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THERMOOXIDATION OF TMAHP-CELLULOSE IN DEPENDANCE TO ITS ANIONIC FORM

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ABSTRACT

With the help of DTA, DTG, elementar analysis of carbonised residue and ESR spectroscopy the thermooxidation of trimethylammoniumhydroxyprophyl (TMAHP)-cellulose in dependance to its anionic form was studied. At 300 °C the percentage of carbon in carbonised residue run in oxidative atmosphere is higher than for sample run in inert atmosphere. The percentage of hydrogen is decreasing simultaneously. The concentration of free radicals in thermolysed residue is also increasing due to the presence of oxygen. We propose that oxygen is abstracting the hydrogen atoms from polysaccharide and unpaired electrons on carbon atoms are formed. At 400 °C the percentage of carbon in residues run at inert atmosphere is higher than for residue run at oxidative atmosphere. Also the concentration of free radicals in residues is greater in inert atmosphere than in oxidative one. That is why we suppose that at this temperature oxygen is bonded to polysaccharide residue and free radicals are terminated. From the semiquantitative DTA we can make the following sequence of samples according to their increasing thermooxidative effect: unmodified cellulose < A-HSO_4^- < A-Br^- < A-I^- < A-NO_3^- < A-$H_2PO_4^-$ < A-CH_3COO^- < < A-HCO_3^- < A-F^- < A-Cl^- < A-OH^-.

INTRODUCTION

There are many factors which are influenting the thermal stability of modified polymer. Some of the methods of thermal analysis which could be used for the study of this subject are: qualitative and semiquantitative DTA, DTG, elementar analysis and ESR spectroscopy of carbonised residues. We used all the mentioned methods for studying the thermooxidation of TMAHP-cellulose in dependance to its anionic form.

MEASURING METHODS

The thermoanalytical measurments were performed on device Mettler TA-1 in dynamic atmosphere of nitrogen, air and oxygen

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(3 dm^3 h^{-1}) using thermocouple Pt Rh 10 % Pt and reheated to 600 °C Al_2O_3 as a standard. The platinum pan was used in the case of ~ 7 mg weights and the high ceramical pan for ~ 100 mg sample weights. The rate of heating was 10 K min^{-1} and the sensibility of DTA was 100 μV. When the qualitative DTA was used the tension differences between observed and referent sample in μV were calculated to kelvine scale using Le Chatelier tables. The semiquantitative DTA was done in oxygen atmosphere after calibration of temperature and heat content using benzoic acid, NH_4NO_3, $LiNO_3$, Bi, KNO_3, Pb, Zn, $MnCl_2$ and Al. The heats of chemical reactions ($\blacktriangle Q$) were calculated from DTA-curve using the relation between apparatus constant and temperature of furnace with the help of ML-09 program for programmable calculator TI-59 (Texas Instruments Inc.).

ESR spectra were measured on X-bond spectrometer (Varian E-4). The measurments were done in glass tubes with inert diameter 2.5 mm. The values of g-factor were determined useing 2,2,6, 6-tetramethylpiperidine-N-oxid. The concentration of spins was related to the concentration of standard (Strong Pitch).

Elementar analysis were done on Perkin-Elmer Elementar Analyser (Model 240).

The samples of TMAHP-cellulose marked in previous work[1] as sample A were used. All other procedures and methods were mentioned also in previous work.[1]

RESULTS AND DISCUSSION

The course of reactions during thermal degradation of ammorphose cellulose could be judged from DTA curves. The unmodified cellulose is showing three exotherm maxima in inert atmosphere. The area of all exotherms of modified cellulose is smaller. It could be supposed that due to smaller area under all DTA exotherms of modified samples the quantity of free radicals in gaseous phase is decreasing as compaired to unmodified cellulose.

When the oxidative atmosphere is used the individual exotherms of DTA curves are moving to lower temperatures and their area under curve is increasing. It is known that the thermooxidative effect is starting to be evident at temperatures lower than 300 °C.[2]

On DTG curves the values of maxima run at oxidative atmosphere are slightly increasing in comparison to inert atmosphere and also moveing to lower temperature.

When the thermal degradation is judged with the help of semiquantitative DTA in oxygen atmosphere, the quantity of heat released in this way could be determined. The heat of reactions determined using this method could be separated in three parts. The sample with the greatest termooxidative effect shows the highest value of $\Sigma\Delta Q_1$ so we can make the following sequence of samples according to their increasing termooxidative effect: unmodified cellulose < $A\text{-}HSO_4^-$ < $A\text{-}Br^-$ < $A\text{-}I^-$ < $A\text{-}NO_3^-$ < $A\text{-}H_2PO_4^-$ < < $A\text{-}CH_3COO^-$ < $A\text{-}HCO_3^-$ < $A\text{-}F^-$ < $A\text{-}Cl^-$ < $A\text{-}OH^-$.

For some of the anionic forms which were thermolysed up to 300 °C in inert atmosphere much greater content of carbon was found as compared to unmodified cellulose ($A\text{-}HSO_4^-$, $A\text{-}I^-$, $A\text{-}Br^-$, $A\text{-}Cl^-$, $A\text{-}H_2PO_4^-$). The percentage of carbon is increasing due to presence of oxygen during thermolysis stopped at 300 °C. The content of hydrogen at residue is decreasing simultaneously. The samples thermolysed in oxidative atmosphere to 400 °C containe lower percentage of carbon as samples run inert atmosphere.

The samples: $A\text{-}I^-$, $A\text{-}H_2PO_4^-$ and $A\text{-}Br^-$ exhibit several times higher concentration of unpaired electrons than unmodified cellulose when the thermolyses was done in inert atmosphere and stopped at 300 °C. When the thermolysis is stopped at 400 °C then the quantity of free radicals formed at inert atmosphere is higher than in oxidative atmosphere (the sample $A\text{-}H_2PO_4^-$ is the exception).

We propose that during thermooxidation oxygen is abstracting the hydrogen atoms from polysaccharide and unpaired electrons on carbon atoms are begining to form at 300 °C. At 400 °C oxygen is bonded to polysaccharide residue and free radicals are terminated.

CONCLUSIONS

So when we summarise the results of all thermoanalytical methods the most suitable method for the study of thermooxidation of TMAHP-cellulose is the semiquantitative DTA.

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