ORIGINAL

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Basic properties of specific wood-based materials carbonised in a nitrogen atmosphere

Abstract The purpose of this study is to develop new porous carbon materials by carbonising wood-based materials. One of the advantages of wood-based materials used as precursors for porous carbon materials is the simple and cost-effective production technique. Moreover, it is possible to make adjustments for a wide range of macro- and micro-structures by selecting different densities and particle sizes. Compared with solid wood, wood-based materials possess much greater homogeneity, isotropy and reproducible characteristics. Another great advantage is the fact that carbon materials can thus be produced from a renewable resource. A broad variety of specifically developed wood-based materials were carbonised to produce porous carbon materials for which characteristics such as density, yield, dimensional changes and surface area were determined. Light microscopy and mechanical testing were applied for further characterisation. The results showed how density and particle size affect the structure of the carbon materials; dimensional changes and mass loss are influenced by the carbonisation temperature, adhesive content and apparent density; increasing particle size decreases flexural strength and increasing apparent density or adhesive content raises flexural strength super-proportionally; and specific surface area increases with rising carbonisation temperatures.

Introduction

Porous carbon materials can be used for a number of applications, including filters, adsorbents, electrodes and catalyst supports. More recently they have

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been found as precursors for reaction-formed structural ceramics and composite materials. Conventional starting materials for the production of porous carbons are phenol formaldehyde polymers, aromatic resins (Fitzer et al. 1969) and furfuryl resins (Constant et al. 1995). Monolithic porous carbon materials can also be obtained by carbonising wood in a controlled thermal decomposition process. In this process the cellular anatomic features of wood are retained in the new carbon material. The structural changes during carbonisation and the physical properties of the resulting chars were investigated in several studies. McGinnes et al. (1971) analysed the dimensional changes occurring on the conversion of wood to charcoal for the tangential, radial and longitudinal planes on the basis of cubes of white oak. Electron microscopic observations revealed that the original microfibrillar orientation of the cell wall had been destroyed in charcoal manufacture and replaced by a smooth "amorphous appearing" wall structure. The dynamic mechanical properties, mass loss and shrinkage of birch which was heat treated in nitrogen were presented by Moor et al. (1974). These authors observed a substantial decrease in rigidity accompanied by a major mass loss and shrinkage. Treatments at higher temperatures produced less additional mass loss and shrinkage, but produced increased rigidity in the char. Byrne and Nagle (1997) demonstrated the applicability of monolithic porous carbon for structural activated carbon and for the impregnation with a polymer to form a carbon/polymer composite. Infiltration of a carbon preform derived from wood with liquid reactants such as silicon or other metallic or non-metallic melts can produce a net shape carbide ceramic. Silicon infiltrated silicon carbide ceramics with anisotropic pore orientation which were obtained from pyrolysed wood are distinguished by a higher strength (in axial direction) at the same level of porosity as conventionally fabricated ceramics (Greil et al. 1998). If a high char yielding polymer like phenolic resin is used for impregnation of wood before carbonisation, a carbon material with superior corrosion resistance and mechanical strength is obtained. These materials are discussed for various industrial uses, such as electromagnetic shields, electrodes or bearing (Okabe et al. 1996). Kercher and Nagle (2002) used commercially available wood-based materials like medium-density fibreboards (MDF) for the production of porous carbon materials. This investigation has shown that the electrical, mechanical and structural properties of carbonised MDF materials make them excellent candidates for lithium-ion and fuel cell components.

In the present study specific wood-based materials were used to produce porous carbon materials. The main purpose of this investigation was to study the influence of wood-based material parameters such as particle size, density and adhesive content on the structure and properties of porous carbon materials.

Experimental

Six different types of particles and fibres were used for the production of wood-based materials in this study. Milled wood fibres with diameters of 40 and 150 μm as well as particles of 1 mm were provided by J. Rettenmaier & Söhne GmbH + Co (Rosenberg, Germany). MDF fibres came from Steico AG (Aschheim, Germany) and surface layer as well as core particles from Pfleiderer

AG (Neumarkt, Germany). The wood-based materials were made by mixing the wood particles or fibres with a powdery phenolic resin (Bakelite) in a stirring device. Subsequently the mixture was pressed to form boards of 10 mm thickness in an uni-axial pressing process at temperatures of 180°C. Carbonisation of the dried (2 h, 103°C) wood-based materials was carried out using specimens sized 600 mm×800 mm in an inert atmosphere (N_2). To make sure the carbon materials remained crack-free, a slow heating rate of 1 K/min was applied up to 500°C. Subsequently a heating rate of 5 K/min was applied up to the peak temperature of 900°C, which was kept for 2 h. After embedding in acrylic resin (LR-White) and cutting into 1 μm slides, the microstructure of the wood-based materials was observed by light microscopy (Zeiss Axiophot). Cross-sections of carbon materials were analysed by incident-light microscopy after being embedded in epoxy resin (Struers SpeciFix 120) and polished (grain size 1 μ;m). To investigate dimensional changes and mass loss, dimensions and masses were measured before and after carbonisation in the dry state. Mechanical testing of the carbon materials was carried out by determining flexural strength by the three point method using a universal testing machine (TesT 112.50kN.L). Test pieces measuring approximately 6mm×10mm×60mm for bending test were obtained from the carbonised specimens in accordance with DIN 51902 (1997). The specific surface area was measured with a high speed gas sorption analyser (Quantachrome Corporation NOVA 2200), and the BET surface area was calculated from the isotherms by the Brunauer-Emmett-Teller (BET) equation (Brunauer et al. 1938).

Results and discussion

Microstructure of porous carbon materials

The microstructure of the porous carbon materials is predominantly influenced by the size and geometry of the particles from which the wood-based materials are produced. Figure 1a–c shows cross sections of those materials with three different particle sizes ((a) milled beech fibres: approx. 40μm×30μm×30μm, (b) spruce fibres: approx. 150μm×30μm×30μm, (c) spruce particles: approx. 1.0mm×0.3mm×0.3mm). For all samples the density was 0.80 g/cm^3 and the adhesive content was 10%. Porous carbon materials were formed from these wood based materials (Fig. 1 d–f). During that process all anatomic features, e.g. pits, and the original morphology of the wood based materials are retained. With decreasing particle size the homogeneity of the porous carbon materials was seen to rise. Pore distribution over the cross section becomes more uniform and the size of the interparticle pores becomes progressively smaller.

Apart from particle size, apparent density is also an important parameter for the structure of wood based materials and hence for porous carbon materials. Figure 2a–f reveals the microstructure of fibreboards with the densities 0.40 g/cm^3, 0.80 g/cm^3 and 1.2 g/cm^3 (a–c) and the corresponding carbon materials (d–f). Adhesive content for these variants is again 10% and the used particles were spruce fibres (approx. 150μm×30μm×30μm). Lower densities in the wood-based materials (Fig. 2a) lead to carbon materials (Fig. 2d) with larger interparticle pores. Increasing the apparent density of the wood-based
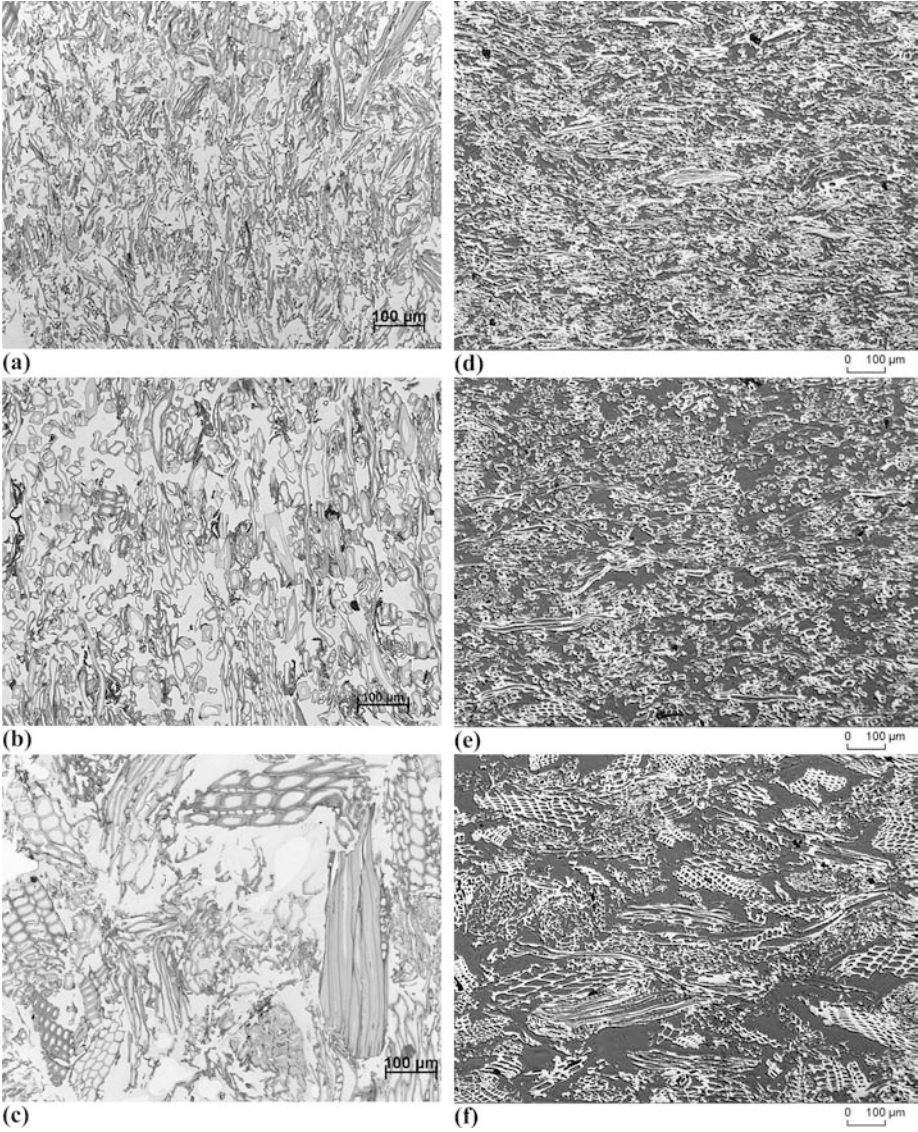
Fig. 1a–f Influence of particle size on the microstructure of wood-based materials (**a–c**), and the resulting porous carbons (**d–f**)

materials (Fig. 2 2) leads to a reduced porosity and smaller pores which is also visible in the resulting carbon material (Fig. 2f). Thus the wood-based material parameter apparent density is a second tool, in addition to particle size, to adjust the internal structure of porous carbon materials.

Mass loss and dimensional changes

Wood-based materials shrink and loose weight during carbonisation. Dimensional changes and mass loss of a fiberboard (milled spruce fibres, apparent
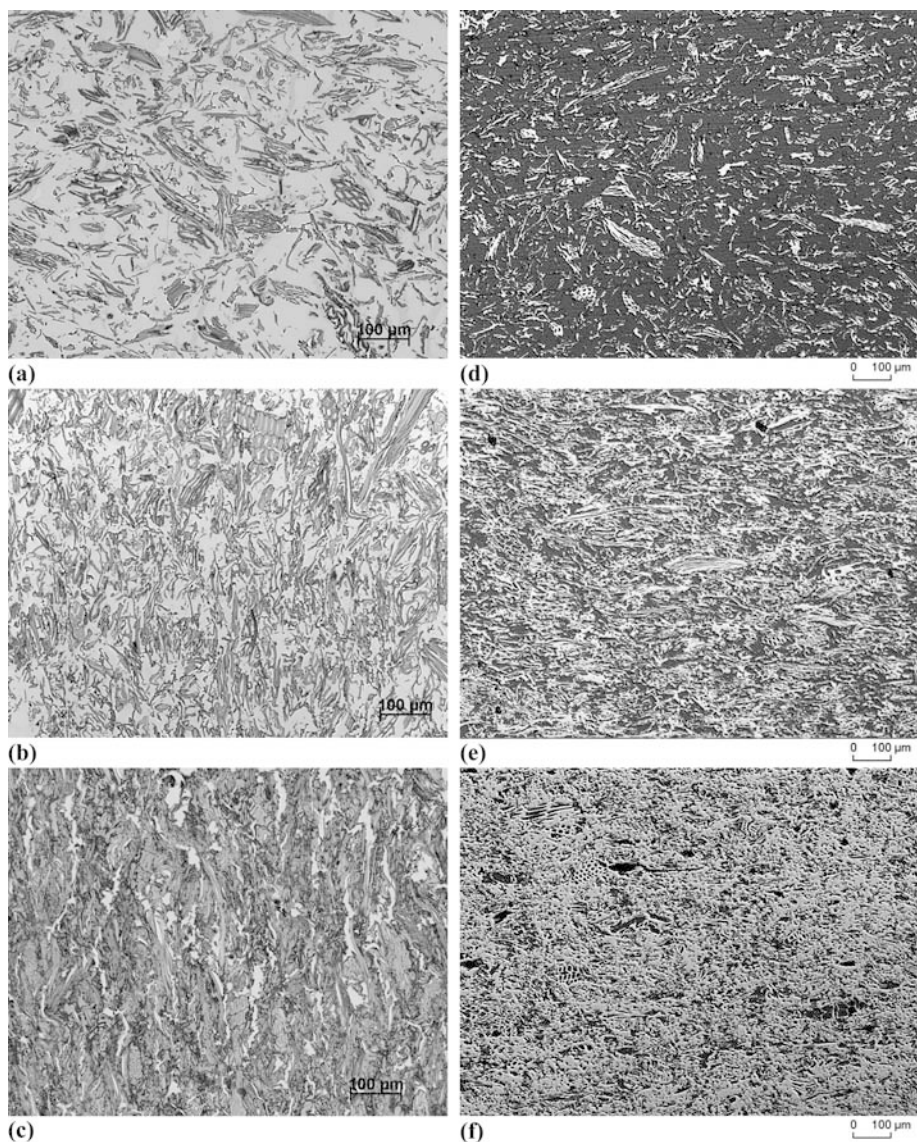
Fig. 2a–f Influence of apparent density on the microstructure of wood-based materials (**a**: 0.4 g/cm^3; **b**: 0.8 g/cm^3; **c**: 1.2 g/cm^3), and the resulting porous carbons (**d–f**)

density 0.80 g/cm^3) are plotted as a function of carbonisation temperature in Fig. 3. Mass and dimensions were found to decrease with rising carbonisation temperature. Similar to mass loss, dimensional changes are greatest at temperatures between 300–350°C, which is consistent with the decomposition of cellulose in this temperature range (Shafizadeh 1983). At 350°C the material lost almost 60% of its weight as well as 25% of its transverse and 10% of its plane dimensions. In addition, the relationship between the reduction in apparent density and carbonisation temperature is shown in Fig. 4. Since mass loss occurs faster than the change in dimensions up to temperatures of 350°C,
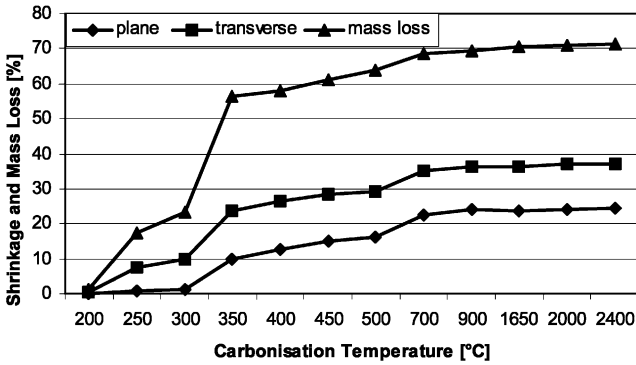
Fig. 3 Shrinkage and mass loss of fibreboards at different carbonisation temperatures
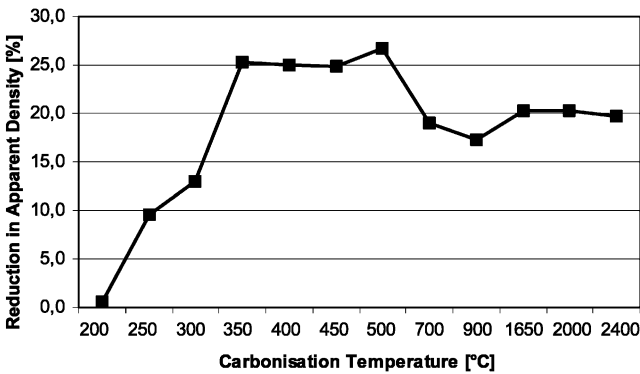

Fig. 4 Reduction in apparent density of fibreboards at different carbonisation temperatures

apparent density is progressively being reduced up to this temperature. Between 350–500°C mass loss and dimensional changes run parallel hence the reduction in apparent density remains constant. Above 500°C shrinkage occurs faster than mass loss with a concomitant decrease in the reduction in apparent density.

Figure 5 shows the relationship between adhesive content and the decrease in dimensions and weight for a material made from milled spruce fibres (apparent density 0.80 g/cm³). As indicated here, the dimensional changes and mass loss decreased with increasing adhesive content. Shrinkage in the plane ranges between 33–36%. Mass loss for the different adhesive contents lies between 57–72%. Because of the fibre arrangement in the direction of the plane during hot pressing, shrinkage in the plane is less than in the transverse direction. Figure 6 shows the reduction in apparent density during carbonisation. Due to the greater impact on mass loss than on dimensional changes, there is less reduction in apparent density with increasing amounts (0–50%)of phenolic resin.

Figure 7 shows the relationship between apparent density of fibreboards and the dimensional changes during carbonisation. With increasing apparent density, shrinkage rose first in the transverse direction. Shrinkage in this direction ranges between 28–39%. Mass loss is not affected by the apparent density. The
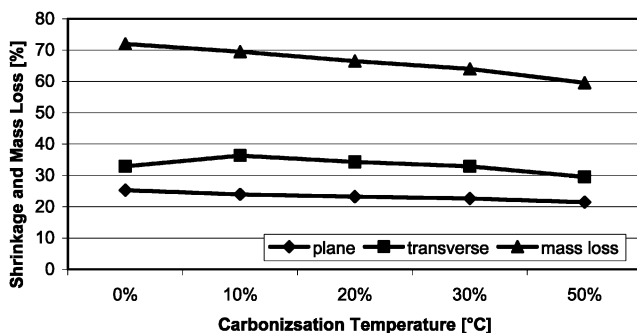
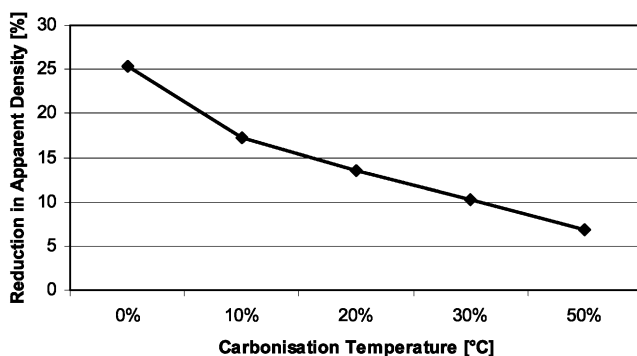**Fig. 5** Shrinkage and mass loss of fibreboards with different adhesive content

Fig. 6 Reduction in apparent density of fibreboards with different adhesive content
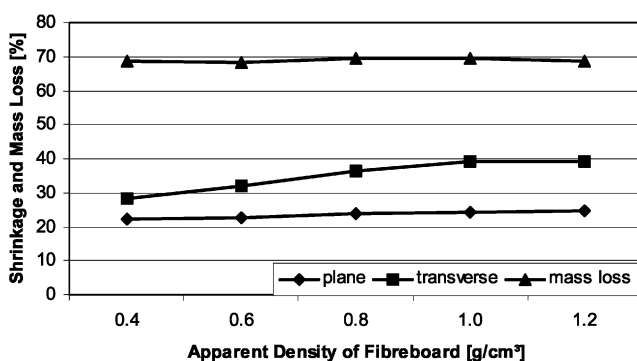

Fig. 7 Shrinkage and mass loss of fibreboards with different apparent densities

effect of this on the reduction in apparent density is illustrated in Fig. 8. Raising the apparent density of the fibreboards causes less reduction during carbonisation. This behaviour is different from that of solid wood, where apparent density after carbonisation was found to be linearly related to wood apparent density (Byrne and Nagle 1997).
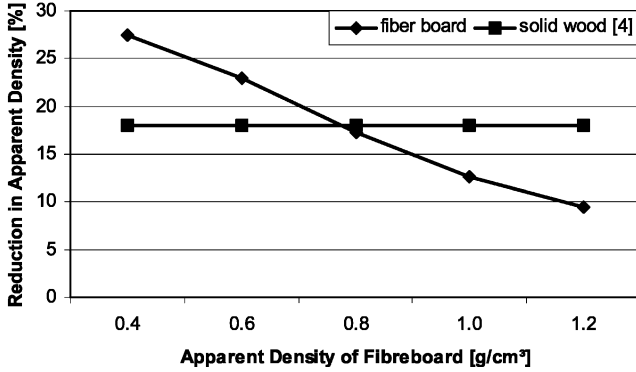
Fig. 8 Reduction in apparent density of fibreboards with different apparent densities compared to solid wood

Mechanical properties

Figure 9 shows the impact of fibreboard apparent density on the flexural strength of the carbon materials. The flexural strength increases super-proportionally with increasing apparent density of the wood-based material. This is due to the effect of an abated reduction in apparent density described in Fig. 8, which leads to an increase in apparent density in the carbon material.

   Besides the internal structure, mechanical properties can also be influenced by wood-based material parameters such as particle size or density. Figure 10 presents the relationship between particle size and flexural strength of the resultant carbon materials. The results suggest that smaller particles lead to higher strength. Boards made from milled beech fibres (40 μm) achieve average values of 27 MPa whereas boards made from larger particles (core particles) only attain 10 MPa. This may be attributable to the fact that more contact points between smaller particles lead to better cohesion. Since the specific flexural strength shows the same tendency, it is suggested that in this case density is not the critical factor influencing the mechanical properties of the porous carbon materials.
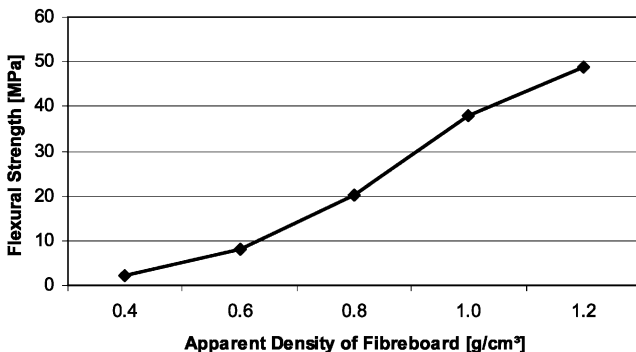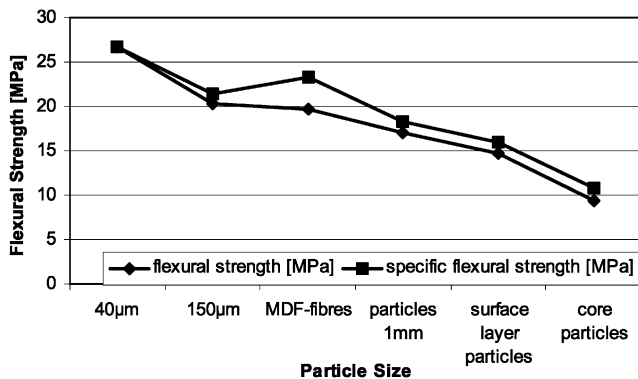

Fig. 9 Relationship between apparent density of fibreboard and flexural strength of porous carbon
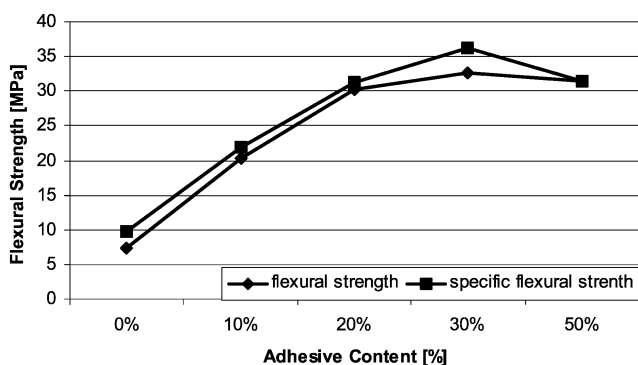
Fig. 10 Flexural strength and specific flexural strength of porous carbon from wood-based materials with different particle sizes

In additional to wood-based material parameters like particle size and density, adhesive content can also affect the flexural strength of the resulting carbon materials. As mentioned above, the flexural strength of the carbon materials depends on the connection between the used wood particles or fibres. Up to a certain degree this connection can be improved by increasing the amount of phenolic resin. Figure 11 shows that the flexural strength of the carbon materials rises monotonically with the increase of the content of phenolic resin up to a share of 30%. In contrast, increasing adhesive content up to 50% does not lead to a further rise of the flexural strength. This may be attributed to the fact that the used particles are already covered completely with phenolic resin at lower adhesive contents so that additional amounts can not improve the connection between the wood particles. As the specific flexural strength again shows the same trend, a density effect can be excluded.

Specific surface area

The specific surface area of porous carbon materials made from fibre boards (apparent density 0,80 g/cm^3, adhesive content 10%) at different carbonisation temperatures was also determined. Figure 12 shows that the specific surface

Fig. 11 Flexural strength and specific flexural strength of porous carbon from wood-based materials with different adhesive content
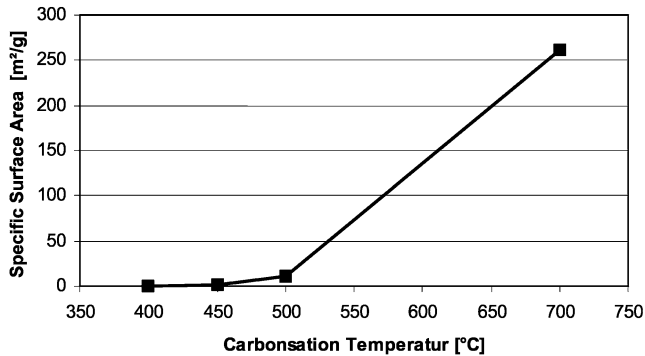
Fig. 12 Relationship between specific surface area and carbonisation temperature

area increases with rising carbonisation temperatures. A maximum of 262 m^2/g was achieved at 700°C. It is assumed that the dehydration of the phenolic resin and wood have an important effect on the surface area of the carbon materials in the course of carbonisation (Fan et al. 2001).

Conclusions

In the present work the influence of wood-based materials parameters (particle size, density and adhesive content) on the properties of porous carbon materials derived from these materials was investigated. The results are summarised as follows:

1. Porous carbon materials suitable for a number of different applications can be prepared conveniently by carbonising specific wood-based materials.
2. The original structure of wood-based materials is retained in the porous carbon material during carbonisation. By varying particle size or density it is possible to tailor a wide range of desired structures in the carbon material.
3. Mass and dimensions were found to decrease with rising carbonisation temperatures. Dimensional changes during carbonisation lessen with increasing adhesive content and become greater with increasing apparent density. Mass loss decreases with increasing amounts of phenolic resin.
4. Smaller wood particles or fibres, a higher density and a higher adhesive content in the raw material lead to higher flexural strength in the porous carbon material.
5. Increasing carbonisation temperatures lead to an increase in surface area up to 262 m^2/g at 700°C.

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