Research Article

XRD Investigation of Some Thermal Degraded Starch Based Materials

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The thermal degradation of some starch based materials was investigated using XRD method. The samples were obtained by thermal extrusion of mixtures of different proportions of starch, glycerol, and water. Such materials are suitable for the manufacturing of low pollutant packaging. Thermal degradation is one of the simplest ways to destroy such materials and this process is followed by structural modification of the local ordering of samples, water evaporation, crystallization, oxidation, or destruction of the chemical bonds. These modifications need to be studied in order to reduce to the minimum production of pollutant residues by burning process. XRD measurements show modification of the local ordering of the starch molecules depending on the temperature and initial composition of the samples. The molecular ordering perturbation is more pronounced in samples with low content of starch.

1. Introduction

The recycling or disposal without pollutant effects of the enormous quantity of residual waste produced daily by the humanity is one of the major challenges of today. One of the solutions is to use biodegradable materials in manufacturing these products [1, 2]. Wood or cellulose could be suitable materials for this purpose, but their use on an industrial scale leads to excessive exploitation of the forests, with negative effects on climate and environment. On the other hand, the destruction of these materials by burning or putrefaction is pollutant. A viable alternative is the use of regenerative materials obtained from crops or other plants with low pollution potential. Starch is one of the most promising materials for this purpose, because it can be easily obtained at low cost from corn, potatoes, or other vegetables and can be fully recycled without any toxic residues [3–5]. However, starch in its natural state has low mechanical properties and low resistance to water and cannot be used for packaging. Improvement of its qualities can be achieved by combination with glycerol, which acts as a plasticizer. Previously, we obtained new materials by thermal extrusion of different

proportions of water, starch, and glycerol [6, 7]. The samples obtained this way are less soluble in water and have enhanced mechanical properties compared with the initial component. Rheological investigation of these samples show specific flow behavior depending on shear stress and temperature [8]. On a microscopic scale, the NMR investigations indicate different mechanisms of relaxation of the transversal magnetization of the protons depending on temperature and sample composition. These findings were correlated with the new physical structures and local molecular organization induced by the synthesis process [9].

The starch and the pure glycerol, in their initial state, can be easily recycled without pollutant effects by hydration or moderate heating, but the product obtained through the plasticizing process has different physical properties compared with the initial components and exhibits different behavior in the presence of water or when submitted to thermal degradation. Heating is one of the easier ways to destroy the used packaging, but this oxidative process leads to important modification of the physical and chemical properties of the materials. Depending on the temperature and duration of the heating we can assist to modification of the organization of

TABLE 1: The composition of samples.

Sample	Starch [%]	Glycerol [%]	Water [%]	Starch/Glycerol ratio	Starch/water ratio
P1	78	19.5	2.5	4	31.2
P2	72	18	10	4	7.2
P3	68	17	15	4	4.5

the matter (crystallization or molecular rearrangement), or modifications on molecular level (oxidation, chemical bond destruction, and decomposition). Awareness and knowledge of these modifications are crucial for the recycling process and demand investigation employing adequate methods. XRD is an appropriate technique to investigate the local organization of such materials. In this work, we performed structural investigation of the components in their pure state and of the samples with different initial composition, all submitted to different heating processes. The experimental data were correlated with the modifications of local order induced by the heating.

2. Materials and Methods

We prepared samples with different content of starch, glycerol, and water, labeled P1–P3. The initial components were corn starch with 21% amylose, 10.76% water content, particle sizes between 2.3 and 37.3 μm and density 0.561 g/cm^3 ; glycerol with 99.5% purity and density of 1.262 g/cm^3 ; and distilled water. The composition of samples is shown in Table 1. Previous publications have shown that concentrations of starch higher than 68% produce sample composition with better results in mechanical properties [10]. These samples were previously investigated by NMR and IR methods [7]. The components were mixed for 30 minutes at room temperature until complete homogenization.

For the samples preparation, we used a corotating twin-screw extruder Collin ZK 25 with controlled gradient temperatures.

The temperatures along the extruder, from the feed zone to the die, are: 30, 50, 100, 130, 140°C and the rotation speed was 220 rot/min. Following preparation, the samples were kept for 24 hours at room temperature, after which a series of samples were heated for 2 hours at 80°C and another series for 2 hours at 140°C. We selected the first temperature, 80°C, below the maximum temperature of processing, and another one at the maximum temperature of processing, 140°C. Visual observation of samples heated at 80°C indicates no apparent changes of color and no degradation by burning. We chose this temperature because DSC investigations, reported in literature, performed on similar starch-water gels, indicate thermal transitions around 70–80°C [11]. Around 140°C, the samples change color and become highly degraded. Other works have reported that the above 170°C amylose structure transformation can be observed [12]. This was a reason to choose a temperature value below the temperature of total degradation. The XRD measurements were performed with Brucker X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.154 \text{ nm}$) at 45 KV and 40 mA. The 2θ range of 10°–90° was recorded with 0.1° resolution.

FIGURE 1: The diffractogram of pure starch before heating (a), and the simulation of the main peaks (b). The graphs were separated on the vertical axis by 50 arb unit for better visualization.

3. Results and Discussion

Starch is a semicrystalline material which contains both the crystalline and amorphous phases, determined by its principal components, the amylose and the amylopectin. The amylose has a linear structure, which produces the crystalline region of the starch, whereas the amylopectin has a branched structure which is responsible for the amorphous phase of the starch [13–15]. The existence of two phases is confirmed by the aspect of the XRD spectrum before the heating. This spectrum is characterized by a broad region between 10° and 27° with some distinctive peaks (Figure 1).

The main peaks are observed at $2\theta = 11.4^\circ, 15.3^\circ, 17.4^\circ, 18.3^\circ$, and 23.1° . A broad peak with low intensity is observed between 19.7° and 20.7° . Similar results were reported by Holder for pure corn starch and waxy corn starch gels [16]. They have found a broad XRD signal between 10 and 30 degrees with peaks at 17 and 19.5 degrees. Other XRD investigations with similar results were reported by Kim et al. for rice starch and rice starch gels [17]. The slight difference between our data and the articles cited above is due to the ratio amylose/amylopectin, determined by different starch provenience: corn in our case, corn and rice in the above references. Quantitative analysis of the ordered structure can be done after simulation of each peak of the spectrum. The main peaks were simulated with Gaussian function $f(\Theta)$ centered on the diffraction angle 2θ , using Kaleidagraph software:

$$f(\Theta) = A \cdot \exp\left(-(\beta \cdot (\Theta - 2\theta))^2\right). \quad (1)$$

TABLE 2: Parameters of the XRD spectrum of the starch in initial state.

2θ [deg]	A [a.u]	β [deg]	d [Å]	$S_{2\theta}$ [a.u]	$S_{2\theta}/S_{\text{tot}}$ [%]
11.4	90	1.3	6.9	125	2.8
15.3	100	1.3	5.2	141	3.1
17 large	145	9.8	4.7	1479	33.5
17.4	105	0.8	4.6	93	2.1
18.3	85	0.9	4.3	55	1.2
19.7–20.7	25	1.3	4.0	35	0.8
23.1	100	1.7	3.4	176	3.9
32 large	80	20.6	2.5	1664	37.7

Θ is the independent variable of the fit. The parameters amplitude A and the half line width β of the function were adjusted until a better fit of the experimental data was obtained. These parameters are presented in Table 2 and the simulated spectrum in Figure 1. The narrow peaks are determined by the ordered alignment of the linear parts of the amylose. These structures behave like the crystalline planes of solid crystal (when they are investigated by X-rays). The characteristic interplanar distance d is given by the Bragg equation:

$$d = \frac{k \cdot \lambda}{2 \sin \theta}, \quad (2)$$

where k is the diffraction order and 2θ is the diffraction angle [18]. The area S under the diffraction peak is proportional with the concentration of the ordered domains in the sample and the width of the signal is correlated with the size of the ordered domains [19].

The ratio between the area of a given peak and the area of the entire spectrum, $S_{2\theta}/S_{\text{tot}}$, is shown in Table 2. From this table, we can see that the ordered domains represent small fractions of the sample. The amorphous domains are dominant (33.5% for the large peak at $2\theta = 17^\circ$ and 37.7% for the large peak at $2\theta = 32^\circ$).

In the next stage of the investigation, a sample of pure starch was heated for 2 hours at 80°C and a second one was heated for 2 hours at 140°C . The XRD spectra of samples degraded at 80°C and 140°C are almost similar, but they differ from the spectrum of the initial starch (Figure 2). The noise effect was reduced by smoothing the experimental data using Kaleidagraph software and a smoothing factor of 1%. The shadow line represents the experimental data as recorded, and the solid line represents the result of the smoothing. In our quantitative analysis, we considered the smoothed data. We used the same quantity of sample, same conditions of exposure, the same number of scans, and the same parameters of the recording of spectra in order to be able to make quantitative comparison between the initial and heated samples. For a given mass of substance, the heated samples contain a reduced proportion of crystalline phase compared with the initial sample. For this reason, the spectra of these samples are rather noisy.

During the heating, the ordered arrangement of the linear parts of the amylose is perturbed, and the branching points of the amylopectin are broken. The result is the degradation

FIGURE 2: The diffractogram of the starch before heating (a), after 2 hours of heating at 80°C (b), and after 2 hours of heating at 140°C (c). The shadow lines represent the experimental data as recorded and the solid lines represent the data after smoothing.

of the ordered phase and the extension of the amorphous phase [20]. Heating the samples induces the increase of the local mobility of molecules, with possible effect in the size reduction of crystalline granules, disentanglement of the chains, and even the scission of some polymeric chains. Reduction of the crystallinity of starch granules at high temperatures has been previously reported by Jenkins and Donald, 1998; Le Bail et al., 1999; Svensson and Eliasson, 1995 [21–23]. As the granule structure becomes increasingly disrupted at higher temperatures, more starch chains, especially amylopectin, could be disentangled, resulting in decreasing of the local order. Decrease of the intensity after heating was also observed for pure starch by Joanna Wojtasz et al. [5]. Reduction of the crystallinity is correlated with the reduction of the intensities of the peaks.

The main structural modifications of the starch appear after the heating at 80°C . The heating at 140°C produces smaller effects compared with the first heating at 80°C . For our discussion, we analyzed the spectrum of starch heated at 140°C . In this spectrum, the intensities of some peaks are reduced and some peaks shift slowly compared with the pure starch (Figure 2). For instance, the peaks at $2\theta = 11.4^\circ$ and 18.3° of initial starch disappear in the spectrum of degraded

TABLE 3: Parameters of XRD spectrum of the starch heated 2 hours at 140°C.

2θ [deg]	A [a.u]	β [deg]	d [Å]	$S_{2\theta}$ [a.u]	$S_{2\theta}/S_{\text{tot}}$ [%]
14.7	10	1.3	5.4	14	0.9
17 large	60	10.7	4.7	611	40
17.1	15	1	4.6	63	4.1
19.7	5	0.9	4.0	4	0.3
22.5	20	1.8	3.5	35	2.3
32 large	30	19.4	2.5	624	41

starch. The peak at $2\theta = 15.3^\circ$ shifts to 14.7° , the peak $2\theta = 23.1^\circ$ shifts to 22.5° , the peaks at $2\theta = 17.4^\circ$, and 18.3° merge into a large peak at 17.1° . The large peak $2\theta = 19.7^\circ$ – 20.7° shifts to 19.7° . Quantitative analysis was done after simulation of the mains peaks of the spectrum using the same procedure as in the case of pure starch before heating. The parameters of the fit for the sample heated for 2 hours at 140°C are presented in Table 3. The shift of the peaks towards small diffraction angles means increase of the interplanar diffraction distance.

The particularities of starch structure are determined by the linkage of the amylose and amylopectin subunits. The amylose subunits are linked mostly α -(1→4) whereas the amylopectin has subunits linked both α -(1→4) and α -(1→6), with about 95% of the glycosidic bonds being α -(1→4) linkages and 5% being α -(1→6). The α -(1→6) linkages in amylopectin cause the polymer to be highly branched [24]. The amylopectin molecular chains form parallel, dense, left-handed double helices with six glucose residues per turn [25]. The two helices are linked in a double helix by an α -1,6 branch point. The double helices can be aligned in two different crystalline lattices: the A-type polymorph [26], which is dense, and the B-type polymorph [27], less dense. Increasing of the thermal agitation during the heating could be favorable to the alignment of starch molecules on the less dense structure, which could explain the small shift of the XRD peaks of pure starch towards small angles for heated samples.

Another effect is the decrease of the ratio between the area of narrow peaks and the area of the entire spectrum (Table 3). That indicates a reduction of the amount of the ordered domains. On the other hand, the largest peaks at $2\theta = 17^\circ$ and $2\theta = 32^\circ$ have greater ratio $S_{2\theta}/S_{\text{tot}}$ in the degraded sample, 40% respectively 41%, compared with 33.5% and 37.7% of the pure starch (Table 3). That means extension of the amorphous domain.

The XRD diffractograms of samples P1–P3, before heating, show different degrees of local ordering depending on the initial composition. In solid starch, most of the molecules are densely packed in an ordered phase and only a small part of the polymer is mobile, in amorphous state [25]. Parts of the same chain can be in a crystalline state, whereas other parts can be in a disordered state [28]. The amorphous parts of the chains are more accessible to water and can easily form gels. Adding water to solid starch is followed by the swelling of the material with the consequence of reducing the crystallinity. Thus, we can explain the differences observed between the spectra of solid starch and samples P1–P3.

FIGURE 3: The XRD pattern of pure starch (a), sample P1 (b), sample P2 (c), and sample P3 (d) before heating.

As in the case of pure starch, the diffractograms of samples P1 to P3 contain a broad region in the domain 10° – 25° with some distinctive peaks with intensities depending on the concentration of starch. For instance, in the spectrum of sample P1 we can see small but distinctive peaks at $2\theta = 12.9^\circ$, 16.9° , 19.7° , and 22° . The intensity of these peaks decreases in the spectrum of sample P2, and they almost disappear in the spectrum of sample P3 (Figure 3). In each of the samples P1–P3 the quantity of starch is decreased, which explains the reduction of the intensities of the narrow peaks. The peak $2\theta = 11.4^\circ$ of pure starch is shifted to $2\theta = 12.9^\circ$ for P2 and P3.

In the presence of water, the mobility of starch molecules increases allowing better packing, better arrangement of branched structure of amylopectin, and thus a more compact packaging of molecules inside the ordered domains. This supposition is in agreement with the model proposed by Kainuma and French, suggesting that glucose polymers form double helices upon addition of water [29]. The effect is the decrease of interplanar distances [30, 31]. The intense peaks at $2\theta = 15.3^\circ$, 17.4° , and 18.3° of pure starch are missing in the spectra of samples P1–P3, but we can see a peak at $2\theta = 16.9^\circ$. The large peak between 19.7° and 20.7° of pure starch becomes narrow and can be seen at 19.7° in the spectra of samples P1 to P3. The peak at 23.1° shifts to 22° in the spectra of P1 and P2 and it is absent for sample P3. This behavior indicates a reduction of the ordered phase when the concentration of starch decreases.

The effect of thermal degradation was also observed for samples P1–P3. These samples were heated for 2 hours at 80°C and 140°C . For sample P1, heated at 80°C , we can see peaks at 12.9° , 16.9° , 19.7° , 22° , and 32° , similar to the initial sample before thermal degradation (Figure 4, curve (b)). However, their intensities and their areas are substantially reduced. That means a decrease of the amount of ordered structure associated with these peaks. At 140°C , the intensity of the peaks diminishes again, the peak at 12.9° become broad, the peak at 19.7° shifts to 20.5° , and the peak at 32° is missing

FIGURE 4: XRD pattern of sample P1 as obtained (a), after 2 hours of heating at 80°C (b), and after 2 hours of heating at 140°C (c). The shadow lines represent the experimental data as recorded and the solid lines represent the data after smoothing.

FIGURE 5: The XRD diffractograms of samples P1–P3 heated 2 hours at 80°C: (a) sample P1, (b) sample P2, and (c) sample P3. The shadow lines represent the experimental data as recorded and the solid lines represent the data after smoothing.

(Figure 4 curve (c)). That shows further decrease of the amount of the ordered phase and increase of the amount of the amorphous phase when the temperature increases. Similar behavior can be seen for samples P2 and P3, but the degradation is more pronounced. The spectra become noisier and the peaks can be difficult to distinguish. For sample P2 heated for 2 hours at 80°C, we can see peaks at 12.9°, 16.9°, and 19.7°, similar to sample P1 (Figure 5 curve (b)). The peak at 22° is missing and the peak at 32° shifts to 33.8°. For sample P3, the entire spectrum is broad with peaks at 18.3° and 20.5° (Figure 5 curve (c)). The ordered structure for this sample at this temperature is strongly affected. The sample is almost entirely amorphous. The concentration of starch decreases in

samples P1–P3 and our results show that the degradation of the ordered phase is more pronounced at low concentration of starch.

4. Conclusion

The effects of thermal degradation of some starch based systems were investigated by XRD. Three systems with different starch concentration were obtained by extrusion technique using glycerol as plasticizer. The systems were investigated before and after thermal degradation. The XRD measurements for pure starch, before heating, indicate the existence of two phases: an ordered one and an amorphous one. The ordered phase is determined mainly by the amylose and branching points of amylopectin, while the amorphous phase is associated with the short-branched chains of amylopectin. Thermal heating at 80°C is followed by partial destruction of its ordered structure. The ordered phase is almost completely destroyed after heating at 140°C.

The ordered phase is also detected for samples P1–P3, but its concentration depends on the initial composition. Samples with high concentration of starch have large regions with ordered structure. After 2 hours of heating at 80°C, most of the ordered phase is destroyed. The degradation continues with temperature increased to 140°C. The degradation of the ordered structure is more pronounced in samples with low content of starch. Heated at 140°C, these samples become almost entirely amorphous.

The XRD investigations demonstrate the role of starch in the thermal stability and local ordered organization of these samples.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

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