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Enhanced Stabilization Reactivity of Coal Tar Based Mesophase Pitch Fiber by Blending PVC Pitch

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PVC pitch prepared at 420 °C for 2 h was blended into a coal tar based mesophase pitch to enhance the stabilization reactivity of the whole pitch fibers. No deterioration of spinnability was recognized after the blending, suggesting their high compatibility. The oxidative stabilization in the air at 270 °C took 120 min for the stabilization of the parent mesophase pitch fibers to maintain its fiber form during the carbonization up to 600 °C, while the pitch fibers from the blends with PVC pitch in 5 or 10 wt% took 80 min to be stabilized. Blended PVC pitch is supposed to be oxidized more easily to react with coal tar derived molecules, enhancing the stabilization reactivity of the whole fiber.

Although mesophase pitch based carbon fiber has been recognized as a strategic material because of its high performance per weight,1,2) low reactivity of the mesophase pitch fibers for the stabilization is one of the most significant or critical problems to be solved to reduce its production cost.3) Mesophase pitch prepared from tarry substances is a kind of diskotic liquid crystal, which consists of highly aromatic molecules of moderate molecular weight,4,5) hence they are very stable for the oxidation at temperatures lower than its softening temperature even if the starting tar is pretreated with hydrogenation procedure.

In the present study, PVC pitch which carried a considerable amount of aliphatic groups was blended into coal tar based mesophase pitch to enhance their stabilization reactivity. The present authors have reported high compatibility of the PVC pitch with coal tar based mesophase pitch without any deterioration of liquid crystal natures of the latter pitch.6)

Coal tar based mesophase pitch used in the present study was prepared from a QI free coal tar pitch after hydro-treatment by THQ (tetrahydroquinoline).7) PVC pitch was prepared from commercial grade PVC by the heat-treatment at 420 °C for 2 hr under a nitrogen flow at the heating rate of 10 °C/min.6,8) Microanalyses of these two pitches are summarized in Table 1. The mesophase pitch was blended with the PVC pitch in 5 or 10 wt% by annealing at 360 °C for 10 min in a Pyrex container (30 mm in dia., 300 mm in length) before the spinning. The mesophase pitch and its blends were spun into the fibers from the nozzle (0.4 mm in dia.) attached to the

Table 1. Microanalyses of pitches

Sample	H	C	N	O[a)]	H/C	fa[b)]	Rnus[c)]	S.p.[d)]	Solubility/wt%			
	wt%							°C	BS	BI-PS	PI-QS	QI
Mesophase pitch	3.9	94.1	1.0	1.0	0.50	0.97	0.55	290	6	41	11	42
PVC pitch	5.9	94.0	0.0	0.1	0.75	0.81	0.80	200	69	13	16	2

a) By difference.

b) Carbon aromaticity.

c) Number of the naphthenic ring in the unit structure

d) Softening point

steel container (the amount of pitch was ca. 10 g) by applying pressurized nitrogen (0.1 kg/cm^2). Pitch fibers from the mesophase and its blends were stabilized at 270 °C by the heating rate of 5 °C/min in the air. The stabilized pitch fibers were further carbonized at 600 °C for 60 min by the heating rate of 10 °C/min in a Pyrex container (30 mm in dia., 600 mm in length) heated in the vertical electric furnace. The degree of the stabilization was examined by the microscopic observation on the shapes and the degree of adhesion of the carbonized fibers.

The mesophase pitch and its blends with PVC pitch in 5 or 10 wt% were both smoothly spun for several minutes into pitch fibers at the same temperature of 350 °C although the softening temperatures of the blended pitches were slightly lower. Figure 1 illustrates the microphotographs of the polished surfaces of the pitch fibers perpendicular to their fiber axis. Both mesophase pitch and its blends pitch fibers exhibited circular and their diameters were well controlled around 20 μm. The well-developed fine mosaic texture was observed in all fibers. Thus, PVC pitch is suggested highly compatible with the mesophase pitch derived from coal tar pitch as reported in a previous paper.[6)]

Figure 2 illustrates the microphotographs of carbonized fibers after the various periods of oxidative stabilization. Most of the fiber strands from the mesophase pitch with the stabilization for 60 and 80 min adhered each other due to the partial fusion at their surfaces, losing the circular shapes, indicating that the stabilization time was insufficient. The fiber strands after the stabilization for 100 min still adhered each other, however their adhesion extent became less and circular shapes were maintained in many cases even when the adhesion took place. The fibers strands stabilized for 120 min showed no adhesion at all, suggesting sufficient stabilization. The fiber strands of the blends with PVC pitch in 5 or 10 wt% (PVC-5 and PVC-10, respectively) after the stabilization for 60 min showed their least adhesion and the most of the fibers maintained circular shapes. Stabilization for 80 min at 270 °C seems to be sufficient to avoid their adhesion completely.

When the carbonized fiber strands from mesophase and blended pitches after the stabilization for 80 min were compared, the skin of the latter strands exhibited finer mosaic texture than that of the former ones, suggesting more extensive oxidation in the latter fiber.

Aromatic molecules of the mesophase pitch should be either polycondensed,

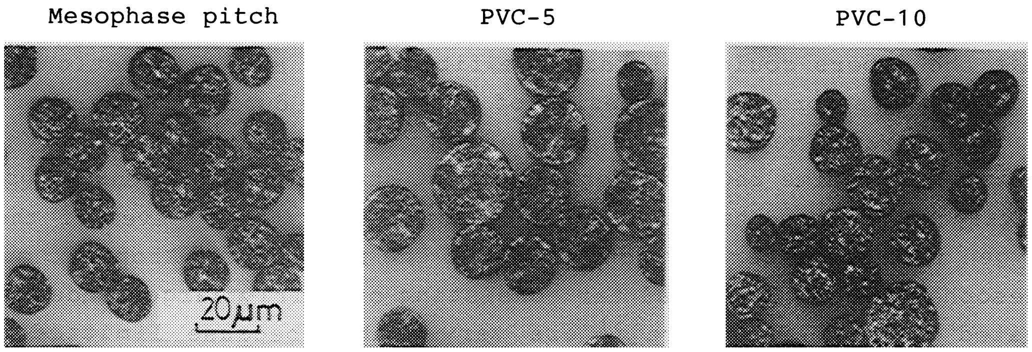

Fig. 1. Optical microphotographs of pitch fibers.

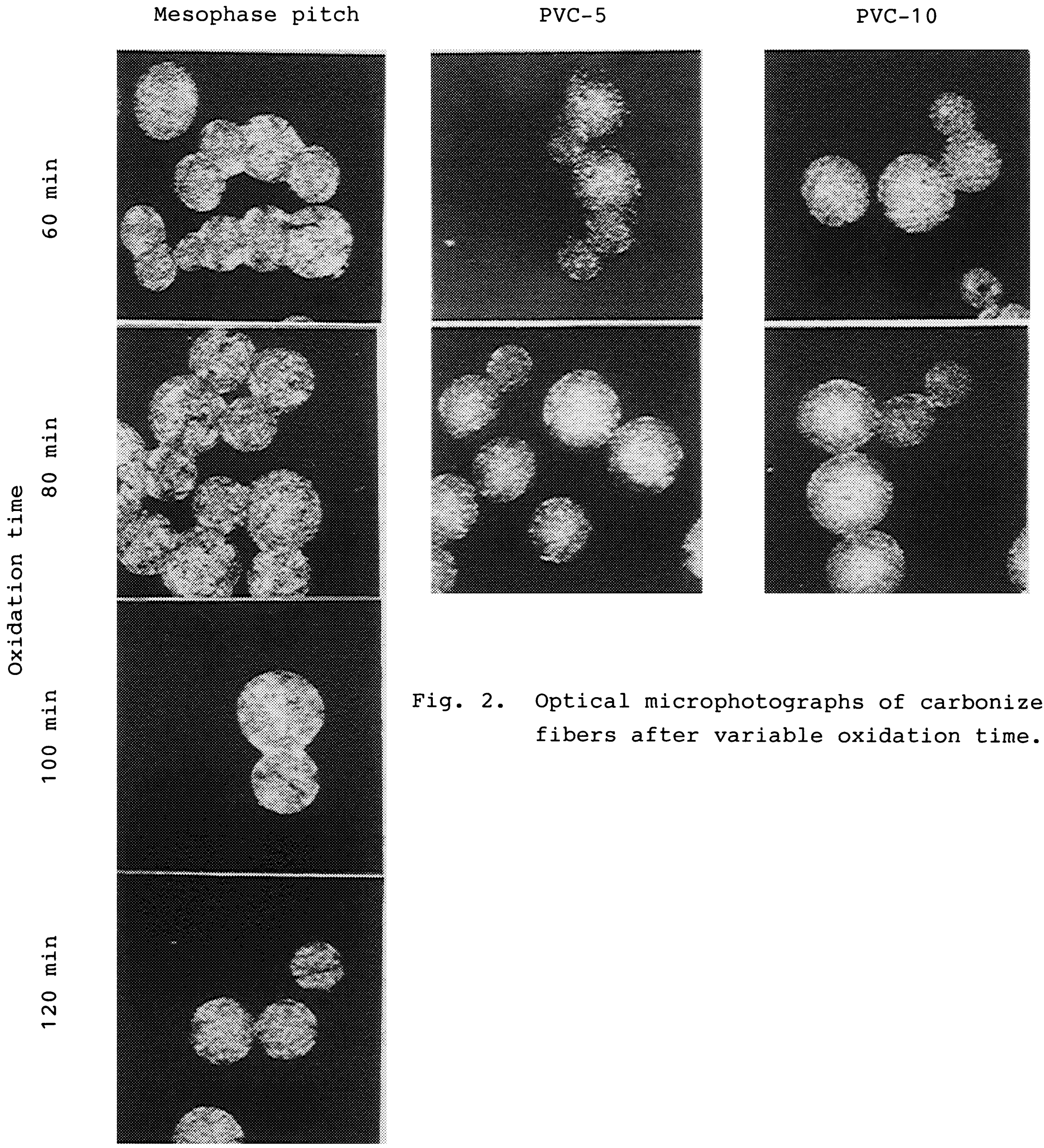

Fig. 2. Optical microphotographs of carbonized fibers after variable oxidation time.

dehydrogenated or oxygenated, and became infusible by the oxidative stabilization, so that the fibers could maintain the fiber shape and orientation of aromatic molecules, and suppress the adhesion of the strands during the carbonization.[9,10] Although the oxidative stabilization can perform such reactions below the softening temperature, the time required for sufficient stabilization strongly depends on the reactivity of the mesophase molecules of the fiber[4,5,11,14] even if the diffusion of oxygen into the fiber may contribute to the reactivity. Aromatic molecules of the mesophase pitch from coal tar consisting of fairly large condensed rings as suggested in the literature[15] are very stable because limitted numbers of naphthenic group and alkyl substituents are required to the mesophase pitch-constituent molecules to obtain the liquid crystal nature through the pyrolytic reaction. In contrast, PVC pitch which consists of olefinic polymers from PVC by the thermal dehydrochlorination, is less condensed and contains significant amounts of alkyl, and/or olefinic structures.[8] Hence, the pitch is easily oxidized and/or polymerized under the conditions of the oxidative stabilization. Such PVC pitch molecules may react with the surrounding molecules of coal tar derived mesophase pitch, or may initiate the chain reactions which can induce the reaction of the latter molecules in oxidation. Thus, the PVC pitch added in a limited amount may work as the trigger of the stabilization reaction of the whole molecules of the pitch fiber.

The present study revealed that a suitable trigger is effective to enhance the stabilization of mesophase pitch based pitch fibers. More reactive trigger may further shorten the time of the stabilization.

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