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THERMAL AGEING OF CELLULOSE WITH NATURAL AND SYNTHETIC ANTIOXIDANTS UNDER VARIOUS CONDITIONS

Studies were undertaken of the influence of both the natural stabilizers present in wood (lignin and extractives) and synthetic antioxidants on the thermal ageing of cellulose. Among the synthetic antioxidants, butylated hydroxytoluene, propyl gallate and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (ethoxyquin) were examined. In order to study the thermal ageing of cellulose with antioxidants, accelerated ageing tests were carried out under various conditions. The ageing tests were performed at a temperature of 95°C in an air and nitrogen atmosphere in anhydrous conditions and at 65% relative air humidity. To study the degradation of the cellulose, size exclusion chromatography was used. The results revealed that ethoxyquin was the best synthetic stabilizer. In addition, butylated hydroxytoluene had stabilizing properties and slowed down the depolymerisation of the cellulose. In turn, the behaviour of the propyl gallate under elevated temperature conditions was the most interesting. This antioxidant, relating to the cellulose degradation process, showed inhibitory as well as catalytic properties under specific conditions. In the ageing conditions applied, the smallest decrease was observed in the average molar mass of the cellulose in the wood without extractives. The results indicate that in this case, lignin played a very important role as a hidden antioxidant. In the presence of the lignin, oxidative the cellulose depolymerisation process proceeded more slowly than with the participation of synthetic antioxidants. The extractives, under elevated temperature conditions, did not show stabilizing properties, and furthermore, they accelerated the degradation of the cellulose.

Keywords: thermal ageing, cellulose degradation, wood, antioxidants, SEC

Introduction

Wood has played an important role in society for a long time. Due to its complex structure, it has unique mechanical, physical and chemical properties. It is

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characterized by its considerable strength, its low price and its interesting decorative and utilitarian value. In addition, it is a readily available and renewable resource. However, in spite of so many advantages, it is also much more exposed to degradation than synthetically obtained materials. Factors that cause wood degradation include elevated temperature, humidity and an oxidizing environment. Cellulose is the main component of wood. Wood strength mainly depends on the physicochemical properties of cellulose. In the literature, some information may be found on the possibility of using natural and synthetic antioxidants for polymer stabilization [Kovářová et al. 1995; Schultz and Nicholas 2000; Pouteau et al. 2003; Gregorová et al. 2006; Košiková and Lábaj 2009; Košiková and Sláviková 2010; Ambrogi et al. 2014]. One of the methods to inhibit or at least reduce the oxidative depolymerisation of cellulose is the application of antioxidants [Schmidt et al. 1995; Strlič et al. 2001, 2004; Vizárová et al. 2014]. The most important antioxidants present in wood include extractives (tannins, flavonoids, stilbenes, lignans) and lignin [Kähkönen et al. 1999; Pan et al. 2006; Pietarinen et al. 2006; Redzynia et al. 2009; Faustino et al. 2010]. Whereas the most widely used synthetic antioxidants in different industries include butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertiary-butylhydroquinone (TBHQ), propyl gallate (PG) and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (ethoxyquin, EQ). 2,4,5-trihydroxybutyrophenone (THBP), nordihydroguaiaretic acid (NDGA) and 2,6-ditertbutyl-4-hydroxymethylphenol (IONOX 100) are less commonly used because of their high cost.

There is little research on the use of the above-listed synthetic antioxidants to study cellulose stability. However, the idea of their application seems to be interesting both from a scientific and a practical view point. In addition, the behaviour of stabilizing compounds at elevated temperatures and their effect on cellulose depolymerisation are still poorly understood. Therefore, an attempt to determine the influence of the natural stabilizers present in wood (lignin and extractives) as well as synthetic antioxidants on the degradation of cellulose was undertaken.

Materials and methods

Ageing tests were carried out on the following materials:

- the non-extracted sawdust of pinewood (*Pinus sylvestris* L.) from the sapwood zone;
- the extracted sawdust of pinewood (*Pinus sylvestris* L.) from the sapwood zone (without extractives) treated with a mixture of chloroform (Chempur, Poland) and 96% ethanol (Chempur, Poland) $(93{:}7)_w$ in a Soxhlet extractor according to the authors' own method [Antczak et al. 2006];
- cellulose – isolated from the above-mentioned extracted pinewood (*Pinus sylvestris* L.) using the Kürschner-Hoffer method [Krutul 2002].

The method consists of the mild nitration (65% nitric acid; Chempur, Poland) of lignin to obtain an alcohol (96% ethanol) soluble nitro derivative. Hemicelluloses and cellulose with a lower degree of polymerisation undergo hydrolysis at reaction conditions;

– the above-mentioned pinewood cellulose with antioxidants – PG, BHT and EQ (Supelco, USA), which were coated on the cellulose fibre using a stirring method [Antczak et al. 2007]. The method consists of immersing a sample of the cellulose in 0.2% antioxidant solution in methanol (Chempur, Poland) and then the total evaporation of the solvent under vacuum while stirring using a vacuum evaporator (Rotavapor R-215, Büchi company).

Accelerated ageing tests in normal atmosphere

At the beginning, the non-extracted and extracted pinewood from the sapwood zone, as well as the cellulose and cellulose with antioxidants (PG, BHT and EQ) were placed in a hermetically-sealed desiccator with P_2O_5 (Sigma-Aldrich, Germany) (in anhydrous conditions). At the same time, for the purposes of comparison, the above-mentioned research material was placed in another hermetically-sealed desiccator with a saturated water solution of $NaNO_3$ (Chempur, Poland) (in conditions of 65% relative air humidity) [Greenspan 1977]. In these vessels the samples were submitted to accelerated ageing tests. The ageing tests were carried out in the thermal chamber (KC 100/200, Elkon company) at 95ºC. The samples were collected every 14 days over a 70 days period and were prepared for SEC (Size Exclusion Chromatography) analysis in order to study the cellulose degradation.

Accelerated ageing tests in a nitrogen atmosphere

In these studies, only the cellulose samples and the samples of cellulose with antioxidants (PG, BHT and EQ) were used. They were placed in a hermetically--sealed vacuum desiccator with P_2O_5. A vacuum pump (V-700, Büchi company) was used to remove the air to 0.66 kPa, and the desiccator was then filled with nitrogen. The procedure was repeated three times. After this, the samples in the desiccator were subjected to accelerated ageing tests. The ageing tests were also carried out in a thermal chamber (KC 100/200, Elkon company) at 95ºC. The samples were also collected every 14 days over a 70 days period and were prepared for SEC analysis in order to examine the cellulose degradation.

Preparation of cellulose samples for SEC analysis

The cellulose samples were prepared using the authors' own procedure, presented in earlier publications [Antczak 2010b; Radomski et al. 2011]. A detailed description of the procedure is as follows: in order to study the cellulose degradation in the aged non-extracted and extracted wood, the

cellulose was isolated using the Kürschner-Hoffer method. All the cellulose samples (50 mg of each) were treated with 50 cm^3 0.01 M $NaBH_4$ (Sigma-Aldrich, Germany) at room temperature (25 ºC). After ca 24 h, the cellulose was filtered through a glass filter (G3), washed with 5% acetic acid (20 cm^3) (Chempur, Poland) and then washed with distilled water until it reached a neutral pH. Following this, the cellulose samples were treated with 1% NaOH (20 cm^3) (Chempur, Poland) in a nitrogen atmosphere for 1 hour using a magnetic stirrer at room temperature (25ºC). The cellulose was then filtered and washed as before. For the next step, the air-dry cellulose samples prepared according to the aforementioned method were subjected to an activation and dissolution procedure. The procedure was carried out in a Baker SPE-12G vacuum system at room temperature (25ºC) and was as follows:

- the cellulose samples (15 mg) were placed in test-tubes (6 cm^3), poured over with distilled water (3 cm^3) and allowed to swell overnight;
- the following day, the samples were transferred to polypropylene tubes with a narrow outlet (8 mm and 0.5 mm – inlet and outlet internal diameters, respectively) and subsequently washed with methanol (Chempur, Poland), filtered and poured over with the next portion of methanol and left for 1 hour; this procedure was repeated twice;
- following this, the samples were washed with DMAc (N,N-dimethylacetamide) (Sigma-Aldrich, Germany), filtered and poured over with the next portion of DMAc and left for 1 hour; this procedure was repeated once and the cellulose with the DMAc was left until the following day;
- the following day, the samples were filtered and poured over with 8% LiCl in DMAc (4 cm^3) (Sigma-Aldrich, Germany);
- the cellulose dissolution in an 8% LiCl/DMAc solvent system was realised using an RM-2M mixer (Elmi company);
- after 1-2 days of continuous mixing, part of the sample (0.2 cm^3) was diluted to 0.5% LiCl (Sigma-Aldrich, Germany) concentration with pure DMAc (3 cm^3);
- finally, the prepared samples were submitted for SEC analysis.

Conditions of SEC analysis

The conditions of the SEC analysis of the cellulose samples were adopted from earlier studies [Antczak 2010b; Radomski et al. 2011]. The analysis was carried out using a HPLC (High Performance Liquid Chromatography) system (LC-20AD, Shimadzu company), which was equipped with a differential refractive detector (RID-10A, Shimadzu), pump (LC-20AD, Shimadzu), degasser DGU-20A (Shimadzu), oven (CTO-20A, Shimadzu) and controller (CBM-20A, Shimadzu). The SEC analysis conditions were as follows:

- 0.5% LiCl/DMAc as the eluent,

- column – cross-linked polystyrene-divinylbenzene gel (PSS GRAM 10000, 10 μ, 8 × 300 mm) connected with a guard column (PSS GRAM 10 μ),
- oven temperature: 80°C,
- flow rate: 2 cm^3/min (the high flow rate was compatible with the column specification),
- injection volume: 0.2 cm^3.

The chromatographic data were processed using PSS WinGPC scientific 2.74 software. Twelve narrow molar mass polystyrene standards (Polymer Laboratories) were used to calibrate the column. The polystyrene standards were prepared as mixed standards in four separate solutions in a 0.5% LiCl/DMAc solvent system. The first standard solution contained polystyrene of the following molar masses: 6 850 000, 565 000 and 11 300 Da, the second: 3 950 000, 170 600 and 2 960 Da, the third: 3 150 000, 66 000 and 1 700 Da, and the fourth: 1 290 000, 28 500 and 580 Da. These polystyrene standards were used to calculate the molar mass of the cellulose according to Mark-Houwink universal calibration:

$$[\eta] = K \times M^{\alpha} \tag{1}$$

where K and α are parameters, which depend on the polymer type, solvent and temperature. For the chromatographic conditions in this study, these parameters were as follows: for the polystyrene $K = 17.35 \times 10^{-3}$ cm^3/g and $\alpha = 0.642$ [Timpa 1991] and for the cellulose $K = 2.78 \times 10^{-3}$ cm^3/g and $\alpha = 0.957$ [Bikova and Treimanis 2002].

Results and discussion

The thermal degradation of the cellulose was examined by SEC after the ageing tests. The relationships between the weight average molar mass (M_w) of the cellulose and the ageing time at 95°C in normal atmosphere (in anhydrous conditions) are presented in figures 1 and 2.

The results of the studies presented in figure 1 indicate that the cellulose with the addition of ethoxyquin was the most resistant to thermal degradation at 95°C in the air (in anhydrous conditions). Furthermore, BHT revealed stabilizing properties and effectively slowed down the rate of cellulose degradation. In turn, the addition of propyl gallate in these conditions had a catalytic influence on the cellulose thermal degradation process. There is some information in the literature that propyl gallate, apart from having antioxidant and stabilizing properties, has pro-oxidizing properties under certain conditions contributing to the acceleration of the degradation of substances such as DNA and carbohydrates [Smith et al. 1992; Aruoma et al. 1993]. These findings were also confirmed by previous studies performed at 130°C. According to these studies,

under aerobic conditions, propyl gallate proved to be the catalyst for the thermal degradation of cellulose [Antczak et al. 2008; Antczak 2010b].

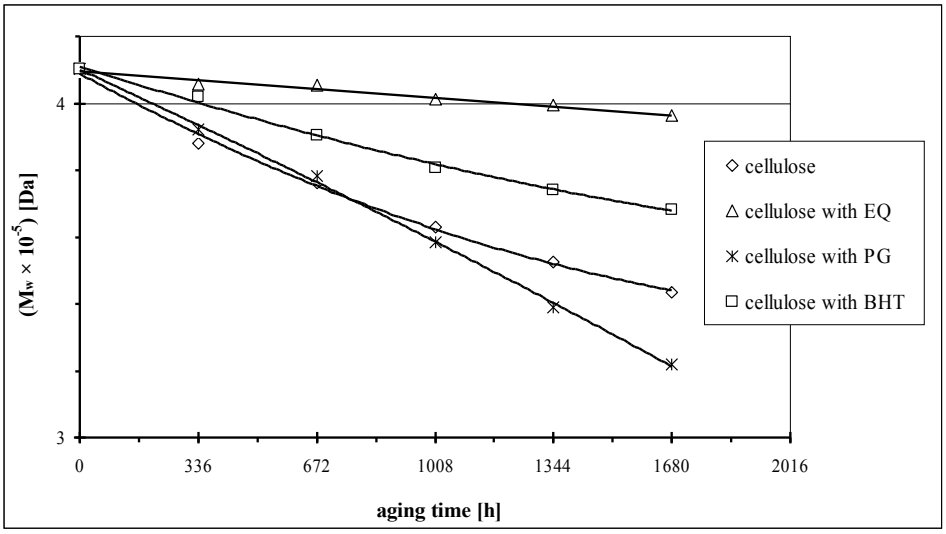

Fig. 1. The relationship between the weight average molar mass (M_w) and ageing time for cellulose and cellulose with antioxidants (EQ, PG and BHT) aged at 95ºC in normal atmosphere and in anhydrous conditions

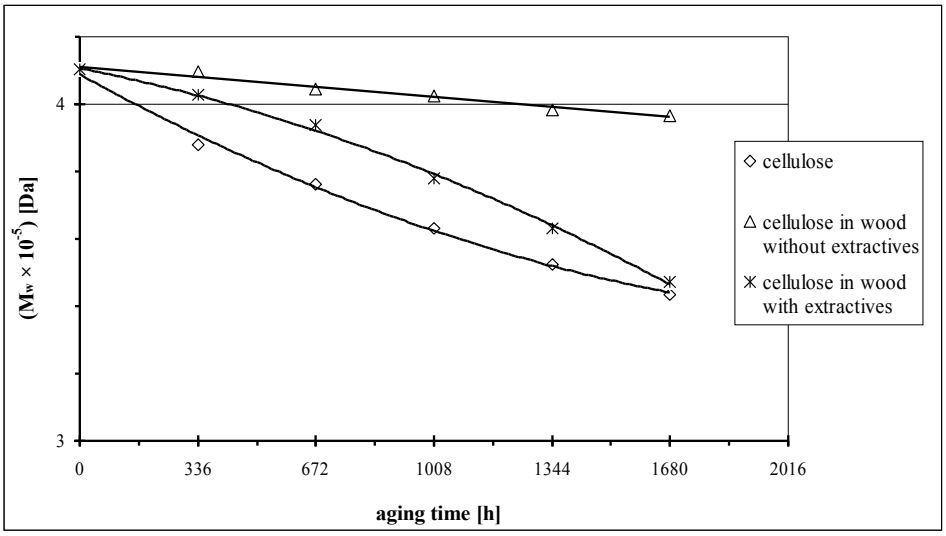

Fig. 2. The relationship between the weight average molar mass (M_w) and ageing time for cellulose, cellulose in wood without extractives and cellulose in wood with extractives aged at 95ºC in normal atmosphere and in anhydrous conditions

The results of the chromatographic analysis for the aged cellulose and cellulose in the aged extracted and non-extracted wood are presented in figure 2. These results indicate that at 95°C in normal atmosphere (in anhydrous conditions) the smallest changes in the weight average molar mass of the cellulose occurred in the extracted wood. The presence of the extractives significantly accelerated the thermal degradation of the cellulose. However, the most significant drop in the weight average molar mass of the cellulose, from the beginning of the ageing process, took place in the case of the pure cellulose.

On the basis of the results of the thermal ageing of the wood at 95ºC (fig. 2), it can be concluded that the most likely cause of the lower degree of cellulose degradation in the wood was the lignin. Barclay et al. [1997], on the basis of their studies, showed that lignin acts as a hidden antioxidant. Phenolic groups of lignin can protect the cellulose, and as a consequence the wood, from the harmful action of radicals formed during ageing. Additionally, a change in the structure due to the cellulose isolation process may have been the reason for the greater degradation of the pure cellulose. It is possible that the chemicals (especially the concentrated nitric acid) modified the crystallinity leading to a material with less thermal resistance. This was confirmed by the results previously obtained using the FT-IR technique [Antczak 2010a]. Based on the results [Antczak 2010a], it appears that pure cellulose subjected to thermal ageing at 130ºC in the air had a higher crystallinity index than cellulose in aged extracted and non-extracted wood. This proves that the cellulose separated using the Kürschner-Hoffer method was, to a great extent, composed of amorphous regions, which at elevated temperatures were more easily degraded.

Figure 3 shows the results of the weight average molar mass of the cellulose and the cellulose with antioxidants (EQ, PG and BHT), which were aged at 95ºC under aerobic conditions in 65% relative air humidity. Based on these results, it can be concluded that the thermal ageing of cellulose under aerobic conditions in 65% relative air humidity caused a sharp reduction in the weight average molar mass of the cellulose. It is certain that the cause of such a large decrease in the molar mass was elevated humidity. In these conditions, the initiation of the hydrolysis reaction occurred, resulting in the rapid disintegration of the cellulose chains.

The addition of antioxidants to the cellulose matrix slowed down the degradation to a certain extent, but its complete inhibition was not possible. The curves describing a decrease in the weight average molar mass of the cellulose with a stabilizer (EQ, PG and BHT) followed a similar course regardless of the antioxidant used (fig. 3).

Figure 4 shows the molar mass distributions of the cellulose and the cellulose with the selected antioxidant – propyl gallate subjected to ageing at 95°C in the air (1008 h) in various relative air humidity conditions. The results confirm that air humidity influenced the degradation process of the cellulose. Based on the results (fig. 4), it can be observed that an increase in relative

humidity caused a shift in the cellulose distribution curve towards a lower molar mass. Firstly, the cellulose chains of the highest molar mass were degraded (the largest loss of the cellulose fraction on the right side of the distribution curve). The addition of the synthetic antioxidant (PG) to the cellulose matrix protected the cellulose to some degree (in a particular part of the fraction of the highest molar mass), but also in this case there was considerable degradation.

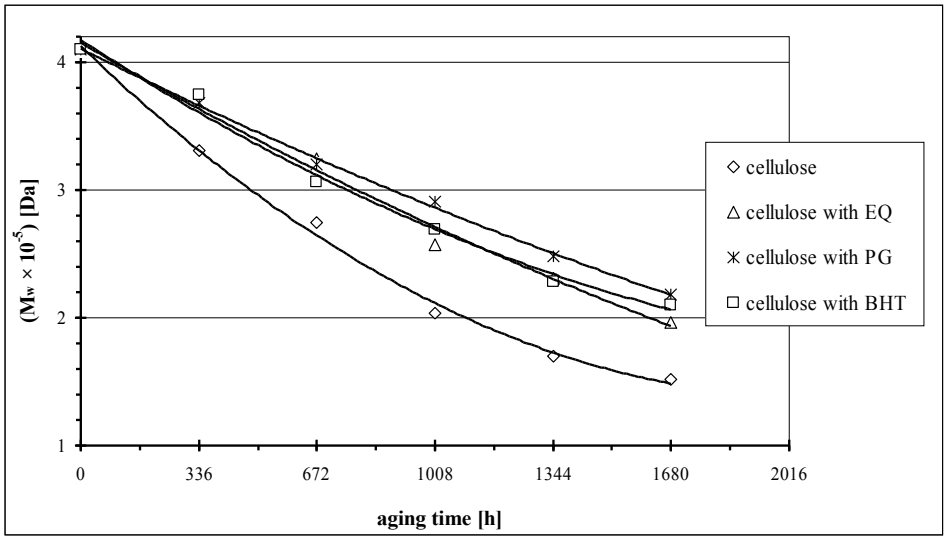

Fig. 3. The relationship between the weight average molar mass (M_w) and ageing time for cellulose and cellulose with antioxidants (EQ, PG and BHT) aged at 95°C in normal atmosphere and in 65% relative air humidity

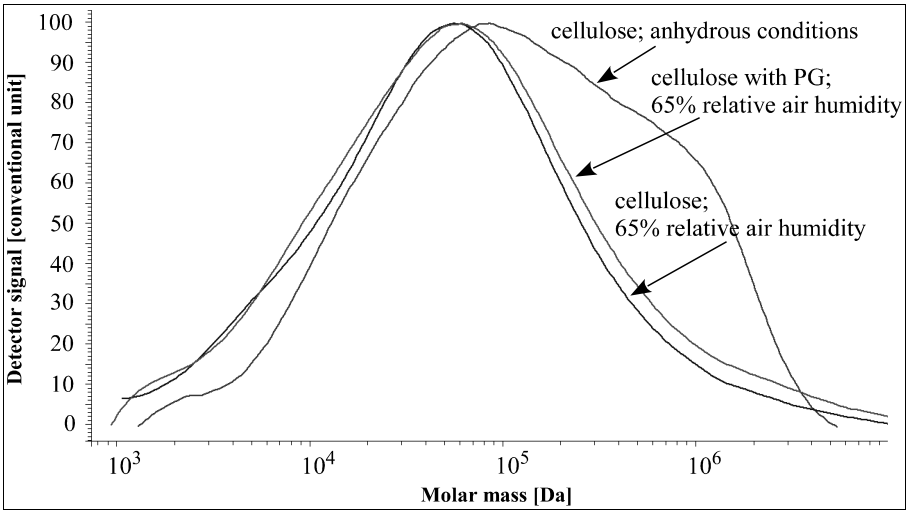

Fig. 4. The molar mass distributions for cellulose and cellulose with antioxidant (PG) aged at 95°C (1008 h) in normal atmosphere and in various (anhydrous and 65%) relative air humidity conditions

Regarding wood ageing at 95°C in the air with 65% relative humidity, it can be seen that the slowest thermal degradation of cellulose occurred in the wood without extractives (fig. 5). This probably means (as earlier) that the lignin had a stabilizing effect on the cellulose degradation process. Furthermore, it appears that in these conditions, the lignin, which may have acted as a natural antioxidant, protected the cellulose more effectively than the synthetic antioxidants (a smaller decrease in the weight average molar mass of the cellulose in the aged wood without extractives than in the presence of the synthetic antioxidants) (figs. 3 and 5). Additionally, changes in the structure due to the cellulose isolation process may have been the cause of the greater degradation of the pure cellulose (as earlier). In turn, the presence of the extractives (as in anhydrous conditions) significantly accelerated a decrease in the weight average molar mass of the cellulose. The high temperature was probably the cause of the extractives' much less efficient stabilizing activity. The decomposition of the unstable low-molecular extractives may have occurred under the influence of the high temperature. As a result of this decomposition, very reactive substances of a radical character may have formed, which accelerated the depolymerisation of the cellulose. Similar results were obtained by other researchers, who observed that extractives reduce the thermal stability of wood and wood composites [Shebani et al. 2008; Poletto et al. 2012; Sheshmani et al. 2012].

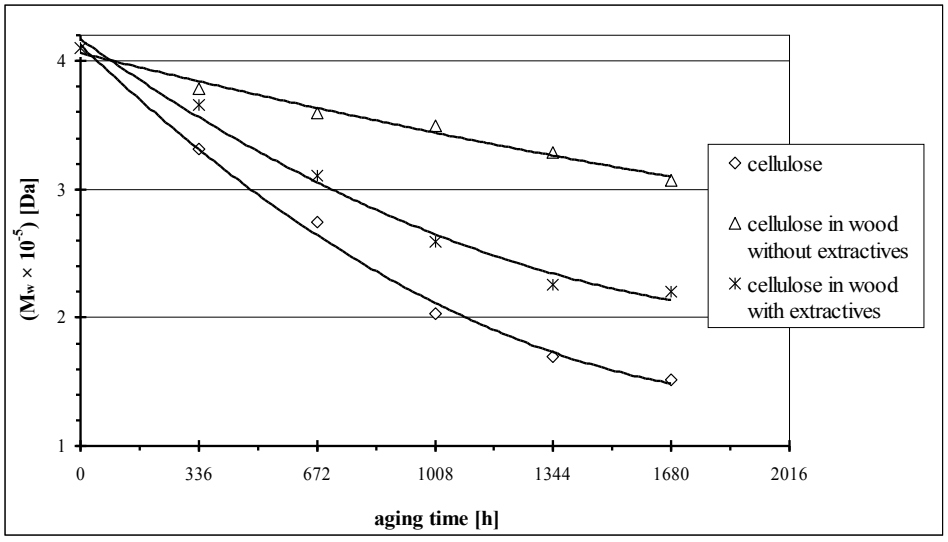

Fig. 5. The relationship between the weight average molar mass (M_w) and ageing time for cellulose, cellulose in wood without extractives and cellulose in wood with extractives aged at 95ºC in normal atmosphere with 65% relative air humidity

Figure 6 presents the molar mass distribution curves of various celluloses aged at 95°C (1008 h) in normal atmosphere with 65% relative air humidity conditions. The distribution of the curves confirms that the cellulose in the aged wood without extractives was the least degraded (the curve is the most shifted to the right). In turn, the presence of low-molecular extractives during the thermal ageing of the wood adversely affected the cellulose, because the molar mass was significantly reduced. As can be observed in figure 6, there was a large difference in the molar mass distribution between the cellulose in the aged wood without extractives, and the aged cellulose with the addition of the synthetic antioxidant (PG). The molar mass distribution curves of the cellulose from the SEC analysis show that, in these ageing conditions, lignin was much a better stabilizer than the synthetic antioxidants used.

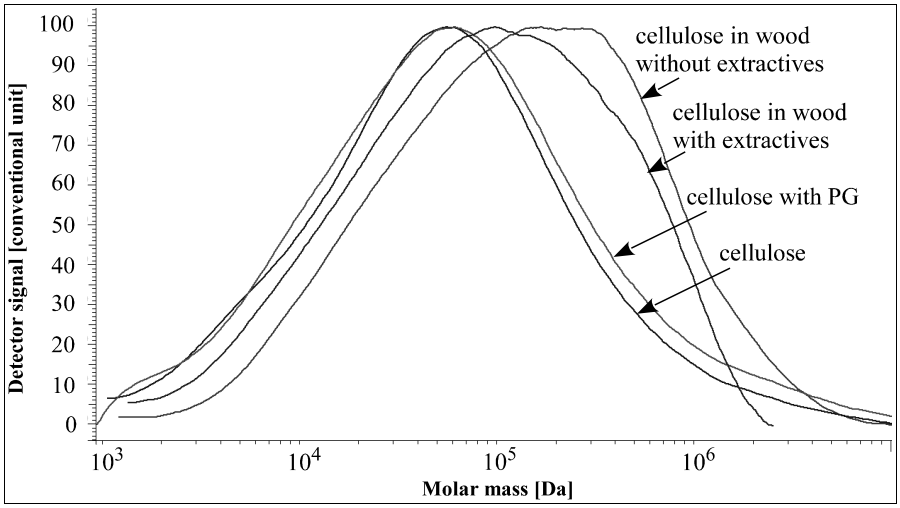

Fig. 6. The molar mass distributions for cellulose, cellulose with antioxidant (PG), cellulose in wood without extractives and cellulose in wood with extractives aged at 95ºC (1008 h) in normal atmosphere with 65% relative air humidity

Figure 7 shows the results of the SEC analysis of the cellulose and the cellulose with antioxidants (EQ, PG and BHT) aged at 95°C in a nitrogen atmosphere in anhydrous conditions. As expected, the stabilizing effect of the synthetic antioxidants (PG, EQ and BHT) during the ageing of the cellulose in a nitrogen atmosphere was observed.

Comparing the changes in the average molar mass of the aged cellulose with the addition of propyl gallate (in a nitrogen atmosphere) with the results of this material aged in the air (figures 1 and 7) in anhydrous conditions, an interesting phenomenon was observed. The propyl gallate at an elevated temperature (95°C) in normal atmosphere (in anhydrous conditions) proved to be a catalyst for the cellulose degradation, whereas under anaerobic conditions it acted as an inhibitor.

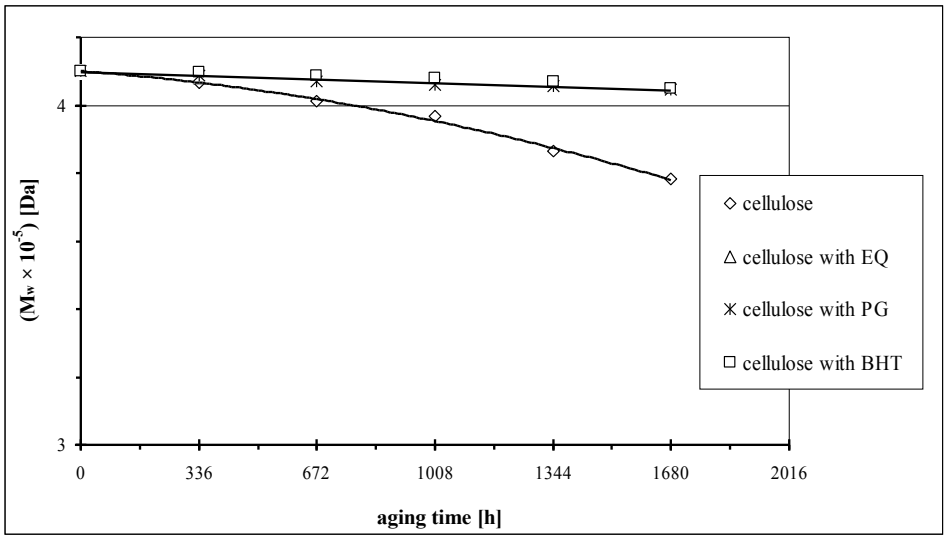

Fig. 7. The relationship between the weight average molar mass (M_w) and ageing time for cellulose and cellulose with antioxidants (EQ, PG and BHT) aged at 95ºC in a nitrogen atmosphere in anhydrous conditions

On the basis of the results obtained in these studies, the hypothesis is confirmed that, in certain conditions (oxygen atmosphere, high temperature), initiation of the oxidation and degradation of the polymer under the influence of antioxidants may occur. In turn, in the absence of oxygen or when there is insufficient oxygen (in a nitrogen atmosphere), this type of reaction does not occur and antioxidants in the majority of cases act as inhibitors of the thermal degradation of polymers.

Conclusions

In this paper, the thermal ageing of cellulose with natural and synthetic antioxidants under various conditions was studied. On the basis of the experiments performed, the following conclusions were drawn:

1. Among the used synthetic antioxidants, ethoxyquin was the best. In addition, BHT also had stabilizing properties and slowed down the depolymerisation of the cellulose.
2. In turn, relating to the degradation process of cellulose, propyl gallate showed inhibitory as well as catalytic properties. PG under aerobic anhydrous conditions accelerated the depolymerisation of the cellulose, while under anaerobic conditions (in a nitrogen atmosphere) and aerobic with 65% relative air humidity it slowed down the process.
3. Furthermore, in the ageing conditions applied, the smallest decrease in the average molar mass of the cellulose was observed in the wood

without extractives. The results indicate that, in this case, the lignin played the role of a hidden antioxidant. In the presence of the lignin, oxidative the cellulose depolymerisation process progressed more slowly than with the participation of synthetic antioxidants.

4. The extractives, at elevated temperature conditions, did not show stabilizing properties, and furthermore accelerated the degradation of the cellulose.

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