the amorphous phase gradually via "interphase" regions of significant thickness. Therefore, it is not likely to develop a simple and general quantitative correlation for the effects of crystallinity on T_g [73].

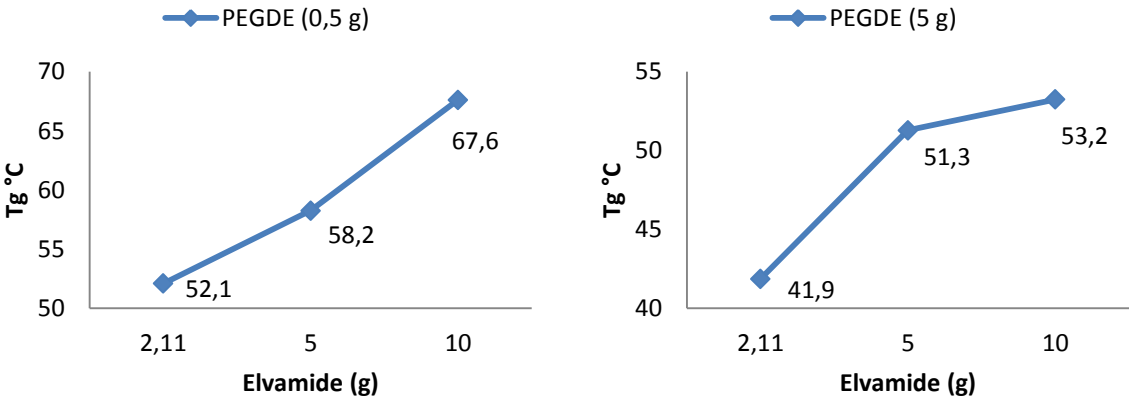

Figure 44 Tg values obtained via DSC for polymer blend consisting of Gluten (40 g), Elvamide and PEGDE

SEM studies were also held to study morphological properties of the blends with compatibilizer. They contain information on the size, size distribution, arrangement and internal structure of the polymer blend components. Thus, toughening effect can be understood via comparing these images to the blends without compatibilizer. Figures 27 (p. 32), 45 and 46 are images of samples containing the same amount of Elvamide (2,1 g) but in which PEGDE content was increased.

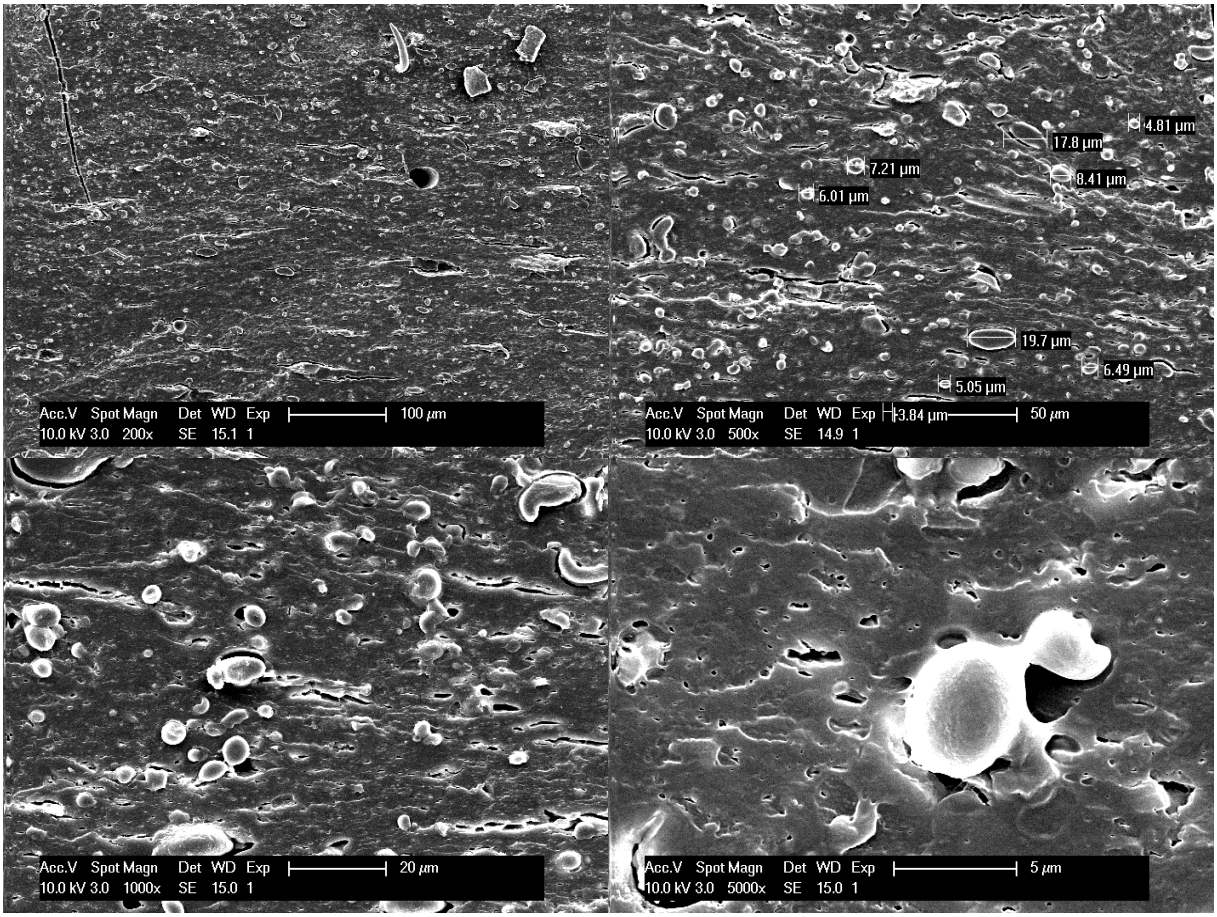

Figure 45 SEM micrographs for Gluten/Elvamide (2,1 g)/PEGDE(0,5 g) blends in different length scales

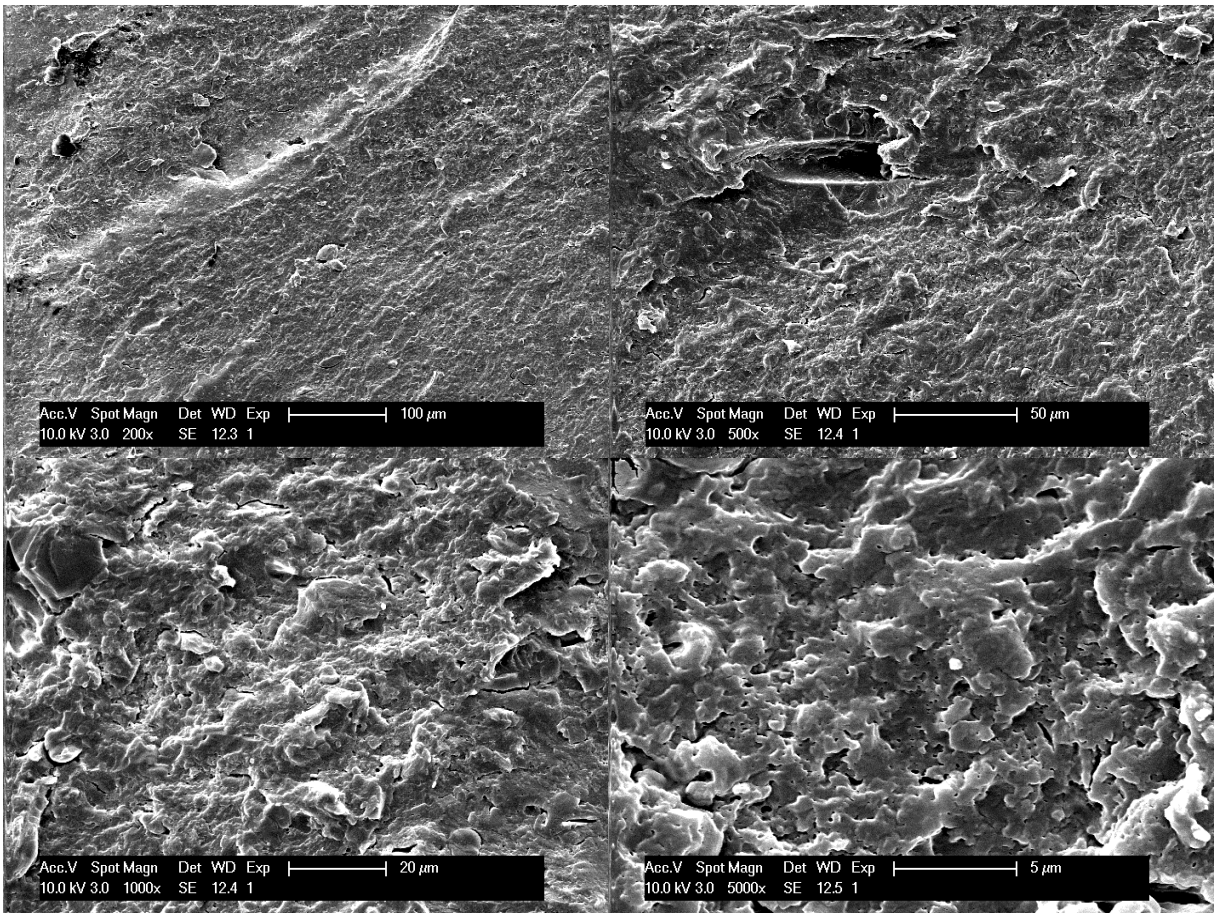

Figure 46 SEM micrographs for Gluten/Elvamide (2,1 g)/PEGDE(2,4 g) blends in different length scales

The sample with 0,5 g PEGDE showed small, finely dispersed nylon particles, whereas the blend containing 2,4 g PEGDE had a continuous arrangement. SEM micrographs obtained for ternary blends correlated with the mechanical properties found by three point bending tests. For example, the sample containing Gluten/Elvamide (5 g)/PEGDE (0,5 g) had reduced values in terms of the strength and modulus which correspond to the presence of cracks and voids observed in the micrographs (Fig. 47). Contacts at the interface in polymer blends were demonstrated with larger magnification.

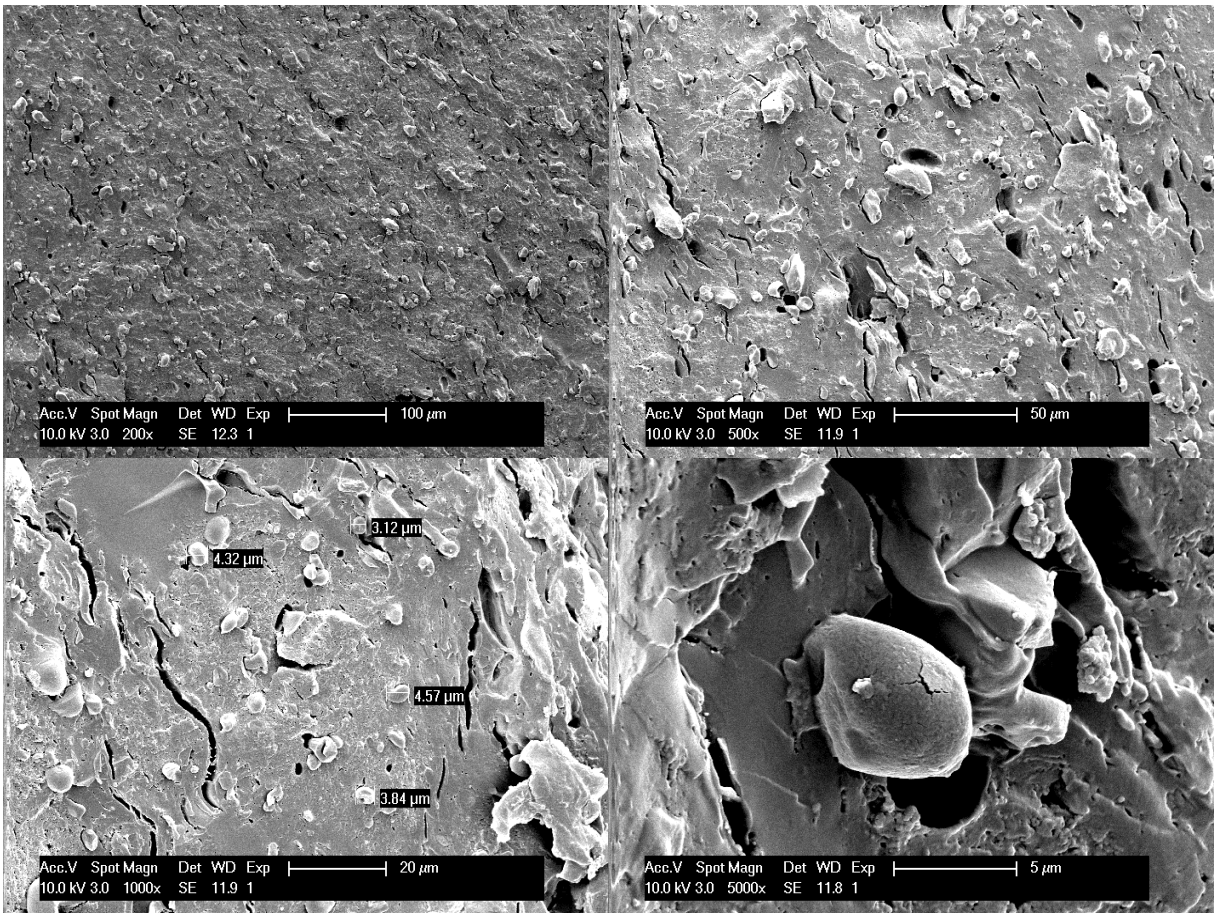

Figure 47 SEM micrographs for Gluten/Elvamide (5 g)/PEGDE (0,5 g) blends in different length scales

Figures 28 (p. 32), 47 and 48 were compared to each other and it was observed that addition of PEGDE increases heterogeneity among samples. Gluten/Nylon blends exhibit finely dispersed small particles whereas wavy surface was observed with addition of PEGDE. Correlation of SEM images and mechanical properties has a critical importance to enhance the properties of material.

In addition, chemical miscibility of the two components, method of mixing, interfacial interaction and compatibilization have to be controlled since those affect the morphology of a multi-component system at a given composition.

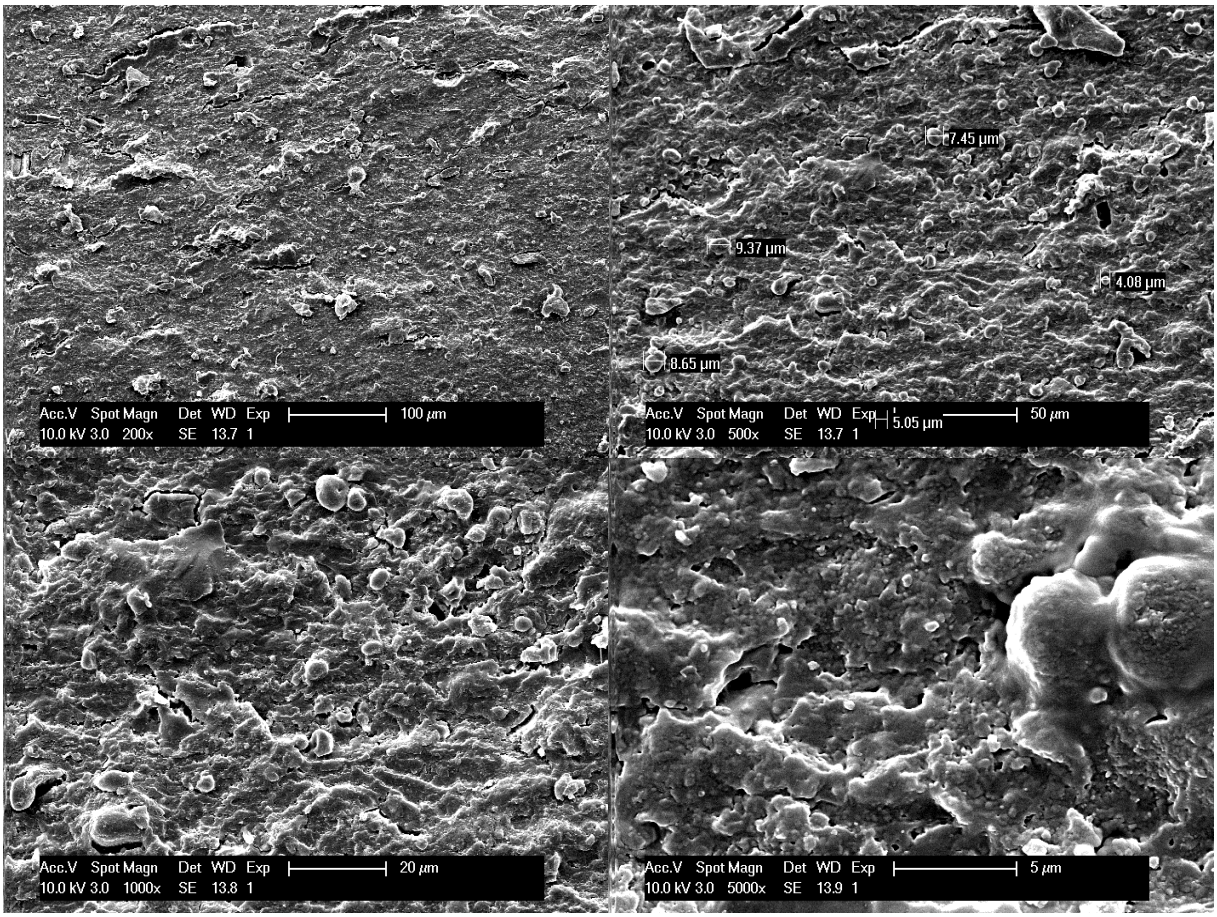

Figure 48 SEM micrographs for Gluten/Elvamide (5 g)/PEGDE (2,4 g) blends in different length scales

Last set of three component blend system was studied with 10 g of Elvamide (20% w/w) and addition of 0,5 and 5 g PEGDE (Fig 49). These samples were outperformed by previous tests. It was observed that, the ultimate strength, toughness and elongation at break were only visibly increased with addition of 5 g PEGDE to ternary blend (Table 12). It was noticed that processing was not feasible and problems due to obtaining blend powder and sieving were encountered.

Table 12 Mechanical properties of three components blend system

Gluten (g)	Elvamide (g)	PEGDE (g)	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
40	10	0	**2,6 ± 0,2**	**42,6 ± 2,4**	**1,7 ± 0,1**	**0,39**
40	10	0,5	**2,5 ± 0,1**	**39,2 ± 0,9**	**1,9 ± 0,1**	**0,44**
40	10	5	**2,2 ± 0,3**	**52,2 ± 1,3**	**3,2 ± 0,1**	**1,03**

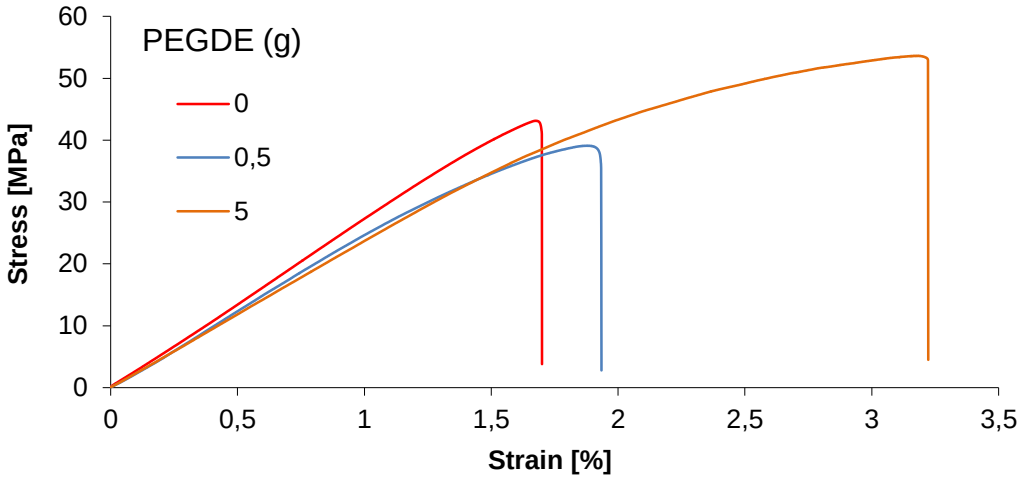

Figure 49 Stress vs. Strain values obtained by 3PB for polymer blend consisting of Gluten (40 g), Elvamide (10 g-20% w/w) and PEGDE

In Fig. 50 SEM micrographs exhibited similarity with gluten/nylon blends, thus finely dispersed small particles were difficult to observe since the nylon content was rather high.

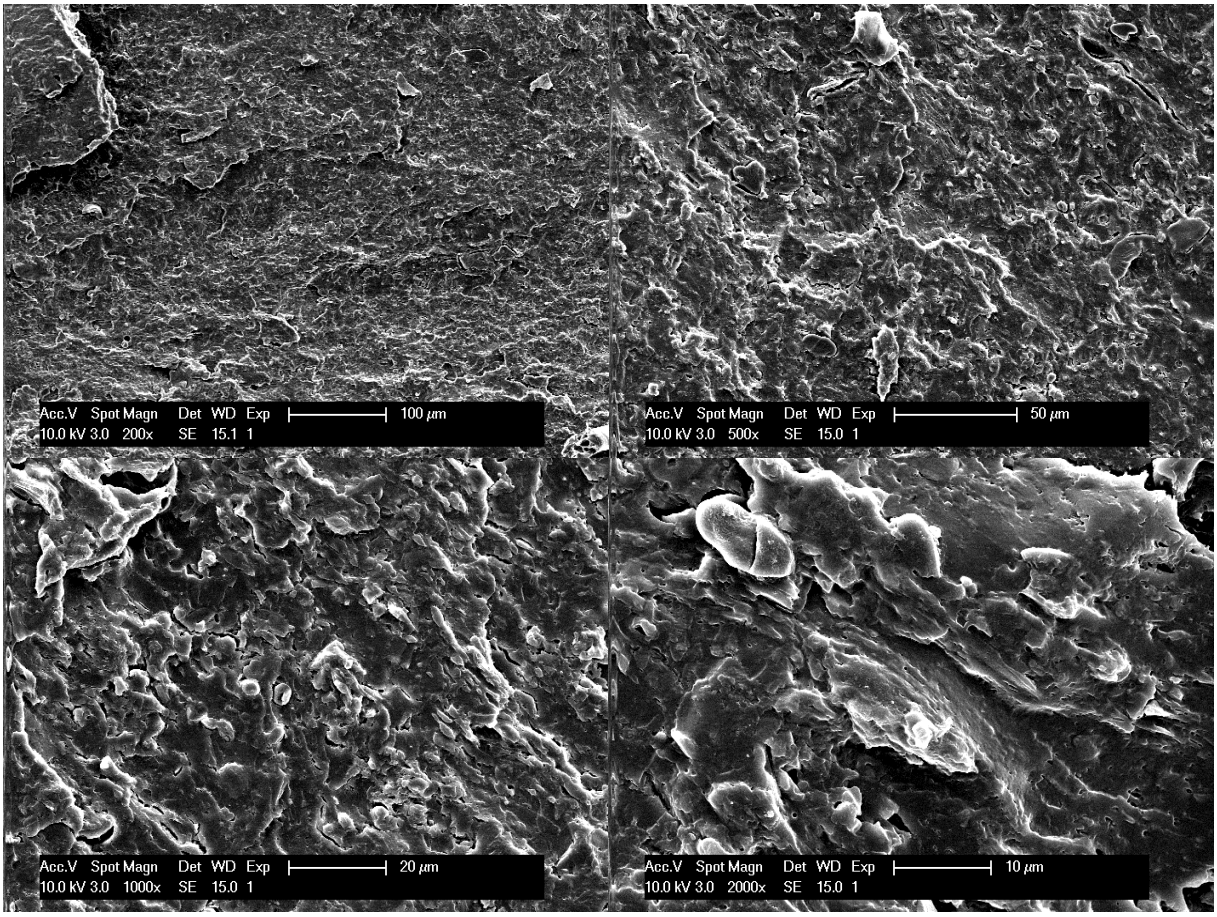

Figure 50 SEM micrographs for Gluten (40 g)/Elvamide (10 g-20% w/w)/PEGDE (5 g) blends in different length scales

To this point, changes of mechanical properties with altered amount of PEGDE were demonstrated within different ratios of gluten/Elvamide. To clearly understand the effect of increased amount of Elvamide, Figures 51 and 52 were studied with constant amount of PEGDE (0.5 g, 5 g). It was resulted that increased amount of Elvamide decreases flexural strength and modulus.

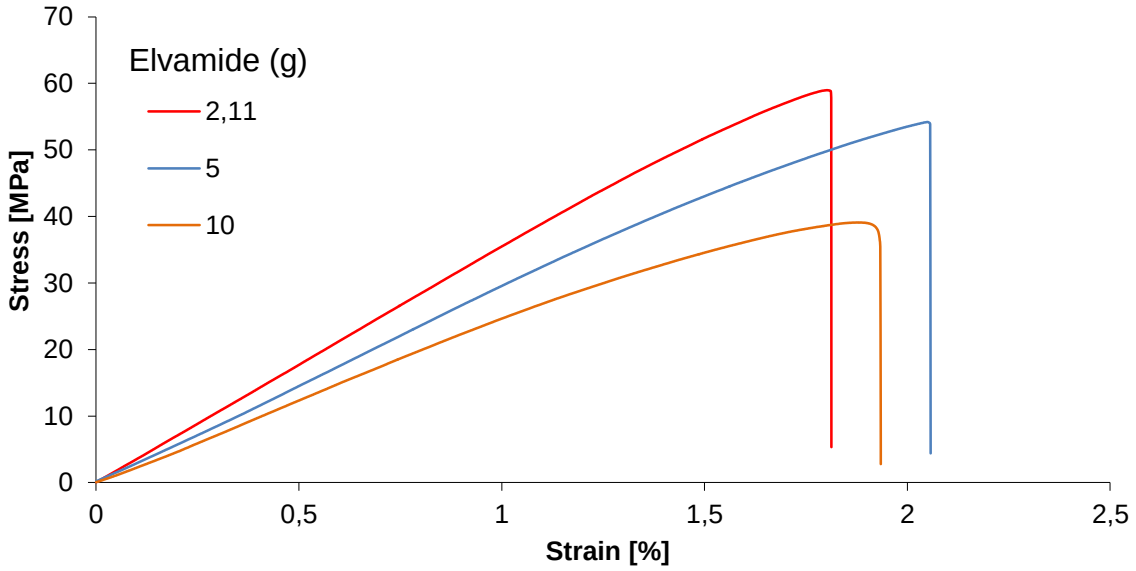

Figure 51 Stress-strain curve for polymer blend consisting of Gluten (40 g), Elvamide and PEGDE (0,5 g)

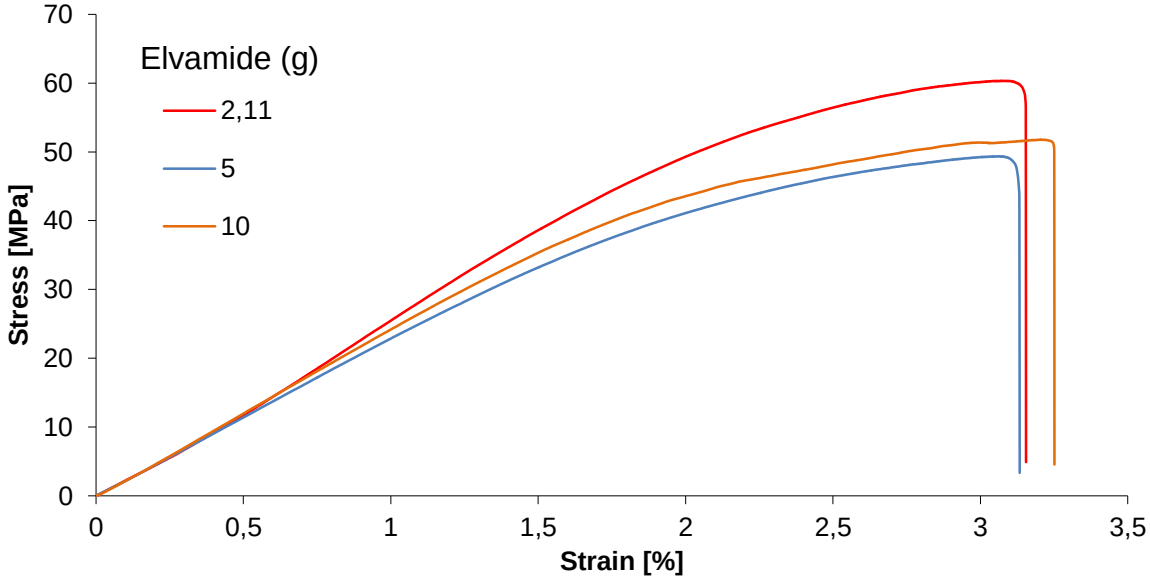

Figure 52 Stress-strain curve for polymer blend consisting of Gluten (40 g), Elvamide and PEGDE (5 g)

4.6. Investigation of Gluten/PEGDE

It was clearly demonstrated that increasing the nylon content does not efficiently increase the mechanical properties of three components blend systems. Another study was aimed to study changes without nylon. Thus study was held with 2.4 g PEGDE and varying the amount of Elvamide (Fig. 53).

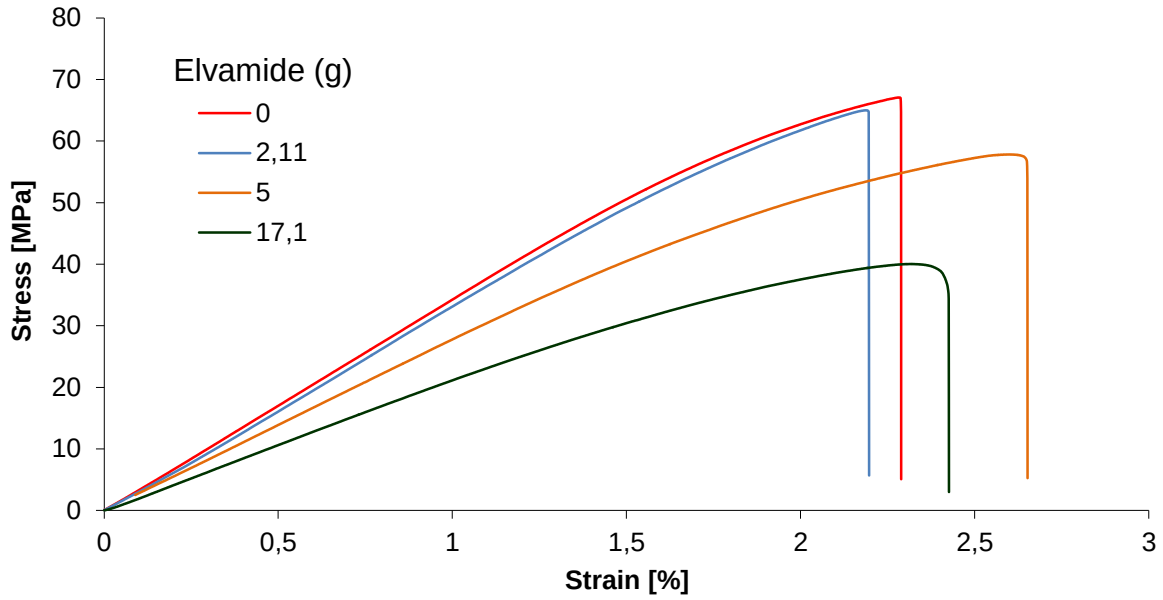

Figure 53 Stress-strain curve for polymer blend consisting of Gluten (40 g), Elvamide and PEGDE (2,4 g)

Table 13 Mechanical properties of blend system Gluten/Elvamide/PEGDE (2,4 g)

Gluten (g)	Elvamide (g)	PEGDE (g)	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
40	0	2,4	**3,4 ± 0,1**	**67,2 ± 1,4**	**2,3 ± 0,1**	**0,87**
40	2,1	2,4	**3,2 ± 0,1**	**63,9 ± 1,8**	**2,2 ± 0,1**	**0,78**
40	5	2,4	**2,7 ± 0,1**	**56,4 ± 2,5**	**2,6 ± 0,2**	**0,84**
40	17,1	2,4	**2,2 ± 0,1**	**40,6 ± 0,6**	**2,4 ± 0,1**	**0,57**

The result was surprising since the sample without nylon displayed the best performance since its flexural strength has highest value together with maximum modulus value. Among all test samples characterized in this thesis; sample consists of gluten/PEGDE has the maximum value of strength. Therefore further experiments should be investigated with blends of gluten/PEGDE and using different PEGDE concentrations.

A DMA experiment held on a gluten/PEGDE blend showed only one T_g maximum in the loss modulus. (Fig. 54) It is suggested that this T_g is due to gluten; therefore PEGDE doesn't exhibit a separate T_g.

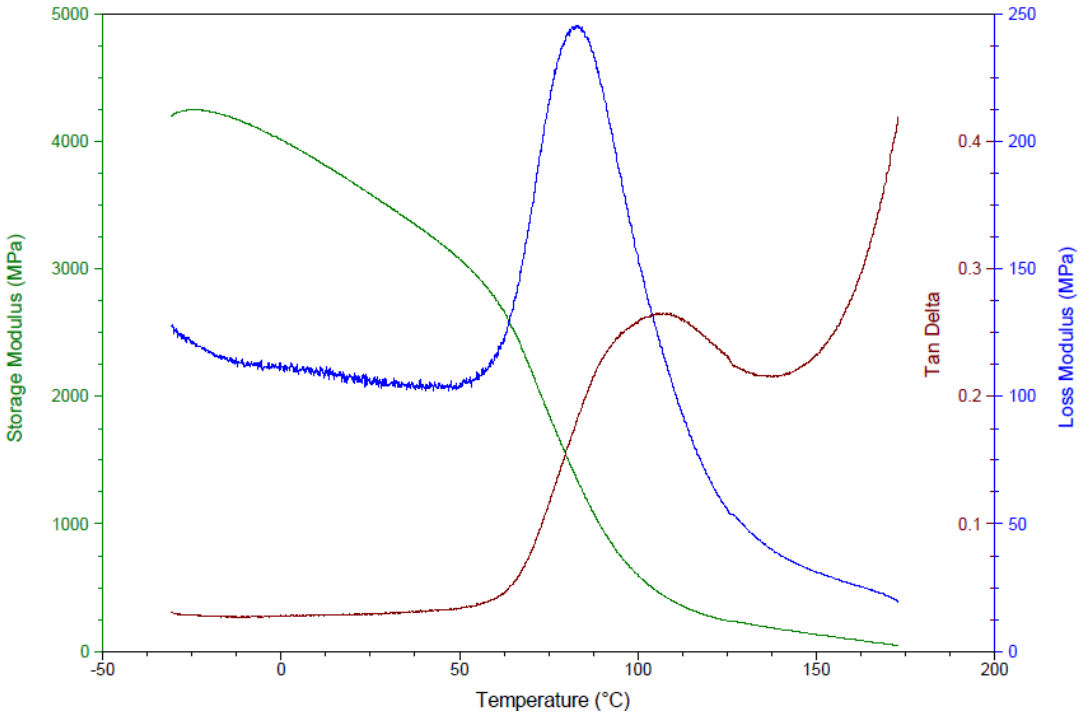

Figure 54 DMA result of blend of Gluten (40 g) and PEGDE (2,4 g) mixed at 110 °C in 500 ml ethanol/water (70% v/v)

The SEM images of gluten/PEGDE blend are shown in Fig. 55 which exhibit rough surface of fracture due to reduced brittleness.

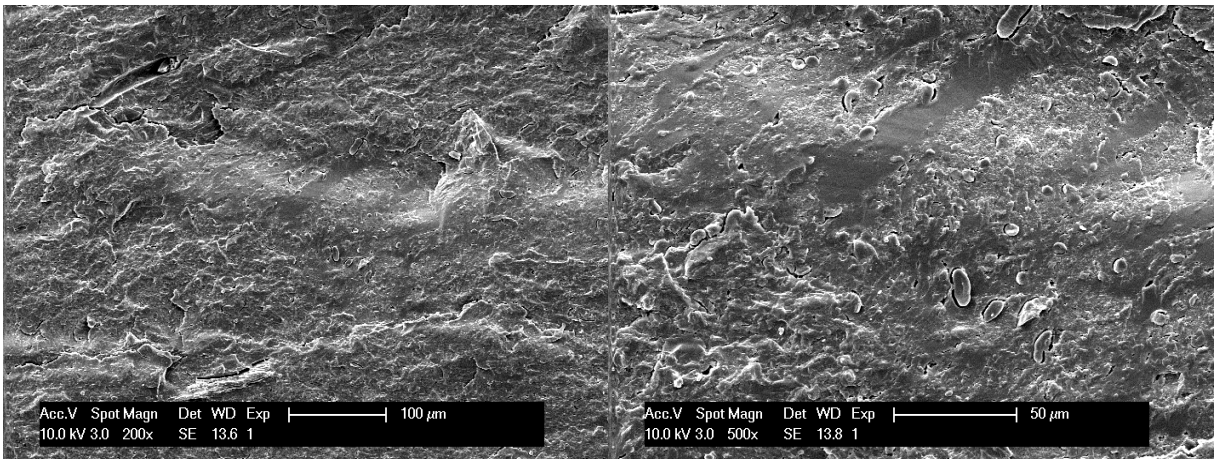

Figure 55 SEM micrographs for Gluten (40 g)/PEGDE (2,4 g) blends in different length scales

On the other hand, ternary blends exhibits two separate T_g values as in the case of gluten/nylon blends. Phase specific T_g values are similar to each other irrespective of the nylon fraction (Table 14). Increase at maximum elongation also demonstrates good adhesion was achieved. Among these set of samples containing 17,1 g Elvamide and 2,4 g PEGDE exhibits poor material performance (Table 13). Storage modulus values obtained via DMA also verifies this behavior for increased amount of Elvamide (Fig. 56).

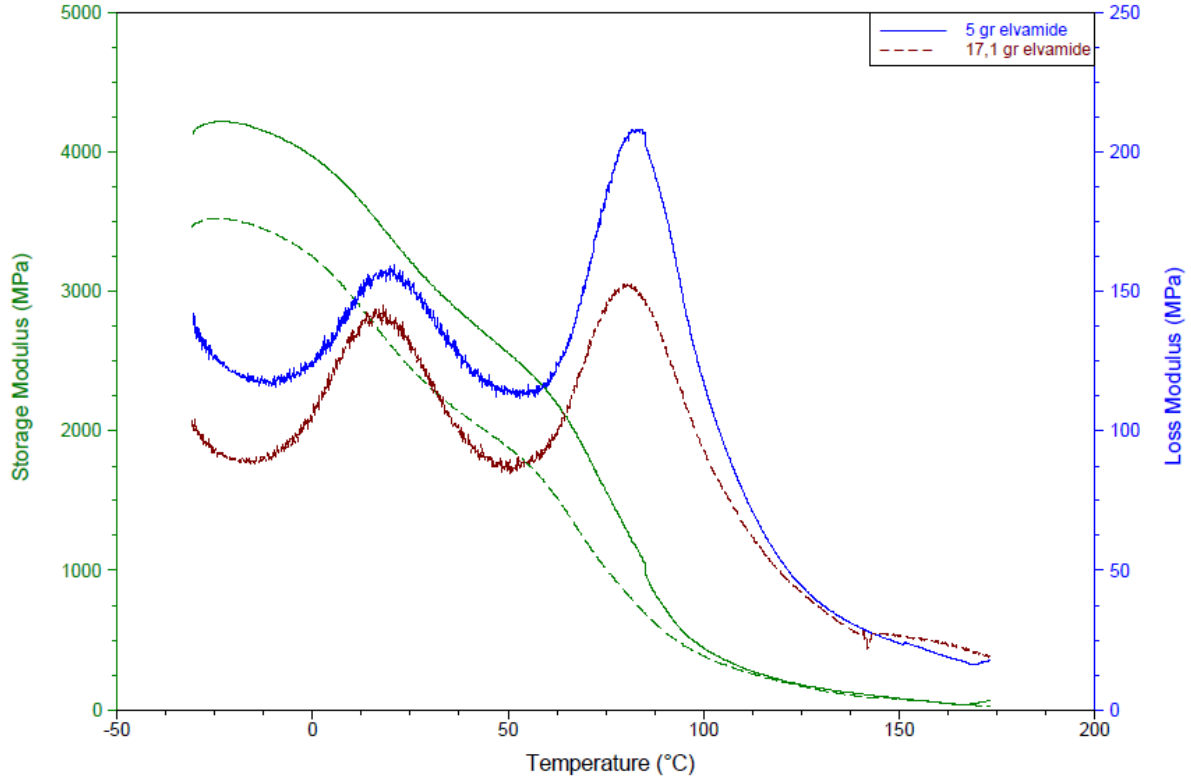

Figure 56 DMA result of blend of Gluten (40 g), Elvamide and PEGDE (2,4 g) mixed at 110 °C in 500 ml ethanol/water (70% v/v)

Table 14 Tg values of polymer blends obtained via DMA and DSC

Gluten (g)	Elvamide (g)	PEGDE (g)	T_g gluten (DMA) °C	T_g Elvamide (DMA) °C	T_g blend (DSC) °C
40	0	2,4	84,3	-	51,7
40	5	2,4	84,1	20,9	59,9
40	17,1	2,4	81,7	18,3	62,7

4.7. Investigation of another compatibilizer

Another multicomponent blend system was investigated with PPGDE (Fig. 57) used as third component (gluten/Elvamide) to study changes of mechanical properties and to compare differences with PEGDE.

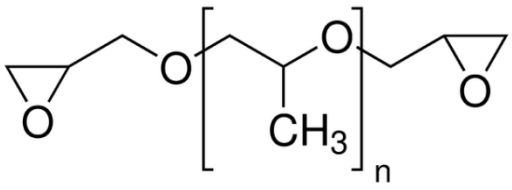

Figure 57 Chemical Structure of poly (propylene glycol) diglycidyl ether (PPGDE) average M_n ~640

The results of mechanical properties obtained via three point bending test are demonstrated in Figure 58.

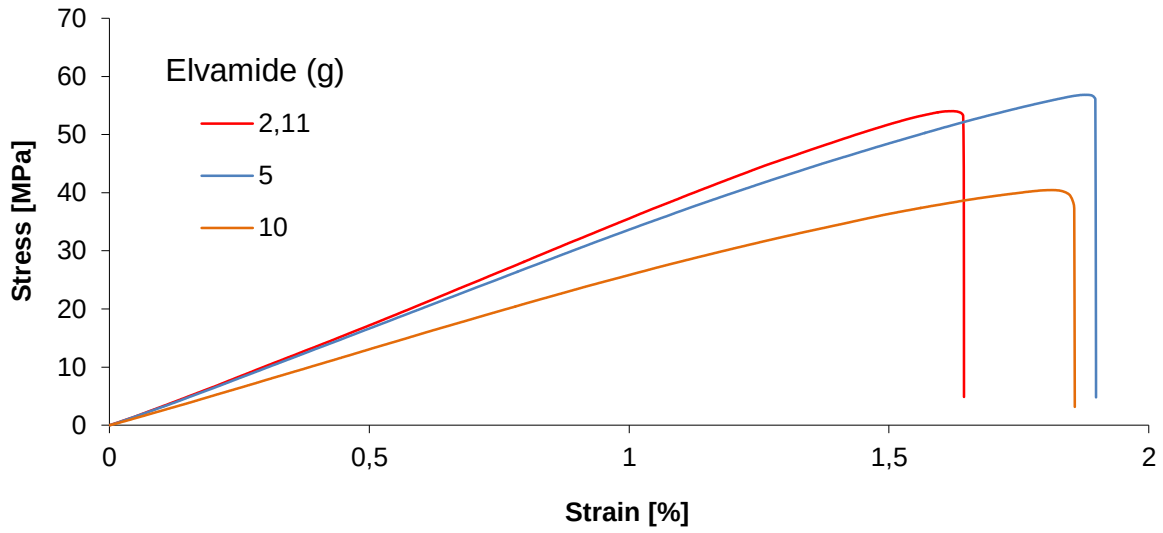

Figure 58 Stress-strain curve for polymer blend consisting of Gluten (40 g), Elvamide and PPGDE (0,5 g)

The results showed similar trend with ternary blend system of PEGDE. (Figure 51) However, another study showed that PPGDE caused a decrease in ultimate strength, toughness and strain at failure with respect to PEGDE. (Table 15)

Table 15 Mechanical properties and Tg values obtained via DSC for polymer blend consisting of Gluten (40 g), Elvamide (2,1 g) and PEGDE (5 g) or PPGDE (5 g)

	T_g (DSC) °C	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
PEGDE	41,9	**2,6 ± 0,2**	**60,1 ± 1,7**	**3,1 ± 0,1**	**1,14**
PPGDE	47,2	**2,5 ± 0,1**	**43,7 ± 1,2**	**2,1 ± 0,1**	**0,51**

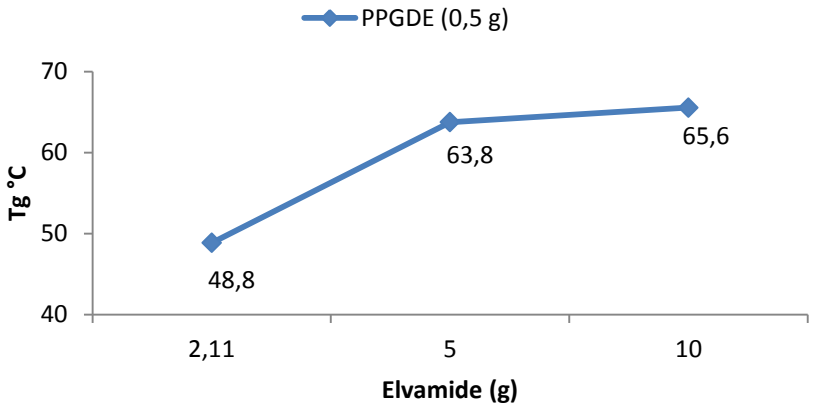

Figure 59 Tg values obtained via DSC for polymer blend consisting of Gluten (40 g), Elvamide and PPGDE (0,5 g)

T_g values were increased again with addition of Elvamide to ternary blends (Fig. 59). The T_g values obtained for different compatibilizers PEGDE (1% w/w) or PPGDE (1% w/w) via DSC for ternary polymer blend consisting of 5%, 10% and 20% w/w Elvamide were very similar.

4.8. Effect of annealing on ternary blends

Firstly, X-ray scattering experiments conducted on non-annealed samples of Gluten/PEGDE (2,4 g) and Gluten/Elvamide (17,1 g)/PEGDE (2,4 g) are shown in Fig.60. Addition of nylon changes the scattering pattern, however crystalline features were not obvious, likely even absent.

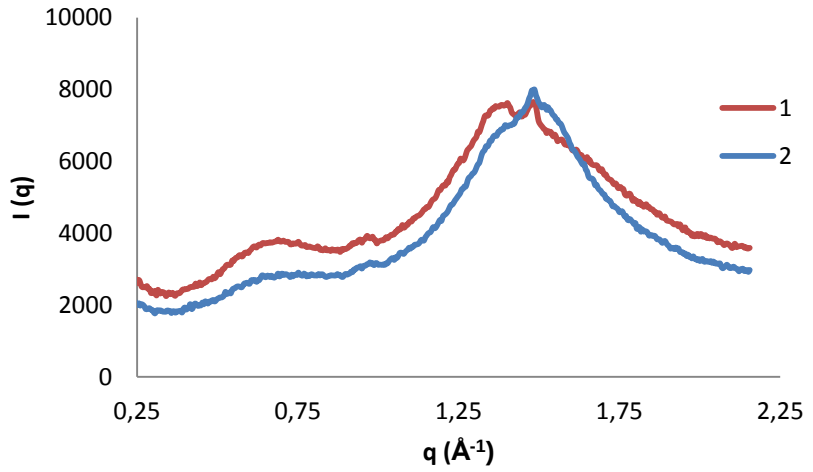

Figure 60 X-ray scattering data for non-annealed blends of Gluten/PEGDE (2,4 g) [1] and Gluten/Elvamide(17,1 g)/PEGDE(2,4 g) [2]

Polymers are often cooled rapidly from the melt when they are being processed industrially. Rate of cooling during solidification should be controlled because time is necessary for chains to move and align into a crystal structure. Therefore, the rate at which the crystals

nucleate and grow become very significant since crystallization is controlled by kinetics[53]. Polymer blends obtained with aliphatic polyamide chains which has inter-chain hydrogen bonding can enhance crystallinity. Thus, the crystallization can be induced by annealing the amorphous polymer at a temperature between the glass transition temperature and the melting point.

It is also known that the addition of compatibilizer not only affects the size and shape of the separated phases; however it may also affect the crystalline form, the size of crystalline entities and the total crystallinity[74].

Thus, some samples were annealed aiming at varying the crystallinity and ultimately also the mechanical properties. Annealing test was also held with polymer blends of gluten/Elvamide (10% w/w)/PEGDE (10% w/w) on samples compression molded for five minutes heating 150 °C and then five minutes cooling to room temperature. These plates were heated again to 80 °C and cooled to room temperature in five minutes to induce crystallinity in the samples. X-ray scattering test gave a similar pattern for annealed sample (Fig. 61). The mechanical properties and T_g values obtained by DMA and DSC of annealed sample [2] exhibit very similar behavior with non-annealed sample [1] (Table 16).

Table 16 Mechanical properties and T_g values of compression molded blends of non-annealed (1) and annealed (2) samples Gluten/Elvamide (10% w/w)/ PEGDE (10% w/w)

T_g gluten (DMA) °C	T_g Elvamide (DMA) °C	T_g (DSC) °C	Modulus (GPa)	Strength (MPa)	Elongation (%)	Toughness (MPa)
71,7	15,2	51,3	**2,2 ± 0,1**	**49,8 ± 1,2**	**3,2 ± 0,3**	**1,00**
75,6	14,3	57,0	**2,2 ± 0,1**	**52,8 ± 2,6**	**3,6 ± 0,3**	**1,22**

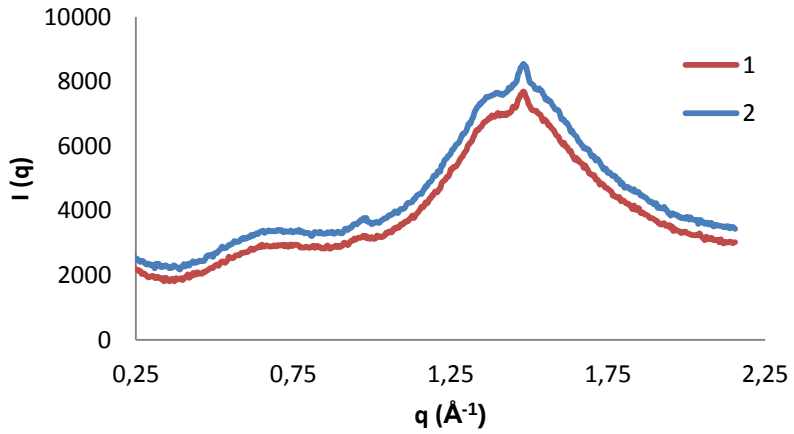

Figure 61 X-ray scattering data for non-annealed blends [1] and annealed blends [2] of Gluten/Elvamide(10% w/w)/ PEGDE (10% w/w)

5. Conclusion

Firstly, the studies were conducted with the polymer blends of wheat gluten and varied amounts of nylon mixed at low temperature. There weren't noteworthy changes in terms of mechanical properties and then the same experiment was repeated with higher temperature of mixing. Toughness values were improved at the expense of modulus and ultimate strength. DMA experiments demonstrated that addition of nylon was more efficient with respect to mixing at low temperature. In general, the mechanical properties obtained with binary blends were not satisfying as modulus and strength were inadequate.

Another experiment investigated the addition of third component to gluten/nylon blends to enhance compatibility and interfacial strength. Those ternary blends verified significant increase in terms of flexural strength and toughness values. The optimum mechanical performance for ternary blends was obtained with 5% w/w nylon.

SEM and DMA investigations of blends revealed the immiscibility of the components. SEM micrographs were compared to mechanical performance of samples. Hence, cracks and voids were related to reduction of mechanical properties due to poor adhesion of phases. Higher strength and elongation at break values are possible after improving compatibility and interfacial strength.

DMA and DSC studies measured the glass transition temperature of polymer blends. For binary and ternary blends, DMA experiments exhibited two separate T_g values whereas only one broad T_g was observed in DSC studies. In general, addition of nylon resulted in increased T_g values which are related to reduced water uptake or change in morphology of nylon phase.

X-ray scattering experiments carried out on both non-annealed and annealed samples of binary and ternary blends to study the crystallinity obtained via nylon phase. Annealed samples exhibited very similar patterns compared to non-annealed samples. On the other hand, addition of nylon to wheat gluten generated another peak at higher q values which is due to crystalline nylon.

A bifunctional epoxide was used as a compatibilizer to improve the adhesion between the gluten and nylon phases. The study demonstrated that the compatibilization of gluten/nylon blends could significantly improve the mechanical performance and modify T_g of wheat gluten based material.

Gluten/PEGDE blend is promising candidate since it has the maximum value of strength with high modulus. Further research is needed on this binary combination.

6. Outlook

The experimental process followed to obtain polymer blends consists of several steps such as mixing components in solvent, drying, grinding and compression molding. In all these multi-step approaches, the resultant polymer could be subjected to repetitive cycles of high processing temperature, which could affect the miscibility of gluten and nylon and also the phase separation between the two at different composition levels. In addition, batch process is disadvantageous with respect to continuous processing. These multi-step approaches can be efficient at the research laboratory level for small-scale production of the blends. However, the multiple steps involved in the production of rigid material make such processes both time consuming and very energy intensive, thus preventing their effective commercial-scale use. A more efficient and effective technique is required that avoids the additional step of pre-mixing and drying before molding. Different processing methods such as intensive mixer-compression, injection or extrusion molding can also be studied since these can result in different mechanical properties like elastic modulus, elongation and tensile strength.

Biodegradation of polymer blended samples should be checked to obtain environmentally friendly material. Although blending gluten with nylon and PEGDE improves its properties and may broaden its applications, the majority of these nylons is derivatives of crude oil and is non-biodegradable[75]. Hence, it is essential to blend gluten with renewable and biodegradable polymers that provide needed performance improvement while not sacrificing biodegradability.

An interesting research was reported to obtain wheat gluten nanocomposites. It is described that, the addition of nanoparticles could enhance the miscibility between the starch and the other components in the gluten nanocomposite, but such miscibility enhancement did not occur in the gluten/PVA blend [29] [76]. Another way to achieve compatibilization is adding a block copolymer in which each of the blocks has similar composition to that of components of polymer blend. Thus morphology can be controlled with an improvement in interfacial adhesion and hence mechanical properties [53].

It is necessary to study wheat gluten protein structure and disulfide bonding patterns to understand chemical changes and its effects. However, it is very difficult to determine the structure of wheat gluten protein since some parts of gluten is insoluble [26].

In addition, it is significant to understand the chemical reactions between the protein chains and the other constituents in the system, the irreversible changes that the protein experiences upon exposure to heat and changes that the protein-based material can undergo with respect to moisture content.

List of Abbreviations and Symbols

AACC	American Association of Cereal Chemists
ASTM	American Society for Testing and Materials
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
E’	Storage modulus
E”	Loss modulus
EDA	Ethyl diamine
HIPS	High Impact Polystyrene
LDPE	Low-Density Polyethylene
MIPS	Medium Impact Polystyrene
NMR	Nuclear Magnetic Resonance
PEGDE	Poly (ethylene glycol) diglycidyl ether
PLA	Poly-lactic acid
PPGDE	Poly (propylene glycol) diglycidyl ether
PS	Polystyrene
PVA	Poly (vinyl alcohol)
RH	Relative Humidity
q	Scattering vector
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
tan δ	E”/ E’
T_g	Glass Transition Temperature
TPVA	Thiolated poly (vinyl alcohol)
WAXD	Wide Angle X-ray Diffraction
WAXS	Wide Angle X-ray Scattering
WG	Wheat Gluten

List of Figures

(Some figures were reproduced from referenced works)

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