In-situ Mesophase Formation in C/C Composites and their Effect on Mechanical Properties

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Abstract

Matrix microstructure plays an important role in controlling the overall performance of the C/C composites which depends on the type of matrix precursor and processing parameters. In the present investigation, composites were developed from T300 carbon fibers with three types of coal tar pitches with different QI contents. These composites were heat treated isothermally between 400-500ºC for different interval of time to develop in-situ mesophase in the composites. Thereafter composites were carbonized at 600 and 1000ºC respectively in an inert atmosphere. These composites were characterized for physico-mechanical properties and microstructure. It is observed that, mesophase formation and type of texture of carbon derived from matrix in composites depends upon Q.I. content in the coal tar pitch. Bending strength of C/C composite was nearly double in case of in-situ mesophase developed composite as compared to the one developed without formation of mesophase. The bulk density of the C/C composites shows interesting behavior with Q.I. content of the pitch.

Introduction

Carbon/carbon (C/C) composites are unique materials that can have high specific thermal and mechanical properties at room temperature as well as at high temperature. Thus, these materials find applications as strategic materials in the areas of aerospace and industrial sectors [Fitzer, E.1983, Fitzer, E.,and Manocha L.M.1998]. The properties of C/C composites are determined by the type of architecture of the fibers and the microstructure of the supporting matrix. The microstructure of a carbon-carbon composite may be described in terms of its porosity, interfaces and texture, and it largely depends on the chemical composition and physical properties of the matrix precursor, as well as on the processing conditions [McEnaney, B. and Mays T, 1993., Rand, B. 1993]. Two main types of the matrix precursors are currently used in the preparation of C/C composites by liquid impregnation resins and pitches. The later offers great possibilities because of the availability of wide range of pitches with different characteristics, their relatively low price and high carbon yield and specially, because of their ability to generate graphitizable matrices. Coal tar pitches are more aromatic, with compounds of higher condensation degree and they contain carbonaceous particles called primary quinoline insoluble (Q.I.) which are generated secondary QI and remain in the pitch. These Q.I. play an important role in the development of microstructure and hence, the mechanical properties of the composites.

Therefore in the present investigation effort was made to develop mesophase in different pitches having different Q.I. content and same pitches were used for the development of in-situ mesophase in C/C composites. The effect of mesophase formation on the mechanical properties of C/C composite was studied.

Experimental

In this investigation three types of pitches of different properties were used (table 1) as a matrix precursor for the development of in-situ mesophase in the composites. Initially, experiments were performed to see how the mesophase were developed in the three different pitches having different Q.I. content. These pitches were heat treated at different temperature from 400 to 475ºC for an interval of one to three hrs. Same conditions were maintained for the development of in-situ mesophase in the composites. The green composites were prepared by using PAN based T-300 carbon fiber as reinforcement and three different pitches as matrices. The composites were initially heat treated at different temperature from 400 to 475ºC for an interval of one to three hrs in an inert atmosphere. Later on, these composites were heat treated at 600 and 1000ºC. The microstructure of pitches and composites were studied by optical microscope and the carbon yield and weight loss of heat treated pitches was studied by TGA (Metter TOLEDO STAR). The C/C composites were characterized for mechanical properties on Instron testing machine (4411) by three point bending technique.

Table 1: Properties of Matrix (different pitches)

Properties	**M1**	**M2**	**M3**
Quinoline insoluble (%)	10	11.1	14.7
Toluene insoluble (%)	37.6	39.8	42.5
Coking value (%)	59	56.2	52
Softening point (ºC)	110	107	104.8
Specific gravity (g/cm^3)	1.34	1.31	1.32

Results and Discussion

Table 2, shows the coking value of resultant pitches after heat treated at 425ºC for different time intervals the yield is higher as compared to the raw pitches, due to the removal of relatively lower molecular weight components from the precursor pitches as well as due to polymerization and condensation reactions taking place between the various planer aromatic molecules present in these pitches. Such reaction obviously leads to the formation and growth of mesophase spherules. This is observed in the optical microscopic investigation of heat treated pitches. Figure 1(a) shows the optical micrographs of M1 pitch after heat treatment at 425ºC for different soaking time. The well developed spheres of mesophase in the pitch along with the QI cluster after 1 hr., of soaking time (M1-425(1)) figure1(a). With increasing soaking time to 3 hrs., quantity of the mesophase spheres formation increases, figure 1b (M1-425(3)).

Table 2. Carbon yield after TGA at 1000ºC in inert atmosphere

Mesophase formation conditions (Temp. ºC)	**M1**	**M2**	**M3**
425 (1)	62	73	81
425(2)	59	76	69
425 (3)	79	85	84

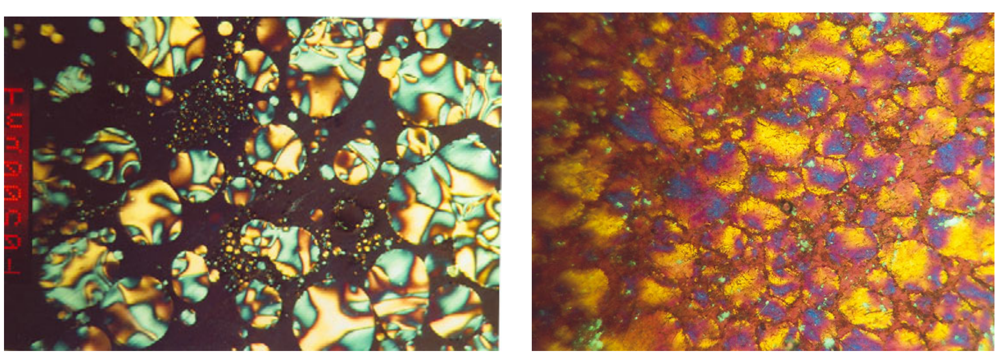

Figure 1. Optical micrographs of M1 pitch after 425ºC for 1 hr and for 3 hrs.

In case of pitch M2, the mesophase spheres of different size in the periphery of primary QI clusters are observed (figure 2). At a later stage (2hrs. soaking time) sphere size increases and regularly distributed in the pitch matrix and Q.I. particles are partly located in the sphere periphery. With increasing the soaking time the mesophase spheres converted in to the coalescence “bulk” mesophase and QI particles occur both as inclusions in the coalesced and separated aggregate of isotropic appearance. On the other hand, in pitch M3, the mesophase sphere growth is restricted even with increasing the soaking time due to the higher content of QI (figure 3).

Figure 4 shows the bulk density of C/C composites at various stages. Initially at green (110ºC) stage, higher density of M1 pitch based composite due to the lower content of Q.I. and lower density of M3 pitch based composite is due to the higher Q.I. Same trend is observed at different stages of processing of the composites up to temperature 1000ºC. The bulk density at 1000ºC heat treated composites is 1.30, 1.2 and 1.17 g/cc for M1, M2 and M3 respectively. The higher density of M1 composites is due to development of higher mesophase content in these composite this leads to larger crystalline size due to laminar type texture of carbon matrix at fiber-matrix interface.

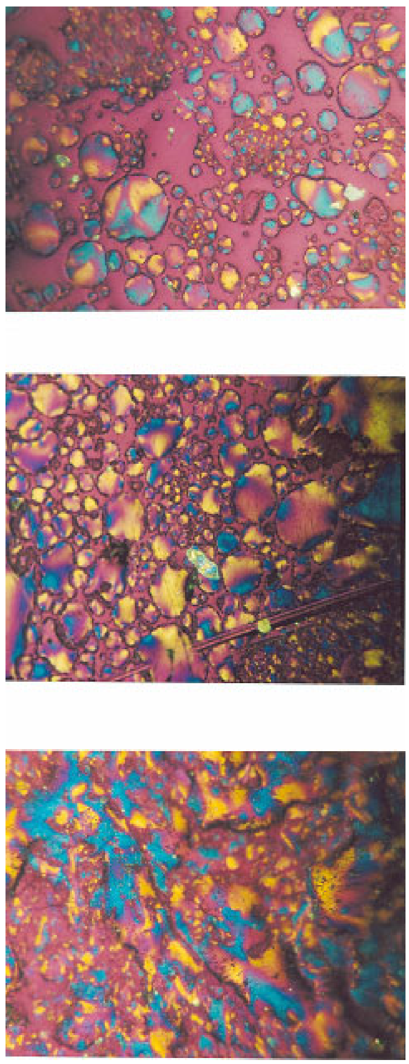

Figure2. M2 pitch heated 425 for 1,2, and 3 hrs.

Figure 3. M3 pitch heated 425 for 1,2, and 3 hrs.

Figure 5 shows microstructure of C/C composites with in-situ mesophase formation at 425ºC and heat treated at 1000ºC. In case of M1 matrix based C/C composites (figure 5a), fiber bundles are relatively well filled with mesophase layers aligned parallel to the filaments (laminar type). As the soaking time increases, width of mesophase layer around the fibers also increases (figure 5b). While in case of M3 pitch based composites, the matrix microstructure of both types laminar and mosaic this is due to higher content of QI figure6(a). It is also interesting to note that lower QI content in the precursor M1 pitch resulted in to poor fiber-matrix interactions (figure 5c). While on the other hand, higher content of Q.I. gives the better fiber-matrix interactions (figure 6a &b).

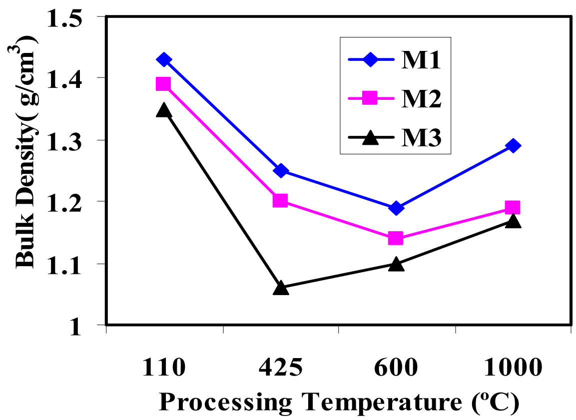

Figure 4: Bulk density with processing stage of composites with different pitches (at 425ºCfor 1hr.)

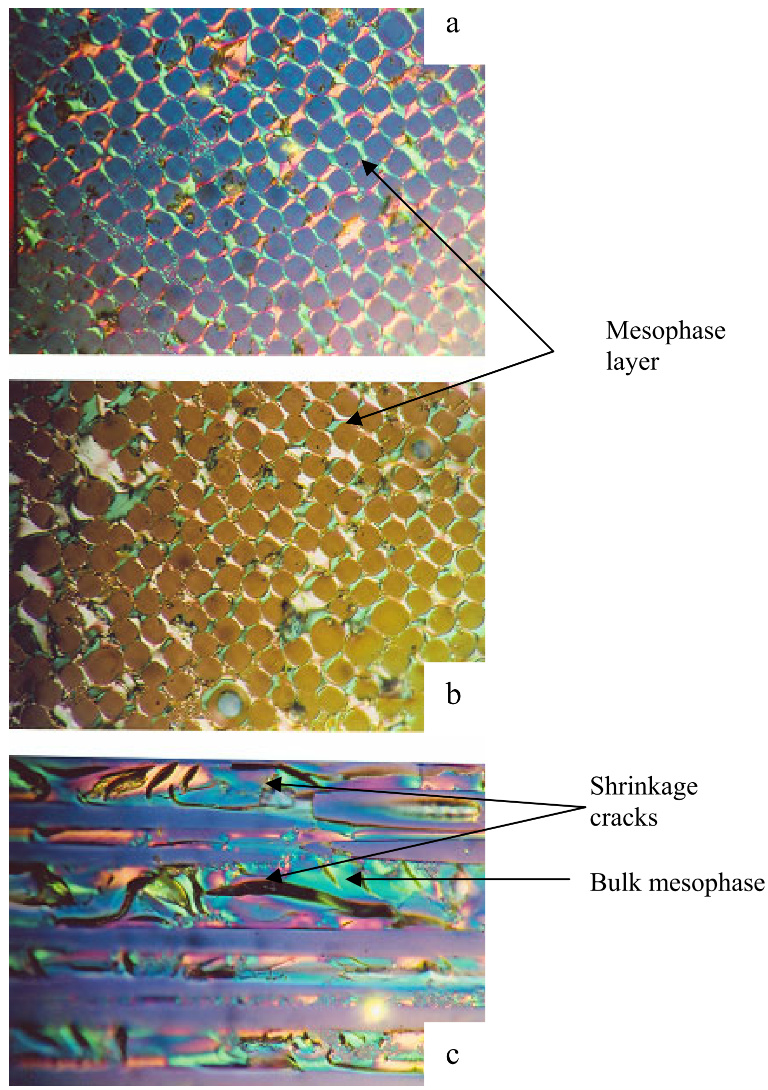

Figure5: Optical micrographs of M1 pitch based C/C composites

mosaics type texture in composite is due to the higher Q.I. content in pitch because the pitch contains solid carbonaceous particles (primary Q.I.) that tend to form clusters giving microstructure of smaller domain size. While other components in the precursor pitch are able to develop anisotropic structure of larger size of domains which tends to orient around the carbon fibers. Figure 7 shows the variation in bending strength with the processing condition of mesophase formation in C/C composites. Before mesophase formation in composites, bending strength is in the order of 80-100 MPa and after mesophase formation strength increases up to 180 MPa in case of M1 pitch based composites where the mesophase formed at 425°C for one hr. With increasing the soaking time and the mesophase formation temperature, bending strength is almost constant or decreases slightly in all the composites. In M1 pitch based composite, bending strength is higher through out the processing stages due to the development of laminar type texture around the carbon fibers and as a consequence weak interface in the composites. However, in M2 and M3 pitch based composites lower value of bending strength is due to strong fiber-matrix interaction as higher QI.

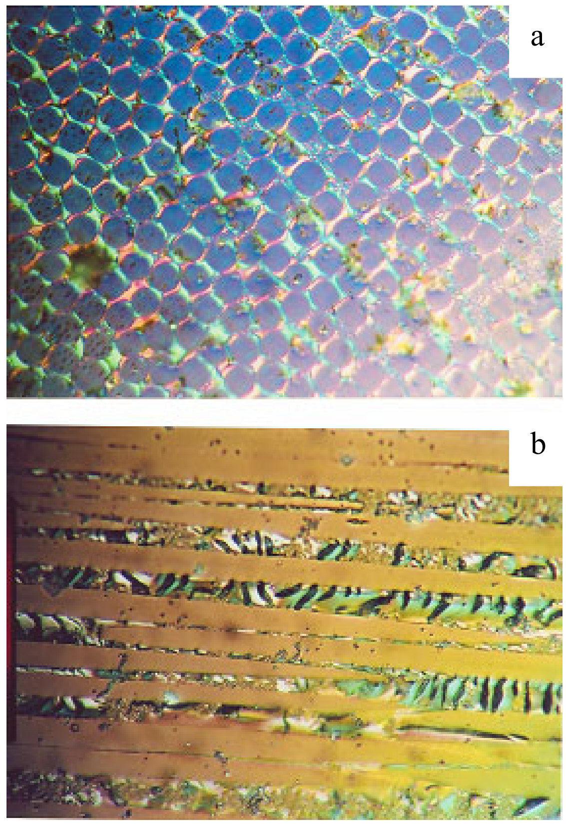

Figure6. Optical micrographs of M3 pitch based C/C composites

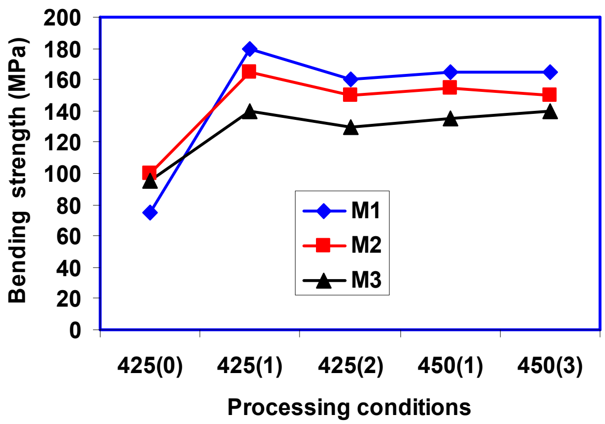

Figure 7: Variation in bending strength with processing stages of mesophase formation in composites.

Conclusions

It is found that, mesophase formation and type of texture of carbon derived from coal tar pitch matrices in composites depends upon Q.I. content. Bending strength of C/C composite is nearly double in case of in-situ mesophase developed composite having low Q.I. content as compared to without mesophase developed at 425ºC. The bulk density is also higher in case of mesophase developed composites and with increasing Q.I. content bulk density of C/C composites decreases.

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