DEVELOPMENT OF POROSITY IN PITCH-BASED C/C COMPOSITES.

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Introduction

The present work is focused on C/C composites made with carbon fibres and coal tar pitch. The objective of this study is to analyse the porosity present in the unidirectional C/C composite after a first impregnation-carbonisation step in relationship with pitch treatment in air. Since opened and closed voids are present in the final C/C composite, their characteristics – amount, size - have been determined using quantitative image analysis.

Experimental

High-strength PAN-based carbon fibres (IPCL, India) were used as a reinforcing agent. A commercial binder coal tar pitch with a Mettler softening point equal to 121°C was taken for the matrix precursor. The manufacturing process for the C/C composite has been reported elsewhere [1]. C/C composite prepared with the as-received pitch will be denominated P; the composites derived from pitch treated in air will be designed by SP-air. The porosity was characterized by image analysis on sections perpendicular to the fibre direction. The porosity determined by image analysis is expressed by the ratio of the total area of voids to the total analyzed area. Moreover, it has been verified that a satisfactorily agreement exists between values of porosity determined by image analysis and by density measurements. Detailed informations on the procedure are given elsewhere [2,3,4].

Results and discussion

A polished transverse section of composite sample P as viewed by video camera is shown in Fig. 1a. The bright areas correspond to carbon fibre tows bound by carbon matrix and the darker ones to voids. Since the C/C composites had only one impregnation cycle of pitch, it is not surprising to find many large voids. In contrast, the aspect of the composite prepared with pitch treated in air, sample SP-air, has a somewhat less developed porous structure (Fig.1b). The size of the voids which essentially correspond to cavities located between the densified carbon fibre tow are ranging between 20µm – 2mm. Moreover, the intratow porous structure has been also determined from optical microscopy views inside densified tows of carbon fibres ranges from 0.5 to 10 µm. In this case, the carbon fibres can be easily differentiated from the surrounding carbon matrix; the voids corresponding to black spots in the observed image. Thus, two voids with different ranges in size can be distinguished from the observation of cross section of the composite: intertow cavities (20µm to 2 mm in size) which constitute the main part of the porosity of the composite and the intratow pores and fissures of much smaller size (0.5-10µm in size). The values of the intertow and intratow porosity are indicated in table 1. The measured total porosity is significant for both type of composites. However, in case of treatment of pitch in air, the intertow porosity is markedly reduced. This observation may be attributed to the fact that a higher viscosity of the pitch induced by its treatment in air will restrict its mobility during pyrolysis. In turn, this will lead to less pronounced debonding between fibre tows. Cumulative intertow and intratow voids fraction is plotted as a function of pore size for the different composites in Fig. 2a and 2b respectively. It can be seen that treatment of pitch in air prior to tow impregnation induces a significant narrowing of the intertow pore size distribution in the composite. In the case of sample P, about 30% of the total pore volume originate from pore larger than 1mm in size whereas for the other one, nearly all voids are smaller than 1 mm in size. Hence, treatment of the pitch in air leads to a significant decrease of the intertow pore size and volume as compared to the untreated pitch-based composite. It appears from Fig.2 (b) that pitch treatment does not have a significant influence on the contribution of the small pores (size below 10 µm) on the overall porosity of the composite. However, it should be noted that the pore size distribution of the intratow porosity is markedly affected by pitch treatment in air since it tends to become narrower (by a factor 2). This fact suggests that the fluidity of the treated pitch is significantly lowered and coalescence of bubbles of volatiles during pyrolysis becomes less feasible. Similar informations have been deduced from the analysis by thermal programmed desorption (TPD) of the volatiles still present in the material and which will be released during thermal treatment. Indeed, experimental results indicate that the carbonisation of the pitch matrix is incomplete during composite processing both for the untreated and the air-treated pitch. It has been shown that upon treatment of pitch in air, the tendency to develop a less accessible or even closed porosity is more pronounced.

Conclusion

The experimental results point out that the treatment in air of pitch used as matrix precursor strongly influences the development of the porosity in the resultant C/C composite. In fact, the treatment of pitch in air induces major changes in the porosity amount and size of voids. In particular, the debonding between fibres is less pronounced in the case of treated pitch which results in a smaller pore fraction at the intertow level. Also, the pore size distribution of the voids located inside the impregnated fibre tows (intratow porosity) becomes narrower after air treatment of the pitch. The development of a important closed porosity in the composite based on treated pitch has been also noted.

References

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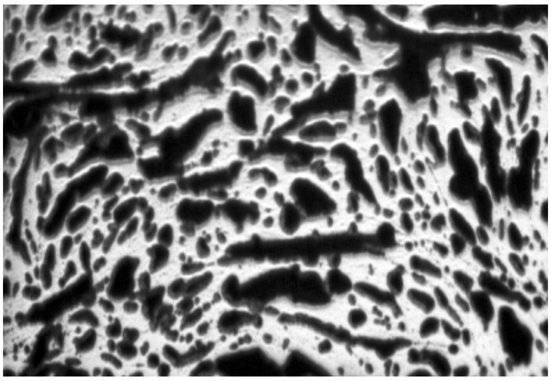
Table 1. Porosity of C/C composites prepared at 1000°C with different types of pitches

Composite	Intertow porosity (%)	Intratow porosity (%)		Total porosity (%)
		in tow	in composite	
P	43	6.0	3.4	46
SP-nit	40	8.1	4.9	45
SP-air	26	4.8	3.6	30



2mm

Fig.1(a) : Aspect of polished section of composite P

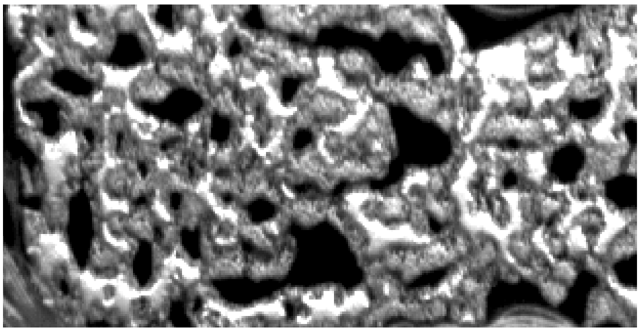


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Fig.1(b) : Aspect of polished section of composite SP-air

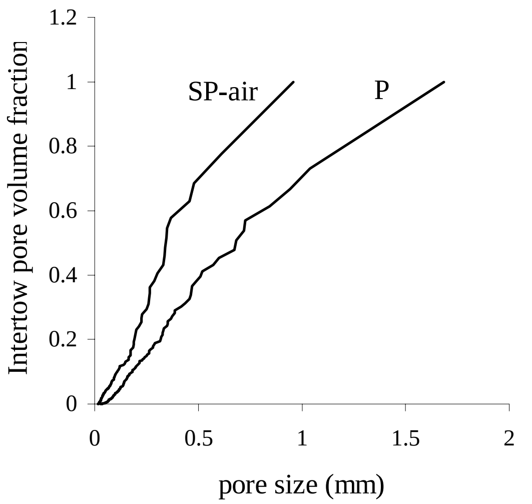

Fig.2(a): Intertow pore volume fraction as a function of pore size for composite P and SP-air

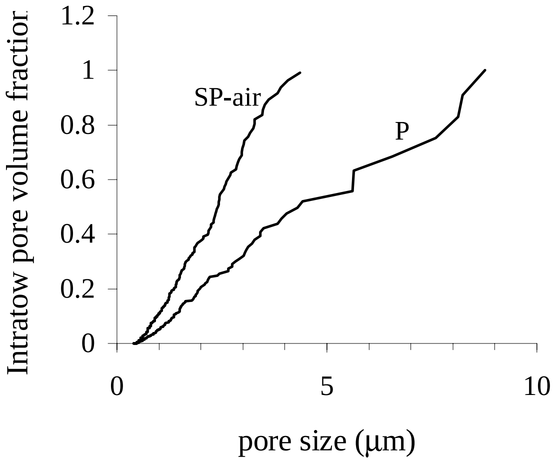

Fig.2(b): Intratow pore volume fraction as a function of pore size for composite P and SP-air