

Effect of Amylose/Amylopectin ratio on physico-mechanical properties of rubber compounds filled by starch

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Abstract: Much research is currently focused on the use of starch as an industrial raw material, which can reduce dependence on non-renewable resources. Pure starches of plants includes 20 -30% of amylose, this value might become to 80% in some starches scarcely, 70-90% amylopectin, approximately 1% fat, protein and minerals. Starches from various sources contain different amounts of amylose and amylopectin, which influence physicochemical properties such as gelatinization, water absorption and paste viscosity. Therefore, amylose/amylopectin (Am/Ap) ratio in starch would effect on physico-mechanical properties of the material which produced from it. The determination of Am/Ap ratio in several samples of starch by a simple modified method was described in this paper and the samples with different Am/Ap ratio were applied as filler in rubber compounds. The physico-mechanical properties of obtained cure rubbers were investigated. The results showed that the physico-mechanical properties of Natural rubber (NR) compounds filled by various starches are mainly correlated with Am/Ap ratio in the starch samples.

Keyword: *Amylose, Amylopectin, Starch, NR, Filler, properties.*

Introduction

Starch is a large and one of the major polysaccharides used by plants for energy storage. It is widespread in seeds, roots and tubers as well as in stems, leaves, fruits and pollen [1]. Plant starches and other polysaccharides comprise the most abundant source of renewable natural products on the planet [2]. Starches and their derivatives are considerable in industrial importance particularly to the food, pharmaceutical, health care, paper, adhesive, cosmet-

ic and paint industries [3-4]. Starch can be used as biodegradable filler in rubber industries. Biodegradable filler have been a subject of interest for recent years because of their potential to protect the environment by reducing non-biodegradable filler. Several publications have reported advances in the production of starch-based biodegradable material [5-6]. The idea of using starch inside synthetic polymer emerged in the 1970s [7]. The first studies were based on introducing starch into the

synthetic matrix at amounts lower than 10% while keeping the granular structure intact. In this case starch is only filler susceptible to enzymatic degradation but unable to affect the mechanical properties of the final material (20-30 Mpa tensile strength and 700-900% elongation at break point for a 90:10 polyethylene: starch blends). A second approach was to use polymer blends. To obtain this morphology, the granular structure of the starch had to be modified (generally by extrusion) to allow thorough mixing of α -glucan and synthetic polymer. The notion of 'starch destructuration' attributable to Tomka [8], refers to the loss of native granular structure and is achieved by melting under shearing and low hydration. These forms of processing, which differ completely from classical pasting obtained in high moisture conditions [9], had already been described in reviews concerning extrusion [10]. Starch destructuration is rather well understood and controlled at the present time. However, the main difficulties encountered in the addition of starch to synthetic polymer are due to the chemical incompatibility of these two types of polymers. Two studies [11] have shown that hydrophilic synthetic polymers such as poly ethylene-co-acryl (acid) or poly (vinyl alcohol) give final blends with acceptable compatibility. Previously several patents have been issued for materials produced by blending starch with one or several synthetic polymers [12-14, 8]. More sophisticated solutions based on the grafting of synthetic fragment have also been reported [15]. The mechanical properties of these materials, which are dependent on the quantity of starch, diminish rapidly when starch level increases (tensile strength ranges from 22 to 28 Mpa and maximum elongation from 260 to 60% when starch level increases from 10 to 60% in a starch-poly(ethylene-co-acrylic acid) blend) [16]. Despite their poor mechanical properties, these materials have been recommended because of their biodegradability, and several commercial

applications have been proposed (e.g. pharmaceutical bottles, container closures, cutlery and cotton swabs). Several studies concerning the mechanical properties of starch of defined botanical origin have shown that the choice of raw material is critical [17-18]. Starch consists primarily of two components, amylose and amylopectin. Amylose is a linear or very lightly branched polymer consisting of several thousand (1-4)- α -D-linked D-glucose units with molecular masses ranging from 2×10^5 to 2×10^6 [5]. Amylopectin is a much larger, highly branched polymer consisting of relatively short segment of (1-4)- α D-linked-glucan units connected by (1-6)- α -D glucosidic link-ages with molecular masses ranging from 107 to 5×10^8 [19-20]. The amylose content in waxy maize can vary from nearly zero to over 50% in some pea and maize varieties. Many of the physicochemical properties of starches that determine their suitability for particular end-uses are dependent on the ratio of amylose and amylopectin and on their molecular weight distributions [21-25] in particular, the ratio of the two types of polysaccharides influences properties such as solubility, viscosity, gel formation and solubilization temperature [22-25]. Therefore the wide variability in the amylose content makes it imperative to have accurate methods for its determination.

Different methods are described in the literature for the determination of the relative amounts of amylose and amylopectin in starch. The estimation of the amylose and amylopectin fraction is possible by means of amperometric or potentiometric titration with iodine [26] or by a colorimetric procedure and, another method which has been used extensively, is near infrared reflectance (NIR) spectroscopy [27], gel permeation chromatography (GPC) and high performance size exclusion chromatography (HPSEC) [28-29]. However; all these methods suffer from some drawbacks. Where as the iodometry method is simple, it suffers from the difficulty in

solubilising the starch completely, which can lead to erroneous results. Uses of various solvents and treatments have been suggested to overcome this problem [30-33]. In this paper particular attention was given to the biodegradation of the starch component as a function of the amylos/amylopectin ratio (Am/AP). A modified and simple method has been used [34-35]. The rubber compounds filled by various sources of starches were prepared for studying of their processability and mechanical properties especially. The research has focused on the study of preparation, structure and properties of NR filled by starch material in rubber compounds, a strategy to prepare high performance starch/rubber compounds and thermoplastic starch/Natural Rubber blends [36-40]. Particular attention in this research gives to the application of the starch component as a function of the amylose/amylopectin ratio and determining of the specific influence of amylopectin content on the physical-mechanical properties in starch/NR compounds.

Experimental

Instrumentation

The starch samples were prepared by soxhlet apparatus, IR analysis were carried out on KBr pellets of sample and the spectra were taken on a FT-IR Spectrum GX. UV Spectroscopy quartz cell (1-cm path-length). The cure characteristics of different compounds were measured at 160°C with MDR 900, HIWA Company, Iran. The compounds were cured in a laboratory press PTP 600, PGH Company at 160°C and 220 KN. Hardness of the samples were measured by a bareiss 49038 Hardness-meter Shore A Type, according to ASTM D2240. Tensile tests were carried out on dumb-bell shaped specimens by M-350-5019. Testometric M350-5KN, Testometric Company, according to ASTM D412.

Materials

Starch samples involves potato, maize, wheat, corn and rice were provided by Mahdaneh, Golokozan, Sadaf, Golmehr, Golha Companies of Iran, and two types of starches as a case study was supplied Sigma-Aldrich Company. Solvents involve 75% (V/V) n-propanol in water, 90% (V/V) dimethylsulfoxide (DMSO) in water provided by Merck Company. KI and I₂ provided by Merck Company. The formulation of rubber compounds filled by various types of starches is showing in Table 1.

Defatted starch samples

Therefore this step is necessary prior to determination of total amylose content, because lipid-iodine complexed interfere with amylose-iodine complex in determination total amylose content, so the amount of amylose content shouldn't be correct. About 5.0 g of starch sample was placed into a filter paper which has been used as an extraction thimble. The lipid was extracted with 150 ml of 75% n-propanol at 85°C for 7 h in a soxhlet extractor. Lipid-free starches were dried at room temperature for 14 h and removed from the thimble. Then oven dried for 24 h at 30 °C.

Dispersion of lipid-free starch

In a flask, 32 mg (± 0.1) of lipid-free starch samples (Table 1) was dissolved in 8ml of DMSO (90%). The solution was stirred at 80°C in a water bath for 10 min until it became transparent and then the samples cooled to room temperature and left for 40 min. When the starch was dissolved completely, an aliquot of 1.0 ml of this solution was mixed with 5.0 ml of freshly prepared iodine reagent and 44.0 ml of distilled water in a 50 ml volumetric flask. The color of all samples was developing after 10 min. The iodine reagent was prepared by dissolving 0.08 g of iodine and 0.27 g of potassium iodide with distilled water in a 250 ml volumetric flask.

Preparation of standard curves

A series of mixtures of pure potato amylose and pure maize amylopectin were prepared in various proportions in order to obtain samples with different percentages of amylose (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 percent amylose). 32 mg of each sample was acted per overhead method as a standard solution. Absorbance spectra at 600 nm were recorded for all samples with GX. UV spectrophotometer. A calibration curve (Figure 1) was plotted for various Am/AP ratio of standard samples. Spectra for blanks of the amylose solutions and the iodine reagent were also recorded. The regression equation 1 for the standard curve was determined to calculate the amylose content of different starch specimens with unknown Am/AP ratio (Table 2)

$$Y = 0.0168X + 0.2138 \quad (\text{equation 1})$$

Where Y = absorbance at 600 and X = %amylose

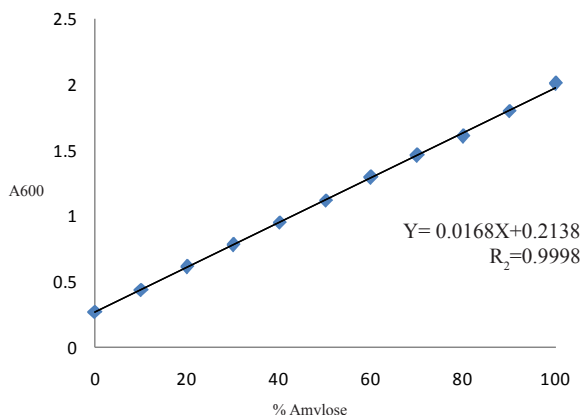


Figure 1 Calibration curve for various amylose ratios of standard samples

Preparation of NR Compounds filled by starch

The starch/ natural rubber compounds were prepared by directly blending unmodified starch powder with natural rubber latex, on a two-roll mill at 75-85 °C. The vulcanizing ingredients and other additive were mixed into the starch/rubber blends (for 15 min). The compositions are shown in Table 2.

Table 1 Formulation of starch/ NR composite

Components	Phr	Company
NR	100	Thaihua, Thailand
Carbon black	10	Pars Tire, Iran
Starch S ₁ =20%, S ₂ =25%, S ₃ =30%, and S ₄ =36% amylose content	50	Mahdaneh-Golokozaan, Golshahr, Iran
Stearic acid	1.5	Acid Chem, Malaysia
ZnO	4	Shekohieh, Iran
TMQ	1	Nanjing, China
S	2.5	Tesduck, Iran
MBTS	0.1	Slexsys, Belgium
TMTD	0.35	Laness, Belgium

Table 2 Determination of amylose content of different starch samples using equation (1)

Number	Starch type	Absorbance at 600 nm	Calculated Amylose content (%)
1	potato	0.7976	30.92±0.04
2	Maize(Golokoza)	0.8867	36.13±0.04
3	Wheat(Sadaf)	0.8785	35.65±0.04
4	Wheat(Golha)	0.7413	27.63±0.04
5	Maize(Mahdaneh)	0.6519	22.40±0.04
6	Rice	0.7613	28.80±0.04
7	Wheat(Golmehr)	0.6957	24.96±0.04
8	Case study(sigma-Aldrich)	0.7299	26.96±0.04
9	Case study(sigma-Aldrich)	1.2940	59.95±0.05

Rheological Measurement

The measurement of the degree of Vulcanization is made directly by determining the torque at 160 °C by MDR rheometer. The start of vulcanization scorch time (TS₂), optimum curing time (TC₉₀), and cure rate index (CRI), minimum torque (ML), and

maximum torque (MH) are shown in Table 3. The higher the torque obtained, the higher the number of cross links created. The maximum torque in table 3 presents the degree of vulcanization or cross link density. The effects of different types of starch on the rheological properties of sample are presented in this table.

Table 3 The rheological properties of unmodified starch/NR

Samples	TS ₂ , Sec	TC 90, Sec	MH, DN.m	ML, DN.m	CRI, sec
S ₁	117	209	9.656	0.552	60.308
S ₂	131	255	9.380	1.242	47.878
S ₃	117	231	11.174	0.690	46.955
S ₄	126	222	10.208	0.966	54.610

Mechanical Properties

To study the stress-strain behavior of rubber compounds (Testometric-M350-5KN, ASTM D412-98 a. Die C) tensile tester was used. The samples were cut from molded sheets in the dumbbell shape, placed in the sample holder and its length, width and thickness were measured. The gage length between the jaws at the start of each test was adjusted to

25 mm and the measurements were carried out at a cross head speed of 500 mm/min. For every value of change in load, displacement was recorded by the computer. In tensile testing machine, the stress is increased slowly and then the elongation of the sample undergoes at each stress level is measured. The process keeps doing this until the sample breaks down. The mechanical properties of Starch/NR blends vulcanized by sulfur are presented in Table 4.

Table 4 Mechanical Properties of the samples

Sample	Tensile (MPa)	Elongation@break (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Hardness (Shore A)	Resilience (%)
S ₁	9.78	620.370	1.69	3.71	52	59
S ₂	9.70	515.240	2.04	4.75	53	60
S ₃	9.82	508.790	2.14	4.91	56	61
S ₄	8.36	505.240	1.93	4.34	56	61

Results and discussion

The various properties of rubber compounds filled by starch depend on Amylose /Amylopectine ratio. In order to find out the exact quantitative relationship between properties and amylopectine content, they were plotted vs. Am/AP ratio (Figures 1-4). For example, the variation in elongation and tensile strength with Am/AP in the compound is shown in Figs 1 and 2 respectively. Tensile strength and elongation at break are ultimate properties of a rubber compound and these are manifestation of a compound's cross-link density and rubberized nature of filler. It is generally observed that samples having optimum cross-link density show higher tensile strength and lower elongation at break. From plot of elongation shown in Fig.1, it is observed that it decreases with decrease in amylopectine content. On the other hand higher concentration of amylopectine in starch causes increase in elongation at break. This type of changing pattern is governed by the increase in flexibility of polymer network caused by the highly branched structure of amylopectine and the more rubberization of starch as filler. As Figure 2 shows it is observed that tensile strength was not significantly changed up to a certain amounts (64%) of amylopectine. Beyond this content the tensile strength decreased as the amylopectine percentage were decreased. It can be concluded that the elastic behavior improved somewhat with decreasing rubberized filler. Therefore, the content of amylopectine influences the property of vulcanizate. The more the percentages of amylopectine, the larger the

possible rubberization of filler (because of highly branched and networking of amylopectine structure).Thehardnessandresilienceofthesamplewith different content of amylopectine are also included. From Fig 3-4, it can be seen that generally the mechanical properties of NR compounds filled by strach did not change appreciably when the content of amylopectine changed.

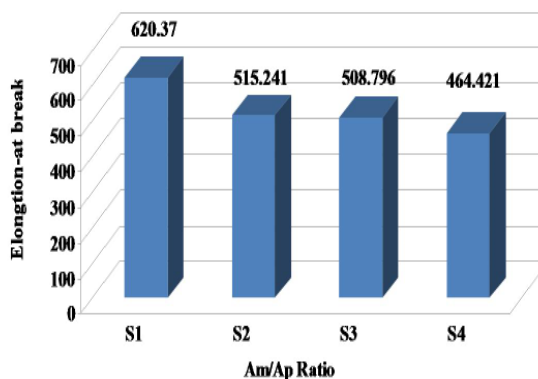


Figure 1 Relation between elongation at break and Am/AP ratio

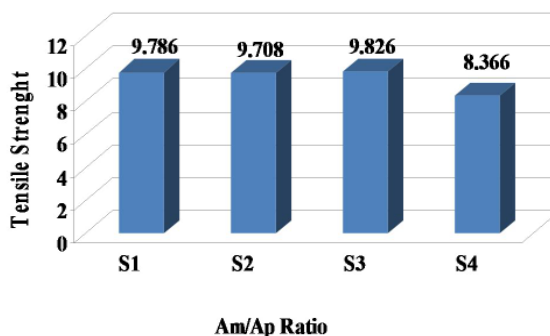


Figure 2 Relation between tensile strength and Am/AP ratio

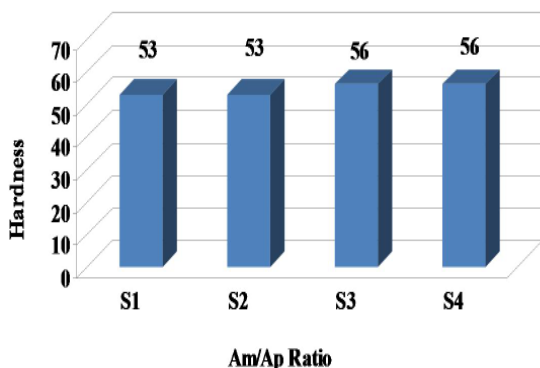


Figure 3 Relation between hardness and Am/Ap ratio

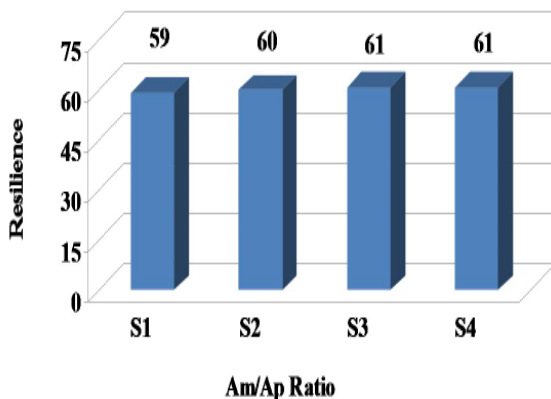


Figure 4 Relation between resilience and Am/Ap ratio

Conclusion

The present results indicate that the content of amylopectine in starch influences the property of rubber samples filled by starch as filler. The larger the contents of amylopectine, the larger the possible rubberization of filler is (because of highly branched and networking structure of amylopectine).

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References

- [1] S. Perez, A. Imberty, *Carbohydr Eur.* 15 (1996) 17.
- [2] W.M. Doane, in *New Crops, New Uses, New Markets*, 1992 Yearbook of Agriculture, office publishing and Visual Communication, US Department of Agriculture, 1992, Ch. 22, pp. 149-153.
- [3] A. Guilbot, C. Mercier, in: G.O. Aspinall (Ed.), *the Polysaccharides*, Vol. 3, Academic Press, Orlando, San Diego, 1985 (pp. 210-273).
- [4] R.P. Ellis, M.P. Cochrane, M.F.B. Dale, C.M. Duffus, A. Lynn, I.M. Morrison, R.D. M Prentice, J.S. Swanston, S.A. Tiller, *J. Sci. Food Agric.* 77 (1998) 298.
- [5] Savary, C., Colonna, P. & Della Valle, G. (1993). *Industrie des Céréales*, 10, 17-29.
- [6] Shogren, R.L., Fanta, G.F. & Doane, W.M. (1993). *Starch*, 8, 276-280.
- [7] Griffin, G.J.L. (1977). U.S. Patent No. 4.021.388.
- [8] Tomka, I. (1988). Warner-Lambert Company, Patent No. 0.282.451.
- [9] Zobel, H.F. (1984). *Starch Chemistry and Technology*, 2nd ed. Academic press, New York, USA, pp.285-309.
- [10] Colonna, P., Tayeb, J. & Mercier, C. (1989). In *Extrusion Cooking*, eds C. Mercier, P. Linko & J. M. Harper ACCC. St. Paul, Minnesota, USA, pp. 247-320.
- [11] Otey, F.H., Mark, A.M. , Mehlretter, C.L. & Russell, C.R. (1974). *Ind. Eng. Chem. Prod. Res. Dev.*, 13, 3453-3455.
- [12] Bastioli, C. (1991). Butterfly s.r.l., Patent No. 91/02024.
- [13] Sachetto, J.P. (1989). Warner-Lambert Company, Patent No. 0.404.723.
- [14] Wittwer, F. & Tomka, I. (1987). Warner Lambert, Patent No. 4.673.438.
- [15] Narayan, R., Lu, Z.J., Chen, Z.X. & Stacy, N. (1988). *J. Polym. Prep.*, 29, 106-107.
- [16] Otey, F.H., Westhoff, R.P. & Doane, W.M. (1980). *Ind. Eng. Chem., Prod. Res. Dev.*, 19, 592-595.
- [17] Arvanitoyannis, I., Kalichevsky, M. & Blanshard, J.M.V. (1994). *Carbohydr. Polym.*, 24, 1-15.
- [18] Bader, H.G. & Göritz, D. (1994). *Starch*, 46, 229-232.
- [19] D. French, in R.L. Whistler, J.N. Bemiller and E.G.

- Paschall (Editors), Starch: Chemistry and Technology, Academic press, Orlando, FL, 1984, p. 184.
- [20] D.J. Manners, Carbohydr. Polym, 11 (1989) 87-112.
- [21] R.F. Tester, W.R. Morrison, Cereal Chem; 67 (1990) 551.
- [22] V.M. Leloup, P. Colonna, A. Buleon, J. Cereal Sci. 13 (1991) 1.
- [23] J. Jana, Pure Appl. Chem. A32 (1995) 751.
- [24] J.P. Greet, Carbohydr. Eur; 15 (1996) 5.
- [25] J.D. Klucinec, D.B. Thompson; Cereal Chem. 79 (2002) 24.
- [26] F.L. Bates, D. French, R.E. Rundle: Amylose and amylopectin content of Starch determined by their iodine starch complexation. J. Amer. Chem. Soc. 1943, 65, 142-148.
- [27] R.D. Delwiche, M.M. Bean, R.E. Miller, B.D. Webb, P.C. Williams: Apparent amylose tance
- [28] S. Kobayashi, S.J. Schwartz, D.R. Lineback: Rapid analysis of starch, amylose and amylopectin by high-performance size-exclusion chromatography. J. Chromatogr. 1985,319, 205-214.
- [29] L.A. Grant, A.M. Dstenson, P. Rayes_Duarte, Determination of amylose and amylopectin of Wheat Starch using high performance size exclusion chromatography. Ceral Chem. 2002,79, 771-773.
- [30] W.R. Morrison, B. Laignelet: An improved colourimetric procedure for determining apparent and total amylose in Cereal and other starches. J. Cereal Sci. 1983, 1, 9-20.
- [31] C.M. Sowbhagya, K.R. Bhattacharya: Simplified Colourimetric method for determination of amylose content in rice. Stärke 1971, 23, 53-56.
- [32] C.A. Knutson, M.J. Grove: Rapid method for estimation of amylose in maize Starches. Cereal Chem. 1994, 71, 469-471.
- [33] S.J. McGrane, H.J. Cornell, C.J. Rix: A simple and rapide colourimetric method for determination of amylose in starch products Starch/Stärke 1998, 50, 158-163.
- [34] McGrance, S.J. Cornell, H.J., and Rix, C.J. 1998. A Simple and rapid colorimetric method for the determination of amylose in starch products. Starch 50: 158-163.
- [35] R. Hoover and W.S. Ratnayake, Memorial University of New foundland St. John's, Canada: Determination of Total Amylose content of starch. Current Protocols in food Analytical Chemistry (2001) E2.3.1- E2.3.5.
- [36] Shogren, R.L. (1992). Carbohydr. Polym., 19, 83-90.
- [37] Jane, J.-L., Lim, S.-T. & Paetau, I. (1993). In Biodegradable polymers and Packaging. Technomic Publishing, pp. 63-73.
- [38] You-ping Wu, Mei-Qin Ji, Qing Qi, Yi-Qing Wang, Li-Qun Zhang, Macromole. Rapid Commun, 2004, 25, 565-570.
- [39] You-ping Wu, Qing Qi, Gui-Hau liang, Li-Qun Zhang, Carbohydrate Polymers, 2006, 65, 109-113.
- [40] a.J.F. Carvalho, A.E. Job, N. Alves, A.A.S. Curvelo, A. Gandini, Carbohydrate Polymers 2003, 53, 95-99.

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