Eur. J. Wood Prod. (2009) 67: 351–355
DOI 10.1007/s00107-009-0347-8

ORIGINALS · ORIGINALARBEITEN

Carbonization of hot-pressed ARBOFORM®-mixtures

G. Scholz · J. Lohr · E. Windeisen · F. Tröger · G. Wegener

Received: 7 August 2008 / Published online: 4 June 2009

Abstract Porous carbon materials have a wide range of technical applications due to their properties including low density potential, mechanical capacity, resistance to heat and corrosion as well as electric conductivity.

Organic materials like phenolic resins or polyacrylnitrile are typically employed as green body for carbon ceramics. However, wood and especially wood-based composites are also suitable as well as hot-pressed ARBOFORM®-powder mixtures from lignin, wood meal and natural additives, which varied with regard to their lignin content as well as partly regarding their additive rates. The objective of the present study was to investigate the influence of some admixed additives of a commercially available wood based composite on carbonization results. The experiment was performed due to its more homogenous material properties in comparison to solid wood. Another aspect was the possibility of forming mixtures of ARBOFORM® by extrusion or injection moulding. Such production processes are already state of the technology and therefore it could be possible to produce complex carbon- and ceramic templates which are difficult to realize by conventional processing methods. Concerning the thermoplastic process step of ARBOFORM® there are further advantages compared with the used wood based panels. The samples were pyrolyzed in a nitrogen atmosphere at a temperature of up to 900 °C. Regarding the absence of cracks, best results were achieved with blend P60 which had a higher content of wood particles. Addition of only 10% of phenolic resin significantly counteracted density reduction.

G. Scholz (✉)
Department of Wood Biology and Wood Products,
Georg-August-University Göttingen,
Büsgenweg 4,
37077 Göttingen, Germany
e-mail: gscholz@gwdg.de

J. Lohr · E. Windeisen · F. Tröger · G. Wegener
Wood Research Munich, Technical University of Munich,
Winzererstraße 45,
80797 Munich, Germany

Karbonisierung heißverpresster ARBOFORM®-Mischungen

Zusammenfassung Poröse Kohlenstoffmaterialen finden aufgrund ihrer Eigenschaften vielfältige technische Anwendungen. Sie haben Leichtbaupotential, sind mechanisch belastbar, hitze- und korrosionsbeständig und elektrisch leitend. Als Grünkörper für karbidische Keramiken dienen typischerweise organische Materialien wie Phenolharz oder Polyacrylnitril. Es eignen sich jedoch auch Holz und insbesondere Holzwerkstoffe sowie die in dieser Untersuchung verpressten ARBOFORM®-Mischungen aus Lignin, Holzmehl und natürlichen Additiven, die hinsichtlich des Ligningehaltes sowie zum Teil auch der Additivzusätze variierten. Es sollte der Einfluss unterschiedlicher Additivzugaben des kommerziell verfügbaren Produkts auf die Pyrolyseergebnisse untersucht werden. Der Versuch erfolgte im Hinblick auf wesentlich homogenere Materialeigenschaften im Vergleich zum Vollholz und ein weiteres Augenmerk galt der Möglichkeit der Formgebung von ARBOFORM®-Mischungen mittels Spritzguss oder Extrusion. Diese Formgebungsverfahren sind bei ARBOFORM® bereits Stand der Technik und damit wäre es möglich, durch diesen Herstellungsweg komplexe Kohlenstoff- und somit auch Keramikformteile zu ermöglichen, welche durch die herkömmlichen Verfahrenswege nur sehr schwer zu realisieren sind. Durch das vorhandene thermoplastische Prozessfenster bei ARBOFORM® ergeben sich damit wei-

tere Vorteile gegenüber den bereits verwendeten, speziellen Holzwerkstoffen.

Um die Umsetzbarkeit der verschiedenen Mischungen in Kohlenstofftemplate zu untersuchen, wurden die Prüfkörper unter einer Stickstoffatmosphäre bis 900 °C karbonisiert. Die mit dem höheren Holzanteil ausgestattete Abmischung P60 zeichnete sich bezüglich ihrer Rissfreiheit aus. Eine nur 10%ige Zugabe von Phenolharz wirkte der Dichtereduktion signifikant entgegen.

1 Introduction

Numerous applications show potential for porous carbon materials, for example electrodes, filters, adsorbents or even precursors for infiltration with silicon under high thermal treatment to produce silicon–carbon ceramics (Treusch 2004, Hofenauer 2004).

Pyrolysis of wood, wood based composites or wood plastic composites has already been described, e.g. by Shafizadeh and Chin (1977), Byrne and Nagle (1997), Kaindl (2000), Sieber et al. (2000), Siegel et al. (2004a), Siegel et al. (2004b), Treusch (2004), Hoffmann (2005), Herzog et al. (2006) and Krischok et al. (2006).

The production of 3-dimensional moulded paddings from solid wood is limited. The carbonization of wood causes an anisotropic shrinkage due to the heterogeneous wood anatomy. According to Davidson and Petterson (2002) the shrinkage of beech wood was 5%–25% in axial direction, 15%–40% in radial diection and 25%–40% in tangential direction. This phenomenon explains the higher risk for cracks and other damages. After pyrolysis and subsequently ceramization a change in the property profiles is the consequence. According to Klingner et al. (2003) irreversible pit closure also inhibited silicium infiltration of pine.

Therefore, special wood based panels were developed for carbonization and ceramization (e.g. Herzog et al. 2006). Such wood based panels are more homogenous and characterized by an isotropic shrinkage during carbonization causing more uniform material properties too. For ceramization, the carbon content is important among others. During carbonization at a temperature of up to 1.600 °C, the carbon yield of lignin (45%) is higher than the one of polyoses and cellulose with 20% (Kaindl 2000). The lignin content of pine and beech for example ranges below 32% (Wagenführ 2000). Practically high amounts of glue with high carbon contents, like phenolic resin were used during the hot pressing process of wood based panels. In this context an opportunity is the use of wood plastic composites. Such materials contain wood particles between 50–70 wt %, use mainly polyethylene, polypropylene or polyvinylchloride as matrix material, and were manufactured by injection moulding or extrusion (Grüneberg 2009).

ARBOFORM® is a processable thermoplastic material. It is manufactured from modified alkali lignin obtained from pulp industry, natural additives as well as annual plant fibres like flax or hemp and wood particles, respectively. The material was developed by the Fraunhofer Institute for Chemical Technology in 1996 and was advanced by Tecnaro GmbH, a spin-off of that same institute. Processing is carried out by injection moulding or extrusion. Density ranges are comparatively high (1300–1400 kg/m^3) without application of foaming additives (Wegener et al. 2006). Such conventional products are extensive stereoscopic moulds and cannot be used for further ceramization. Another opportunity is hot pressing of plasticized moulding material similar to curable plastic or thermoplastic composite production. It is possible to work within density ranges below 800 kg/m^3 and up to 1.400 kg/m^3. Density ranges between 850–1.000 kg/m^3 are interesting for ceramization.

ARBOFORM® possesses some good properties suitable for successful pyrolysis. The thermoplastic processable material is comparatively isotropic, consists of capillary particles and has a carbon content of about 50 wt %. Compared to wood based panels, used for pyrolysis and ceramization, it has the advantage of a great variety of shapes. It is a much more homogenous material compared to solid timber. In this report, the effects of mass losses as well as the reduction of volume and density of different ARBOFORM®-mixtures and the influence of some additives are considered. Pyrolysis temperature of 900 °C was chosen because of an almost complete mass loss of wood and phenolic binder caused by decomposition of organic compounds (Treusch 2004). Specimen density constituted approx. 900 kg/m^3 avoiding bubbling and minor density reduction and providing good infiltration velocity of silicium with optimal silicium carbide yield (Treusch 2004, Hofenauer 2004).

2 Material and method

Three different types of powdery ARBOFORM® mixtures were used for hot-pressing of panels. Mixtures of P60, P45 and F45 were provided by Tecnaro GmbH. The features of each mixture are as follows: P60 consists of 60% wood particles, 30% are based on Kraft lignin and 10% on natural additives. Type P45 differs from that mixture by possessing more lignin and 45% wood particles. Type P60a (reference) was partially modified with 10% phenolic resin (P60b) and 20% ammonium phosphate provided by Sigma-Aldrich (P60c) which had a lower density of 850 kg/m^3. These types have more or less the same isodiametric particle sizes. In Table 1 several mixtures of S150Tra are presented for comparison. These fibres of 70–150 µm in size came from *Picea abies* and were glued with distinct phenolic glue contents (taken from Treusch 2004). The same

Table 1 Variables, mass losses as well as reduction of volume and density of different materials after carbonizationa
Tabelle 1 Kennwerte verschiedener Materialien sowie Masse-, Volumen- und Dichtereduktionen nach der Pyrolyse

Material	Producer	Wood content [%]	Phenolic content [%]	Carbon content [%]	Mass loss [%]	Volume reduction [%]	Density reduction [%]
P60a	Tecnaro	60	–	54.7	66	61	14
P60b	Tecnaro	54	10	57.0	64	60	9
P60c	Tecnaro	48	–	43.7	61	46	28
P45	Tecnaro	45	–	58.4	65	61	10
F45	Tecnaro	45	–	59.1	64	60	11
S150TRa*	Rettenmaier	90	10	48.6	70	63	18
S150TRb*	Rettenmaier	70	30	51.2	65	60	11
Lignin**	MWL			63.8	n.d.	n.d.	n.d.
Phenolic	Bakelite			76.1	n.d.	n.d.	n.d.

* According to Treusch (2004)
** Milled wood lignin (MWL) according to Fengel and Wegener (2003)

phenolic type (Novolak JK63, Bakelite company) was used for investigating the test mixtures.

Addition of these substances was carried out by mixing them in a stirring device followed by pressing of boards ($200 \times 160 \times 10\,mm^3$) at a temperature of 180 °C. Oven-dried (103 °C) specimens with a size of $50 \times 50 mm^2$ and varying thickness between 10–15 mm were pyrolyzed. According to Treusch (2004) carbonization took place by applying a gaseous heat vector (N_2) under inert conditions at a temperature of up to 900 °C.

Determination of carbon content was carried out by means of C-analysis (element analyzer CHN-O-Rapid, Heraeus). Therefore, approx. 10 mg of milled material was weighed within tin boats. Acetanilide was used as reference material.

3 Results and discussion

The results of carbonization are presented in Figs. 1–2 and Table 1 (the measured carbon content refers to the accomplished CHN-analyses).

The application of ammonium phosphate effectively contributes to lower dimension shrinkage. Otherwise type P45 shows small cracks at the edges. F45 is covered with small whitish bubbles, possibly provoked by additives, and shows first signs of deformation.

Thickness shrinkage is decreasing with lower content of wood particles or when applying special additives (Table 1). According to Treusch (2004) the increased thickness loss can be explained by more contacts between the particles during the manufacturing process in tangential direction. This applies to all apart from F45 presumably because of more isodiametric particles.

Carbon yield for special wood based panels constitutes between 28%–30% using pyrolysis at 900 °C (Treusch 2004). In other investigations, a carbon yield of the used phenolic resin of approx. 60% (Treusch 2004) was detected thermo-gravimetrically. One possible explanation for the increasing carbon yield could be higher carbon amounts in lignin or phenolic resin. Addition of 10% phenolic resin led to a reduction in density of approx. 9% (Fig. 1 and Table 1) which is favourable compared to optimized wood based panels with a phenolic resin content of 30% (Treusch 2004).

The application of flame retardant ammonium phosphate should facilitate carbonization. Contents between 10%–20% are established within fibre boards (Deppe and Ernst 1996). The high amounts of that chemical caused an extraordinary low volume shrinkage provoking a high reduction rate of density (Figs. 1 and 2, Table 1). On the one hand, this could be good for a sequencing silicium infiltration. On the other hand, it is most likely that high contents of phosphor are within the carbon templates. The last-mentioned fact is important for silicium carbide yield or resulting poisonous phosphines at high temperature treat-

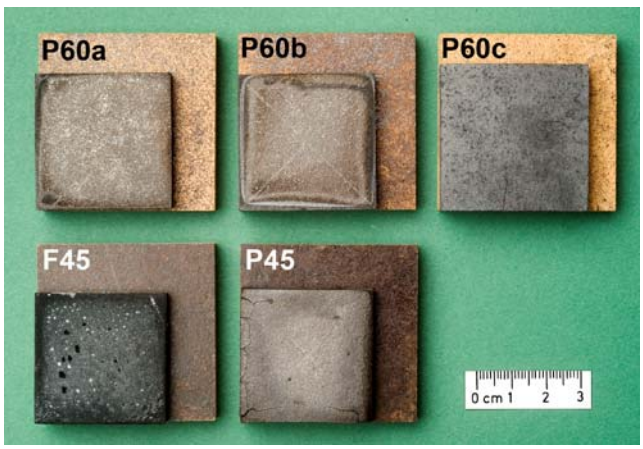

Fig. 1 Specimens before and after carbonization
Abb. 1 Prüfkörper vor und nach der Karbonisierung

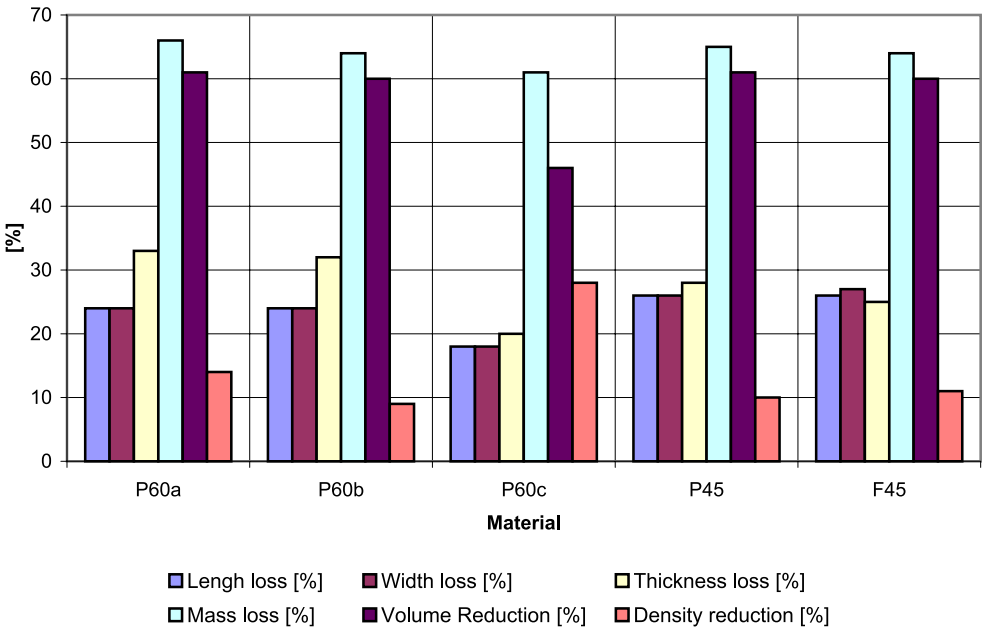

Fig. 2 Dimensional losses and mass losses as well as volume and density reduction of hot-pressed ARBOFORM®
Abb. 2 Dimensions- und Volumenschwund, Massenverlust sowie Dichtereduktion der ARBOFORM®

ment. Furthermore, such heterogeneity can lead to problems in applications like electrodes within storage batteries.

During carbonization, mass losses between 62%–75% are reported for wood based composites (Treusch 2004, Hofenauer 2004). The reduction of utilised raw materials is of economic interest. Otherwise these comparatively inexpensive materials are renewable and available in great quantities. Basic material components like lignin and wood fibres are by-products of the pulp and wood industry, and are locally and regionally accumulated. An important fact is, that the density of carbon templates can be obtained by means of calculating the required density of the corresponding wood based composite (Hofenauer 2004).

4 Conclusion

Hot-pressed ARBOFORM® can be applied for carbonization. Great opportunities exist concerning wide modification possibilities regarding particle geometry, binder systems and additives (e.g., carbonization aid, increasing carbon yield). An important fact is the purity of that material due to the occurrence of calcium in P60. In literature, sodium contents for F45 after pyrolysis have been described (Krischok et al. 2006). These impurities are disturbing for special applications like storage batteries or infiltration with silicium. However, they could be avoided by using lignin of other sources or by chemical cleaning of the applied matter High density can be critical because of bubbling in consequence of insufficient gas flue, and cracks may occur by reason of anisotropy (Treusch 2004, Hofenauer 2004, Krischok et al. 2006). Lower densities are important to avoid these effects, e.g. by means of hot-pressing types. In accordance to Treusch (2004) the shrinkage of thermoplastic processable wood based composites can also be calculated.

The material properties of ARBOFORM® are comparable with special wood based panels developed for carbonization. The advantages of the applied material are described in the introduction. It is essential that commercially used ARBOFORM® is still processable at minor densities with thermoplastic behavior by extrusion or injection moulding. Therefore, further research is necessary.

Acknowledgement The authors gratefully thank Tecnaro GmbH for providing ARBOFORM®-mixtures.

References

Barton T, Bull L, Klemperer W, Loy D, McEnaney B, Misono M, Monson P, Pez G, Scherer G, Vartuli J, Yaghi O (1999) Tailored porous materials. Chem Mater 11(10):2633–2656

Burchell T (1999) Carbon materials for advanced technologies. Pergamon, Amsterdam

Byrne C, Nagle D (1997) Carbonized wood monoliths – characterization. Carbon 35(2):267–273

Davidson KO, Petterson JBC (2002) Birch wood particle shrinkage during rapid pyrolysis. Fuel 81:263–270

Deppe H-J, Ernst K (1996) MDF. DRW-Verlag, Leinfelden-Echterdingen

Fengel D, Wegener G (2003) Wood – chemistry, ultrastructure, reactions. Reprint (once de Gruyter). Kessel, Remagen

Grüneberg T (2009) Wood polymer composites (WPC)-processing technologies, chemical modification of wood and natural fiber components and improvement of selected properties. In: Kharazipour A, Schöpper C, Müller C, Euring M (eds) Review of Forests, Wood Products and Wood Biotechnology of Iran and Germany – Part III. Universitätsverlag Göttingen, Göttingen, pp 55–69

Herzog A, Vogt U, Kaczmarek O, Klingner R, Richter K, Thoemen H (2006) Porous SiC ceramics derived from tailored wood-based fiberboards. J Am Ceram Soc 89(5):1499–1503

Hofenauer A (2004) Entwicklung spezieller Holzwerkstoffe für die Herstellung Silicium-infiltrierter Siliciumkarbid-Keramik. PhD thesis. Holzforschung München. Technische Universität München. Online available. http://mediatum2.ub.tum.de/node?id=603609 (accessed 14 Dec 2007)

Hoffmann C (2005) Herstellung und Eigenschaften von SiSiC-Keramiken aus biogenen Fasermaterialien. Shaker, Aachen

Kaindl A (2000) Zellulare SiC-Keramiken aus Holz. PhD thesis. Technische Universität Nürnberg/Erlangen

Klingner R, Sell J, Zimmermann T, Herzog A, Vogt U, Graule T, Thurner P, Beckmann F, Müller B (2003) Wood-derived porous ceramics via infiltration of SiO_2-sol and carbothermal reduction. Holzforschung 57(4):440–446

Krischok S, Himmerlich M, Ahmed SIU, Kauffmann A, Pfitzer J, Huber M, Bengel W, Schaefer JA (2006) Biannual report 2005/2006. Technische Universität Ilmenau, pp 136–137

Shafizadeh F, Chin PPS (1977) Thermal deterioration of wood. In: Goldstein IS (ed) Wood Technology: Chemical Aspects. ACS-Symposium Series No. 43, Washington DC, pp 57–79

Sieber H, Hoffmann C, Kaindl A, Greil P (2000) Biomorphic cellular ceramics. Adv Eng Mater 2(3):105–109

Siegel S, Boden G, Petasch U (2004a) Biogene Keramik – eine Alternative? Teil 1. Keram Z 56(3):156–163

Siegel S, Boden G, Petasch U (2004b) Biogene Keramik – eine Alternative? Teil 2. Keram Z 56(4):234–238

Treusch O (2004) Poröse Kohlenstoffmaterialien auf der Basis spezieller Holzwerkstoffe. PhD thesis. Holzforschung München. Technische Universität München. Online available. http://mediatum2.ub.tum.de/doc/603515/document.pdf (accessed 27 June 2007)

Wagenführ R (2000) Holzatlas. 4. Ausgabe. Fachbuchverlag, Leipzig

Wegener G, Windeisen E, Scholz G, Schrader C, Pfitzer J, Nägele H (2006) Material alliance of lignin with natural fibres. Proceedings of the 9th European Workshop on Lignocellulosics and Pulp, Wien, pp 126–129