Formation and Behavior of Mechanoradicals in Pulp Cellulose

DAVID N.-S. HON, *Department of Forestry and Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

Synopsis

The mechanical degradation of pulp cellulose fiber was studied at ambient temperature and at 77°K. ESR findings reveal that mechanical degradation occurs via free-radical routes. Three types of mechanoradicals contributing singlet, doublet, and triplet ESR signals are identified. The singlet signals are derived from the alkoxy radicals at C_4 positions as a consequence of the cleavage of glucosidic bonds, the radical pairs generated at C_1 positions contributing the doublet signals. Triplet signals are derived from the C_2 and C_3 positions due to the cleavage of C_2 and C_3 bonds. Of these radicals, alkoxy radicals are the most stable at ambient temperature. Carbon radicals are capable of interacting rapidly with oxygen molecules to produce peroxy radical intermediates, where alkoxy radicals are inert toward oxygen molecules. ESR study also reveals that cellulose mechanoradicals are capable of initiating vinyl polymerization. MMA propagating radicals are identified when the monomers are in contact with cellulose mechanoradicals. The ability of mechanoradicals to initiate graft copolymerization from cellulose fiber is discussed.

INTRODUCTION

Wood cellulose is one of the most important natural resources for pulp fibers. In order to convert wood raw materials into end products of pulp and fiber, wood has to be delignified and defibered in terms of chemical and mechanical treatment. Generally, cellulose fibers as produced by the pulp mills are unsuitable for the manufacture of paper in that they need to be treated mechanically by beating and/or refining processes in order to produce the desired qualities in the finished paper and paperboard. It is obvious that in the pulping process, starting with debarking and chipping to beating and refining, mechanical treatment is an inevitable process.

Mechanical treatment of cellulose fiber shows that a repeated crushing action causes a breakdown of fibers, a decreased degree of polymerization, and a decreased crystallinity of cellulose fibers.[1] In view of this, the mechanical effects on cellulose fibers have emerged as a fundamental problem of the pulp and paper industry.

The fact that cellulose fiber is degraded by mechanical force has been known since 1921,[2] and over the years many papers on mechanical degradation of cellulosic materials have appeared. Especially during the past 15 years, industrial necessities have required scientists to study mechanical reactions by the use of suitable laboratory equipment for the purpose of elucidating the effects of mechanical action. Many techniques have been developed and studies made on the effect of controlled mechanical action on individual fibers, or on aggregates of fibers. Hess and his co-workers[3–6] had shown that the molecular vibrational energy produced in ball-milling cellulose is sufficient to rupture inter- and intramolecular hydrogen bonds and covalent bonds. Mechanical energy is also

Journal of Applied Polymer Science, Vol. 23, 1487–1499 (1979)

0021-8995/79/0023-1487$01.00

able to disaggregate and disorder the crystalline structure as well as to change the molecular weight distribution. Years later, Assarsson et al.[7] also found that carbon-to-carbon as well as carbon-to-oxygen bonds were ruptured by mechanical force.

The formation of mechanoradicals has been convincingly established for mechanochemical reactions in cellulose fibers. The presence of mechanoradicals was confirmed by reacting them with radical acceptors (iodine, nitric oxide, and oxygen)[8–11], by mass-spectrometric measurements,[12,13] and by electron spin resonance (ESR) techniques.[11,14–19] However, the mechanism of mechanoradical formation as well as the nature of these radicals and their role in relation to mechanical degradation are not yet clearly elucidated. Moreover, it has been known that mechanoreactions can be used as a tool for the preparation of block and graft copolymers,[20] yet very few studies have been carried out to investigate the capability of mechanoradicals in cellulose fiber to initiate vinyl copolymerization, although this is an important approach to improving pulp fiber characteristics.

The present investigation sets out to establish the mechanisms of free-radical formation by mechanical force, and to elucidate the behavior of these radicals in their chemical environment and the capability of these radicals to initiate vinyl graft copolymerization onto cellulose fibers.

EXPERIMENTAL

Materials

Commercial NSSC pulp from softwood (Douglas fir, *Pseudotsuga menzieii* (Mirb.) Franco) was used as the cellulose sample. In order to prevent undesired factors influencing the primary results from the cellulose fiber, the lignin component of the sample was removed by hypochlorite, as described by Norman and Jenkins.[21]

Glucose and cellobiose used as low molecular weight compounds were reagent-grade commercial samples. They were used as received without further purification. Methyl methacrylate used as a monomer was purified by distillation under reduced pressure.

Methods

Grinding mechanical energy was delivered to the cellulose fiber by milling the sample in a specially designed 30-ml Pyrex flask charged with 0.5 g air-dried sample and 0.5 g Pyrex beads. This flask was vibrated vertically at about 15 cycles/sec by a modified amalgamator manufactured by the Lima Electric Motor Company. The schematic diagram of the milling apparatus is depicted in Figure 1. For experiments at ambient temperature, millings were carried out in nitrogen or in oxygen; low-temperature (77°K) millings were carried out under vacuum, in liquid nitrogen, or in liquid air (mostly oxygen) at liquid nitrogen temperature. After the sample was milled for 3 hr, liquid nitrogen was introduced into the milling flask, and the sample was washed and transferred together with the liquid nitrogen to an ESR sample tube (E in Fig. 1), which was inserted into a Dewar flask filled with liquid nitrogen. Subsequently, the liquid nitrogen in the ESR

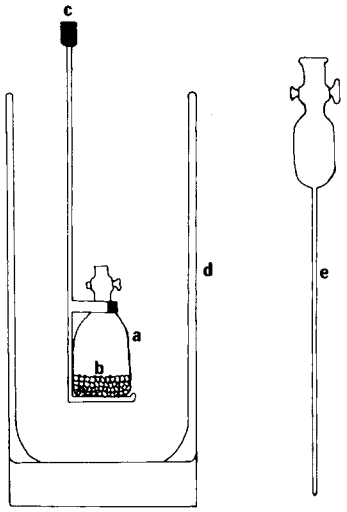

Fig. 1. Schematic sketch of low-temperature ball-mill apparatus: (a) glass flask; (b) glass beads for milling; (c) vibrator connection; (d) Dewar flask containing coolant (liquid nitrogen); (e) ESR sample tube.

sample tube was pumped away with a vacuum pump, and the tube was sealed for ESR measurements.

ESR spectra were measured with an x-band ESR spectrometer (Varian E-12, 100 kHz field modulation). To avoid distortion of the spectra by a power saturation, the ESR measurements were carried out at a microwave of 3 mW. The g-value was measured by comparison with the strong pitch provided by Varian Associates. In all cases, ESR spectra were recorded at 77°K.

Estimates of the changes in degree of polymerization (D.P.) during millings were made from intrinsic viscosity values $[\eta]$ obtained by using a capillary viscometer. The measurements were carried out in a thermostat at 25.00 ± 0.05°C in cupriethylenediamine solution, and converted to D.P. by using the equations[22]

$$[\eta] = KM^{\alpha}$$

$$\text{D.P.} = 156[\eta]$$

Graft copolymerization was carried out under vacuum in a milling system consisting of 0.3 g cellulose and 0.5 ml methyl methacrylate for certain periods. The copolymerization products were washed with water and extracted with acetone for 48 hr to remove homopolymers. The percent grafting was taken as the percentage weight increase of the original cellulose sample.

RESULTS AND DISCUSSION

General Mechanochemistry of Polymers[23]

The basic principle underlying mechanochemical polymeric reactions is the scission of carbon–carbon, carbon–oxygen, or other chemical bonds within the backbone of a polymer macromolecule under the influence of an applied mechanical stress. The mechanochemistry of polymers includes processes in which

mechanical stress initiates or accelerates the development of chemical reactions or influences them in some other way.

Basically, in the mechanical process, when a polymeric solid or liquid is subjected to an applied stress, individual macromolecules deform to try to reach new equilibrium positions. When the resulting mechanical forces acting on the polymer overcome intramolecular forces holding the polymer together, rupture of primary chemical bonds may take place. Mechanochemistry thus involves a reaction for which the activation energy is supplied mechanically. Its consequence is chain rupture and subsequent formation of macroradicals or mechanoradicals. The magnitude of the experienced internal forces that lead to chain rupture depends predominantly on the stress and on the local molecular structure. Usually the crosslinks or the junction points of entangled molecules are considered the position of high energy, although the maximum might be midway between entanglements. The reactivity and the fate of macroradicals in mechanically degraded polymers depends on the particular environment in which they are formed as well as the structure of the polymer in question. They can participate in a wide variety of reactions to form new terminal groups. In the presence of free-radical scavengers such as oxygen, a peroxy compound may result. In an inert atmosphere in the absence of radical scavengers, recombination, disproportionation, or other reactions may occur. All of these reactions will influence the physical, mechanical, and chemical properties of the polymer. These general aspects of mechanochemistry are undoubtedly applicable to the cellulose macromolecule.

Change of Degree of Polymerization

It has been known that a decrease in the degree of polymerization (D.P.) of the cellulose macromolecule takes place when the polymer is subjected to mechanical stress. In order to provide a fundamental understanding of mechanical force on cellulose fiber by the milling system in this study, change in D.P. of cellulose was examined. Results are shown in Figure 2. It was recognized that the D.P. of cellulose fibers decreased when the polymer was milled either in the presence of nitrogen or in oxygen; and the magnitude of decrease was accelerated by the presence of oxygen. As will be discussed later, it was found that mechanoradicals were generated in cellulose fibers by mechanical force. It is probable that mechanoradicals are rapidly scavenged by oxygen molecules eliminating the possibility of radical recombination reactions; hence, the rate of decrease in D.P. is enhanced. This was also substantiated by the identification of peroxy radicals by ESR studies, as reported in a subsequent section. It is clear that the D.P. of the milled samples leveled off after 6 hr of milling in both cases.

Formation of Mechanoradicals in Cellulose Fiber

In order to procure information on mechanoradical formation in mechanically degraded cellulose, the treated samples were prepared for ESR studies. As a consequence of the absence of intrinsic free radicals, no ESR signals were detected from cellulose fiber prior to any mechanical treatment, namely, milling.

When cellulose was milled under vacuum for 3 hr at ambient temperature and

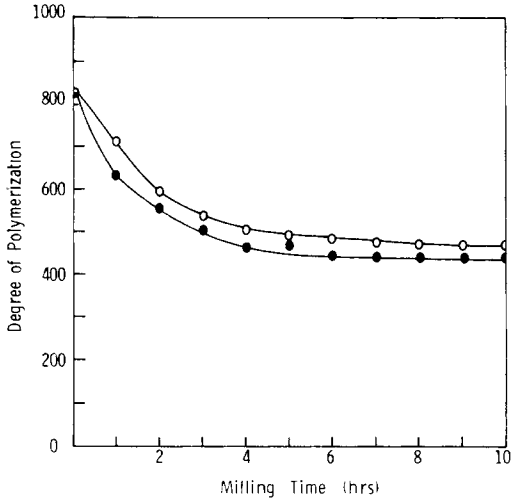

Fig. 2. Decrease of degree of polymerization of cellulose during glass-bead milling in (○) nitrogen and (●) oxygen at ambient temperature.

measured by the ESR spectrometer at 77°K, a poorly resolved multiplet signal with a g-value of 2.003 was detected; when the sample was milled under vacuum at 77°K, a weak five-line signal was detected, as shown in Figure 3. Sample milled at ambient temperature required a larger modulation than that milled at 77°K. In other words, the overall ESR signal intensity was 18 times more intense for the sample milled at 77°K than that milled at ambient temperature. This demonstrates that labile mechanoradicals were unable to survive at ambient temperature. Only the long-lived mechanoradicals can survive at ambient temperature.

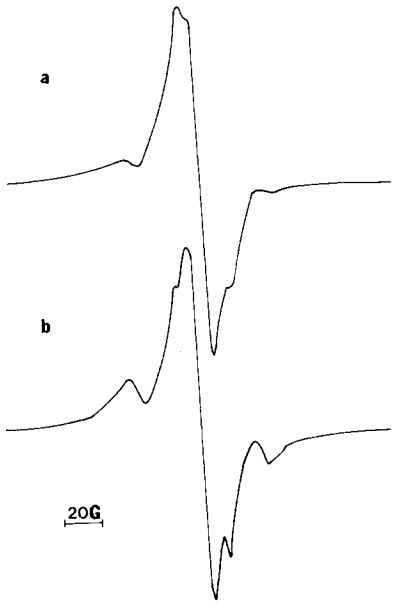

Fig. 3. ESR spectra of cellulose milled under vacuum at (a) ambient temperature and (b) 77°K for 3 hr. Spectra well recorded at 77°K.

After the samples were milled under vacuum for 3 hr at ambient temperature and at 77°K, oxygen was introduced into the sample 60 min prior to ESR measurements. It is noteworthy that although the ESR line shapes for both samples were not altered, the intensities of the signals were reduced to 16% and 38% of their original values respectively for samples milled at ambient temperature and at 77°K. This demonstrated that mechanoradicals were intercepted or interacted with oxygen molecules. However, no peroxy radicals were detected in either sample.

When cellulose fiber was milled in the presence of oxygen at ambient temperature, a very weak singlet signal was detected from the sample; when the sample was milled in the presence of liquid air or in liquid nitrogen at 77°K a different feature of interest was readily recognized. The typical spectrum observed is shown in Figure 4. This spectrum displayed definite symmetrical properties, representing the powder pattern of axially symmetrical ESR peaks. The g-values of $g_{\parallel}$ and $g_{\perp}$ are 2.007 and 2.034, respectively ($\bar{g} = 2.021$). Because of the similarity of the ESR pattern as well as the g-value to those from the peroxy radicals formed in cellulose and other polymers irradiated with light,[24,25] we see that mechanoradicals generated in cellulose fiber are capable of reacting with oxygen molecules to produce peroxy radicals. It is surprising that peroxy radicals were identified when the sample was milled in liquid nitrogen. It must be recognized, however, that it is extremely unlikely that liquid nitrogen can be purified and completely free from all traces of oxygen. Thus, peroxide radicals are formed from the interaction of mechanoradicals and traces of oxygen even at 77°K. Apparently, certain transient mechanoradicals produced in cellulose fiber were trapped at 77°K. These radicals are mobile and are capable of interacting with oxygen molecules to produce peroxy radicals. As previously indicated, no peroxy radicals had been detected when oxygen was introduced into the sample at 77°K,

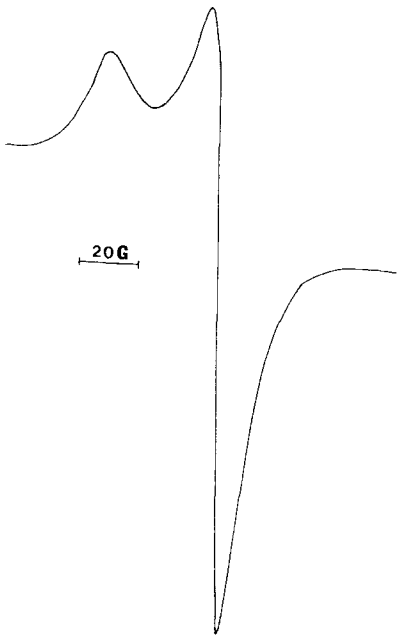

Fig. 4. ESR spectrum of cellulose milled in liquid nitrogen at 77°K and recorded at 77°K.

which was milled at ambient temperature or at 77°K. This difference in reactivity of radical reactions may be attributed to the low diffusion and reactivity of oxygen toward mechanoradicals occluded or inaccessible in fibers at this low temperature. From this observation, it is evident that oxygen present in the milling system was activated by mechanical energy; and the probability that oxygen molecules will trap transient mechanoradicals generated at the newly formed surface of cellulose fiber is high.

In order to obtain more information on the mechanical degradation of cellulose, D-glucose and cellobiose were used in the identical milling conditions as those for cellulose at 77°K. No ESR signals were detected from either sample, demonstrating that free radicals were not produced in low molecular weight compounds. The formation of mechanoradicals in cellulose fiber is primarily due to the scission of the polymer backbone.

Finally, it should be mentioned here that experiments in which the test samples were replaced with powdered Pyrex glass showed that Pyrex beads were not responsible for the ESR signals.

Stability of Primary Mechanoradicals in Cellulose Fiber

All of the ESR observations in our experiments were carried out at 77°K. It has been noted that mechanoradicals formed in cellulose fiber are capable of undergoing secondary reactions, implying that mechanoradicals generated in the system are very active. Hence, it is necessary to pinpoint the stability of mechanoradicals at this temperature, i.e., at 77°K. For this purpose, the sample after milling at 77°K was transferred to a sample tube, which was then inserted into a Dewar flask with liquid nitrogen and placed into the ESR cavity for measurements without any warming. The intensities of the ESR spectra were examined for a long time. The first observation was made immediately after milling. There was practically no change in the intensities of ESR spectra of any samples. The line shapes of the spectra also did not change throughout this experiment. Therefore, it is clear that mechanoradicals formed in cellulose fibers are very stable at 77°K.

However, when samples after milling at 77°K are treated repeatedly for a certain duration at ambient temperature, an array of spectra indicating changes in the hyperfine structure as the resonance signal decayed were observed. For the sample milled at 77°K under vacuum, the decay of ESR signals as a consequence of decay of mechanoradicals is shown in Figure 5. When the sample was warmed to 298°K for 30 sec and the spectra recorded again at 77°K, the intensity of the spectra decreased, and the five-line signal was transformed to a three-line signal as shown in Figure 5(b). It is obvious that a signal having a principal peak of 23.5 gauss splitting constant had disappeared. This signal has been assigned to be derived from a doublet component.[26] When the sample was warmed at 298°K for 20 min, the three-line signal decayed further, and only a singlet signal with a splitting constant of 17 gauss remained. This change also infers that the radicals corresponding to the triplet component (34 gauss splitting constant) of the spectrum had disappeared. This change of ESR profile by the "warm-up" process suggests that the spectrum shown in Figure 5(a) is not a single spectrum originating from a single radical species but is the superposition of three radical species corresponding to a singlet, a doublet, and a triplet component. It is

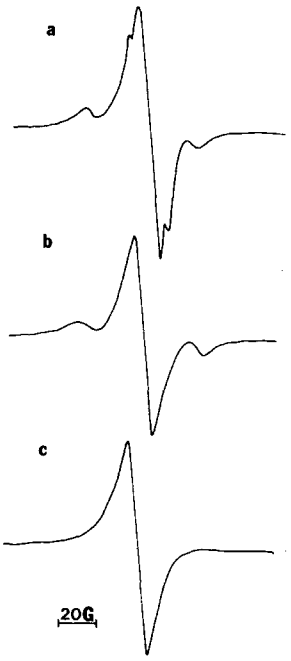

Fig. 5. Change and decay of ESR spectra of cellulose after milling under vacuum at 77°K for 3 hr: (a) initial spectrum observed at 77°K immediately after milling without any warming; (b) warming for 30 sec; (c) warming for 20 min at 298°K and recorded at 77°K.

obvious that of these three mechanoradicals, the one attributed to the singlet signal had the highest stability at 298°K.

Different aspects of mechanoradical decay were observed from the sample milled in oxygen or liquid nitrogen at 77°K. The change in the asymmetrical pattern of peroxy radicals upon the "warm-up" process is shown in Figure 6. It is apparent that when the milled sample was warmed to 298°K for 6 min, the asymmetrical spectrum was transformed to a singlet spectrum with a splitting constant of 18 gauss. The overall intensity of the signal also dwindled. Accordingly, it can be deduced that the peroxy radicals were very unstable at 298°K (they underwent secondary reactions rapidly) whereas the mechanoradicals which generated a singlet signal were relatively stable at this temperature. It is very interesting that neither doublet nor triplet signal was observed during the "warm-up" process. This clearly indicates that the mechanoradicals corresponding to doublet and triplet signals interacted with oxygen to form peroxy radicals at 77°K during milling. The mechanoradicals corresponding to the singlet signals were inert toward oxygen molecules.

Mechanisms of Mechanoradical Formation in Cellulose Fiber

ESR findings reveal that at least three kinds of mechanoradicals were formed in cellulose fiber during mechanical action. These radicals correspond to singlet, doublet, and triplet ESR signals. Of these radicals, those corresponding to the doublet and triplet signals are unstable at 298°K and are capable of reacting with oxygen molecules to produce peroxy radicals; those radicals corresponding to

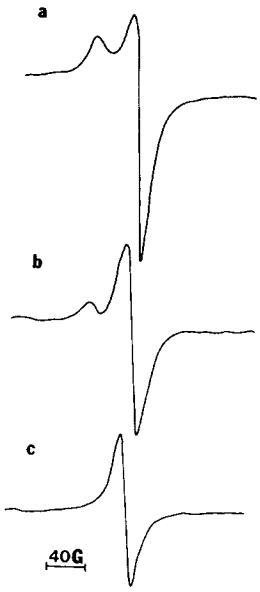

Fig. 6. Change and decay of ESR spectrum of cellulose after milling in liquid nitrogen at 77°K: (a) initial spectrum observed at 77°K immediately after milling without any warming; (b) warming for 3 min; (c) warming for 6 min at 298°K and recorded at 77°K.

the singlet signal were rather stable at 298°K and did not interact with oxygen molecules.

Moreover, the decrease in D.P. of cellulose fiber after milling clearly demonstrated that chain scission of the polymer took place by mechanical action.

Accordingly, with the rupture of the glucosidic bonds, namely, depolymerization, two radical sites are concurrently produced in cellulose molecules. The two possible ways that glucosidic bonds may rupture are shown in eqs. (1) and (2):

$$R_{cell}—C_1—O—C_4—R_{cell} \xrightarrow{M.E.} R_{cell}—C_1—O\cdot + \cdot C_4—R_{cell} \quad (1)$$

$$R_{cell}—C_1—O—C_4—R_{cell} \xrightarrow{M.E.} R_{cell}—C_1\cdot + \cdot O—C_4—R_{cell} \quad (2)$$

where R_{cell} represents the cellulose molecule and M.E. is mechanical energy.

Mechanoradicals generated at $\cdot C_4—R_{cell}$ sites may be expected to interact with protons at C_4, C_3, and C_5 positions to exhibit an intricate spectrum which has not been detected in this work. It is plausible to consider that $R_{cell}—C_1\cdot$ and $\cdot O—C_4—R_{cell}$, as denoted in eq. (2), were actually formed, generating a doublet and a singlet signal, respectively. The presence of these radicals has been recognized in photoirradiated pulp cellulose,[26,27] and their corresponding singlet and doublet ESR ignals resemble those observed in this study.

Furthermore, in the mechanical process, the deformed cellulose fiber may also exert a drag on the carbon-to-carbon bonds along the polymer molecules. When the C_2–C_3 bonds were ruptured, mechanoradicals thus formed would exhibit triplet signals.[27] While cleavage of C_1–C_2, C_3–C_4, C_4–C_5, C_5–O, and C_5–C_6 may occur, the corresponding signals derived from these signals have not been detected in this study. Therefore, it is reasonable that the three-line signals observed in this study were due to the cleavage of C_2–C_3 bonds in cellulose molecules. The other possibility is that free radicals generated at C_2, C_3, C_4, and C_6

positions by dehydrogenation reactions may generate triplet signals; however, under mechanical stress this reaction is unlikely.

Based on these experimental data, it can be stated that the singlet signals are derived from the alkoxy radicals ($R_{cell}—C_4—O\cdot$), whereas the triplet signals are derived from carbon radicals located at the C_2 and C_3, the doublet signals from C_1 positions. These carbon radicals interacted with oxygen molecules to produce peroxy radicals.

Comparison with Other Work

Several ESR studies on mechanical degradation of cellulose have appeared in the literature. The results reported are compared with those of the present work.

Ott[11] observed a diffuse multiplet ESR signal from cotton linters after milling them at ambient temperautre. He indicated that three types of radicals may be produced in cotton cellulose but failed to interpret the spectrum observed. It is believed that if he could have carried out his experiment at low temperature such as at 77°K, he would have detected ESR spectra with better resolution for interpretation. Likewise, Urbanski[18] observed a singlet signal from cellulose after milling. No interpretation was attempted by the author.

Abagyan and Butyagin[17] reported that several types of mechanoradicals were observed in polysaccharides after milling at 77°K. Their ESR interpretation is entirely contrasted with our observation. The comparison of these results on cellulose after milling is shown in Table I.

From the study of decrease of D.P. as well as from the available doucments on ESR spectra of cellulose and other polymers, we believe that the mechanoradicals generating the singlet and doublet signals are derived from $R_{cell}—C_4—O\cdot$ and $R_{cell}—C_1\cdot$ radicals due to the cleavage of glucosidic bonds. However, Abagyan and Butyagin indicated that radicals with a free valence on the oxygen atom, which could have been formed during the cleavage of the glucosidic bonds, were not detected in their work. They further interpreted the singlet signals they detected as corresponding to radicals with a free valence localized on the oxygen atom, but with uncertainty.

We did not detect the signal of the quadruplet which they interpreted as corresponding to the primary radicals with a free valence at the C_5 position. It is hard to think that the cleavage of carbon-to-hydrogen bonds at C_5 could be caused by mechanical force. There is a possibility that the radicals at the C_5

TABLE I
Comparison of ESR Spectra of Cellulosic Mechanoradicals

ESR	Hon[a]	Abagyan and Butyagin[b]
Singlet	$R_{cell}—C_4—O\cdot$	oxygen radicals (?)
Doublet	$R_{cell}—C_1\cdot$	$R_{cell}—O\cdot$
Triplet	rupture of C_2–C_3 bonds	—
Quadruplet	—	$R_{cell}—C_5\cdot$ (due to hydrogen abstraction)

[a] This work.

[b] Abagyan and Butyagin.[17]

position can be generated as a result of hydrogen abstraction by other mechanoradicals. If this reaction occurred, the radicals at C_5 thus formed should be secondary radicals rather than the primary radicals as stated by the authors.

Finally, it is worthwhile noting here that we do not intend to deny the different spectra observed by other investigators. The reasons for this apparent contradiction could be due to difference in milling or the nature of the cellulose fibers used.

Ability of Cellulose Mechanoradicals to Initiate Graft Copolymerization

Mechanoradicals were essentially produced in cellulose by means of mechanical treatments. These mechanoradicals may be used as reaction sites for the initiation of vinyl polymerization which would result in graft copolymers of cellulose. Based on this principle, the ability of cellulose mechanoradicals to initiate copolymerization was pursued.

After cellulose was milled under vacuum at 77°K for 3 hr and transferred to a sample tube for ESR measurement at 77°K, a five-line spectrum was observed as shown in Figure 7(a) [previously shown in Fig. 3(b)]. Following this, 0.5 ml of methyl methacrylate (MMA) was injected into the sample tube. No change of ESR pattern was recognized. The sample tube was subsequently allowed to warm up to 298°K for 2 min; and, recorded again at 77°K, the five-line ESR spectrum of the cellulosic mechanoradicals was converted to an asymmetrical multiplet spectrum [Fig. 7(b)], and these signals were further intensified when the sample was warmed for 5 min at 298°K. When the sample was further warmed at 298°K for 10 min, the ESR spectrum observed at 77°K was a nine-line spectrum, as shown in Figure 7(d). This nine-line spectrum originated from characteristic propagating radicals of MMA for polymerization.[28] These propagating radicals of MMA were not detected when the monomer was added to untreated cellulose fibers in identical experiments. This clearly indicated that propagating radicals of MMA were created by contact of MMA with cellulosic mechanoradicals. Subsequently, cellulosic mechanoradicals are capable of initiating vinyl copolymerization. In light of this finding, graft copolymerization of MMA onto cellulose fiber was carried out at ambient temperature by introducing monomer to fiber prior to milling.

Although it was found that propagating radicals of MMA were created by the contact of MMA with cellulosic mechanoradicals at 77°K, graft copolymerization of MMA onto cellulose fiber was not significant at ambient temperature. Results of grafting are 3%, 8%, and 25% for 1, 2, and 3 hr of reactions, respectively. At ambient temperature, MMA molecules may not transfer or penetrate sufficiently or efficiently enough to trap the unstable cellulosic mechanoradicals before they undergo secondary reactions. The use of swelling agents for the milling system may eliminate this difficulty. It should be mentioned here that from this preliminary study, it is obvious that much work is necessary regarding grafting conditions before any definite conclusion can be drawn about the efficiency of the grafting reaction as well as the detailed mechanisms of the graft copolymerization.

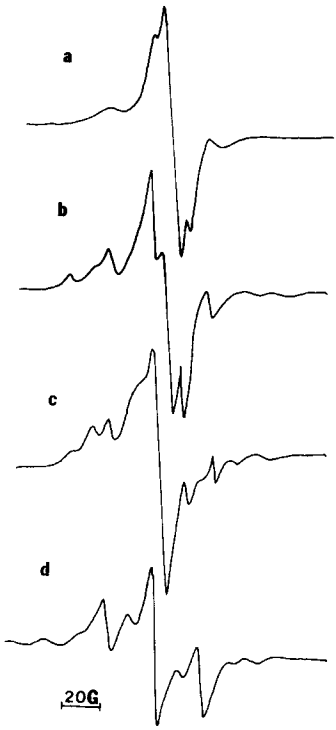

Fig. 7. Changes in ESR spectra of cellulosic mechanoradicals: (a) initial spectrum observed at 77°K immediately after milling; cellulose after milling was contacted with MMA and warmed at 298°K for (b) 2 min; (c) 5 min; (d) 10 min and recorded at 77°K.

CONCLUSIONS

This study reveals that cellulose fiber is susceptible to degradation by mechanical treatments. The degradation process occurs via free-radical routes. Three kinds of ESR signals, namely, singlet, doublet, and triplet, corresponding to three different kinds of mechanoradicals produced in cellulose fiber, are identified during the mechanical treatments. Mechanoradicals contributing the singlet signals are derived from the alkoxy radicals at the C_4 position due to depolymerization, that is due to the cleavage of glucosidic bonds. This reaction is substantiated by the observation of a decrease in D.P. after milling the sample. The radical pairs generated at the C_1 position after the cleavage of glucosidic bonds contribute the doublet signals. Triplet signals are derived from C_2 and C_3 positions due to the cleavage of C_2 and C_3 bonds. Among these radicals, the alkoxy radicals are the most stable at 298°K. It is found that carbon radicals are capable of interacting with oxygen molecules to produce peroxy radicals; alkoxy radicals are inert toward oxygen molecules. ESR study also reveals that cellulose mechanoradicals are capable of initiating vinyl polymerization. When MMA contacts mechanoradicals, propagating radicals of MMA are identified. However, a high degree of graft copolymerization of MMA onto cellulose fiber is not recognized. Further investigation on the optimization of experimental conditions for graft copolymerization seems to be needed.

References

1. L. F. McBurney, *Mechanical Degradation in Cellulose and Cellulose Derivatives*, E. Ott, H. M. Spurlin, and M. W. Graffin, Eds., Part 1, Interscience, New York, 1954, p. 191.
2. P. Waentig, *Text. Forsch.*, **3**, 154 (1921).
3. K. Hess, Steurer and H. Fromm, *Kolloid-Z.*, **98**, 148, 290 (1942).
4. K. Hess and K. E. Heumann, *Ber.*, **75B**, 1802 (1942).
5. K. Hess and E. Steurer, *Z. Phys. Chem.*, **193**, 234 (1944).
6. H. Grohn and W. Deters, *Faserforsch. Textiltech.*, **13**, 544 (1962).
7. A. Assarsson, B. Lindberg, and O. Theander, *Acta Chem. Scand.*, **13**, 1231 (1959).
8. J. A. Howsman and R. H. Marchessault, *J. Appl. Polym. Sci.*, **1**, 313 (1959).
9. C. Simionescu and C. Vasiliu-Oprea, *Cellul. Chem. Technol.*, **2**, 155 (1968).
10. C. Simionescu, C. Vasiliu-Opera, and L. Sarosi, *Celul. Hirtie*, **17**, 403 (1968).
11. R. L. Ott, *J. Polym. Sci.*, **A2**, 973 (1964); see also R. L. Ott, Ph.D. Thesis, Lawrence College, Appleton, Wisconsin, 1963.
12. A. N. Dubinskaya and P. Yu. Butyagin, *Vysokomol. Soedin.*, **B9**, 525 (1967).
13. V. A. Malchevskii, O. F. Pozdnyakov, V. R. Regel, and M. G. Falkovskii, *Vysokomol. Soedin.*, **A13**, 2078 (1971); *Polym. Sci. USSR*, **9**, 2334 (1971).
14. P. Yu. Butyagin, *Dokl. Akad. Nauk SSSR*, **140**, 145 (1961).
15. T. N. Kleinert and J. R. Morton, *Nature*, **196**, 334 (1962).
16. K. Ulbert and P. Yu. Butyagin, Dokl. Akad. Nauk SSSR, **149**, 1194 (1963).
17. G. V. Abagyan and P. Yu. Butyagin, *Vysokomol. Soedin.*, **7**, 1410 (1965).
18. T. Urbanski, *Nature*, **216**, 577 (1967).
19. V. A. Malchevskii and V. A. Zakrevskii, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **15**, 276 (1972).
20. A. Casale and R. S. Porter, *Adv. Polym. Sci.*, **17**, 1 (1975).
21. A. G. Norman and S. H. Jenkins, *Biochem. J.*, **27**, 818 (1933).
22. E. H. Immergut, B. C. Rånby, and H. F. Mark, *Ing. Eng. Chem.*, **45**, 2483 (1953).
23. N. K. Baramboim, *Mechanochemistry of Polymers*, translated from Russian by R. J. Moseley, W. F. Watson, Ed., Rubber and Plastic Research Association of Great Britain, Maclaren, London, 1964.
24. D. N.-S. Hon, paper presented at the 174th National Meeting of the American Chemical Society in Chicago, Illinois, August 28–September 2, 1977.
25. S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Polym. Sci.*, **A1**, 605 (1963).
26. N.-S. Hon, *J. Macromol. Sci.-Chem.*, **A10**, 1175 (1976).
27. N.-S. Hon, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2497 (1976).
28. D. Campbell, *Macromol. Rev.*, **4**, 91 (1970).

Received March 2, 1978
Revised April 7, 1978