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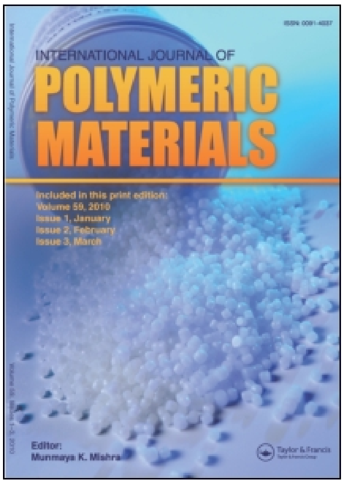

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D. C. Prevorsek[a]; R. K. Sharma[a]
[a] AlliedSignal Inc., Morristown, New Jersey, USA

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TOWARDS A NON-CVD PROCESS FOR HIGH-PERFORMANCE C–C COMPOSITES: PART I

D. C. Prevorsek and R. K. Sharma
AlliedSignal Inc. Morristown New Jersey, USA

With the objective to develop a non-CVD process for C–C composites we investigate the effects of pyrolysis conditions on rheological and chemical characteristics of various pitches. Pyrolysis processing windows were also established for subsequent pultrusion and resin transfer molding of carbon fibers preforms.

Keywords: pitches, mesophase, pyrolysis, processibility, C–C composites

INTRODUCTION

The objective of this research was to establish the feasibility of non-CVD process for the manufacture of high performance C–C composites. The working hypothesis was that the porosity caused by the pyrolysis of the matrix can be eliminated or reduced to acceptable levels by applying the pressure on the preforms during pretreatments, carbonization and graphytization steps. In conventional processes, the porosity is controlled by costly CVD OR CVI steps.

We also assumed that the optimal performance of the final product will depend on the level of the mesophase (I.E. The liquid crystalline component of the pitch). Thus, the entire process and matrix selection and its pretreatments were investigated using mesopitch content as a major process and product variable.

Part I of this study covers our matrix research (pyrolysis) and studies of impregnation of carbon fiber assemblies suitable for carbonization and graphitization.

OVERVIEW OF MATRIX RESEARCH

A great deal of literature [1–4] has been devoted to the pyrolysis of pitches because of their importance as precursors for high modulus carbon fibers. Studies of the carbonization of coal tar or petroleum pitches have confirmed

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Address correspondence to D. C. Prevorsek, P.O. Box 677, Hood River OR 97031, USA.

that the principal features of graphitic and pregraphitic micro-structures are established in a relatively narrow range of temperatures near 450°C in which the pyrolysing mass exists as a viscous anisotropic phase, *i.e.*, as a mesophase in the terminology of liquid crystals. The molecules in the precursors, such as coal tar and petroleum based pitch materials consist of polynuclear, planer aromatic hydrocarbons as well as lower molecular weight, lower melting compounds. The latter play an important role in the softening temperature of the pitch and facilitate the significant intermolecular motions leading to mesophase formation. However, the low molecular weight components must be removed (physically removed or chemically polymerized to a higher molecular weight) to stabilize the material without large rearrangements after fabrication.

During the early stages of the pyrolysis, the various pyrolytic reactions result in an increase in the average molecular weight of the fluid. With increasing carbonization temperature, increasing fluidity of the system increases the diffusivity of the system leading to an enhanced probability of molecule–molecule interactions which result in the formation of the nematic liquid crystals from the aromatic molecules. Chemical bonding between the constituent molecules of the liquid crystal leads to a polymeric, anisotropic stable phase, called the mesophase, which consists of small spherules. As pyrolysis proceeds further, the spherules continue to grow at the expense of the isotropic fluid phase until they eventually touch each other. If there is sufficient plasticity at this stage then the mesophase spherules respond to the requirement of minimum surface energy and become spherical. When two spherical particles meet coalescence occurs and the two adopt a single spherical shape having a lamelliform morphology where the surface of the mesophase spheres is made of the molecules with their planes at right angles to the sphere surface. The formation of the mesophase is irreversible and it is relatively insoluble in benzene and pyridine.

The nucleation, growth and percolation of gas bubbles within the mesophase can produce extensive plastic deformation by which the microstructure is both oriented and reduced to finer structure. The microstructural refinements can be intensified by purposefully applying mechanical deformation to the mesophase while it is still plastic. In general stacking sequences of the constituent molecules in the nematic liquid crystals are maintained in the mesophase and established in the anisotropic carbon formed therefrom.

Thus, the anisotropic carbons possess an imperfect, pregraphitic structure which is progressively perfected, with increasing temperature, towards graphite. The degree of anisotropy and the detail of the stacking sequences influence graphitization which is essentially the removal of the stacking defects in the original carbon. The ability to graphitize increases as the size of the elemental domains of the bulk mesophase increases. Thus, the properties of the graphitized material closely depend on the structure of the mesophase (extent of order and molecular perfection) which in turn, is dependent on the chemical and structural properties of the material of pitch and the carbonization conditions. Control of the carbonization conditions for a given pitch thus offers a method of controlling the properties of the graphitic material.

EXPERIMENTAL

Materials

The pyrolysis experiments were carried out on petroleum and coal tar pitches listed below:

Petroleum pitches	Ashland Pet Co A-240, Aerocarb 70 and Aerocarb 80
Coal tar pitch	Allied 15-V

Pyrolysis Apparatus and Pyrolysis Conditions

Pyrolysis of the various pitches was carried out as a function of

a. temperature (365°C to 465°C)
b. soak time (1 hr to 16 hr)
c. atmosphere (argon or hydrogen)
d. pressure (15 psi to 70 psi)

Normal pressure experiments were carried out in a Lindburg Box Furnace consisting of a 1200°C box furnace, a retort and a programmable temperature control. Prior to use, the interior of retort was calibrated for temperature for various heating rates and final temperatures used in actual experiments. The retort inside the box furnace allowed for the maintenance of controlled atmosphere (argon or hydrogen) during pyrolysis. In a typical pyrolysis experiments, a covered porcelain or quartz crucible containing 15–20 g of crushed pitch was placed in the retort at room temperature. The retort was purged with argon at one atmosphere for half an hour to expel any oxygen from the system. The temperature was raised at 10°C per minute to the desired pyrolysis temperature and held constant there for the desired soak time. At the end of experiment, the heating was terminated and the sample allowed to cool to room temperature. During the entire process argon at one atmosphere pressure was passed through the retort at about

20 cc per minute. The volatiles given out were carried away by the purging argon and caught in a trap inside. The solid pyrolysis residue was removed and weighed. The reactor used for high pressure experiments consists of a cylindrical vessel made of stainless steel ($\sim$7 cm diameter, 25 cm height). The reactor is heated by an electric furnace incorporating a programmable temperature controller. The temperature was measured by a thermocouple placed in the reaction mass. In a typical experiment the furnace was heated to the desired pyrolysis temperature.

A known weight (15 – 20 g) of crushed pitch was added to the reactor which was then locked with pressure tight lid, evacuated, and filled with desired gas (argon or hydrogen). After the desired pressure was reached the reactor was placed in the furnace and allowed to reach final temperature. During heating and the final pyrolysis the pressure was kept constant by slow bleed of excess pressure. At the end of the experiment the reactor was removed from the furnace and allowed to cool down and solid residue was removed and weighed.

Sample Characterization

The pyrolysis residues prepared under different conditions were analyzed for meltability, solubility, char yield, chemical structure and morphology using the standard techniques of TGA, solvent extraction, infra-red analysis, X-ray and microscopy.

Summary of Results

Pyrolysis yields, *i.e.*, the fraction of the original pitch left as residue after the pyrolysis experiment, were found to be dependent on the experimental conditions. The yields decreased with an increase in temperature and soaking time. Hydrogen atmosphere accelerated the rate of pyrolysis relative to argon. The hydrogen gas and pressure also result in an increased yield relative to argon at normal pressure.

The pyrolysis residues were extracted with quinoline and toluene as solvents. Toluene being the poorer solvent, the toluene insoluble fraction Q_iT_i includes the quinoline insoluble fraction Q_i. The Q_i fraction is generally regarded as a measure of mesophase content and consists of nonmeltable oriented liquid crystalline domains of higher molecular weight material. The quinoline soluble but toluene insoluble fraction Q_sT_i, on the other hand, consists of lower molecular weight material and can be made to melt depending on the pyrolysis conditions. The solubility data show that milder pyrolysis conditions (time and temperature) favor the formation of Q_sT_i structures whereas more and more of highly oriented Q_i is formed as the pyrolysis conditions become more severe. Formation of Q_i is also enhanced in the presence of hydrogen relative to argon.

Measurement of toluene insoluble and quinoline insoluble contents of the pyrolysis residue produced under a given condition (Figs. 5a and 5b) shows that the toluene insoluble content (Q_iT_i) is always larger than the quinoline insoluble content (Q_i). In other words, there are formed oriented domains which are soluble in quinoline but insoluble in toluene. These fractions must have a lower molecular weight than the ones which are insoluble in quinoline.

However, the results in Table 1 show that, by proper selection of pyrolysis time and temperature, it is possible to produce pyrolysis residues with identical amounts of total liquid crystal domain (total L_c%) but having different amounts of low molecular weight and high molecular weight components. The relative amounts of these components can be expected to influence the melt processibility of the mesopitch since the low molecular weight material is more readily meltable than the high molecular weight material. The choice of pyrolysis conditions can thus provide a method to vary the composition of the mesopitch for optimal processibility.

Char yields of the pyrolysis residues and solvent insolubles were measured by heating to 1000°C in Helium, the char yields are seen to increase with pyrolysis time and temperature. For a given pyrolysis experiment the char yield is the highest for Q_i fraction followed by Q_iT_i, Q_sT_i and the pyrolysis residue. Under the conditions of char yield measurement all elements, other than carbon and sulfur (*e.g.*, oxygen, hydrogen, nitrogen, *etc.*) still present in the material are removed. This results in a corresponding reduction in weight of the sample being measured. Since char yield, Cy, is defined as

$$Cy = W_c/W_i \times 100 = (W_c - W_r)/W_i \times 100$$

where W_i is the initial weight of the sample of the sample W_c is the weight of char after measurements and W_r is the weight removed during measurement, W_r is a measure of the amount of removable O_2 H_2 and N_2 present in the sample. The higher the value of char yield, the lower the amount of these elements in the sample being measured.

A process parallel to and a consequence of O_2 H_2 and N_2 removal is the increase in molecular weight of the residue due to polymerization. The critical issue is whether removal of these elements uniquely determines the structure and molecular weights of the residue or we can control it and

TABLE 1 Effect of pyrolysis conditions on the molecular weight of L_c domains

Temperature °C	*Time/Hours*	*Total L_c, %*	*Low M_w, %*	*Low M_w total L_c, %*
410	6.0	67.5	45	67
420	2.5	67.5	36	53

TABLE 2 Effect of pyrolysis temperature, time, environment and pressure on char yield of residue

Pyrolysis					
Temp°C	*Time, hr*	*Gas*	*Pressure psia %*	*Pyrolysis yield %*	*Char yield of residue %*
420	4	A_r	15	84	78
440	2	H_2	85	84	90
420	6	A_r	15	82	81
420	2	H_2	15	82	79
420	16	A_r	15	79	89
420	4	H_2	15	79	81

change it by changing the processing conditions. Residue can be controlled by controlling the pyrolysis conditions. As an example, the data in Table 2 show three sets of results where the pyrolysis yields of the two experiments in a set are the same but the char yields are different. The difference is caused by the difference in pyrolysis conditions used for the two experiments.

Although the char yields of the fraction Q_i and Q_sT_i depend on pyrolysis conditions, the char yields of the pyrolysis residues are almost independent of conditions during pyrolysis. Their values depend only on the total Q_i or Q_sT_i content. Thus, a wide variety of time, temperature and atmosphere combinations which yield the same value of Q_i or T_iQ_i can be used to produce pyrolysis residues of desired char yield. The set of variables used in actual fabrication will be influenced by the ease or complexity of the experiment required.

X-ray diffraction analysis of selected samples was carried out to determine the interlamellar spacing (d) and the coherence length (L). Smaller values of d and larger values of L are a measure of higher order and thicker domain size. Results show that d spacing may be used to differentiate between some very poor samples, but provide no resolution for samples that are treated at more severe conditions. The coherence length L is, however, more sensitive to temperature and time of pyrolysis. The coherence length increased with increase in temperature and time of pyrolysis.

Morphology of selected fractions was studied by optical and scanning electron microscopy (SEM). One of the samples, was prepared by pyrolyzing the pitch at 420°C for 2 hours at normal pressure; the other sample studied was prepared under similar conditions, except that the pressure was maintained at 85 psia during pyrolysis. Pyrolysis residue from the first sample contained a mixture of Q_i, Q_sT_i and Q_sT_s where as the residue from high pressure experiment was 100% Q_i. The optical micrograph of the first sample showed circular shaped spheres (mesophere spheres) of various sizes.

The areas within the circles were birefringent indicating preferred orientation of molecules. The areas outside of circles were isotropic. It is clear that the pyrolysis time and temperature used do not lead to a complete conversion to merophase.

The morphology of the second sample prepared under high pressure is very different from the above in that the entire sample has become a highly oriented birefringent mass. The higher rate of mesophase formation under high pressure has led to total conversion to merophase which is a very viscous liquid, and is deformed by high pressure to produce large domains of oriented material. Complete conversion to mesophase under pressure was also shown by complete insolubility of the pyrolysis residue in quinoline. Most importantly, the high pressure samples already indicate the incipient formation of curved layer structures (splay type disclinations) that reflects the plasticity of the sample and the capability of this product to form large layered structures that can conform to the tortuous space between the fibers and surround the fibers without large discontinuity (well defined crystal boundaries) in the crystal structure. This observation has implications in C–C composite samples formed from highly oriented mesopitch and carbon fibers where molding is carried out under high pressures.

The common feature of infra-red analysis of the various samples appear to be; (1) under milder pyrolysis conditions the loss of aliphatic hydrogen, such as $—CH_3$ groups, is smaller but the loss increases steadily as the pyrolysis conditions become more severe, and (2) conversion of disubstituted rings to multi-substituted rings (aromatic conversion) follows the opposite trend *i.e.*, the aromatic conversion is greater at milder conditions than at more severe conditions. The energy involved is used to either remove aliphatic hydrogen (*e.g.*, $—CH_3$ groups) or convert the aromatic rings to higher levels of substitution.

In our earlier discussions it was seen that Q_i and T_i fractions formed at more severe pyrolysis conditions, which according to IR results are accompanied by higher aliphatic H_2 loss but very little aromatic conversion, also had the highest values of char yield, were the most birefringent and had the highest order as measured by X-ray diffraction.

Thus, the IR results confirm that the higher char yields are the result of larger removal of aliphatic hydrogen during pyrolysis and not the aromatic conversion. On the other hand lower values of char yield for Q_i and T_i fractions prepared under relatively milder conditions are due to the lower loss of aliphatic hydrogen during pyrolysis. The increase in aromatic conversion under milder conditions is perhaps due to the bridging of aromatic rings by $—CH_3$ groups or the presence of CH_3 groups on the surface of multi-substituted structures. The presence of such groups could also explain the relatively lower packing order seen by X-ray diffraction in the samples prepared under milder conditions.

OVERVIEW OF IMPREGNATION RESEARCH

Rheological Properties of Mesophase Pitch

Rheological characteristics of mesophase pitches have a strong influence on the processability of the preform fabrication (impregnation) process. In addition to processability, it has been suggested that the rheological characteristics of mesophase pitches affect the growth and coalescence of mesophase spheres during the mesophase formation process. The rheological behavior of heat treated pitches varies depending on the degree of heat treatment (pyrolysis), in other words, degree of mesophase formation. The results of investigations on the rheological behavior of mesophase pitches have been reported in the literature [5 – 10].

Rheological studies [5] on petroleum and coal tar pitches reported in the literature suggest that when the pitches are exposed to heat, their viscosity increases due to formation of anisotropic phase (mesophase). When exposed to low temperatures, the pitches exhibit Newtonian behavior, but when exposed to high temperatures, they exhibit non-Newtonian behavior such as shear thinning viscosity [8]. Nazem [9] has reported that viscoelastic behavior was observed with mesophase pitches.

A study reported by Wiecek [6] shows the effects of temperature on the viscosity of pitches. His results show that the viscosity of mesophase pitches increases gradually as the temperature increases and when the temperature exceeds a certain temperature, the viscosity increase rapidly (see Fig. 1). In addition, the rheological behavior of mesophase pitches varies depending on the heat treatment conditions even though the mesophase contents are the same. In other words, the mesophase prepared at a lower temperature for a prolonged period may give the same level of mesophase content as that prepared at a higher temperature for a shorter period of time. However, their rheological behavior is different, suggesting that the molecular weights of liquid crystals in the mesophase are different.

Bhatia *et al.* [7] investigated the effects of additives on the rheological characteristics of coal-tar and petroleum pitches. They reported that both types of pitches exhibited Bingham plastic behavior with certain yield stresses at a temperature range between 85 – 180°C and the addition of a carbon powder (*e.g.*, petroleum coke or natural graphite powder) to the pitches resulted in a considerable increase in viscosity but had no significant effects on the temperature dependence of their viscosity. However, the addition of carbon black to the pitches resulted in a decrease in viscosity.

Balduhn and Fitzer [8] reported that non-Newtonian behavior of pitches was observed at high temperatures above 300°C and the viscosity went through a maximum and minimum in the temperature range of 420°C, confirming the observation of Collet and Rand [8]. They attributed this phenomenon to the formation and growth of mesophase. They reported also

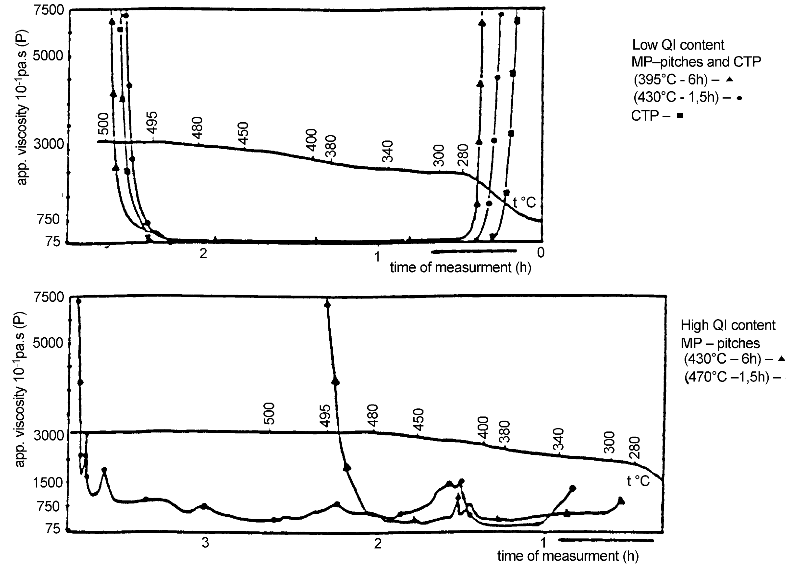


FIGURE 1 Typical temperature *vs.* rheological behaviour of pitches.

that the nucleation and coalescence of mesophase were retarded by the flow and motion but the growth rate was increased.

Fitzer *et al.* [10] made an attempt to correlate the rheological behavior of pitches with their microstructures. They determined the mesophase content of pitch by optical anisotropy. Their study showed that optically isotropic pitches behaved nearly as Newtonian fluids with slight non-Newtonian characteristics at low temperatures but optically anisotropic pitches exhibited non-Newtonian characteristics showing shear rate dependent viscosity and also yield stress.

These studies show that the pitches treated at about or below 460°C are viewed as an emulsion of mesophase droplets suspended in a continuous isotropic liquid phase. As the mesophase content increases, coalescence of the mesophase droplets occurs at about 460°C or higher temperatures, and an interlock network structure of mesophase is formed. The behavior of interlock network structure resembles that of a two-phase polymer melt. At still higher temperatures, there appears to be a phase inversion and then mesophase becomes the continuous phase in which the isotropic phase is dispersed as droplets. It has been reported by Collet and Rand [1] that at above 460°C, the viscosity of mesophase go through a maximum which seems to support the theory of forming an interlock network type microstructure.

Our studies also show that mesophase droplets were formed during pyrolysis and the deformation of the droplets were observed in the reactor due to shearing motion generated by the stirrer. The deformation of droplets under shear fields is commonly observed with liquid emulsion systems.

Viscosity Measurement

Apparent viscosity of mesophase pitches was measured using Brookfield viscometer Model HATDV. Figure 2 shows the schematic diagram of the viscosity measurement apparatus, *i.e.*, rotational viscometer and capillary viscometer.

In measuring the viscosity of pitches, the rotational viscometer was mostly used in this study. It consists of coaxial cylinder and spindle (rotor), both made of stainless steel. The coaxial cylinder was equipped with electrical heating elements and a nitrogen purge line. The viscosity measurement was carried out under nitrogen atmosphere to prevent oxidation.

A predetermined amount of pitch sample was charged to the cylinder. The amount of sample was determined such that the spindle should be just immersed when the pitch sample was melted. Then the cylinder was covered with a lid and purged with nitrogen for about one hour. After nitrogen purge, the sample in the cylinder was heated at a rate of 3°C per minute with nitrogen purge. When the sample was stabilized at the desired temperature, the spindle was turned on at a rotational speed to attain a desired shear rate. After stabilized, the torque reading was taken to calculate the viscosity. The shear rate was varied by adjusting the rotational speed of the spindle.

The viscosity was measured as a function of temperature at several different shear rates. The temperature was varied from 310°C to 450°C.

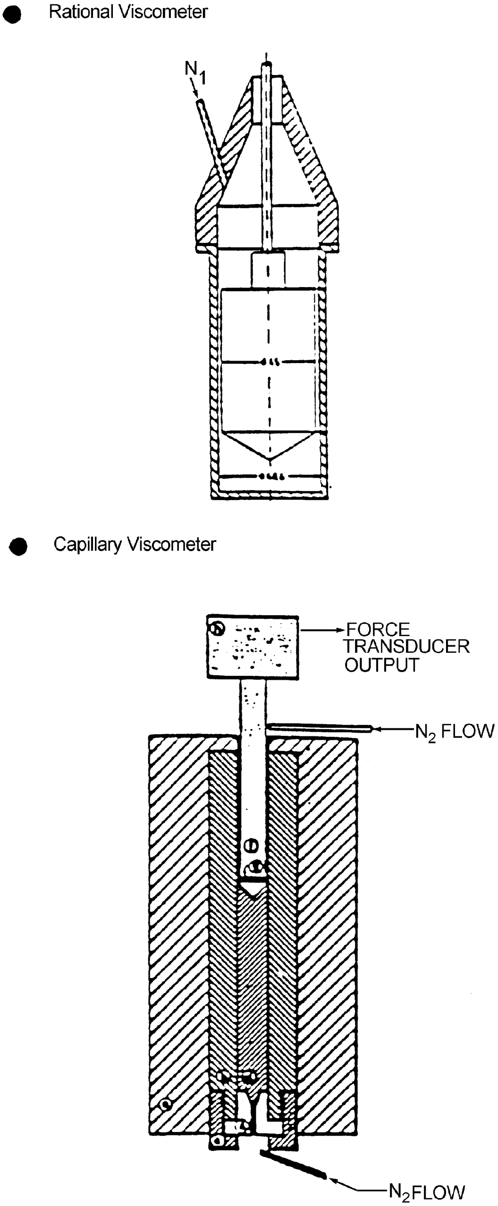
Viscosity of Mesophase Pitch

Figure 3 shows the typical behavior of Ashland A-80 pitch before heat treatment. The viscosity of A-80 varies from 10 poises to 0.5 poises in the temperature range of 325°C to 425°C. When the pitch was heat treated at elevated temperatures, its viscosity increased as shown in Figure 4. It is seen that the pitch treated at 440°C for two hours shows a substantial increase in viscosity exceeding 100 poises, suggesting that an appreciable amount of mesophase has been formed. On the other hand, the pitch treated at 260°C for a prolonged time still shows only a slight increase in viscosity, indicating that the rate of mesophase formation is very slow at low temperatures. Further investigation on the rheological behavior of various mesophase pitches will be carried out and will be reported in a separate report.

PULTRUSION IMPREGNATION

Experimental Set-Up and Procedure

A bench scale pultrusion impregnation experimental set-up was designed for pultrusion processability evaluations. The experimental set-up (Fig. 5)


● Rational Viscometer

● Capillary Viscometer

FIGURE 2 Schematic diagram of viscometers.

consists of a fiber feeding creel, impregnation bath, take-up device and cutter (pelletizer). The impregnation bath was designed to control the mesophase temperature and resin pick-up. The impregnation experiments

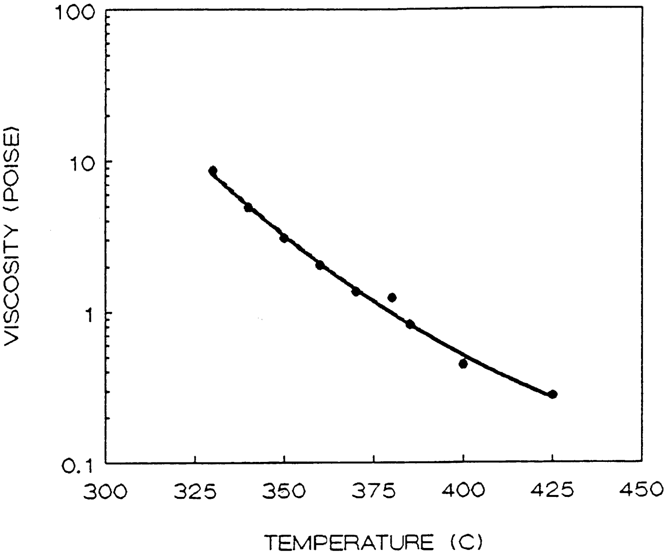


FIGURE 3 Rheological behaviour of Ashland A-80 pitch.

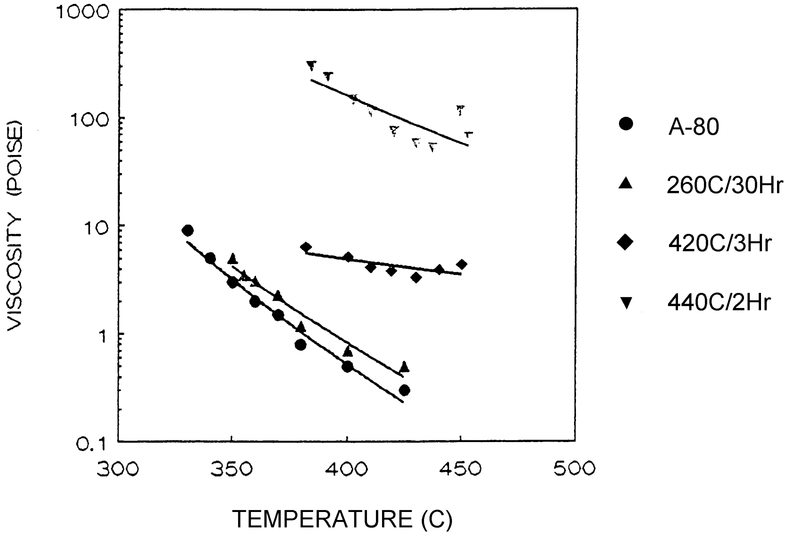


FIGURE 4 Rheological behaviour of mesophase pitch with different heat treatment.

were conducted under nitrogen atmosphere as described here: A known amount of sample (mesophase pitch) was charged into the impregnation bath. Then, the bath was purged with nitrogen and the bath temperature

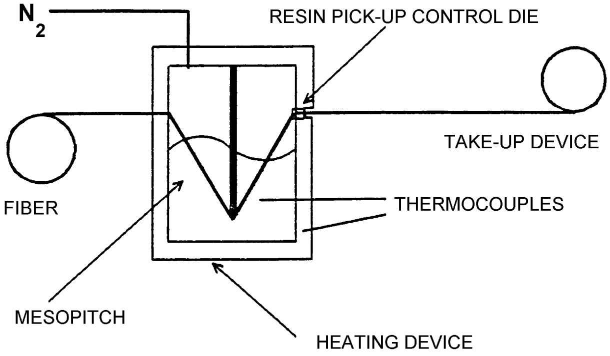


FIGURE 5 Schematic diagram of pultrusion apparatus.

was increased using the electrical heater to the processing temperature. When the temperature of the sample was stabilized, the carbon fiber (yarn) was fed to the impregnation bath. In the bath, the fiber was guided to go through the pitch and the excess amount of resin picked up by the fiber was removed using the exit die so that the resin content in the fiber could be controlled. The fiber used was PAN base carbon fiber and various heat treated mesophase pitches were used.

Processing Window of Pultrusion

The processability was measured by the resin pick-up, uniformity and surface roughness. Table 3 summarizes the results of pultrusion impregnation experiments. As can be seen from Table 4, the resin pick-up was generally very good ranging from 60% to 85% by weight for all samples evaluated. The uniformity of impregnation was examined using SEM, which indicated the fiber was fairly uniformly impregnated.

The processing window of mesophase pitches for pultrusion impregnation is shown in Figure 6 in terms of mesophase preparation conditions. It is seen that the pitches treated above 440°C appear very difficult to process. At 420°C, the pitches treated longer than three hours may not be pultrusion impregnated. In terms of rheological properties, as shown in Figure 7, the highest viscosity range for pultrusion impregnation is about 100 poises. In Figure 8, the processing window is presented in terms of QI and TI.

Pultrusion with Post Heat Treatment

As shown above, high mesophase content pitches show poor processability, thus the mesophase content in the pultruded fiber may be limited. An alternative route to increase the mesophase content in the pultruded fiber is to increase the mesophase content after pultrusion. An experimental

TABLE 3 Mesophase formation conditions (Ashland A-80 petroleum pitch)

Sample ID	*Temperature* (°*C*)	*Time* (*hrs*)	*Batch* (*g*)	*Weight loss* (*wt*%)	*QI* (*wt*%)	*TI* (*wt*%)	*PI* (*wt*%)	*THFI* (*wt*%)
01222	450	6	300	12.6				
01242	400	6	300	11.0				
01302	450	4	300	12.1				
02042	450	2	300	12.6				
02102-1	400	1	300	6.1	1.2	56.2		
02102-2	400	2	300	7.8	2.9	63.4		
02112-1	420	1	300	9.8	5.9	64.7		
02112-2	440	1	300	13.2	28.7	84.1		
02262	440	1	2000	7.1	43.1	91.2	67.3	83.9
03072-1	420	2	300	10.6	12.3	71.2		
03072-2	440	2	300	10.3	43.6	94.2		
03162-1	400	3	300	12.3	6.9	64.5		
03162-2	420	3	2000	8.8	17.8	69.8	63.3	
03162-3	440	3	300	12.4	48.6	96.1		
04032-1	440	2	2000	11.6	56.0	98.9		96.8
04032-2	420	2	2000	4.1	19.5	71.5	84.7	93.0
05132-1	440	1	2000	4.7	26.0			
05132-2	450	4	2000	10.0	97.0	92.8		
05202	400	1	2000	3.0	1.6	62.3		
06292-1	440	1	2000	5.1	20.2	75.8		
06292-2	440	1	2000	5.4				
08062	440	1	2000	5.0	24.0	68.1		

apparatus designed to induce *in situ* mesophase formation reaction after pultrusion as shown in Figure 9. The fiber yarn is pultruded following the pultrusion procedure and exposed to a temperature controlled heating tunnel which has two different temperature zones. The results are summarized in Tables 4–6.

Table 4 shows that when the pitch treated at 400°C for 2 hours was pultruded and exposed to 450°C at the post heat treatment, the QI was increased from 2.9 to 5.5%. When the pultruded and post heat treated at 450°C was again further exposed to 500°C, the QI was increased from 5.5 to 7.6%. The post heat treatment was continued up to 600°C, the final QI reached 46% from the original 2.9% QI.

This experiment indicated that if the heating zones of the heating tunnel are constructed such that their temperature increases from 450°C to 600°C successively, the QI in the pultruded carbon fiber can reach 46%, which can not be achievable otherwise. Tables 5 and 6 show the results of the post heat treatment experiments with different mesophase pitches. Note that 98% QI was achieved from 18% QI when the pitch was heat-treated at 420°C for 3 hours.

TABLE 4 Pultrusion processing conditions

			Heat treatment		*Resin*	*Processing*		
Sample ID	*QI* (*wt*%)	*TI* (*wt*%)	*Temp* (°*C*)	*Time* (*Hrs*)	*pickup* (*wt*%)	*Temp* (°*C*)	*Speed* (*ft*/*min*)	*Surface condition*
02282	43.1	91.2	440	1	88	440	5.7	smooth
03182	12.3	71.2	420	2	78	420	5.7	smooth
03192	17.8	69.8	420	3	79	420	5.7	smooth
04082	6.9	64.5	400	3	54	400	5.7	smooth
04092*	–	100	440	1	72	440	5.7	smooth/rough
04222	56	98.9	440	2	80	440	5.7	smooth/rough
04232	56	98.9	440	2	84	440	5.7	smooth/rough
04272	1.2	56.2	400	1	81	400	5.7	smooth
04282	2.9	63.4	400	2	56	400	5.7	smooth
05292	19.5		420	2	79	420	5.7	smooth
06012	56	98.9	440	2	72	440	3.6	smooth/rough
06092	26		440	1	78	440	5.7	smooth
06102	26		440	1	80	440	5.7	smooth
06112	26		440	1	75	440	5.7	smooth

* THF extracted residue after heat treated.

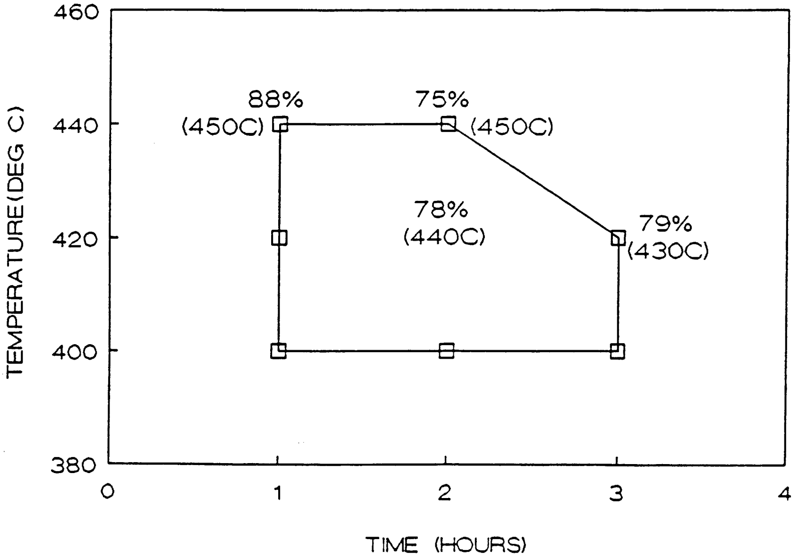


FIGURE 6 Processing window of pultrusion impregnation process in terms of heat treatment conditions.

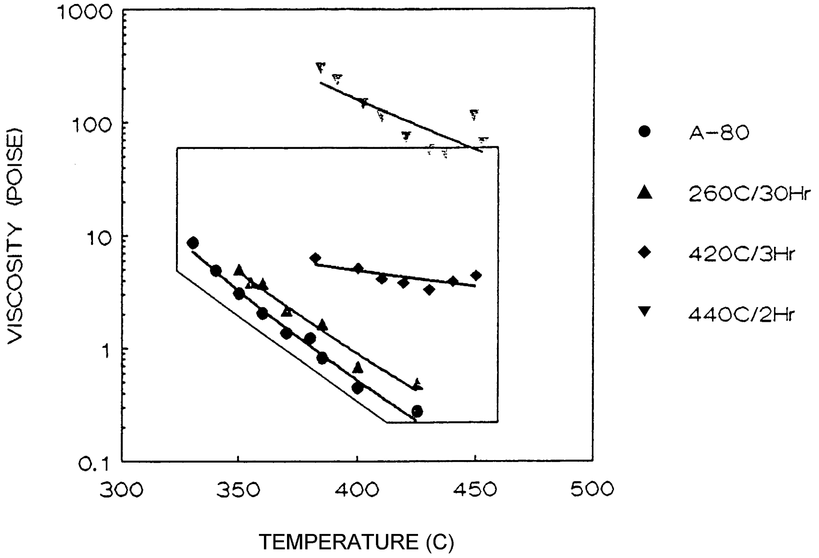


FIGURE 7 Processing window of pultrusion impregnation process in terms of viscosity.

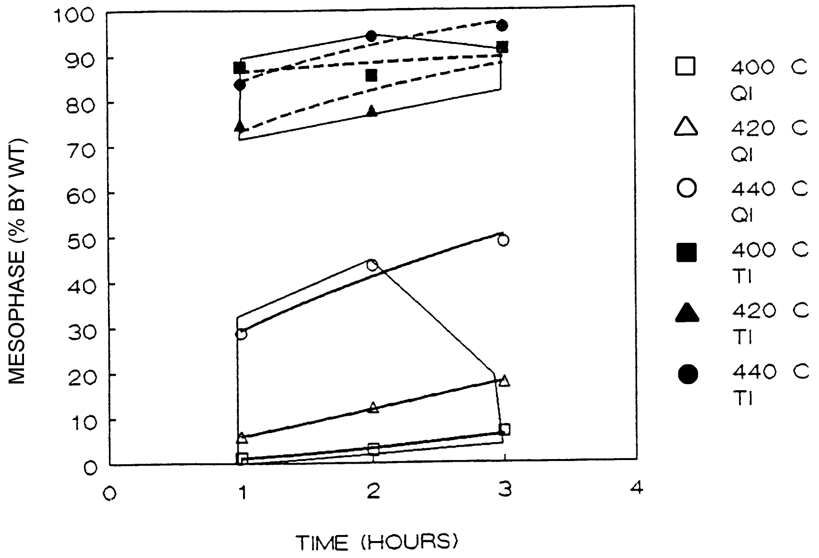


FIGURE 8 Processing window of pultrusion impregnation process in terms of quinoline and toluene insolubles.

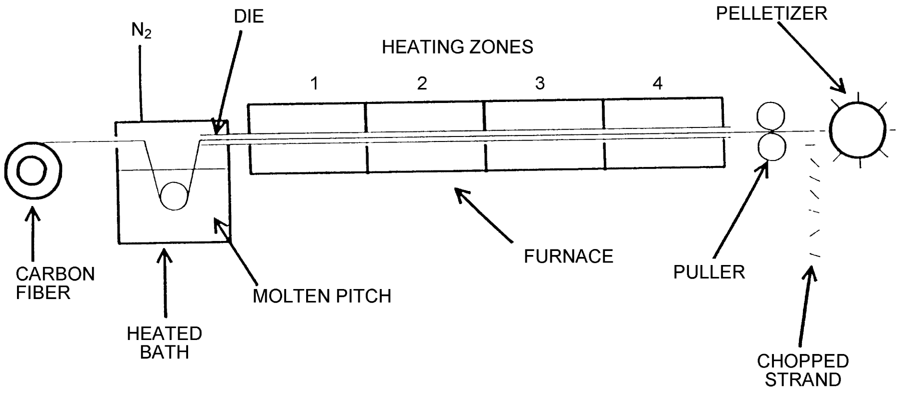


FIGURE 9 Schematic diagram of *in situ* mesophase formation after pultrusion impregnation.

TABLE 5 Pultrusion with post heat treatment. Pitch impregnation material heat treated 400°C for 2 hours

Furnace temperature		*Line speed*	*Resin*	*QI*
Zone #1	*Zone #2*	*(ft/min)*	*(wt%)*	*(wt%)*
–	–	5.4	85	2.9
450	450	4.7	82	5.5
500	500	4.1	78	7.6
500	500	3.1	78	11
550	550	3.6	69	11
550	550	3.6	65	15
600	600	3.6	63	15
600	600	3.1	61	41
600	600	3.1	60	46

TABLE 6 Pultrusion with post heat treatment. Pitch impregnation material heat treated 420°C for 3 hours

Furnace temperature		*Line speed*	*Resin*	*QI*
Zone #1	*Zone #2*	*(ft/min)*	*(wt%)*	*(wt%)*
–	–	5.7	84	18
450	450	3.6	83	19
500	500	3.6	78	21
550	550	3.1	72	24
600	600	5.4	64	69
650	650	5.4	59	98

RESIN TRANSFER MOLDING (RTM)

RTM Experimental Set-Up and Procedure

An experimental apparatus for evaluating RTM processability was designed as shown in Figure 10. The mold was designed such that the pitch is injected from the bottom and the mold can be pressurized to enhance the penetration of the pitch. Another feature is that a reservoir is installed at the exit of the mold so that a continuous flow of pitch can be maintained. The resin transfer molding process procedure is described as follows:

A 3-dimensional non-woven preform was placed in the mold and the mold was closed. At the same time, a sufficient amount of mesophase pitch was charged into the feed reservoir and the whole system was then purged with nitrogen. Then, the mold and both feed and exit reservoirs were heated to the processing temperature. During heating, the valve between the mold and feed reservoir may be left open or closed if desired. When the temperature of the

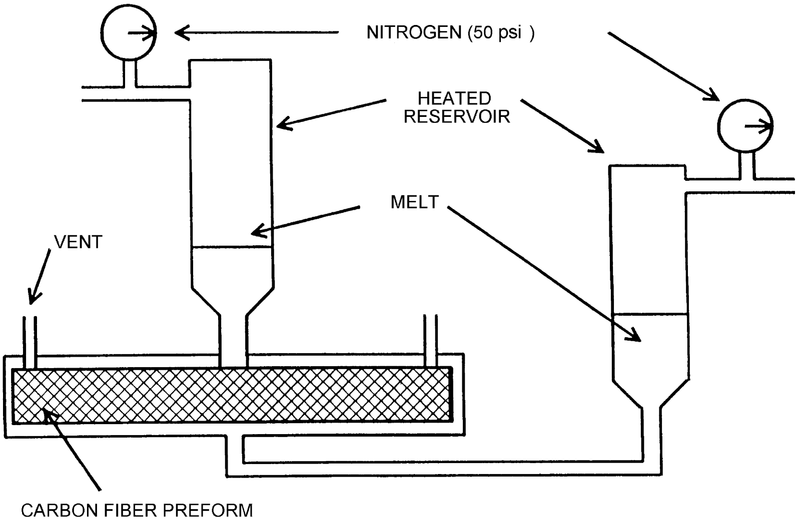


FIGURE 10 Schematic diagram of resin transfer molding apparatus.

pitch in the reservoir was stabilized, the pitch was charged to the mold by pressurizing the reservoir with nitrogen. When the pitch started overflowing through the vent lines, the vent valves were closed and the excess pitch was collected in the exit reservoir. The pressure at both reservoirs were maintained at 50 psia throughout the duration of the process.

In order to further increased the mesophase content of the pitch in the mold, the mold temperature was increased to 450°C and maintained at that temperature for the desired period of time. When the molding process was completed, the temperature of the mold and the reservoirs were cooled down to ambient temperature and the impregnated preform was discharged.

Processing Window of RTM

The processability was measured by the resin content in the preform, uniformity and density. Table 7 summarizes the results of the RTM impregnation experiments. As can be seen from the Table 8, the resin content and density were generally very consistent from batch to batch. The resin content ranges from 55 wt% to 60 wt% and the density ranges from 1.1 g/cc to 1.3 g/cc with a void content 10 vol% ~ 26 vol%. The uniformity of impregnation was examined using SEM, which indicated that the fiber was fairly uniformly impregnated.

The processing window of mesophase pitches for RTM appears very similar to that of pultrusion impregnation as shown in Figure 6 in terms of

TABLE 7 Pultrusion with post heat treatment. Pitch impregnation material heat treated at 440°C for 1 hour

Furnace temperature		*Line speed*	*Resin*	*QI*
Zone #1	*Zone #2*	(*ft/min*)	(*wt%*)	(*wt%*)
–	–	16.4	85	17
450	450	4.0	83	19
500	500	4.0	79	22
550	550	4.0	71	26
600	600	4.0	62	70
650	650	11.5	61	96

TABLE 8 Resin transfer molding petroleum pitch

			Heat treatment		*Processing*			*Void*	*Pitch*
Sample ID	*QI* (*wt%*)	*TI* (*wt%*)	*Temp* (°*C*)	*Time* (*Hrs*)	*Temp* (°*C*)	*Time* (*Hrs*)	*Density* (*g/cc*)	*content* (*vol%*)	*content* (*wt%*)
05182	0	5.3	0	0	350	0.5	1.33	8.8	62
05222	1.6		400	1	420	0.5	1.13	–	55
06182			440	1	450	0.083	1.03	35	57
06232			440	1	450	1.0	1.08	30	61
07142			440	1	450	1.5	1.15	25	63
07172			440	1	450	1.5	1.23	20	64.4
07232			440	1	450	1.5	1.16	25	62.5
07272			440	1	450	2.0	1.18	23	61.8
07302			440	1	450	1.75	1.19	23	62.8
08032			440	1	450	1.5	1.18	23	62.8
08052			440	1	450	2.25	1.18	23	62.9
09012			440	1	450	2.5	1.15	25	64.4
09082			440	1	450	2.0	1.14	26	65.5
09102			440	1	450	2.0	1.14	26	64.7
09152			440	1	450	2.0	1.14	26	64.3

mesophase preparation conditions. It is seen that the pitches treated above 440°C appear to be difficult to process. It is recognized that the RTM process requires a pitch with a better processability than the pultrusion process in order to achieve uniform impregnation. Thus the maximum viscosity range for RTM is estimated to be about 50 poises.

CONCLUSION

Based on the results of this study, we concluded that the selection matrix materials and pretreatments we investigated will allow us to arrive at intermediate products which after carbonization and graphitization under pressure will have density and properties comparable to those of present CVD or CVI C–C composites.

REFERENCES

[1] Brooks, J. D. and Taylor, G. H. (1965). *Carbon*, **3**, 185.
[2] White, J. L. and Price, R. J. (1974). *Carbon*, **12**, 321.
[3] White, J. L. and Shaeffer, P. M. (1989). *Carbon*, **27**, 697.
[4] Marsh, H. and Walker, P. L. Jr. (1979). In: "*Chemistry and Physics of Carbon*", Walker, P. L. and Thrower, P. A. Ed., **15**, 229.
[5] Collett, G. W. and Rand, B., "Rheological Investigation of Coal-tar Pitch during its Transformation to Mesophase", *Fuel*, **57**, 162, March, 1978.
[6] Wiecek , I., "*Rheological Properties of Mesophase Pitches from Coal Tar Pitch*".
[7] Bhatia, G., Aggarwal, R. K., Chari, S. S. and Jain, G. C. (1977). "Rheological Characteristics of Coal Tar and Petroleum Pitches with and without Additives", *Carbon*, **15**, 219.
[8] Balduhm, R. and Fitzer, E. (1980). "Rheological properties of Pitches and Bitmina up to Temperatures of 500°C", *Carbon*, **18**, 155.
[9] Nazem, F. F., "Rheology of Carbonaceous Mesophase Pitch", *Fuel*, **59**, 851, December, 1980.
[10] Fitzer, E., Kompalik, D. and Yudate, K., "Rheological Characteristics of Coal-tar Pitches", *Fuel*, **66**, November, 1987.