The structure and mechanical properties of sheets prepared from bacterial cellulose

Part 2 *Improvement of the mechanical properties of sheets and their applicability to diaphragms of electroacoustic transducers*

Y. NISHI
Sony Research Centre, 174 Fujitsuka-cho, Hodogaya-ku, Yokohama 240, Japan
M. URYU
Sony Corporate Research Laboratories, 1-7-4 Konan, Minato-ku, Tokyo 108, Japan
S. YAMANAKA, K. WATANABE, N. KITAMURA
Central Research Laboratories, Ajinomoto Co., Inc., 1-1 Suzuki-cho, Kawasaki-ku, Kawasaki 210, Japan
M. IGUCHI, S. MITSUHASHI
Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

A sheet obtained from bacterial cellulose had a remarkably high modulus of elasticity as reported in Part 1 of this series. The Young's modulus of a sheet prepared by squeezing and drying a gel-like pellicle of bacterial cellulose was found to be >15 GPa. In addition, it has been found that treatment of the gel-like pellicles or dried sheets of bacterial cellulose with alkaline and/or oxidative solutions improves the mechanical properties significantly, and the Young's modulus of the resulting sheets approaches 30 GPa. In this paper, improvement of the mechanical properties of bacterial cellulose sheets by the removal of impurities is investigated and the applicability of bacterial cellulose to diaphragms of electroacoustic transducers is discussed.

1. Introduction

In recent years, a variety of materials has been introduced for the preparation of diaphragms for electroacoustic transducers, i.e. loudspeakers, headsets, etc. Some physical requirements for materials to be used for acoustic diaphragms are high Young's modulus, high internal loss, low density and high sound propagation velocity.

Traditionally, diaphragms of loudspeakers are made from paper (so-called "cone paper") formed with cellulose fibres, because the material can be processed into a lightweight diaphragm with a relatively high internal loss (or tan δ). Cone paper, however, has a too limited range of Young's modulus (E) and sound propagation velocity (C) to provide satisfactory flexural rigidity, and attaining sufficient expansion of the width of the reproduction frequency band is difficult.

Light metals such as aluminium and titanium (E = 70 and 110 GPa, respectively, and $C = 5\,000\,\mathrm{m\,sec^{-1}}$ for both) are also used as diaphragm materials for loudspeakers, especially for tweeters. However, tan δ of these metals is restricted to a very low value, around 0.001. It may safely be said that few materials are known to combine high E or C with a high tan δ.

As reported in Part 1 [1] of this study, a sheet prepared from a gel-like pellicle of bacterial cellulose (BC) has been found to have the highest E ever known in two-dimensional organic materials. A preliminary investigation showed that this material possessed a number of desirable features for a transducer diaphragm material. In this paper, improvement of the mechanical properties of BC sheets by alkaline and/or oxidative treatment and the effect of the concentration of the treatment solution have been studied and the applicability to a transducer diaphragm is discussed.

2. Experimental procedure

2.1. Production of bacterial cellulose

Procedures for the fermentative production of BC pellicles were described in Part 1 [1] of this series.

2.2. Treatment solutions

NaOH 0 to 12% (wt/wt) aqueous solutions were prepared with deionized water and the concentration was determined by titrating with a 0.1 N HCl solution.

NaClO 0 to 1.0% (wt/wt, as active Cl) solutions were prepared by diluting a commercial NaClO solution (active Cl ~ 5%) and the concentration of active Cl was determined by iodometry [2]. Usually, a commercial NaClO solution contains a small amount of NaOH and its concentration in the 1.0% NaClO solution was determined to be 0.84% by acid titration. In order to eliminate the effect of the NaOH

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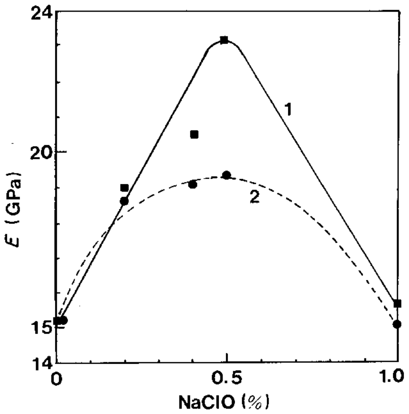

Figure 1 Dynamic Young's modulus of NaClO treated sheets plotted against NaClO concentration. Curve 1, Method B; Curve 2 Method C.

concentration, all the NaClO preparations were adjusted to contain the same amount of NaOH as the 1.0% NaClO solution by adding NaOH.

2.3. Preparation of sheets

A gel-like pellicle of BC as-produced was washed thoroughly in running water and was used as the starting material. BC sheets were prepared by the three different procedures.

Method A. A washed gel-like pellicle was sandwiched between two stainless steel plates to squeeze out water, and then dried at 120° C under pressure of $1\,\mathrm{kg\,cm^{-2}}$.

Method B. A gel-like pellicle was soaked in treatment solutions for 15 h followed by washing completely with running water. The pellicle was then squeezed and dried in the same way as described in Method A.

Method C. Dried sheets prepared by Method A were soaked in the treatment solution for 15 h followed by a complete wash with running water. Treated sheets were dried between two stainless steel plates at 120° C under $1\,\mathrm{kg\,cm^{-2}}$ pressure.

2.4. Measurement of physical properties

E and tan δ were measured by the vibrating reed method. Rectangular specimens, 5 mm wide and 40 mm long, were cut from BC sheets and were used

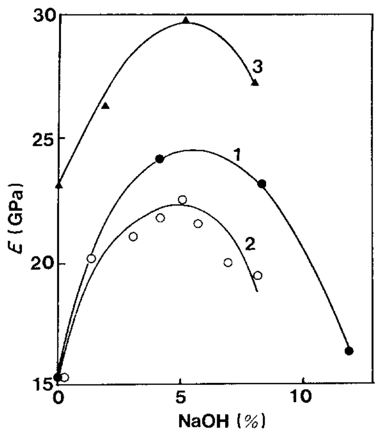

Figure 2 Dynamic Young's modulus of NaOH treated sheets plotted against NaOH concentration. Curve 1, Method B; Curve 2, Method C; Curve 3, double treatment with NaClO and NaOH solutions (for details, see text).

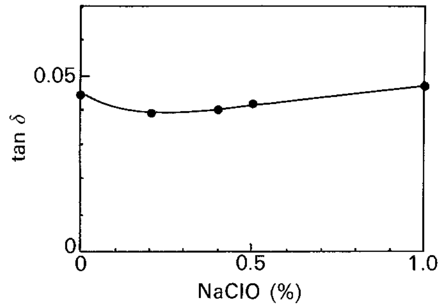

Figure 3 Effect of NaClO treatment on tan δ of BC sheets.

for measurement. E was calculated as usual from the resonant frequency and dimensional parameters [3] and tan δ was obtained from the sharpness of the resonant peaks [4]. C was calculated as the square root of E divided by density (ρ).

3. Results

3.1. Young's modulus of sheets

Fig. 1 shows the effect of NaClO concentration on E of the sheets prepared by Method B from the gel-like pellicle treated with NaClO solutions (Curve 1). The figure shows that E increased with increasing NaClO concentration, passed through a maximum at 0.5%, and then decreased. The sheets prepared by Method C showed a similar tendency (Fig. 1, Curve 2).

The effect of NaOH concentration is shown in Fig. 2. Similar results as in the NaClO treatment can be observed, and the optimum NaOH concentration was 5%. E of the sheets prepared by Method B was somewhat higher than E of those prepared by Method C in both NaOH and NaClO treatments.

An NaOH treatment following the NaClO treatment, or vice versa was also attempted. Sheets were prepared by Method B from 0.5% NaClO treated pellicles and then treated subsequently with NaOH solutions of various concentrations followed by drying by Method C. The sheets obtained showed much higher E than the sheets prepared by single treatment with a NaOH or NaClO solution (Fig. 2, Curve 3).

The highest values of E and C were about 30 GPa and $5000\,\mathrm{m\,sec^{-1}}$, respectively, which were attained when the sheets obtained by Method B using a 0.5% NaClO solution was further treated with a 5% NaOH solution followed by drying through Method C. It must be noted, however, that the treatment with a mixed solution of NaOH and NaClO was less effective and E of the sheets treated with a solution containing 5% NaOH and 0.5% NaClO was only 19.2 GPa.

3.2. Internal loss

Internal loss (tan δ) of a sheet prepared by Method A was determined to be 0.044, which was comparable to ordinary cone paper. Because materials of high modulus, in general, show limited internal loss, it was anticipated that an increase of E by the treatments would bring about an unavoidable drop in tan δ. As shown in Fig. 3, however, the decrease of tan δ after NaClO treatment was only moderate and the value remained at a satisfactory level for acoustic materials, despite the significant increase of E as observed in

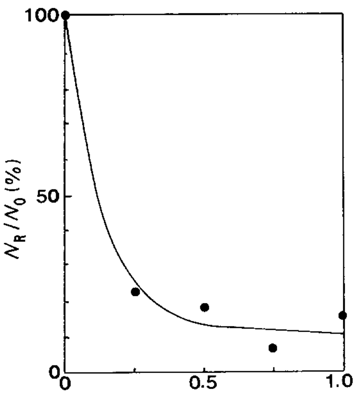

Figure 4 Effect of NaClO concentration on amounts of Kjeldahl nitrogen remaining in the BC sheets after NaClO treatment. N_R, nitrogen in sheets after treatment; N_0, nitrogen in sheets before treatment.

Fig. 1. The effect of NaOH on tan δ was as slight as that of NaClO.

4. Discussion

4.1. Effect of NaClO treatment

It is believed that three factors are responsible for determining the elastic modulus of a cellulosic sheet [5].

1. The elastic modulus of the fibres. For well-bonded sheets of long and straight fibres, the modulus of the sheet is experimentally of the order of one-third of the modulus of the fibres.

2. The degree of bonding. Because of the transfer of load from the fibre to the network near the ends of the fibre, the modulus falls short of the theoretical value, and the extent to which it falls short depends on the degree of bonding.

3. The presence of curl, kinks or crimps. This lowers the modulus of the sheet.

The NaClO treatment was considered to dissolve the non-cellulosic components (NCC) in BC. NCC were found to be mainly nitrogen-containing compounds such as proteins and nucleic acids derived from bacterial cells and the culture broth. Fig. 4 shows the Kjeldahl nitrogen remaining in the BC sheets after treatment with NaClO solutions of various concentrations. It can be seen from Fig. 4 that 80% to 90% of the nitrogen was removed by the treatment.

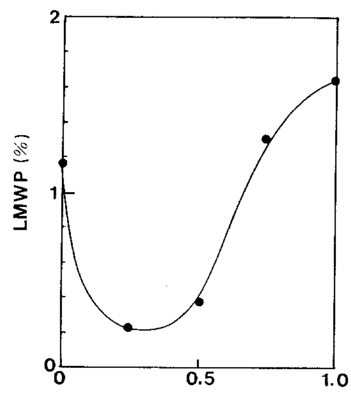

Figure 5 LMWP amounts remaining in NaClO treated BC sheets plotted against NaClO concentration.

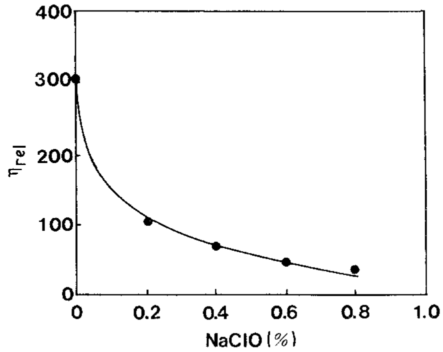

Figure 6 Effect of NaClO treatment on relative viscosity of BC/dimethylacetamide/lithium chloride solution.

NaClO treated BC was soaked in a 18% NaOH solution to extract polysaccharides other than α-cellulose [6]. From the infrared spectrum, the extracts were identified to be a polysaccharide homologue, presumably low molecular weight polysaccharides (LMWP).

It is not likely that LMWP was dissolved completely during the course of the NaClO treatment but it is probable that small amounts of LMWP were left undissolved in the sheets. Fig. 5 shows the amount of LMWP remaining in BC sheets after the treatment with NaClO solutions, measured by analysis of alkali (18% NaOH) extracts using the phenol–sulphuric acid method [7]. It is seen that a 0.25% NaClO solution removed LMWP effectively from BC sheets but LMWP had a greater tendency at higher NaClO concentrations.

Because it was considered that the concentrated NaClO solutions oxidized and degraded cellulose, changes of the molecular weight of BC were examined from the solution viscosities. BC treated with NaClO solutions of various concentrations was dissolved at a concentration of 1% (wt/wt) in a 90/10 mixture of dimethylacetamide and lithium chloride [8], and the viscosity was measured by a conventional method with a rotational viscometer. As shown in Fig. 6, the relative viscosity, η_{rel}, decreased significantly with NaClO concentrations indicating that disintegration of the molecular chains of BC occurred through oxidation to produce LMWP and caused the increase of LMWP at higher NaClO concentrations (Fig. 5).

Removal of NCC from BC would have increased the probability of direct or close contact between cellulose fibrils, resulting in the formation of strong intra- and inter-fibrillar hydrogen bonds. Too concentrated NaClO solutions, however, induced the destruction of the cellulose fibrils and changed the mechanical properties of the sheets.

The optimum NaClO concentration of 0.5%, observed in Fig. 1 with respect to the Young's modulus, corresponds to the concentration in which a large portion of NCC was removed (Fig. 4) and the loss of strength of the fibrils by molecular degradation was not considered to be fatal at this concentration.

As an oxidative treatment solution, the effect of H_2O_2 was also examined. Similar results as in the NaClO treatment were observed and the highest E of 24.8 GPa was obtained with a slightly alkaline solution of 0.75% H_2O_2.

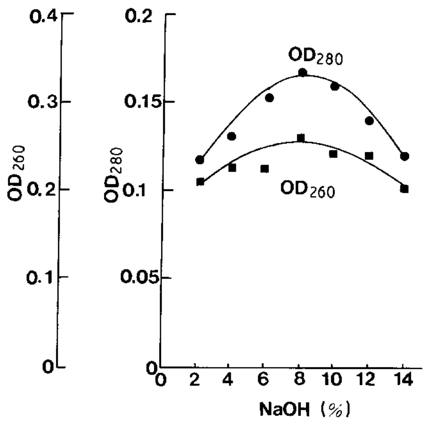

Figure 7 Proteins and nucleic acids leached out into an NaOH solution plotted against NaOH concentration. OD_{260} and OD_{280}: see text.

4.2. Effect of NaOH treatment

NaOH solutions were also considered to dissolve NCC. Fig. 7 shows the amounts of proteins and nucleic acids leached out into the NaOH solution from BC sheets and they were determined by measuring the optical densities at 280 nm (OD_{280}) and 260 nm (OD_{260}), respectively, with an ultra violet spectrophotometer. It is observed in Fig. 7 that the extracted NCC increased with the concentration of NaOH solution, passed through a maximum at 8% and then decreased.

With concentrated NaOH solutions above 6%, however, significant shrinkage or curling of the BC sheets was observed and the higher the concentration of the NaOH solution, the more severe were these deformations of the sheets. The reason for the decreased dissolution of NCC in concentrated NaOH solutions is not clear, but one possibility is that these components were confined within the cellulose texture owing to the severe shrinkage of the sheets and that the dissolution was thereby impeded.

Fig. 8 shows the LMWP remaining in the BC sheets after treatment with NaOH solutions measured by the same method used in Fig. 5 and little disintegration of fibrils was indicated even at higher NaOH concen-

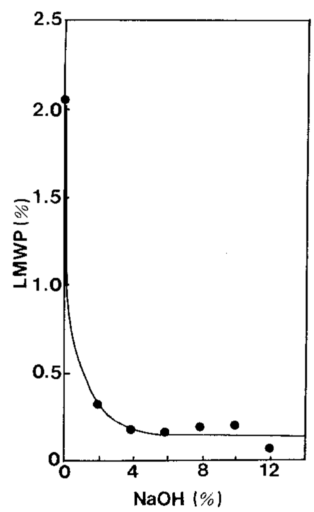

Figure 8 LMWP remaining in NaOH treated BC sheets plotted against NaOH concentration.

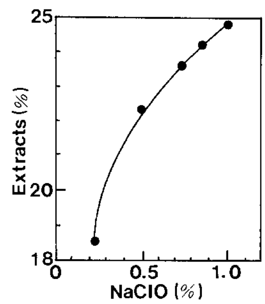

Figure 9 Amounts of NCC and LMWP extracted by mixed solutions of 5% NaOH and NaClO of various concentrations.

trations. The results in Figs 7 and 8 suggest that the optimum NaOH concentration for the highest E might be 8% but experimentally a 5% NaOH solution gave the best results (Fig. 2). In an 8% NaOH solution, shrinkage and curling of fibrils were so severe that the decrease of the strength of sheets was unavoidable and this caused the shift of the optimum NaOH concentration from 8% to 5%, where little deformation of sheets was observed.

The treatment with mixed solutions of NaOH and NaClO was not so effective as independent treatments with each solution. Fig. 9 shows the amount of the extracts from BC sheets with the solutions consisting of 5% NaOH and NaClO of various concentrations. In Fig. 9, an abrupt increase of extracts is observed at higher NaClO concentrations and this may be attributed to the formation of a considerable amount of LMWP as a result of the extensive degradation of BC by the synergistic effect of the mixed solutions.

When a BC sheet is soaked in the treating solutions, swelling by water causes the rearrangement of interfibrillar hydrogen bonds which may bring about changes of mechanical properties of the sheets. To examine the possibility that swelling is responsible for some portions of the changes of the sheet properties by the treatments described in this work, the effect of swelling on the properties of BC sheets was investigated. The sheets prepared by Method A were soaked in distilled water overnight and then dried by Method C. The changes of the properties are shown in Table I and the effects were confirmed to be negligibly small.

5. Conclusion

E of the BC sheet prepared by treatment with the solutions described above reached 30 GPa, and C was estimated to be in the neighbourhood of 5000 m sec^{-1}. In addition, tan δ was encouragingly high for a material of high modulus, and these characteristics are most desirable for an acoustic material, especially for a transducer diaphragm material. For example, tan δ of the BC sheet with C of 5000 m sec^{-1} described above was 0.04, which was comparable to ordinary

TABLE I Effect of swelling of BC sheets in water on the acoustical properties of BC sheets

	E (GPa)	ρ (kg m^{-3})	tan δ	C (m sec^{-1})
Before soaking	15.1	1280	0.04	3420
After soaking	15.4	1310	0.04	3430

cone paper. E and C of cone paper, however, are 1.5 GPa and 1600 m sec^{-1}, respectively, and both are far below the values for BC sheets. On the other hand, materials with the same order of C as the BC sheet, aluminium and titanium for example, show only very low tan δ, at most 0.001. Because acoustic materials are required to have both high E (or high C) and high tan δ at the same time, the BC sheet may be considered to be a highly satisfactory material.

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