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Plasticizers for Protein-Based Materials

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Abstract

This study presents a practical approach to select plasticizers for proteins. It is a case study on thermoformed wheat gluten, considered here as a model protein, and it involved 30 plasticizer candidates. The approach consisted of selecting plasticisers (30 wt%) based on visual examination, rheological and molding behavior of the dough, and finally tensile data. There was no unique relationship between the torque behavior of the dough and the mechanical properties of the films. Nevertheless, the extensibility and dough analysis indicated that the most promising plasticizers were as follows: glycerol, linear glycols, ethanol amines, diols, and trimethylolpropane. Further, considering also the stiffness, it was concluded that the most efficient plasticisers were those that contained three hydroxyl groups and the linear glycols of intermediate size. Out of those, glycerol stood out as having the highest extensibility and lowest stiffness and strength. In an attempt to predict the mechanical properties of the films based on several physical data of the compounds, it was observed that there was a weak nonlinear relationship between the stiffness/strength and the size (molecular weight/molar volume), polarity and molar refractivity of the compound. The stiffness/strength decreased with an increase in these physical parameters.

Keywords: proteins, wheat gluten, plasticisers, compression molding, mixing

1. Introduction

Protein-based films have generally low oxygen permeability in dry conditions due to the high amount of hydrogen bonds. However, the hydrogen bonds also make the films brittle in dry conditions, and a plasticizer is needed for the film to have desirable ductility [1–4]. Several factors must be taken into account when choosing between different possible plasticizers, and

the perfect plasticizer is probably not to be found. Plasticizer and protein materials must have similar polarity to be compatible. Insufficient dispersion of the plasticizer in the protein matrix results in a material with properties depending on the internal variation in plasticizer concentration. The molecular weight and chemistry/polarity of the plasticizer affects its diffusion properties and therefore the migration from the protein matrix and the long-term properties of the protein material. There are numerous reports on plasticized protein-based films, including matrices from plants such as soy, pea, sunflower, and wheat proteins and zein [5]. Animal-based protein matrices include sodium caseinate, keratin, gelatin, collagen, and whey and myofibrillar proteins. Plasticisers have also been an important factor to consider in biocomposites [6].

The most commonly used plasticizer for protein films is glycerol, which is miscible in most proteins, but several other plasticizers have also been studied [7–12]. Examples are polyfunctional alcohols such as sorbitol, propylene glycol, and di- and triethanolamine [1, 4, 7, 8, 10, 11, 13–20]. Often, more than one plasticizer has been used, for example water and glycerol [21], glycerol and trehalose [22], and glycerol and dendritic polyglycol [23]. An interesting direction toward new types of plasticisers is low-molar-mass proteins (hydrolysates). However, as reported by Nuanmano et al. [24] on the plasticization of fish myofibrillar proteins, that glycerol is more effective than the hydrolysates (gelatin-based) at similar contents. Both glycerol and sorbitol are harmless as plasticizers for films in contact with foodstuff and are also frequently used as sweeteners in foodstuffs [13]. It was interesting to compare the number of papers with the search words “glycerol” and “plasticizer” with those on “phthalate” and “plasticizer”. The total number in the former and latter case was 48,600 and 89,800 (Google Scholar). In the years 1980, 1990, 2000, 2010, and 2015, the papers on glycerol plasticizer were 330, 520, 1270, 3640, and 5150. The same numbers for PVC plasticizer were 800, 1310, 2450, 4490, and 6020. It shows that glycerol, as a plasticizer for bio-based materials, is investigated to almost the same extent as the phthalates, being a common plasticizer for petroleum-based plastics (mainly PVC). The interest in glycerol is also increasing with time.

The potential migration of plasticizers is an important aspect to consider when choosing plasticizer. Migration of plasticizers leads to a decrease in fracture strain [11, 12]. Even though the film becomes more ductile with increasing plasticizer content, it is important to keep the content as low as possible because of barrier property issues; the gas/vapor permeabilities, generally, increase with increasing plasticizer content [25]. In general, a compromise between permeability and extensibility has to be made [11, 26–28]. In fact, a compromise has to be made also between ductility and stiffness/strength, since they normally go in opposite directions with increasing plasticizer content. Several less hygroscopic plasticizers, such as mono-, di-, or oligosaccharides and urea, have also been studied in solution cast films. Amphipolar plasticizers such as octanoic and palmitic acids, dibutyl tartrate and phthalate, and mono-, di-, and tri-glyceride esters have also been studied in solvent cast protein films such as WG and zein. Still, glycerol and triethanolamine have so far seemed to be the most appropriate plasticisers for films of proteins such as whey or wheat gluten [7, 11, 12]; however, sorbitol is also a commonly used plasticizer [29]. These plasticizers have mostly been evaluated for solution cast films [30, 31], and only a limited number of studies have been reported for

thermoformed gluten-based matrices with plasticizers [32–39]. In fact, for the most common plastic processing method (injection molding), only a few studies have been performed on the effects of plasticizers [40, 41].

There is no study, to our knowledge, that compares a very large set of different types of potential plasticizers for thermoformed wheat gluten films. This study focuses on a practical evaluation of potentially interesting plasticizers for use in thermoformed wheat gluten films. The outcome should be valid not just to WG, but also to proteins of different origins like pure or modified whey [42] and blood meal [43] proteins. The number of potential plasticizers is high, and these have to be carefully selected to avoid poor film properties and issues relevant, for e.g., the barrier properties, migration, aging behavior, sealing properties [44], printing properties, and cost. Which properties that are most interesting depend on the specific application, but the thermoforming and mechanical properties are of fundamental importance for most applications. This is also why these properties have been compared and evaluated, as a function of plasticizer type, in this study.

2. Experimental

2.1. Materials

The wheat gluten powder was supplied by Reppe AB, Lidköping, Sweden. The additives added for plasticizing purposes are presented in **Table 1**. The selection was based on polarity, melting, and boiling temperatures.

2.2. Blending procedure

About 350 g wheat gluten powder and 150 g of plasticizer were blended using a food processor (WATT; DUKA AB, Sweden) at the lowest speed, “Speed 1” (about 95 rpm), for 60 s. About 40 g of the blend was then transferred to a Brabender plasticorder PL2000 with a M50EHT measuring head and kneaded at 50 rpm for 2 min. The torque and the temperature were monitored with Brabender correlation program version 2.2. The starting temperature was set to 50°C.

2.3. Water adding procedure

Gluconic acid lactone, PEG 150, PEG 200, PEG 400, sorbitol, and xylose, respectively, were also mixed with small amounts of water (20% of the plasticizer content) for improved miscibility with the gluten powder. The water used was deionized and was blended in with the plasticizer.

2.4. Visual evaluation of the mixtures

The mixtures were visually evaluated during mixing. The focus was on crack formation, visible separation of the additive and the protein, and also on “apparent” dough brittleness. The visually “most promising” additive/gluten mixtures were chosen for compression molding.

Additive	T_m^a (°C)	T_b^a (°C)	Purity	Supplier
1,2-propanediol	-59	187.6	98%	Fluka, The Netherlands
1,3-propanediol	-27	214–216	99.6%	Aldrich, USA
1,4-butanediol	16	230	≥99.9%	Merck KGaA, Germany
2-propanol	-89	82.4	≥99.9%	Sigma-Aldrich GmbH, Germany
Adipic acid	151–154	265	≥99.9%	Sigma-Aldrich GmbH, Germany
Diethanolamine	28	217	99%	Sigma-Aldrich
Gluconic acid lactone	117	–	≥99.9%	Sigma-Aldrich GmbH, Germany
Glycerol	18	290	99.5%	Karlshamns Tefac AB, Karlshamn, Sweden
Lactic acid	53	–	≥99.9%	Sigma-Aldrich GmbH, Germany
Myvacet™ 5-07 ²⁹	41–46	–	–	Quest International Inc., USA
Myvacet™ 9-08 ²⁹	-12 to -14	–	–	Quest International Inc., USA
Myvacet™ 9-45 ²⁹	4–12	–	–	Quest International Inc., USA
Octanoic acid	16–17	237	≥99.9%	Sigma-Aldrich GmbH, Germany
Diethylene glycol	-10	245	99%	Sigma-Aldrich
Triethylene glycol	-7	278	99%	Sigma-Aldrich
Tetraethylene glycol	-6	314	99%	Sigma-Aldrich
Octaethylene glycol	-4	327	≥99%	Sigma-Aldrich GmbH, Germany
Ethylene glycol	-13	197	99.5%	Merck KGaA, Germany
SAIB™ 90EA ³⁰	–83°C	78°C	–	Eastman Chm. Co., USA
Sorbitol	95	296	≥98%	Sigma-Aldrich, USA
Succinic acid	185–187	235	≥99.9%	Coleman & Bell Co., USA
Trimethylolpropane	58	292–297	≥99%	Perstorp Specialty Chemicals AB, Perstorp, Sweden
Triethanolamine	21	208	≥99.9%	Riedel-de Haen GmbH, Germany
Xylose	144–145	–	≥99%	Sigma-Aldrich GmbH, Germany

^a T_m and T_b are melting and boiling points.

Table 1. Additives that were mixed with the wheat gluten powder.

2.5. Preparation of compression-molded films

The wheat gluten powder and the additives were blended using a food processor (WATT; DUKA AB, Sweden) at the lowest speed, “Speed 1” (about 95 rpm), for 30 s and thereafter at

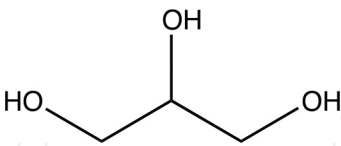



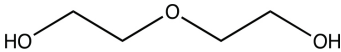

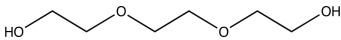

“Speed 3” (about 200 rpm) for 1 min. Five grams of the mixture was then put in a frame and pressed into 0.5 mm thick films at 120°C for 3 min at a pressure of 100 bar. The compression-molded gluten sheet was cut into a square following the frame and put on Mylar films for 1 h. The press used was a Laboratory Press Polystat 200T #7105, Servitec Maschinenservice GmbH, Wustermark, Germany.

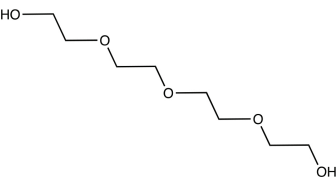
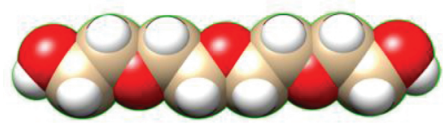
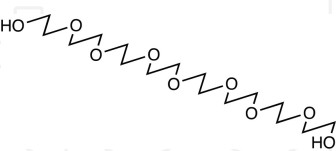
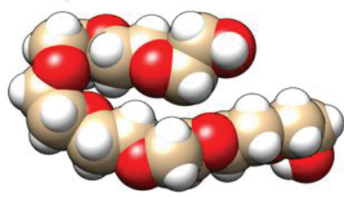
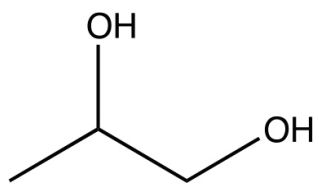
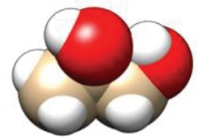
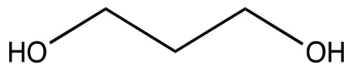
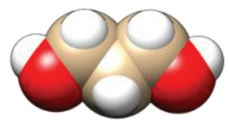
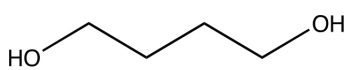
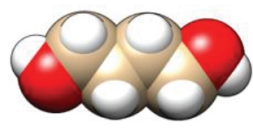
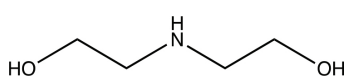
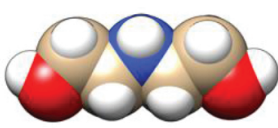
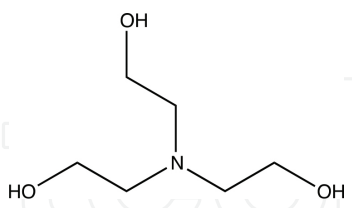
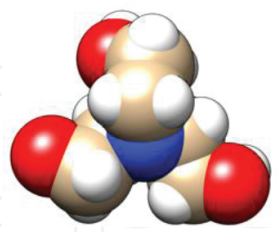
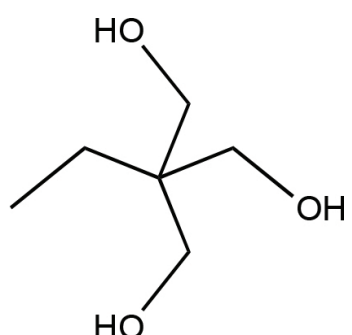
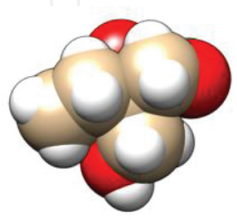
2.6. Tensile testing

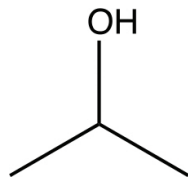

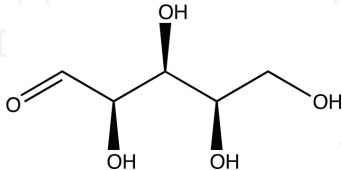
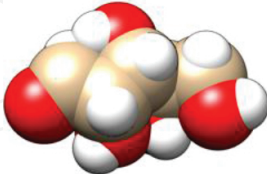
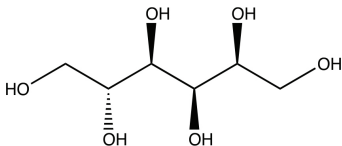
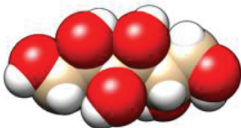
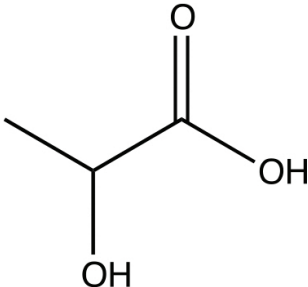
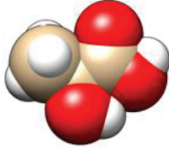
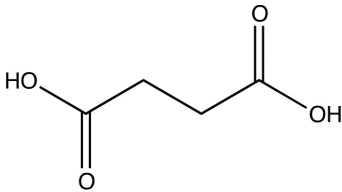
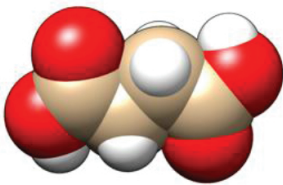
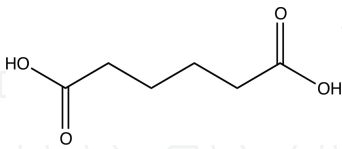
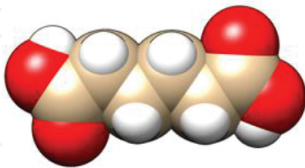
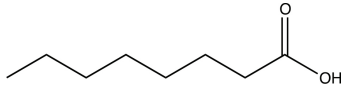
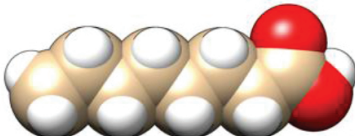
The Young's modulus, tensile stress, and fracture strain (maximum tensile strain) were measured on samples, punched from the pressed gluten/additive films. Ten specimens, with a size described by EP 04/ISO 37-3 (with a test area of 4 × 40 mm), from each sample were measured by a Zwick Z010 tensile tester using the sensor 0.5 kN, controlled by TestXpert 7.11. A preload of 0.5 N applied with a speed of 100 mm/min was used. The entire tests were also performed at 100 mm/min. The tensile test and the 24-h preconditioning were performed at 50% RH and 23°C. The average values for each sample are presented.

3. Results and discussion

The molecular structure and properties of the compounds evaluated here are given in **Tables 2** and **3**. To narrow down the number of potential plasticisers the mixing/compounding and molding properties were first evaluated before going further with mechanical characterization of the compression-molded films. Very early six different compounds (four different starch syrups, octanoic acid, and pentaerythritol) were discarded due to very poor mixing with WG.

Additive	Molecular structure	Van der Waals volume
Glycerol		
Ethylene glycol		
Diethylene glycol		
Triethylene glycol		

Additive	Molecular structure	Van der Waals volume
Tetraethylene glycol		
Octaethylene glycol		
1,2-propanediol		
1,3-propanediol		
1,4-butanediol		
Diethanolamine		
Triethanolamine		
Trimethylolpropane		

Additive	Molecular structure	Van der Waals volume
2-propanol		
Xylose		
Sorbitol		
Lactic acid		
Succinic acid		
Adipic acid		
Octanoic acid		

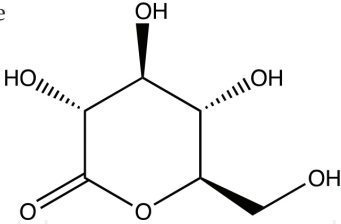
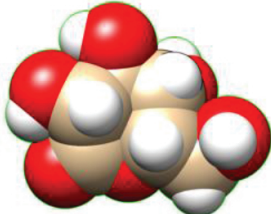
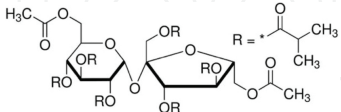
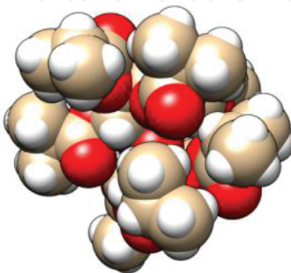
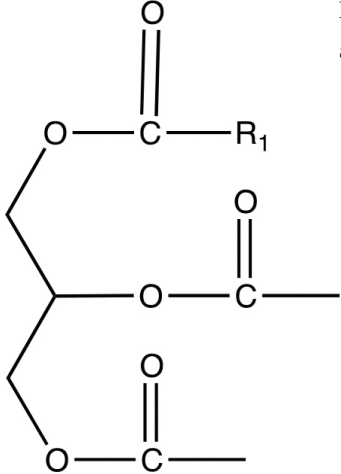
Additive	Molecular structure		Van der Waals volume
Gluconic acid lactone			
SAIB™ 90EA			
Myvacet™ 5-07			R ₁ : fatty acid chains based on 30% palmitic acid and 70% stearic acid
Myvacet™ 9-08	As 5-07	R ₁ : fatty acid chains based on 47% lauric acid, 18% myristic acid, 12% stearic acid, 10% palmitic acid, 13% others	
Myvacet™ 9-45	As 5-07	R ₁ : fatty acid chains based on 73% oleic acid (isomers), 18% myristic acid, 13% stearic acid, 10% palmitic acid, 4% others	

Table 2. Additive properties.

Additive (0.43 g additive/g WG)	Density ^a (g/cm ³)	Molecular weight (g/mol)	Crit. molar volume ^b (cm ³ /mol)	Specific volume (cm ³ /g)	Amount added ^c (mol/g WG)	Volume added ^d (cm ³ /g WG)	Functional groups added ^e (mol/g WG)	Log P ^f	tPSA ^g	MR ^h (cm ³ /mol)
Glycerol	1.260	92.1	254.5	0.794	0.0047	0.341	0.0140	-1.33	60.69	20.27
Ethylene glycol	1.200	62.1	185.5	0.825	0.0069	0.355	0.0138	-0.79	40.46	14.21
Diethylene glycol	1.120	106.1	315.5	0.893	0.0090	0.384	0.0189	-0.95	49.69	25.14

Additive (0.43 g additive/g WG)	Density ^a (g/cm ³)	Molecular weight (g/mol)	Crit. molar volume ^b (cm ³ /mol)	Specific volume (cm ³ /g)	Amount added ^c (mol/g WG)	Volume added ^d (cm ³ /g WG)	Functional groups added ^e (mol/g WG)	Log P ^f	tPSA ^g	MR ^h (cm ³ /mol)
Triethylene glycol	1.127	150.2	445.5	0.887	0.0029	0.382	0.0057	-1.1	58.92	36.06
Tetraethylene glycol	1.129	194.2	575.5	0.886	0.0022	0.381	0.0044	-1.26	68.15	46.99
Octaethylene glycol	1.130	370.4	1095.5	0.885	0.0012	0.381	0.0023	-1.88	105.07	90.68
1,2-propanediol	1.036	76.1	235.5	0.965	0.0057	0.415	0.0113	-0.47	40.46	18.9
1,3-propanediol	1.060	76.1	241.5	0.943	0.0057	0.406	0.0113	-0.68	40.46	18.81
1,4-butanediol	1.017	90.1	297.5	0.983	0.0048	0.423	0.0095	-0.23	40.46	23.41
Diethanolamine	1.097	90.1	332.5	0.912	0.0048	0.392	0.0095	-1.17	52.49	27.24
Triethanolamine	1.124	149.2	446.5	0.890	0.0070	0.383	0.0201	-1.31	63.93	38.44
Trimethylolpropane	1.150	134.2	417.5	0.870	0.0070	0.374	0.0224	-0.22	60.69	33.95
2-propanol	0.785	60.1	216.5	1.274	0.0072	0.548	0.0072	0.38	20.23	17.53
Xylose	1.525	150.1	390.5	0.656	0.0070	0.282	0.0266	-2.71	97.99	31.75
Sorbitol	1.489	182.2	461.5	0.672	0.0024	0.289	0.0142	-2.94	121.38	38.44
Lactic acid	1.200	90.1	240.5	0.833	0.0048	0.358	0.0143	-0.51	57.53	18.65
Succinic acid	1.572	118.1	307.5	0.636	0.0036	0.274	0.0073	-0.64	74.6	21.93
Adipic acid	1.360	146.1	419.5	0.735	0.0029	0.316	0.0059	0.2	74.6	31.13
Octanoic acid	0.910	144.2	507.5	1.099	0.0030	0.473	0.0030	2.43	37.3	39.7
Gluconic acid lactone	1.610	178.1	411.5	0.621	0.0024	0.267	0.0121	-2.44	107.22	35.58
SAIB™ 90EA ³⁰	1.110	846.9		0.901	–	0.387	–	–	–	–

^aIf not stated otherwise, the density was obtained from PubChem and at 15–25°C. The value for 1,3-propanediol was obtained from *chemicalbook.com*.

^bCritical molar volume.

^cAmount of additive added in moles.

^dAmount (volume) of additive added based on the specific volume and molecular weight.

^eAmount of functional groups added based on the molecular weight and the number of functional groups per molecule.

^fLogarithm of the partition coefficient in n-octanol/water. The ratio of the solubility of the additive in n-octanol and water, the larger the more hydrophobic the additive is. Log P, tPSA and MR obtained from CS Chembiodraw Ultra.

^gTotal polar surface area.

^hMolar refractivity.

Table 3. Additive properties.

3.1. Additive/WG blends that were evaluated only qualitatively (visually and by hand) during and after mixing and compression molding, due to poor miscibility/mixing and/or brittleness

Xylose and *gluconic acid lactone*, with and without water, gave both an inhomogeneous WG dough with a clear phase separation. The resulting compression-molded films were very brittle

with properties similar to the molded pure wheat gluten powder. The use of SAIB™ 90EA [45], which is a low-viscous liquid with 90% sucrose acetate isobutyrate and 10% ethyl acetate that is used in, for example, coatings and in nail-polish lacquers, resulted in a homogeneous dough with potential for further development. However, the molded films were too brittle. Three grades of acetylated monoglyceride (AMG, Myvacet™ 5-07, 9-08, and 9-45 [46, 47]) were mixed with WG. The 5-07 grade (which is an AMG with 50% acetylation) has been used previously in WG formulations, although not with the primary purpose of plasticizing the film [48]. This grade gave an inhomogeneous dough, and the resulting compression-molded film was brittle. The mechanical flexibility was too poor to proceed with further film development at this stage. Myvacet™ 9-08 and Myvacet™ 9-45 (fully acetylated using, respectively, hydrogenated coconut oil and partially hydrogenated soybean oil as fat sources) did not dissolve in the WG. The resulting molded films fell apart due to extensive brittleness. *Lactic acid* made the dough highly viscous and sticky, which prevented longer mixing in the Brabender. The pressed films were too soft and sticky to be further tested.

The use of *succinic* and *adipic acid* resulted in doughs that were quite homogeneous and viscous. The molded films were at warm conditions (when they were released from the compression molder) flexible. However, they turned out to be inhomogeneous with a significant amount of trapped air bubbles and turned brittle when cooled to room temperature. The *2-propanol* did not yield a dough when mixed with WG. The blend could be described as a wet powder rather than a dough. The compression-molded films were very brittle and could not be tensile tested. The largest glycol tested here, *octaethylene glycol* (PEG 400), yielded an inhomogeneous dough and was only very poorly mixed with the WG powder. The film had an uneven surface but parts existed which were homogeneous and smooth. However, the overall impression was, however, that the films were like pressed powder. The compression-molded films had similar appearance to molded WG powder without plasticizer and were too brittle to be tensile tested.

3.2. Additive/WG blends that were evaluated with respect to rheological and tensile properties

Glycerol serves here as a reference plasticizer due to its well-known excellent plasticizer efficiency. Its torque and temperature evolution during the 2-min mixing in the Brabender are given in **Figure 1a**. The temperature was steadily increasing from 50°C and reached the maximum temperature after 2 min (76°C). The torque was also steadily increasing reaching a maximum torque of 18.4 Nm at the end of the experiment.

The use of *ethylene glycol* (PEG 60) and *diethylene glycol* (PEG 100) resulted in doughs that seemed appropriate for, for example, extrusion. The resulting maximum and final torque values were high (similar to glycerol, **Table 4**), and the PEG 60 mixed faster with the WG powder (a faster rise in torque) than PEG 100. The reason to that is most likely the lower melting temperature of PEG 60. The maximum temperature during the 2-min mixing occurred close to or at the end of the experiment and was, for both glycols, slightly lower than for glycerol. The resulting compression-molded films were homogeneous and mechanically flexible. *Triethylene glycol* (PEG 150) yielded a dough that was sticky and that had a low viscosity/torque throughout the mixing step (**Table 4**). The resulting temperature increase was also low. An

even constantly lower torque, with no temperature increase, was observed when mixing *tetraethylene glycol* (PEG 200) with WG. Still, a homogeneous dough and a flexible film were obtained.

The diols *1,2-propanediol*, *1,3-propanediol*, and *1,4-butanediol* all gave homogeneous doughs and initially flexible films. However, they became less flexible after 1 day (see the mechanical section below). There were no clear correlation between molecular size and rheological behavior in this group (**Table 4**). The largest torque values and temperature increase were observed for *1,3-propanediol*, whereas the lowest torque values and temperature increase were observed for *1,4-butanediol*.

Diethanolamine and *triethanolamine* gave homogeneous doughs and flexible films. The torque remained very low throughout the mixing step and the temperature remained low. A similar torque and temperature behavior were observed for *trimethylolpropane* (TMP) (**Figure 1b**), which also resulted in a homogeneous dough and flexible film. Based on the different rheological behaviors and the apparent plasticizer efficiencies of the analyzed additive/WG combinations, it is concluded that it is not possible to predict the plasticizer efficiency based on the torque/temperature behavior during mixing. This is most clearly illustrated in **Figure 1** where two of the most efficient plasticisers gave two very different torque/temperature-time curves.

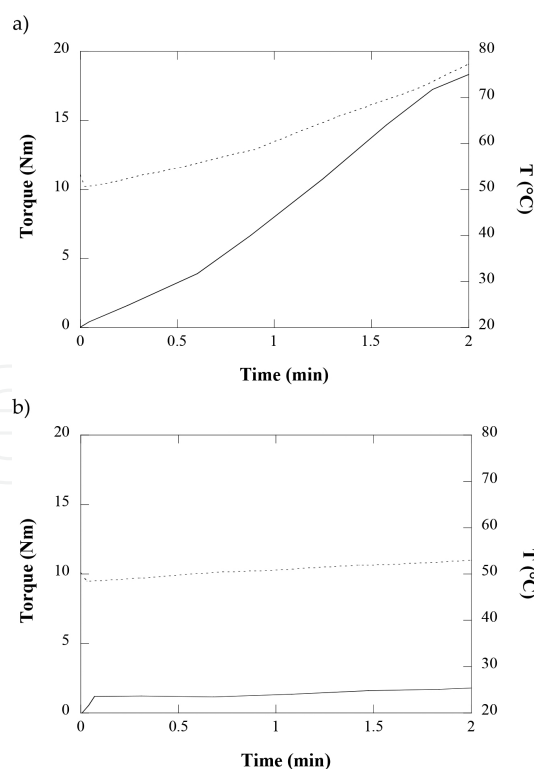


Figure 1. Torque (solid line) and temperature (broken line) as a function of mixing time in the Brabender. (a) Glycerol and (b) trimethylolpropane.

Additive	τ_{\max}^a	T at τ_{\max}^b	Time to τ_{\max}^c	τ_{Final}^d	T _{final} ^e
Glycerol	18.4	76	2.0	18.4	76
Ethylene glycol	17.2	71	1.8	15.2	71
Diethylene glycol	15.2	70	2.0	15.2	70
Triethylene glycol	8.4	59	2.0	8.4	59
Tetraethylene glycol	0.5	50	2.0	0.5	50
1,2-propanediol	3.4	52	2.0	3.4	52
1,3-propanediol	15.1	67	2.0	15.1	67
1,4-butanediol	0.5	45	0.2	0.5	49
Diethanolamine	0.7	49	1.2	0.7	49
Triethanolamine	0.8	50	0.7	0.7	51
Trimethylolpropane	1.8	53	2.0	1.8	53

^aMaximum torque (Nm).
^bTemperature at maximum torque (°C).
^cTime to maximum torque (min).
^dFinal torque (Nm).
^eFinal temperature (°C).

Table 4. The thermomixing properties of wheat gluten with plasticisers.

In **Figure 2**, the tensile curves of the compression-molded films with the most interesting additives are displayed, and in **Table 5**, their mechanical properties are given. The WG with glycerol showed the greatest fracture strain and the lowest modulus and maximum stress. The curve shape (**Figure 2a**) indicated a clear yielding (non-linearity in the curve) before fracture. The scatter in the tensile properties was also among the lowest, indicating good mixing/high miscibility (**Table 5**). TMP, not tested in wheat gluten before, showed a fracture strain above 100% and somewhat higher modulus and maximum stress as compared to glycerol. The scatter in these parameters was also higher than for glycerol. Triethanolamine and, in particular, diethanolamine were not as effective plasticisers as glycerol and TMP. However, the scatter in data (mixing efficiency) was similar to that of glycerol in the case of maximum stress and fracture strain (triethanolamine). It seemed as if the additives with three hydroxyl-terminated arms (glycerol, TMP, and triethanolamine) were better plasticizers than the linear diethanolamine.

The range in mechanical properties was large within the oligoethylene glycol family (**Figure 2b** and **Table 5**). The highest extensibility (fracture strain) was observed for triethylene glycol (**Figure 2b**), which value was close to that of TMP. In fact, its modulus was lower than that of TMP, but higher than that of glycerol. The smallest glycol (ethylene glycol) showed poor plasticizing properties with a high modulus and maximum stress and low fracture strain. The scatter in data within this family was lowest for the two most effective plasticisers (triethylene and diethylene glycols). Their scatter in modulus and maximum stress was on the same order as that of glycerol.

As for ethylene glycol, the propanediols and the 1,4-butanediol had high modulus, maximum stress, and low fracture strain (**Figure 2c** and **Table 5**). It is amazing how the plasticizing efficiency increases when a “flexible” ether linkage is inserted in the middle of the molecule (compare mechanical data of 1,4-butanediol and diethylene glycol, **Tables 2** and **4**). The effect is somewhat larger than putting an N–H group in the same place (compare 1,4-butanediol and diethylenamine). If a third hydroxyl group is placed on the central carbon, a sizeable improvement is observed (compare 1,3-propanediol and glycerol).

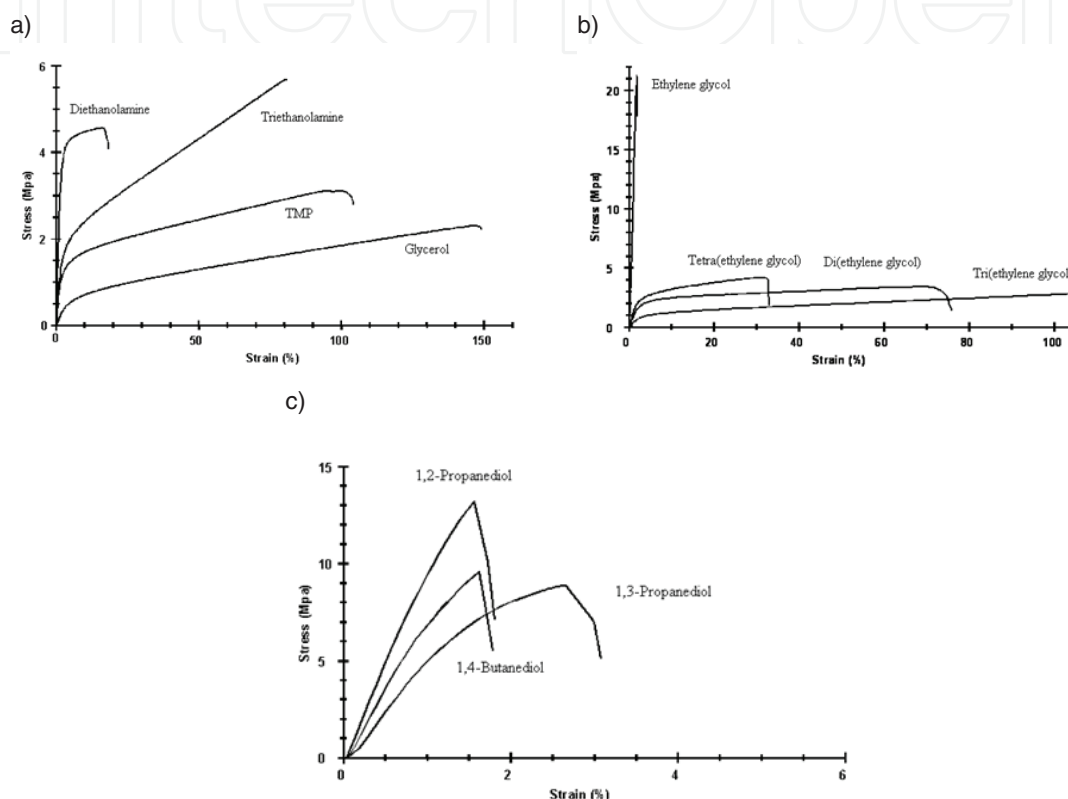


Figure 2. Tensile curves.

In general, the modulus and yield stress of tough polymers go hand in hand whereas the fracture strain is not a simple function of these [49]. Here, we show that the modulus and strength (maximum stress) are basically linearly related (**Figure 3a**). For those blends that show a clear yielding, it is also obvious that the stiffer materials also show larger yield stresses (**Figure 2**). There does, in general, not exist a clear correlation between stiffness/strength and fracture strain when tough and brittle materials of different types are investigated together. A material can be stiff and brittle or stiff and tough. Here, however, the fracture strain decreases in a nonlinear fashion with increasing stiffness (**Figure 3b**) or strength (not shown), where there is a lesser correlation at higher stiffness and strength. This shows that for the same polymer matrix (WG), the addition of additives that alter the mechanical properties, such as those with a higher or lower plasticizing ability, the four mechanical parameters (modulus, yield stress, maximum stress, and fracture strain) are clearly interrelated.

Additive	E ^a	R. E ^d	σ_{\max}^b	R. σ^e	ϵ^c	R. ϵ_b^f
Glycerol	27 ± 2	7	2.4 ± 0.2	8	152 ± 10	7
Ethylene glycol	1532 ± 218	14	21.5 ± 4.2	20	2 ± 0.5	25
Diethylene glycol	133 ± 10	8	3.4 ± 0.2	6	66 ± 9	14
Triethylene glycol	77 ± 9	12	2.8 ± 0.2	7	99 ± 12	12
Tetraethylene glycol	206 ± 68	33	4.4 ± 0.9	20	34 ± 20	59
1,2-propanediol	1068 ± 103	10	13.2 ± 0.9	7	2 ± 0.2	10
1,3-propanediol	647 ± 63	10	9.0 ± 1	11	3 ± 0.9	30
1,4-butanediol	875 ± 55	6	9.9 ± 0.9	9	2 ± 0.3	15
Diethanolamine	280 ± 39	14	4.5 ± 0.3	7	16 ± 4	25
Triethanolamine	151 ± 24	16	5.7 ± 0.4	7	78 ± 6	8
Trimethylolpropane	108 ± 21	19	2.9 ± 0.6	21	104 ± 23	22

^aYoung's modulus (MPa).
^bMaximum stress (MPa).
^cElongation at break (%).
^dRelative standard deviation of modulus data.
^eRelative standard deviation of stress data.
^fRelative standard deviation of strain at break data.

Table 5. Mechanical properties of wheat gluten materials.

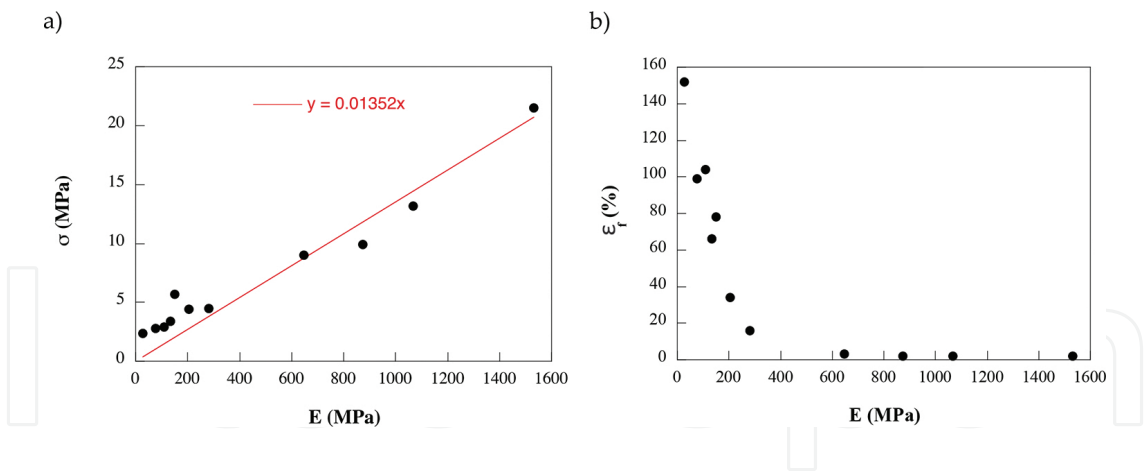


Figure 3. (a) Maximum stress versus modulus and (b) fracture strain versus modulus for the additive/WG materials in Table 5.

It was important to see whether it was possible to predict the plasticizer efficiency, or its trends, from any easily obtained parameter characterizing the additive. The mechanical parameters (Table 5) were correlated with all the physical parameters in Table 3. No specific correlation was observed between the mechanical properties and the density, specific volume, amount/volume of additive added (mol/g WG or cm³/g WG), functional groups added, and log P. In fact, none of the physical parameters in Table 3 could be used to predict the trends in the

observed fracture strains. On the other hand, when plotting the size and the modulus against the critical molar volume, a trend was observed (**Figure 4a** and **b**). The stiffness decreased in a nonlinear way with increasing size of the additive, with a vanishing correlation at larger additive sizes. The modulus was correlated with the additive polarity, in terms of the tPSA (total polar surface area) (**Figure 4c**). The correlation was less than with the molecular size; however, two regions were clearly separated, a low polarity region (low tPSA) with high modulus and a high polarity region with low modulus. Finally, in **Figure 4d**, the modulus was plotted against the molar refractivity (MR), which is also a measure of the polarity (and the size) of the additive. Here, the correlation was similar as for molecular size (**Figure 4a** and **b**), with a nonlinear decrease in stiffness with increasing modulus. When plotting the same type of data for maximum stress rather than modulus, the same relationships were observed, which was not a surprise since stiffness and strength were linearly dependent (**Figure 5**). To conclude, of all the parameters listed in **Table 2**, only the molecular size and/or the polarity was affecting the mechanical properties (only stiffness and strength) in a systematic way, although the correlation was relatively poor.

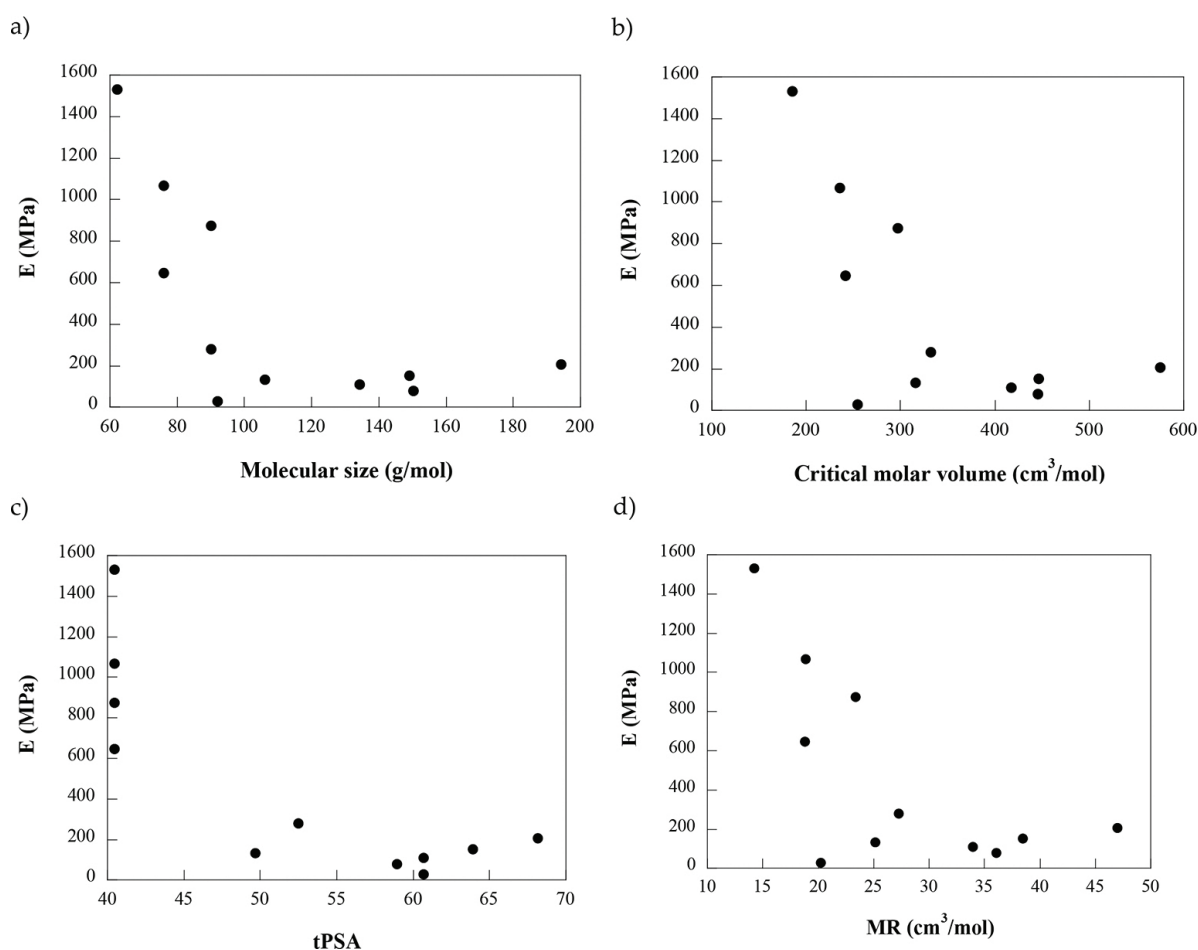


Figure 4. Modulus versus additive (a) molecular weight, (b) critical molar volume, (c) total polar surface area, and (d) molar refractivity.

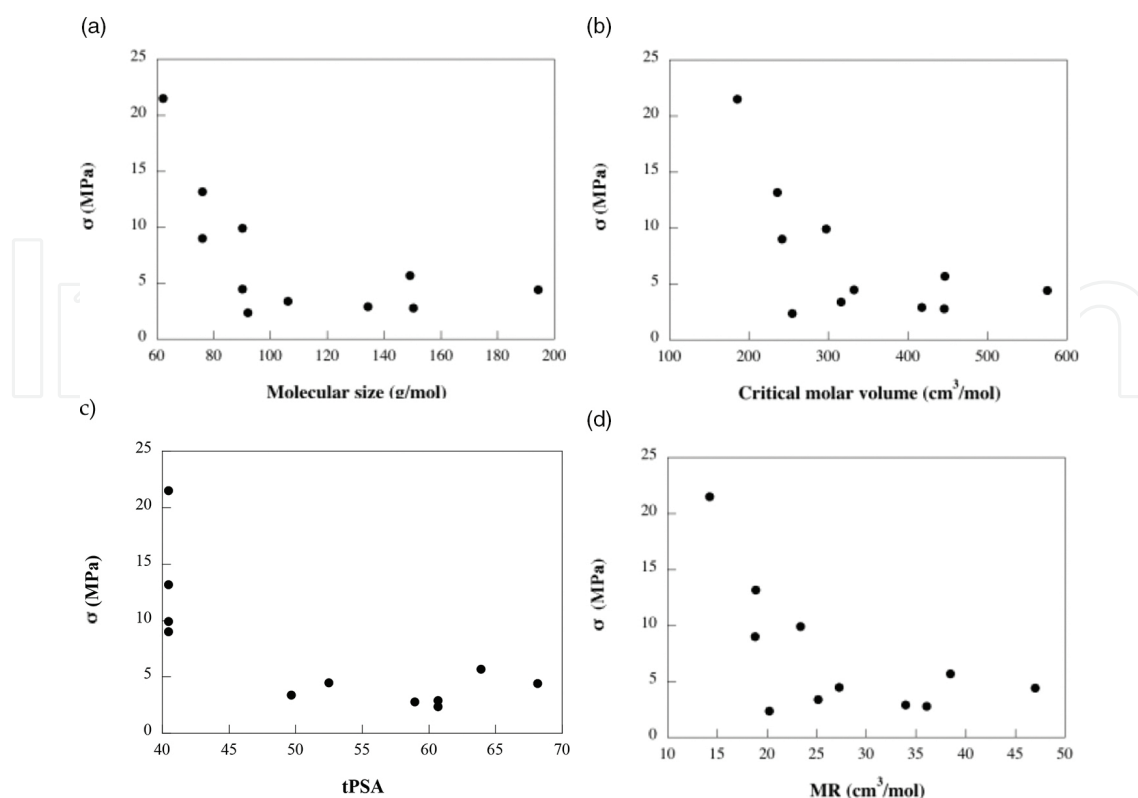


Figure 5. Maximum stress versus additive (a) molecular weight, (b) critical molar volume, (c) total polar surface area, and (d) molar refractivity.

4. Conclusions

Of the extensive number of additives/plasticizers that were tested, having different molecular weights, polarity, melting and boiling temperatures, glycerol was shown to be the most efficient plasticizer for thermoformed gluten films. The most efficient plasticisers, considering stiffness and extensibility, were those that contained three hydroxyl groups and the linear glycols of intermediate size. It should be stated, though, that only the short-term mechanical data were analyzed, and no aging and relative humidity effects were explored. All thermoformed plasticizer/gluten mixtures were studied at equal mass concentration of plasticizer, an issue that can be further elaborated; different plasticizers have different efficiency and should thus also be further studied as a function of plasticizer concentration. Still, several plasticizers in this study seemed to be fully blended with gluten after <2 min of thermomixing. Regrettably, there did not seem to be a unique relationship between the torque behavior and the final mechanical properties of the films. However, there was a weak nonlinear relationship between the stiffness/strength and the size (molecular weight, molar volume) and the polarity/polarizability (tPSA and MR) of the compound. The mixing conditions (i.e. shear forces, time, and temperature) may differ from extrusion; hence, this study should thus be considered as a first attempt to determine appropriate plasticizers for thermoformed gluten films.

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