

Improving the sintering behavior of mesocarbon-microbeads for the manufacture of high quality carbon products using a joint promoter comprising carbon black and glycidyl methacrylate



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HIGHLIGHTS

- Qualities of sintered MCMB product was effectively improved by CB and GMA additives.
- CB and GMA exert a mutual cooperative effect on the sintering reactions of MCMBs.
- High bending strength (142 MPa) carbonized carbon-blocks were obtained.

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ABSTRACT

Carbon-black (CB) and glycidyl methacrylate (GMA) were used together as a joint promoter to improve the quality of sintered mesocarbon products. The results show that, in addition to inhibiting the condensation of β -resin at $\sim 200^\circ\text{C}$, GMA reduces the formation of volatile pyrolysis products during MCMB sintering at $\sim 300\text{--}550^\circ\text{C}$, while CB accelerates pyrolysis and lowers the temperature at which the evolution of volatile components begins. Our observations suggest that a cooperative effect, between CB and GMA, improves sintering behavior during sintered mesocarbon product manufacture, resulting in the formation of carbonized carbon blocks with high bending strengths (142 MPa) and high densities (1.87 g cm^{-3}).

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1. Introduction

The manufacture of high performance carbon blocks is attracting significant attention, due to their increasing use in high-technology applications, e.g. in the electric, metallurgical, nuclear, and chemical industries. Mesocarbon-microbead (MCMB) sintering is recognized as leading manufacturing method because of the excellent compressibility, and the rapid low temperature sinterability of MCMB materials [1–6]. Although the sintered mesocarbon products have high densities and good friction characteristics, they have unacceptable mechanical properties [5–7]. Much effort has been devoted to studying MCMB sintering reactions and improving the mechanical properties of the resulting products. Various additives, such as: ZrB_4C [5], Ti/Ni [8], carbon-

black (CB) [9,10], carbon-nanotube [11], SiC [12], and Ti [13] have been shown to promote the sintering reaction and improve the products' mechanical strength. In addition to the kinetic aspects of the reaction, the physical properties of the viscous raw materials, e.g. their contacting patterns and fluidities, are critical determinants of MCMB sintering outcomes. A higher β -resin content (i.e. the difference between toluene insoluble (TI) and quinoline insoluble (QI) compounds) and a better MCMB contacting pattern were found to favor the fluidity and sinterability of the 'clumpy' mixtures and to improve the bending strength of the products [11,14–16]. The reason for this is that the reactions are not fully homogenous [14–17]. However, the β -resin content of the MCMB raw materials must be limited, as an excess will promote bursting of the carbon matrixes, due to the release of volatiles during degradation [15,18,19]. The fluidity change of the raw materials can also affect neck-formation [2] between the MCMBs and consequently alter the product's resulting strength. The viscosity of the raw materials decreases initially with an increase in temperature,

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but increases rapidly when the sintering temperature is higher than the onset temperature for β -resin condensation [20]. The viscosity increase (hardening of the materials) at the initial low temperature stage tends to hinder neck-formation among the MCMBs. Taking these facts into account, and remembering that the β -resin content is a key factor in MCMB sintering [4,6,21,22], it is apparent that promoting material fluidity and reducing the destructive effects from pyrolysis gas evolution are important strategies for improving the quality of sintered mesocarbon blocks. However, very few studies have focused on these aspects, thus techniques for producing high quality sintered mesocarbon products need further investigation.

In this work, CB and glycidyl methacrylate (GMA) were used as joint reaction-promoters to modify the sintering behavior of the β -resin and improve the quality of the sintered mesocarbon products. GMA provides reactive functionality (epoxy and methacrylate) [23,24] to react with the intermediate species from the pyrolysis reaction to reduce the formation of volatile gases, while CB accelerates pyrolysis during sintering [9,10]. The effects of the promoters on improving the sintering behavior of β -resin, and enhancing the mechanical strength of the sintered mesocarbon products, were investigated.

2. Experimental details

Solid-resin containing a high β -resin content (65.6 wt %) and a low QI content (12.4 wt %), and MCMBs having a high QI content (ca. 99 wt %) and a low β -resin content (0.3–0.6 wt %) were provided by the China Steel Chemical Corp. (Taiwan). The average particle sizes of the solid resin and MCMB were 4.87 and 10.74 μm , respectively. The MCMBs were completely blended with the solid-resin and the various additives (BP-2000 CB 8 wt %, GMA 2 wt %) using a high-speed mixer (HSM-25, She-Hui Machinery Co., Taiwan) in dry form at 200 rpm for 15 min, and then submitted for modeling by cold isotropic compression (1600 kg cm^{-2}) in a cylindrical rubber mold (7.70 cm diameter and 14.2 cm length) using a Nikkiso CL-49-22-30 cold isostatic presser. The β -resin content of the green sample blocks was altered by changing the solid-resin/MCMB ratio. The β -resin contents had the same composition. These qualities facilitated examination of the dependence of the sintering behavior and the resulting product quality on the reaction-promoters and β -resin contents. The green sample blocks were carbonized in a Carbolite CWF-1100 furnace using a carbonization time-temperature sequence given in our previous paper [15]. The weight of the samples, before and after the carbonization, was measured in milligrams to determine the weight loss during the procedure. The molecular weight distribution of the solid-resin was determined using a MALDI-TOFMS (Autoflex III, Bruker Daltonics GmbH, Leipzig, Germany). The thermal behavior of the solid-resin and the MCMB raw material was examined by thermogravimetry (TGA) using a Perkin-Elmer SDT-Q600 Thermogravimetric Analyzer/Differential Thermal Analyzer (DTA). The bending strength of the sintered mesocarbon blocks was measured using a three-point fixture on an MTS Sintech 10/GL testing machine (method based on ASTM C 1161-02), while the density was measured by the Archimedes drainage method. Scanning electron microscopy (SEM) images of the carbon blocks were obtained using a JEOL-JSM 6300 SEM.

3. Results and discussion

3.1. Effects of GMA and CB on the molecular weight distribution and β -resin content of the heated solid-resin

The solid-resin, with and without GMA and CB, was heated at 170, 190 or 210 $^{\circ}\text{C}$ in a nitrogen environment for 2 h to examine the

efficacy of the reaction-promoters in inhibiting material condensation during the initial low temperature sintering process. The results, see Fig. 1, show that the heated (190 and 210 $^{\circ}\text{C}$) original solid resin (SR) show additional higher molecular weight peaks that result from condensation polymerization of low molecular weight compounds into larger molecular species (e.g. 2300 g mol^{-1}) [20,25,26], while the heated samples with the GMA (SR_{GMA}), CB (SR_{CB}) and CB + GMA (SR_{CG}) do not.

These results reveal that condensation polymerization of the solid-resin at ~ 200 $^{\circ}\text{C}$ was inhibited by GMA and CB.

The TI, QI and β -resin contents of the various heated solid-resins (measurements based on ASTM D 7280 and JISK 2425), are shown in Table 1. The results indicate that the fraction of higher molecular weight components (determined from TI and QI values), of the heated SR, are higher than those of SR_{GMA} , SR_{CB} and SR_{CG} . For example, the SR heated at 190 $^{\circ}\text{C}$ has a higher TI value (95.5%) compared to SR_{GMA} , SR_{CB} and SR_{CG} , whose TI values are 87.4%, 88.1% and 86.6% respectively. These results and those in Fig. 1 clearly show that the degree of condensation of the solid-resin, occurring at ~ 200 $^{\circ}\text{C}$, was significantly reduced in the presence of GMA and CB. In addition, the results also show that the TI (89.2%) and QI (62.4%) contents of the heated SR_{CG} are lower than those of the

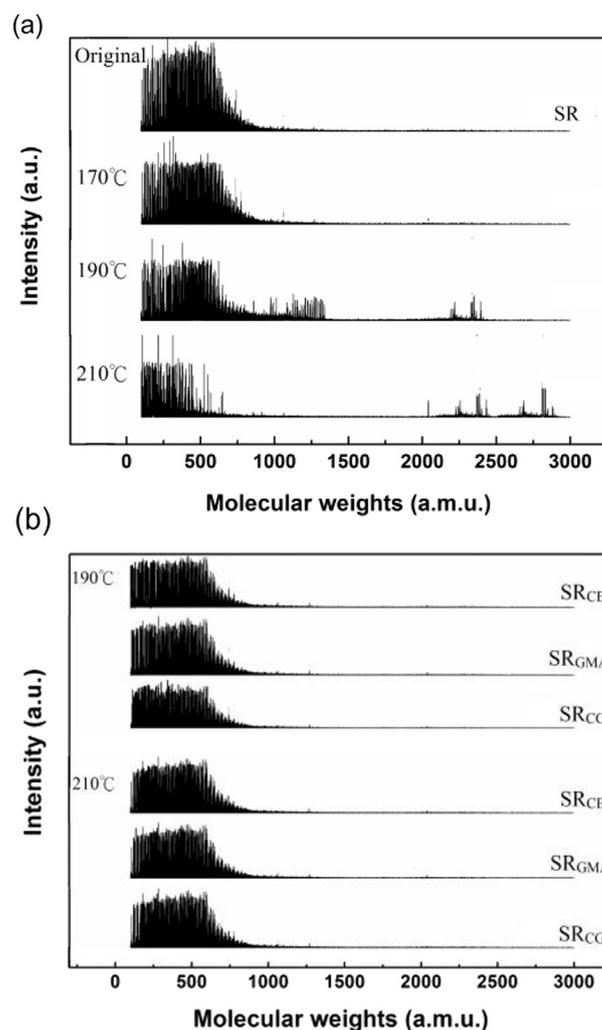


Fig. 1. Molecular weight distribution of: (a) the original and heated SR, (b) heated SR_{CB} , SR_{GMA} , and SR_{CG} . SR: solid-resin without additives. SR_{CB} , SR_{GMA} , and SR_{CG} are solid-resin with CB, GMA and CB + GMA, respectively. Additive content: CB 8 wt %, GMA 2 wt %.

Table 1

The TI, QI and β -resin of the heated solid-resin with and without GMA and CB additives.

No.	Samples	Heating temp. ($^{\circ}\text{C}$)	Content (wt%) ^a		
			TI ^b	QI ^c	β -resin ^d
1	SR	190	95.5	41.7	53.8
2	SR _{CB}	190	87.4	32.2	55.2
3	SR _{GMA}	190	88.1	33.6	54.8
4	SR _{CG}	190	86.6	31.0	55.6
5	SR	210	99.5	81.7	17.8
6	SR _{CB}	210	89.6	65.9	23.7
7	SR _{GMA}	210	90.2	68.8	21.4
8	SR _{CG}	210	89.2	62.4	26.8

^a Measurements based on ASTM D 7280 and JIS K2425.

^b Toluene insoluble.

^c Quinoline insoluble.

^d The difference of TI and QI.

SR_{GMA} and SR_{CB} heated under the same conditions, suggesting that there is a cooperative effect between GMA and CB that inhibits condensation of the solid-resin.

These facts were confirmed by the TGA/DTA curves at $\sim 200^{\circ}\text{C}$ which are presented in the following section.

3.2. TGA/DTA behavior of the solid-resin with and without GMA and CB

The TGA/DTA behavior of the solid-resin, with and without, CB and GMA is shown in Fig. 2. The low temperature weight loss rate

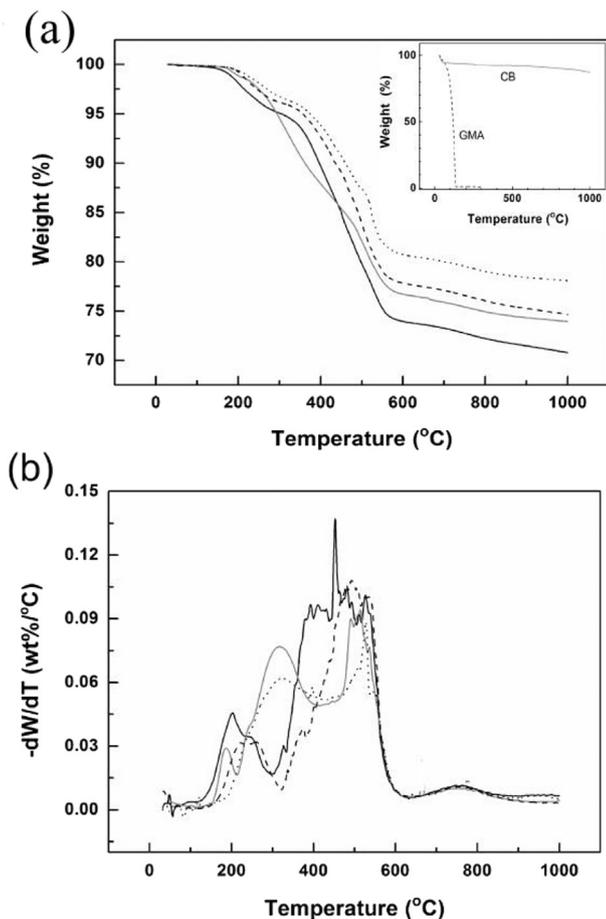


Fig. 2. Measurements of: TGA (a) and DTA (b). SR (heavy solid line), SR_{CB} (light solid line), SR_{GMA} (---) and SR_{CG} (····) in nitrogen atmospheres. Heating rate $10^{\circ}\text{C min}^{-1}$. Additive content: CB 8 wt %, GMA 2 wt %.

($-\text{dW}/\text{dT}$) at $\sim 200^{\circ}\text{C}$ for both SR_{CB} and SR_{GMA}, is smaller than that for SR. This result also supports the results in Table 1 and Fig. 1, showing that the evolution of volatiles, due to condensation was inhibited by CB and GMA.

Moreover, the high temperature $-\text{dW}/\text{dT}$ at $300\text{--}550^{\circ}\text{C}$ of the SR_{CB} shifts negatively (i.e. the onset temperature shifts from 300 to 210°C), indicating that the CB promoted pyrolysis of the solid-resin and accelerated pyrolysis driven gas evolution. Similar thermal behavior of MCMB in the presence of CB was also obtained by Menéndez et al., who suggested that this phenomenon was attributable to adsorption, by the CB, of most of the volatile components and a lowering of the temperature to the partial polymerization of heavy volatiles [10]. The volatiles released at around 550°C have been found to comprise mainly methane [2,14,27].

On the other hand, the high temperature $-\text{dW}/\text{dT}$ peak of the SR_{GMA} remains in the original temperature range ($300\text{--}550^{\circ}\text{C}$), but has a lower $-\text{dW}/\text{dT}$ value in the range $300\text{--}450^{\circ}\text{C}$. This indicates that GMA reacted with pyrolysis intermediates, e.g. methyl radicals [24], generated during the sintering and thereby inhibited the formation of volatiles.

The total weight loss of the SR below 1000°C was 29.2%, while SR_{CB}, SR_{GMA} and SR_{CG}, lost 26, 25.3 and 21.9%, respectively, thus showing that both CB and GMA reduced the evolution of volatiles during sintering. Moreover, the weight loss of the SR_{CG} is much less than that of SR_{GMA} or SR_{CB}. This result suggests that there is a cooperative effect when using the two reaction-promoters in combination. This can be due to GMA inhibiting the formation of pyrolysis volatiles, while CB accelerates the pyrolysis reaction and reduces the onset temperature for volatile evolution.

3.3. Improvement of bending strength and density of the carbonized carbon blocks in the presence of CB and GMA

The results of bending strength tests for the carbonized carbon blocks without the reaction-promoters (CC) in the raw materials, and those with CB (CC_{CB}), GMA (CC_{GMA}) and CB + GMA (CC_{CG}) are shown in Fig. 3. The bending strength of the various carbon blocks increases linearly with an increasing β -resin content in the mixtures, as reported in our previous paper [15]. The highest bending strength (142 MPa) was obtained from CC_{CG} samples having 14.4% β -resin content in the raw materials. This is 1.5 times the highest bending strength (96 MPa) obtained from the CC samples, and 1.4–3.5 times the bending strength of the sintered mesocarbon

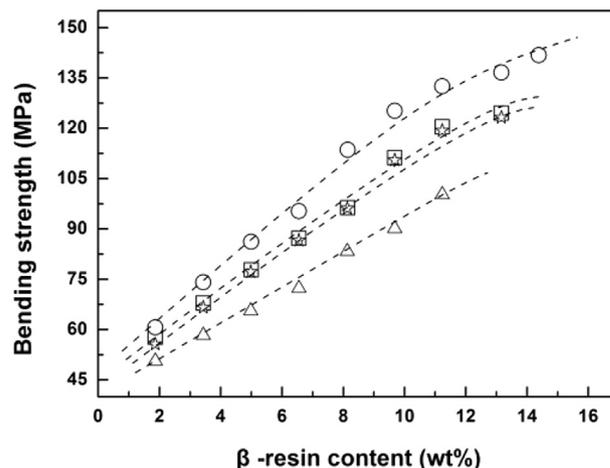


Fig. 3. A comparison of bending strength of the various carbonized carbon blocks (\circ) CC_{CG}, (\square) CC_{CB}, (\star) CC_{GMA} and (Δ) CC.

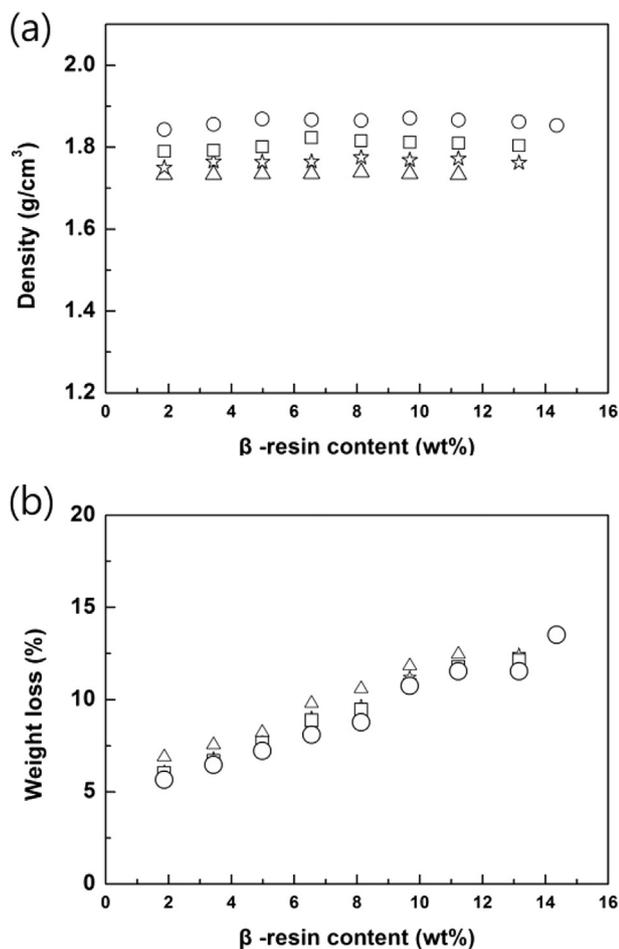


Fig. 4. Dependence of the (a) density (b) weight loss of (○) CC_{CG}, (□) CC_{CB}, (☆) CC_{GMA} and (△) CC on the β -resin content of the green samples.

products, prepared at the same carbonization temperature range i.e. 1000–1100 °C [18,21,28–31]. The CC_{CG} with a higher β -resin content (15.2%) showed burst phenomena during carbonization; indicating that the maximum tolerable β -resin content for the CC_{CG} samples is ~14.4–15.2%. The maximum tolerable β -resin content for the CC_{CG} samples is higher than that for the CC, CC_{CB} and CC_{GMA} samples: note, burst phenomenon for the CC, CC_{CB} and CC_{GMA} samples was observed with β -resin contents of 13.2, 14.4 and 14.4%, respectively. These results obviously show that the formation of volatiles from the degradation of the β -resin was inhibited and that the destructive effect on the carbon blocks was effectively reduced by the combined use of the reaction-promoters during sintering. Thus, the addition of CB and GMA allows a higher β -resin content for the MCMB raw materials, i.e. they enable the use of materials having a higher fluidity and sinterability for the manufacture of high strength sintered mesocarbon products.

The bending strength increase of CC_{CG} is 10–36 MPa when compared to CC, and 7–20 MPa when compared to CC_{CB} and CC_{GMA}. These results support the suggestion that there is a cooperative effect between CB and GMA that improves the qualities of the sintered MCMB products.

The densities of the various carbonized carbon blocks are shown in Fig. 4. The results indicate that the CC_{CG} samples have a constant value of 1.87 g cm⁻³ when the β -resin content is 5–15 wt%, which decreases slightly with a decrease in the β -resin content to below 5.0 wt%. The density of the CC_{CG} is ca. 7% higher than that of CC (1.73–1.74 g cm⁻³). The density dependence of the carbon blocks on the β -resin content is quite similar to that reported by Gao et al. [21], i.e. a maximum density (1.76 g cm⁻³) with an optimum β -resin content of 8.9 wt %, such minor differences are attributable to the MCMB β -resin content and the contacting patterns varying with preparation procedures [15]. The weight losses of the various CC_{GMA} samples are 1–2% smaller than those of the CC samples with the same β -resin content (Fig. 4(b)).

These results further show that the joint use of CB and GMA effectively inhibits the formation of pyrolysis volatiles and reduces the weight loss during the sintering, as indicated in Fig. 2.

Fig. 5 shows SEM images of various carbonized carbon blocks' fracture surfaces. The microstructure of the CC (Fig. 5(a)) shows

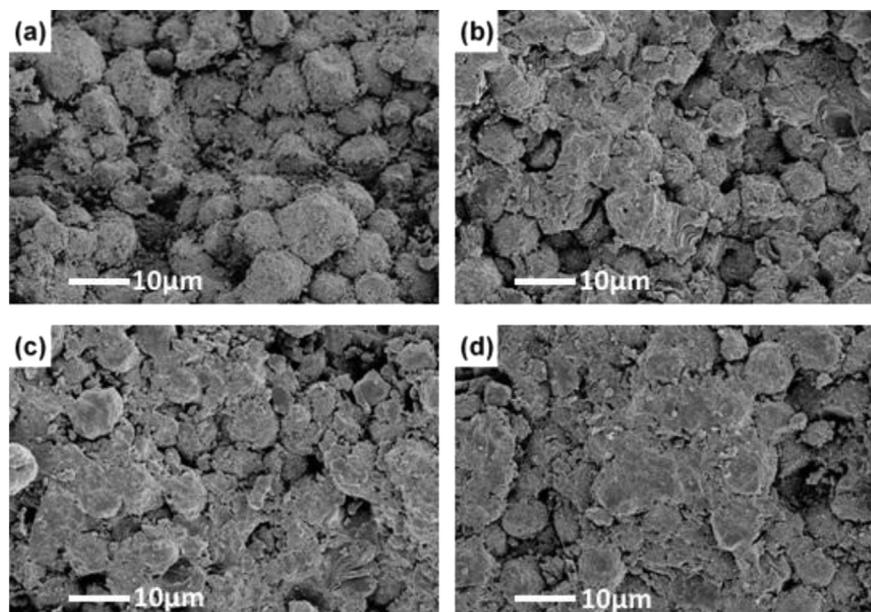


Fig. 5. SEM images of the fracture surface of the carbonized (a) CC, (b) CC_{CB}, (c) CC_{GMA} and (d) CC_{CG} sample with 11.2% β -resin content.

that sintering-necks appeared among the MCMBs; however, the appearance of pores and cracks suggests that sintering-necks are lack solidity. In contrast, the microstructures of the CC_{CB} , CC_{GMA} and CC_{CG} samples are shown to be relatively firm and well-connected - especially that of CC_{CG} (Fig. 5(d)). This result is further indication that the quality of the sintered mesocarbon products was improved significantly as a result of improvements in the fluidity and sinterability of the MCMB materials in the presence of CB and GMA.

4. Conclusions

The preparation of high quality carbon blocks by MCMB sintering in the presence of CB and GMA was investigated in this work. The results show that CB and GMA exert a cooperative effect that leads to an improvement in MCMB sintering. The joint use of CB and GMA inhibits the condensation of β -resin, reduces the formation of volatiles from pyrolysis at the initial low temperature stage, increases the maximum tolerable amount of β -resin, while simultaneously promoting the fluidity and sinterability of the MCMBs and is thus a very useful and practical method for improving the quality of sintered mesocarbon products. The maximum bending strength and density of the carbonized samples, manufactured in the presence of CB and GMA are respectively 50% and 7% higher than when made in their absence.

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