Journal of Thermal Analysis, Vol. 10 (1976) 59—64

THERMOOXIDATIVE INVESTIGATION OF SILYLATED CELLULOSE DERIVATIVES

A. BORBÉLY-KUSZMANN, E. BRANDT-PETRIK, G. LIPTAY, and J. NAGY

Institute for Inorganic Chemistry, Technical University 1521 Budapest

(Received December 12, 1975)

Cellulose substituted by organosilicon groups represents a new type of modified cellulose. The silylation changes the physical and chemical properties of cellulose drastically. The thermoanalytical investigation of differently trimethylsilylated cellulose derivatives was carried out under static conditions in air atmosphere. The DTA curves of the cellulose used as starting material are different from those of its silylated derivatives. In the latter a new characteristic exothermic peak appears in the range 320—370°. The value of this maximum depends on the grade of silylation, being shifted towards higher temperatures with higher degrees of substitution.

In recent decades an increasing number of researchers have applied thermoanalytical methods to solve problems connected with natural and synthetic polymers. Differential thermoanalysis is suitable for characterizing the various sorts of polymers, for investigating the thermal and thermooxidative features of the polymers, for following polymerization and depolymerization processes, and for studying hydration and dehydration phenomena.

A number of research-workers have dealt with the thermal analysis of cellulose and its derivatives. Their results were summarized by Hornuff and co-workers [1, 2, 3]. As silylated cellulose ethers are a new class of modified cellulose, we set out to investigate the thermooxidative features of these trimethylsilyl derivatives.

Cellulose, which is one of the most important natural polymers, contains one primary and two secondary hydroxy groups in its glucose units. When these hydroxy groups are partially or fully trimethylsilylated, substituted cellulose derivatives are obtained which are soluble in apolar solvents.

Our aim was to investigate how the thermooxidative properties of cellulose are influenced by silylation.

Experimental

The thermoanalysis was carried out by using a complex thermoanalytical apparatus made by the Hungarian firm "MOM". The same experimental parameters were applied in the case of all measurements, so we had the possibility to compare the results obtained. A sample of 100 mg was submitted to analysis. The rate of heating was 10°/minute. The investigations were carried out in a platinum crucible in a static air atmosphere, using α-Al_2O_3 as reference material.

Results and discussion

We first investigated the regenerated cellulose used as starting material for synthetizing the trimethylsilyl cellulose ethers.

Figure 1 shows the thermal curves of the regenerated cellulose. According to the TG curve, this material contained nearly 5 weight per cent water bound by sorption. This amount of water was lost in the temperature interval from 40° to 150°, to the accompaniment of an endothermic peak in the DTA curve. The absorbed and crystal water left the cellulose at various temperatures. The leaving of the water is followed by a nearly weight-stable period, after which the decomposition process (which starts above 250°) becomes intensive and an exothermic peak appears in the DTA curve, slightly shifted in comparison to the DTG peak. During this decomposition process the heat produced by the oxidation of the decomposition products surpasses the energy demand of the endothermic decomposition process. Above 350° the slow thermooxidative decomposition of the products

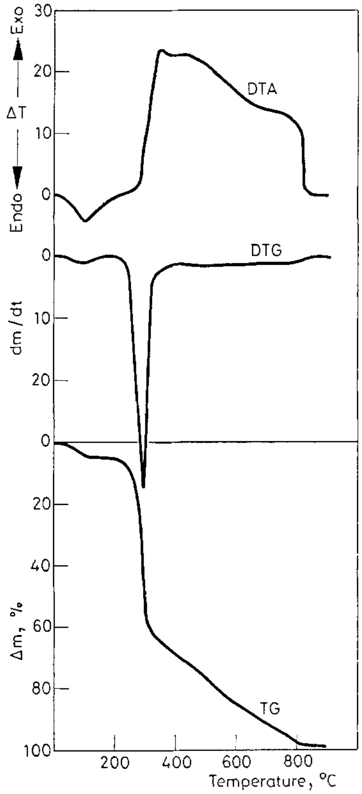

Fig. 1. Thermal curves of regenerated cellulose

takes place. The slow exothermic process seen in the DTA curve is characteristic for all kinds of regenerated cellulose.

The trimethylsilyl-cellulose derivatives investigated were prepared according to our published method [4]. The trimethylsilyl-cellulose products were synthetized by using hexamethyldisilazane as silylating agent, pyridine as solvent and trimethylchlorosilane as catalyst of Lewis acid type. The degree of silylation of the products obtained was different, and is referred to as the degrees of substitution per glucose unit.

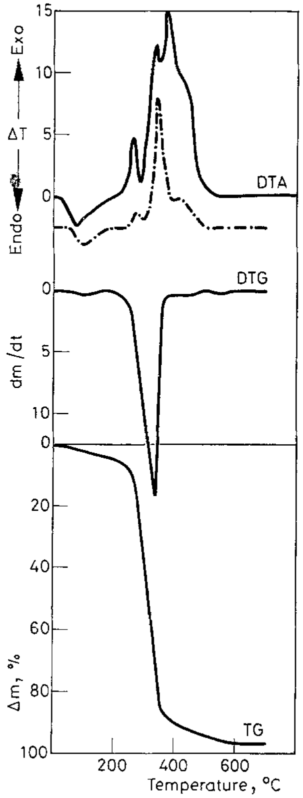

Fig. 2. Thermal curves of a silylated cellulose and the DTA curve of another silylated cellulose with a different degree of substitution

Figure 2 shows the TG, DTG and DTA curves of a silylated cellulose, and the DTA curve of a silylated cellulose with a different degree of substitution. In this latter the characteristic features of the silylated cellulose can be even better seen. The starting section of the DTA curve reveals an endothermic process due to the presence of solvents which can not be removed completely from the gel-like samples. The amount of solvents varied in the different samples. The presence of these traces of solvents can be seen in the DTG curves as well.

The curves of the silylated cellulose is quite different from that of the starting material, and consequently the thermal properties of the cellulose were altered by the substitution. In the DTA curves the broad peak of the regenerated cellulose starting at 280° is changed to two or three distinct peaks in the case of the silylated samples. In the latter no water is present, this being decomposed during the silylation reaction.

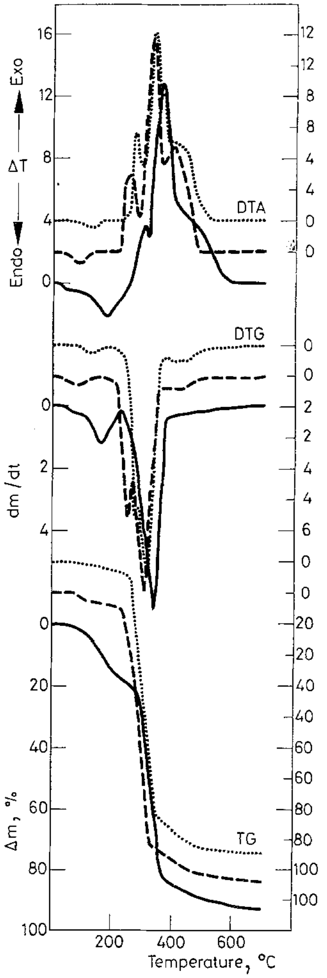

Fig. 3. Thermal curves of silylated cellulose derivatives produced during different reaction times: 2 hours —; 6 hours – – –; 8 hours . . .

In Fig. 3 the thermal curves of a set of samples can be seen, which were prepared using a similar excess of the silylating agent, but differ in the duration of the reaction. The DTA curve characteristic of the silylated cellulose appears already after 2 hours. The broken and the dotted lines correspond to 6 and 8 hours, respectively. With increasing reaction time the first and second maxima of the DTA curve increase. After 8 hours the first maximum decreases. The following differences can be detected in the DTG curve. After 2 hours of silylation only one inflexion point appears. After 6 and 8 hours the appearance of separated peaks shows the progress of the silylation. The thermooxidative properties of the different samples can be explained by taking into consideration simultaneously the other properties, such as for instance the degrees of substitution and the average molecular weight.

In the first 2 hours of the reaction mainly the surface and the amorphous parts of the cellulose molecules are silylated and are resolved. These resolved parts are immediately further silylated by the large excess of the silylating agent. With the prolongation of the reaction progressively less silylated products are resolved and consequently the degree of substitution and the average molecular weight decrease; the DTG curve exhibits a double decomposition process and in the DTA curve the first maxima is increased. After 8 hours the partly silylated fragments are further silylated, and consequently the degrees of substitution and the average molecular weight increase once more. In the DTA curve the double decomposition process is less pronounced and the first peak of the DTA curve is decreased

Table 1

Characteristic data of different silylated cellulose derivatives, depending on the silylation reaction time

Reaction time, hour	Degree of substitution	Average molecular weight $\overline{M}$	DTA Peak, 1 °C	DTA Peak, 2 °C	DTG Peak, 1 °C	DTG Peak, 2 °C
2	1.40	$2{,}46.10^4$	310	370	300 (inf)	340
6	0.92	$2{,}00.10^4$	250	340	240	300
8	1.15	$2{,}38.10^4$	280	340	270	320

Table 1 lists the degree of substitution, the average molecular weight, the maxima of the DTA curves of the silylated samples, the reaction duration and the temperatures of the DTA and DTG peaks. From these data it can be seen that the characteristic maxima of both the DTA and DTG curves depend on the degree of silylation. With increasing degree of silylation the thermostability of the products is increased, despite the fact that as a result of the substitution the amount of H-bonds originally present decreases. This fact can be explained by the different bond energies: the energy of the Si–O bond is 106 kcal/mole and that of the C–O bond is only 70 kcal/mole. Furthermore, by silylation of the hidroxy groups the intra- and intermolecular condensation processes are repressed. The decomposition of the silylated hydroxy groups produces hexamethyldisiloxane, which could be detected by g.l.c. The activation energy of this, however, is much greater than that of the formation of water from the corresponding hydroxy groups.

References

1. G. Hornuff and H. J. Jakobasch, Faserforsch. Textiltech., 18 (1967) 282.
2. G. Hornuff and R. Schäfer, Deutsche Textiltechnik, 18 (1968) 110.
3. G. Hornuff and R. Schäfer, Faserforsch. Textiltech., 23 (1972) 466.
4. J. Nagy, K. Becker-Pálossy, A. Borbély-Kuszmann and E. Zimonyi-Hegedüs, Periodica Polytech., 18 (1974) 91.

Résumé — La cellulose substituée par des groupes silico-organiques représente un nouveau type de celluloses modifiées. La présence du silicium change complétement les caractéristiques physiques et chimiques de la cellulose. L'étude thermo-analytique de divers dérivés de la cellulose triméthylsilylée a été effectuée dans l'air en atmosphère statique. Les courbes ATD de la cellulose utilisée comme matériau de départ sont différentes de celles de ses dérivés silylés. Pour ceux-ci, un nouveau pic exothermique caractéristique apparaît entre 320 et 370°C. La température du maximum du pic dépend du degré de la silylation et se déplace vers les valeurs plus élevées si le degré de substitution augmente.

Zusammenfassung — Die durch Organosilikongruppen substituierte Zellulose stellt einen neuen Typ modifizierter Zellulose dar. Die Silylierung ändert die physikalischen und chemischen Eigenschaften der Zellulose drastisch. Die thermoanalytische Prüfung verschieden trimethylsilylierter Zellulosederivate wurde in Luft unter statischen Bedingungen durchgeführt. Die DTA-Kurven der als Ausgangsmaterial eingesetzten Zellulose sind von denen ihrer Silylderivate verschieden. In den letzteren erscheint ein neuer charakteristischer exothermer Peak im Bereich von 320 bis 370°C. Die Temperaturlage dieses Maximums hängt vom Silylierungsgrad ab und wird bei höherem Substitutionsgrad in Richtung höherer Temperaturen verschoben.

Резюме — Введение кремний—органических групп в целлюлозу дает новый тип модифицированной целлюлозы. Наличие таких групп сильно изменяет физические и химические свойства целлюлозы. В статических условиях в атмосфере воздуха было проведено термоаналитическое исследование целлюлозы с различной степенью замещения триметилсилильными группами. Кривые DTA целлюлозы, используемой в качестве исходного материала, отличаются от кривых ее силильных производных. Для последных появляется новый характерный экзотермический пик в области 320—370°C. Значение этого максимума зависит от степени силилирования и сдвигается в более высокотемпературную область с увеличением степени замещения.