ORIGINAL ARTICLE

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Activated carbon sheet prepared from softwood acetic acid lignin

Abstract As an example of activated carbon (AC) moldings, AC sheets were prepared from thermoplastic acetic acid lignin by lamination. The resulting AC sheets are a new type of product that can be applied as water and air cleaners. Powdered softwood acetic acid lignin (SAL) was molded into sheets by a thermal pressing method. When the sheet was carbonized under a stream of nitrogen at 1000°C, it was deformed with expansion and contained much foam. The deformation during carbonization was suppressed by the addition of pulp to the lignin. A sheet prepared by mixing lignin with pulp was directly carbonized without thermostabilization. The carbonized sheet was activated with steam for 2h. The resulting AC sheet had adsorption properties, such as specific surface and iodine adsorption capacity, comparable to those of commercial AC powders or granules. Furthermore, the AC sheet had a larger capacity to adsorb methane than did the commercial AC powder. Therefore, SAL seems to be a promising source for the AC moldings.

Key words Activated carbon moldings · Activated carbon sheet · Cellulosic material · Methane adsorption · Pore distribution · Softwood acetic acid lignin · Thermostabilization
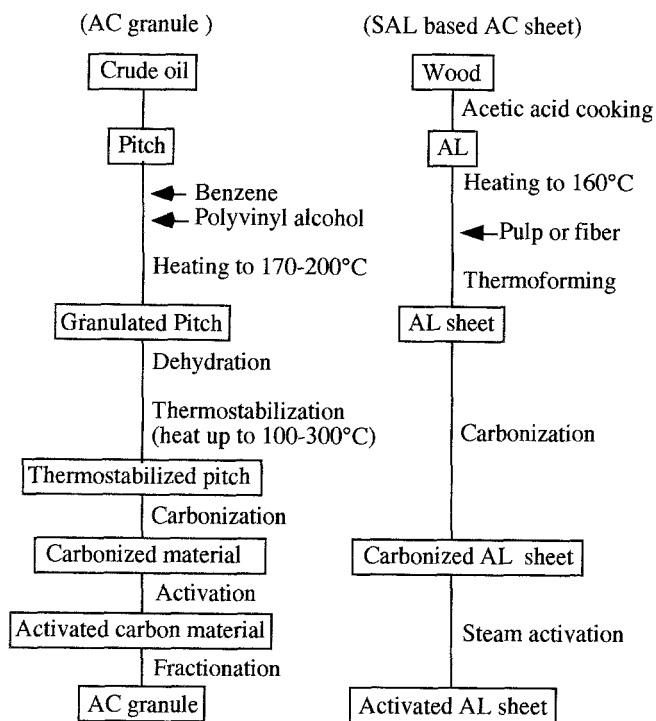
Introduction

Activated carbons (ACs) are excellent adsorbents for the pollutants and contaminants in industrial and domestic fields. AC is classified into three categories with respect to forms: powdery, granular, and fibrous. These forms affect the performance and handling of AC. AC powder has been used widely as a deodorant and decolorant since the end of the seventeenth century because of its rapid rate of adsorbing unwanted materials. Recently, AC powder from peat moss was utilized as the adsorbent for dioxins in the garbage incinerator. However, AC powder has some disadvantages. For example, it cannot be reused and scatters as small particles in the environment. The other AC forms, granule and fiber, have been developed to solve these problems. These ACs are considered for AC moldings. The AC fiber has the best adsorption property among the AC but is expensive. For industrial use, the AC granules have been utilized. AC granules have been developed by mixing pitch or coal with synthetic polymers, as shown in Fig. 1.[1] Such a complicated procedure during manufacture and the use of large quantities of solvents and additives are disadvantages of AC granules, leading to a high production cost. A requisite of AC moldings is thermoplasticity. Taking the utilization of unused biomass into consideration, thermoplastic technical lignins[2] that are by-products in the pulping process seem to be suitable sources for manufacture of AC moldings. In fact, molded AC granules have been produced from lignin that was obtained as a residue of wood saccharification.[3,4]

Acetic acid lignin (AL) obtained from spent liquor of atmospheric acetic acid pulping was considered the most suitable raw material for manufacture of AC moldings among the isolated lignins, as AL had unique thermal properties. In fact, AL from hardwood (HAL) had a fusion property so it could be converted to AC fiber after fusion spinning, as reported previously.[5,6] By contrast, AL from softwood (SAL) was not converted because it had only a thermal property that allowed glass transition (i.e., thermoplasticity) but not a fusion property.[7] However, SAL could also be spun and converted to carbon fibers (CFs) by removing the high-molecular-mass fraction from SAL.[8] On the production of CFs from SAL, the SAL fibers were suggested to be thermostabilized during the spinning.[9] This resulted in omission of the thermostabilization process during production of carbonaceous material from SAL. Such a thermal feature of SAL was expected to be an advantage for preparing AC moldings.

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(AC granule)   (SAL based AC sheet)

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┌──────────┐              ┌──────┐
│ Crude oil │              │ Wood │
└──────────┘              └──────┘
     │                        │ Acetic acid cooking
  ┌───────┐                 ┌────┐
  │ Pitch │                 │ AL │
  └───────┘                 └────┘
     │◄─ Benzene              │ Heating to 160°C
     │◄─ Polyvinyl alcohol    │
     │ Heating to 170-200°C   │◄─Pulp or fiber
     │                        │ Thermoforming
┌───────────────┐          ┌──────────┐
│ Granulated Pitch │        │ AL sheet │
└───────────────┘          └──────────┘
     │ Dehydration            │
     │ Thermostabilization    │ Carbonization
     │ (heat up to 100-300°C) │
┌────────────────────┐     │
│ Thermostabilized pitch │   │
└────────────────────┘     │
     │ Carbonization         │
┌──────────────────┐      ┌──────────────────┐
│ Carbonized material │     │ Carbonized AL sheet │
└──────────────────┘      └──────────────────┘
     │ Activation            │
┌────────────────────────┐ │ Steam activation
│ Activated carbon material │ │
└────────────────────────┘ │
     │ Fractionation         │
┌────────────┐           ┌──────────────────┐
│ AC granule │           │ Activated AL sheet │
└────────────┘           └──────────────────┘
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Fig. 1. Scheme for preparation of activated carbon (AC) granules and sheet from petroleum pitch and softwood acetic acid lignin (SAL), respectively

Recently, some pollutants have affected human health, so-called environmental hormones, as evidenced by medical symptoms. This type of environmental pollution has drawn considerable attention. It is desirable to remove potential pollutants of this nature from the air, soil, and water. The occurrence and species of pollutants diversify year by year. Concomitantly, the need for ACs is diversifying. To meet the demand, AC moldings, not only AC granules but also various shapes of ACs are expected to be required. For instance, thin AC sheets are needed for use in narrowly spaced refrigerators. Furthermore, an AC sheet with large adsorption capacity would be required for manufacture of compact cleaners used to clarify water and air. This can be accomplished by using an AC block made of many laminated AC sheets. Thus, production of AC moldings larger than AC granules are of primary importance. There are few reports about large AC moldings including AC sheets, although the preparations of carbonized board from woody wastes[10] and its AC with a dimension of 25 × 25mm[11] has been reported. Such AC moldings must be readily made from thermoplastic sources, without the use of solvents and additives, by a thermal pressing method.

Except for the production of fine fibers, the thermal moldings do not require a fusion property in the starting materials. Starting materials with thermoplasticity are adequate for the preparation of moldings. Therefore, SAL is expected to be easily transformed into AC sheets by a combination of the thermal pressing method and direct carbonization without removal of the high-molecular-mass fraction.

In this study AC sheets were prepared from SAL as an example of large AC moldings. The procedure for preparing the AC sheet and its adsorption properties are reported.

Materials and methods

The SAL powder was prepared by atmospheric acetic acid pulping of todo fir (*Abies sachalinensis* Masters) as described previously.[8] SAL powder was heated at 160°C for 30min under reduced pressure (approximately 0.8kPa), and then it was packed in a cylindrical stainless mold 5cm in diameter; the mechanism is similar to that of the pelletizer for infrared measurement. The mold was pressed under 29.4MPa, a value on an equipped gauge, by a laboratory press machine. After 30min of pressing it was heated at 200°–220°C for 15min. When the temperature of the mold was cooled to 70°C, the resulting SAL sheet was taken out from the mold. The SAL sheet was carbonized at 1000°C for 1h under a nitrogen stream in an electric furnace. The heating rate was 180°C/h. After carbonization, the carbon sheet was activated with steam at 900°C (heating rate 750°C/h) for 40–120min in the furnace.[12] The steam was introduced into the furnace with nitrogen at a flow rate of 450ml/min. The volume ratio of steam to nitrogen was 49.9%. AC sheets were prepared from a mixture of SAL and either acetic acid pulp[13] or viscose rayon. Commercial AC powder and granules were used as references for evaluating the adsorption properties and were purchased from Wako Pure Chemicals (Japan).

The morphological change during carbonization was evaluated by thermomechanical analysis (TMA).[7] Specific surface area was measured with nitrogen on a Belsorp 28 (Nippon Bell, Japan). Adsorption capacity to methane was measured at 25 °C on a Omnisorp 100 (Coulter, Japan). Prior to the measurement of gas adsorption, samples were dried at 200°C for 4h under reduced pressure. Adsorption capacities of ACs to iodine and methylene blue were measured according to JIS K-1474, provided the sample weights were 0.3g. The capacities to iodine and methylene blue were determined at 15min and 8h after mixing the ACs, respectively.

Results and discussion

Thermal pressing of SAL into sheets and
their carbonization

When SAL from which the high-molecular-mass fraction was removed was converted to CF precursory fibers before carbonization, it was found to be thermostabilized during fusion spinning.[9] Accordingly, we assumed that molded SAL might be carbonized directly without thermostabilization. In addition, it might keep the original shape during the carbonization. A sheet with a diameter of 5cm and a thickness of 3.8mm, as a precursor for the AC sheet, was prepared by the thermal pressing method from 6g of SAL

**Table 1.** Dimensions of SAL-based sheets before and after carbonization

Condition	Diameter (mm)	Thickness (mm)
Before carbonization	50	3.8
After carbonization		
SAL	61 (1.22)	6.8 (1.78)
SAL with 1.7% pulp	57 (1.14)	24 (6.32)
SAL with 10% pulp	41 (0.82)	3.1 (0.82)
SAL with 20% pulp	38 (0.76)	2.3 (0.61)

The values in parentheses are after/before carbonization size ratios and are averages of three specimens
SAL, softwood acetic acid lignin

Fig. 2. Thermomechanical analysis (TMA) curves for SAL-based sheets with various contents of pulp. (*1*) with 1.7% pulp; (*2*) with 10% pulp; (*3*) with 20% pulp

that was thermally treated at 160°C under reduced pressure for 30min to remove volatile materials. The resulting sheet was carbonized directly under a stream of nitrogen. The carbonized sheet was deformed markedly with expansion and much foam, probably due to both the ejection of thermal decomposition materials from the sheet and the thermoplasticity of SAL. Thus, to make a precursor AC sheet, direct carbonization of the SAL sheet was unsatisfactory.

Cellulosic materials such as pulp and viscose rayon have no thermoplasticity – only thermal decomposition. We have added these cellulosic materials to SAL not only to suppress deformation but also to strengthen the mechanical property of the sheet. First, viscose rayon at a length of about 3cm was added. The deformation during carbonization was drastically repressed by the addition of 1.7% rayon fibers, although slight expansion did occur. This result suggested that cellulosic material was useful for suppressing deformation, and that complete suppression would be attained by its addition in large quantity.

Acetic acid pulp was used as an antiexpansion cellulosic material, as pulps were less expensive than viscose rayon. The precursory sheet was prepared from a mixture of the pulp and SAL powder in various ratios by a sandwich-like mixing method and was subjected to carbonization. Table 1 shows the sizes of the carbonized sheets. The sheet made from only SAL was expanded to 1.2-fold of the diameter and 1.8-fold of the thickness. The sheet with 1.7% pulp was deformed significantly. By contrast, the sheet with 10% pulps shrunk only slightly, and the sheet with 20% pulp shrunk drastically, especially in the thickness direction. To clarify the mechanism of volume change upon carbonization, the change in thickness was evaluated by TMA (Fig. 2). The sheet with low content of pulp (1.7%) thickened at an early stage of heating, whereas the sheets with high contents of pulp thickened up to 350°C, and then began to shrink. In particular, the sheet with 20% pulp expanded to the smallest extent, and shrinking began at the lowest temperature. In general, the carbonization reaction is complete at about 700°C. Accordingly, shrinking may continue to the end of carbonization. Therefore, the sheet with 20% pulp was transformed into a tightened, carbonized sheet. For production of AC granules, thermostabilization is a tedious and costly process, as shown in Fig. 1. By adding pulp, the precursory sheet for AC sheet could be prepared by direct carbonization without thermostabilization.
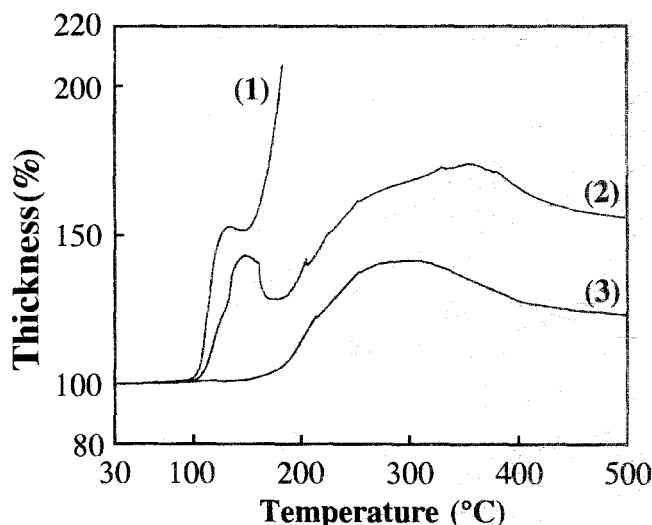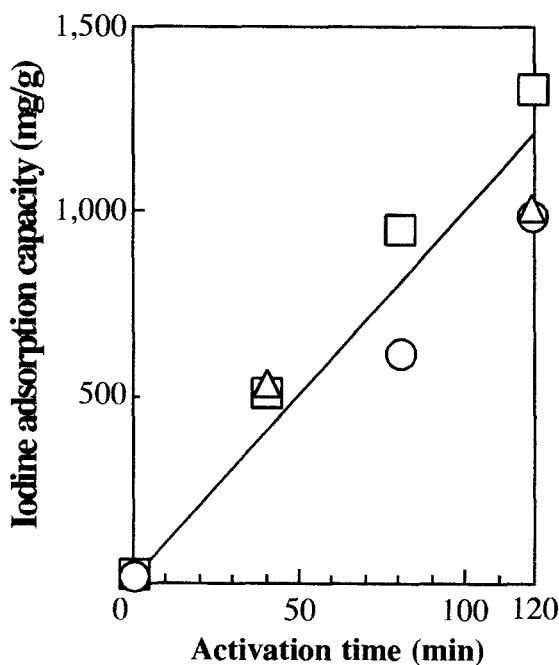
Activation of carbonized sheet

When the CF from HAL was activated with steam that was introduced into an electric furnace concomitantly with a stream of nitrogen,[6,12] satisfactory adsorption properties of the resulting ACF (comparable to those of commercial AC) were obtained by the activation time of 40min. However, the activation conditions seemed to be insufficient for the effective activation of SAL-carbonized sheet, as the surface area of the carbonized sheet was much smaller than those of carbon fibers. Hence, the effect of the activation time on surface area and iodine adsorption were investigated in addition to the activation yield. Japan industrial standard (JIS) provides criteria for evaluating the adsorption property of AC based on the iodine, methylene blue, and benzene adsorption capacity. Among the measurements, iodine adsorption capacity was easily determined only by titration. In this study, the relation between activation time and iodine adsorption was examined to clarify the activation efficiency.

Figures 3 and 4 show the relation of activation time with activation yield and iodine adsorption, respectively, where the data from all the AC sheets prepared from SAL with different cellulosic materials are summarized. The prolonged activation time brought about a decrease in activation yield because of oxidative aging of carbon with steam. On the other hand, the iodine adsorption capacity of AC sheet was markedly increased with the prolonged time. Thus, there was a negative correlation between the activation yield and iodine adsorption capacity. Consequently, iodine adsorption capacity of AC sheets comparable to that of commercial AC powder (1150mg/g) (Table 2) was found to be at an activation time of 120min.

The surface area of AC is the most important parameter for characterizing the performance of AC. In general, it is calculated from the isotherm of nitrogen adsorption at various relative pressures (P/Ps), and is represented as the spe-
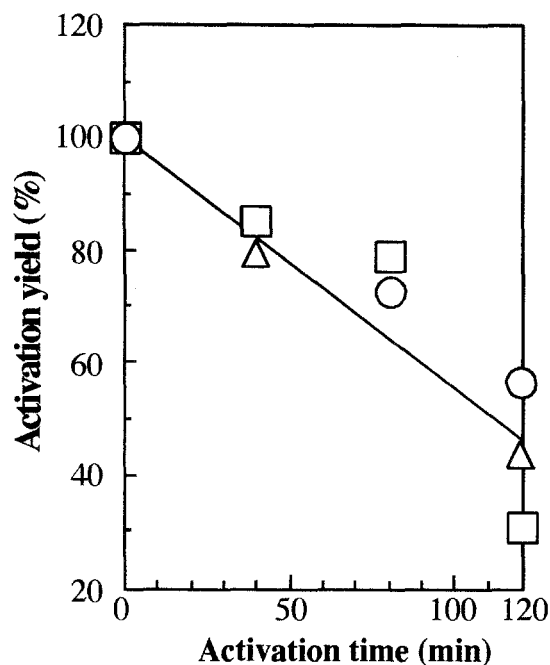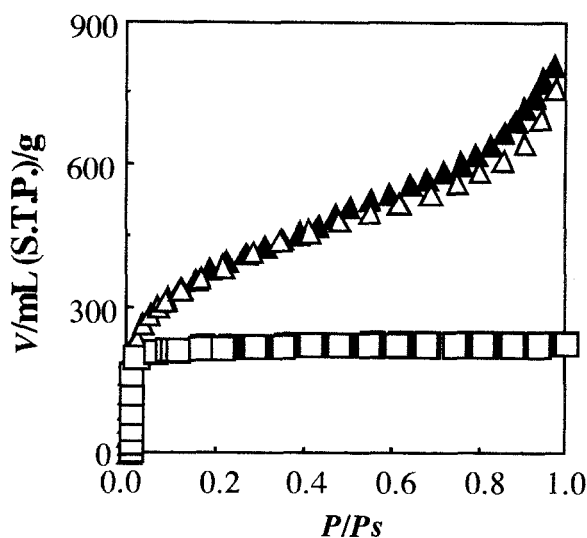
Fig. 3. Relation between activation time and activation yield of AC sheet. *Squares*, AC sheet from SAL; *triangles*, AC sheet from SAL with viscose rayon; *circles*, AC sheet from SAL with pulp

Fig. 5. Adsorption-desorption isotherms of AC powder and AC sheet that was prepared from SAL by steam activation for 40 min. *Open and filled triangles*, adsorption and desorption isotherms of AC powder, respectively; *open and filled squares*, adsorption and desorption isotherms of AC sheet, respectively. V/mL $(S.T.P.)/g$ is the volume of nitrogen at standard temperature (298 K) and pressure (101.3 kPa). P/Ps is the relative pressure to saturation pressure of nitrogen

Fig. 4. Relation between activation time and iodine adsorption capacity of AC sheet. *Squares*, AC sheet from SAL; *triangles*, AC sheet from SAL with viscose rayon; *circles*, AC sheet from SAL with pulp

Table 2. Adsorption properties of AC samples

Sample	Langmuir's surface area (m^2/g)	Adsorption capacity (mg/g)	
		I_2	Methylene blue
AC sheet[a]			
SAL with 1.7% pulp	1560	1100	124
SAL with 10% pulp	1350	1270	81
SAL with 20% pulp	1290	1360	97
HAL-based ACF[b]	1360	1520	115
Commercial			
AC powder[c]	1220[e]	1150	97
AC granule[d]			
Intact	nd	485	50
Shattered	1440	1270	196

I_2 and methylene blue adsorption capacity were measured at 15 min and 8 h after mixing AC samples, respectively
AC, activated carbon; HAL, hardwood acetic acid lignin; ND, not determined
[a] These samples were activated for 120 min. The values are the average of two or three specimens
[b] Activated carbon fiber was prepared from HAL
[c] Commercial AC powder was made from coconut shell
[d] Commercial AC granule was pruchased from Wako Pure Chemicals, Japan
[e] These values were calculated by BET method

cific surface area. A satisfactory isotherm of the sheets before activation could not be obtained, which implied that the specific surface area of the sheets was too small to measure precisely. By contrast, the isotherms of AC sheets was obtained, suggesting an increase in surface area upon steam activation. Figure 5 shows the adsorption-desorption isotherms of commercial AC powder and the SAL-based AC sheet without pulp that was activated for 120 min. The isotherm diagram of the AC powder was similar to that for type IV adsorbent in the BDDT classification,[14] and the diagram of the AC sheet was classified as type I. The specific surface area of type I and IV adsorbents could be
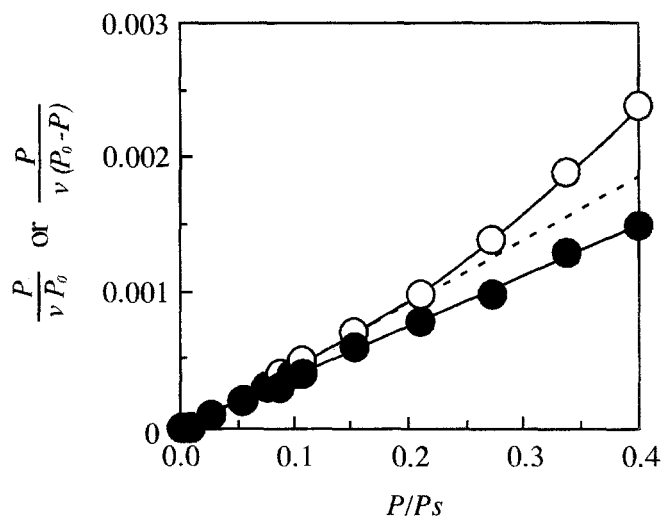
Fig. 6. Langmuir's (*filled circles*) and BET (*open circles*) plots of AC sheet prepared from SAL by steam activation for 120 min
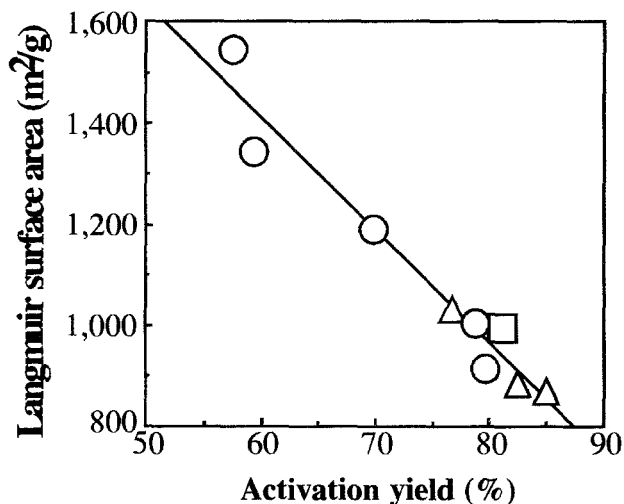

Fig. 7. Relation between activation yield and specific surface area of AC sheet calculated by Langmuir's plot. *Squares*, AC sheet from SAL; *triangles*, AC sheet from SAL with viscose rayon; *circles*, AC sheet from SAL with pulp

calculated by Langmuir's equation[15] and the BET equation,[16] respectively. The plot of the AC sheet fitted into Langmuir's plot better than into the BET plot, as shown in Fig. 6. Therefore, the specific surface area of AC sheets was calculated by Langmuir's equation. Figure 7 shows the relation between activation yield and specific Langmuir's surface area. As expected, Langmuir's surface area was increased dramatically by the decrease in activation yield. A similar tendency was found for the relation between the activation yield and iodine adsorption capacity. Thus, iodine adsorption capacity is closely related to the specific surface area. These results suggested that the prolonged activation time improved the adsorption property of the AC sheets but decreased the activation yield.
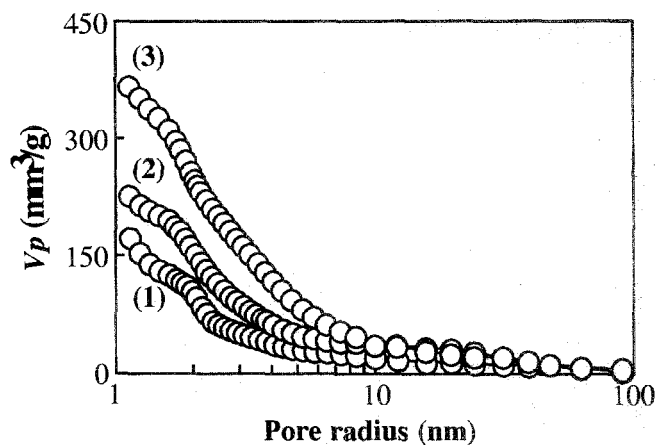

Fig. 8. Cumulative pore volume distributions of ACs sheet with various contents of pulp: (*1*), with 1.7% pulp; (*2*), with 10% pulp; (*3*), with 20% pulp

## Adsorption properties of AC sheets from a mixture of SAL and pulp

The adsorption properties of various AC samples are listed in Table 2, where specific surface areas of AC samples (except for the AC sheet) were calculated by the BET equation. The adsorption capacity of the commercial AC granule to iodine and methylene blue was measured under two conditions: intact granules and shattered granules prepared with a mortar. The Japan Industrial Standard states that the measurement of adsorption capacity of AC granules be performed with shattered granules.

The AC sheets with pulp had an adsorption property similar to that of commercial AC powder after steam activation for 2 h, in contrast to 40 min of activation of HAL-based carbon fibers. The specific surface area of the AC sheet decreased with an increase in the pulp content in the sheet. Interestingly, the iodine adsorption capacity was enhanced by the increase in pulp content. By contrast, the AC sheet made from 1.7% pulp content had the highest adsorption capacity to methylene blue among the sheets tested. Thus, the specific surface area did not affect the adsorption of adsorbates in the AC sheets.

Because the adsorption properties of the AC sheets were assumed to be influenced not only by specific surface area but also by the volume of the adsorption site in the sheet, the distribution of pore volume was estimated by the Dollimore-Heal method[17] from nitrogen desorption. Figure 8 shows the cumulative pore volume versus pore radius. In general, mesopores and micropores with a radius of less than 25 nm are directly involved in the adsorption of adsorbates due to capillary condensation. Mesopores with a radius of less than 10 nm were formed by the increase in pulp content; in particular, the sheet with 20% pulp had the largest pore volume with a radius of less than 5 nm. This indicates that a large volume of adsorption sites contributes appreciably to the specific adsorption property of the AC sheet.

As shown in Fig. 9, the morphological change of the sheet with a high pulp content upon activation was observed by scanning electron microscopy (SEM). The original sheet

Fig. 9. Scanning electron micrographs of the sheet with 20% pulp before (**A**) and after (**B**) activation. **C** Cross section of the sheet after activation

(bar = 3μm)   (bar = 3μm)   lignin pulp lignin
   (bar = 430μm)
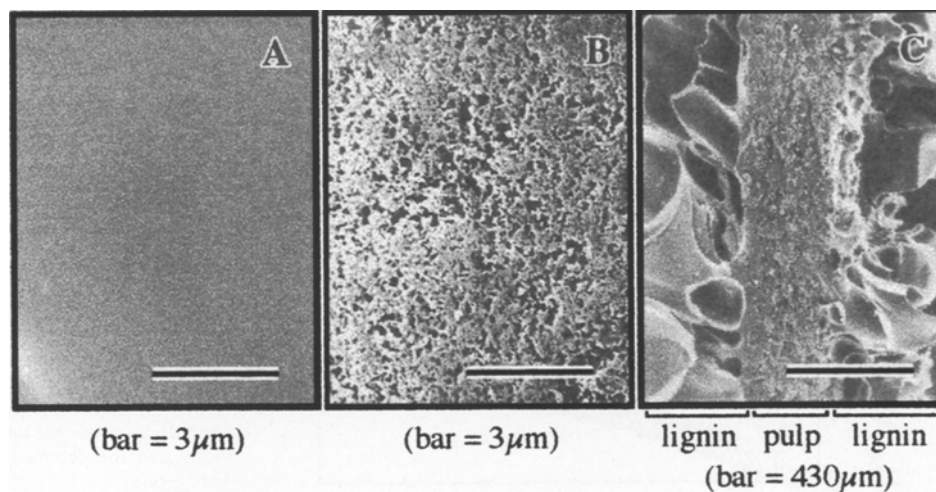
was prepared by inserting pulp between SAL powders (the sandwich-like method). The smooth surfaced carbonized sheet with small pores (Fig. 9A) was transformed into a porous one by steam activation (Fig. 9B). Figure 9C is a cross section of the AC sheet. The central bundle was attributable to the pulp, because tangled fibers were observed when the region was magnified. Accordingly, both outside layers were comprised of SAL. After activation, the outside SAL layer of the sheet was destroyed and become small compartments, but the pulp was found to reside inside the sheet probably as fibrous AC. The development of mesopores in the AC sheet with high pulp content was attributed to the residual pulp.

Adsorption rate dependence on the morphology of AC moldings

The AC granule was considered to be useful for AC moldings. The shattered AC granule had better adsorption capacities than the intact granule for two adsorbates tested, as shown in Table 2. This difference of capacities between the two forms was attributable to the adsorption rate. This means that the intact AC granule has a slow adsorption rate. Actually, adsorption of methylene blue by the intact AC granule did not reach equilibrium, and the capacity was very low for an adsorption time of 8h, as shown in Fig. 10. Thus, the adsorption rate of AC molding is highly dependent on the morphology. AC sheets, however, showed a more rapid adsorption rate than AC granules, though their sizes were bigger than the granules. In particular, the AC sheet with 20% pulp was the highest. The adsorption rate of the AC sheet, of course, was slower than those of ACF.[6] These results also suggested that the residual pulp in the sheet as fibrous AC contributed to relatively rapid adsorption.

Methane gas adsorption

Methane sometimes causes air pollution in chemical factories. To remove the gas from the atmosphere, methane gas adsorption of AC sheet was investigated. The adsorption
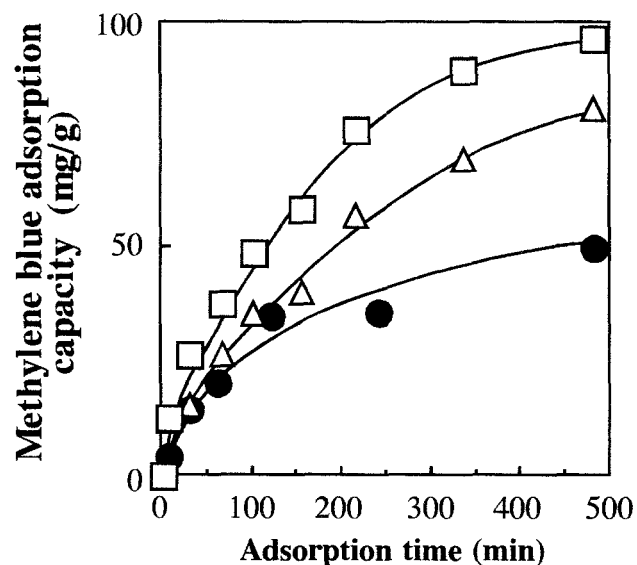

Fig. 10. Methylene blue adsorption rate of the AC granules and the AC sheet. *Circles*, AC granules; *triangles*, AC sheet with 10% pulp; *squares*, AC sheet with 20% pulp

capacity of commercial AC powder was 13.4ml/g at the relative pressure of one, whereas that of the AC sheet with 10% pulp was 35.9ml/g: 2.8-fold that of the AC powder (Fig. 11). Fibrous AC (ACF) was reported to adsorb gaseous adsorbates, such as benzene and ozone.[18] Such high adsorption capacity to methane resulted from the adsorption property of fibrous AC into which the pulp was transformed. Therefore, AC sheets with pulp are an excellent adsorbent to combat air pollution.

Conclusions

Activated carbon sheets were prepared from SAL, although they were deformed during carbonization. The morphological change in the sheet was improved by adding more than 10% pulp. The residual pulp likely played a role as fibrous AC in the adsorption. Therefore, the AC sheet is a potential
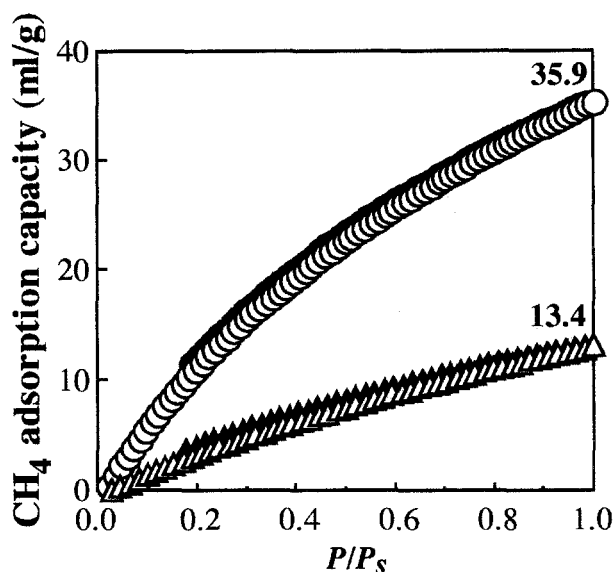
Fig. 11. Adsorption-desorption isotherms of AC powder and AC sheet with 10% pulp to methane. *Open and filled triangles*, adsorption and desorption isotherms of AC powder, respectively; *open and filled circles*, adsorption and desorption isotherms of AC sheet, respectively

adsorbent for removal of water and air pollutants. In addition, SAL is a promising raw material for AC moldings.

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