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Silver Up-Take by Modified Pitches

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Abstract

The modification of coal-tar pitch has been carried out by heat treatment of pitch at different temperatures in the range (300°-400°C) for different times (2-5 hrs) in air and nitrogen. The pitch heat treated in air at lower temperature (300°C) exhibit increase in softening point by 20°C as compared to only 2°C when treated in nitrogen. The changes are faster in air than in pure nitrogen. Pitch as such as well as after heat treatment were further treated with metal complexes by solution route. Silver intake has been found to increase from 0.5 to 0.8 % in nitrogen treated pitch while the uptake is found to decrease for pitches treated in air at 350°C for 5 hrs. Experiments have also been made to incorporate silver into PAN and PAN-ox fibers through solution route. The metal intake has been found to be more in PAN-ox fibers than in PAN as such. Metal loaded carbon composites have been made by using metal loaded fibers as well as cokes. These composites as such exhibit higher surface oxygen complexes but decrease after activation.

Keywords : *Modified pitches, Metal loaded carbon, Carbon fibers, Composites, Surface oxygen complexes, Electrical conductivity*

1. Introduction

Porous carbons as such as well as with impregnated metal ions find applications as adsorbents, decoloriser, unique catalysts for oxidation-reduction, electrical-magnetic devices, magnetic wave absorbers, antibacterial agents etc. For most of these applications pitches are used as precursor for host carbon materials. Pitches as such have low coke yield. In order to increase coke yields, pitches are modified through different routes such as heat treatment, chemical treatment [1-3] etc. Pitch modified by heat treatment undergoes polymerization, whereas chemical treatment results in dehydrogenation and condensation. These treatments raise the softening point and increase the yield of carbon. Heat treatment in nitrogen blowing leads to polymerization of pitch. On further heat treatment at 400-450°C, these macromolecules result in the formation of mesophase structure in pitch [4]. Modification by air blowing promotes the crosslinking between adjacent aromatic molecules, suppress the evaporation of light fraction and stacking of large aromatic molecules, thus retarding the formation of liquid crystalline mesophase [5]. Modification of pitch by incorporation of metals such as silver, copper, iron and platinum has been carried out by several researchers [6] to develop new types of stable metal-carbon complexes and metal loaded carbon fiber. Fine silver particles have strong antibacterial activity against stapplococcis and E.Colie and carbon fibers loaded with silver have been used as biocidal materials [7, 8]. Active carbon impregnated with chromium-copper-silver has been used for protection of respiratory tract. Pitch based carbon fiber containing Fe show magnetic anisotropy of Fe specie in carbon matrix [9, 10]. In literature not much work is reported on development of carbon-metal complexes with different carbon precursors. The incorporation of metal ions into carbon will depend upon the chemical nature of the precursor, processing (heat treatment temperature) and other physical characteristics of the precursor. The modified pitches consist of molecules or molecular chains with different functionalities and hence should behave differently when treated with metal salts, to make carbon-metal complexes. Present work was undertaken to study the role of carbon precursor in making carbon-metal complexes. Modified pitches, modified by heat treatment in air and nitrogen were taken as carbon precursor and metal salts were taken as the source for metal ions.

2 Experimental

2.1. Raw Material

Binder coal-tar pitch of following specification was used in the present studies.

Sample	S.P. in °C	Coke Yield %	Q.I %	C/H ratio
Binder coal-tar pitch	110	56	10	1.831

(where, S.P. softening point, Q.I. quinoline insoluble)

2.2. Modification of Pitch

The pitch was modified by heat treatment at different temperatures in the domain 350-450°C either in nitrogen or air to control the polymerization/crosslinking.

2.2.1. Heat treatment of pitches under nitrogen

Pitch was modified by heating in nitrogen atmosphere at temperature 300-400°C for 2-5 hrs. with continuos stirring.

2.2.2. Heat treatment of pitches by air blowing

In this case the pitch was modified by heating it at 300-350°C for different times (2-5 hrs.) under continuous bubbling of air through the liquid mass.

2.2.3. Metal impregnated pitches

50-200 gm of heat treated pitch and 1-2% of $AgNO_3$ were dissolved separately in quinoline to make solutions. These were then mixed under constant stirring for 16 hrs. to get uniform mixing. The excess of quinoline was removed by vacuum distillation. The solids thus obtained were metal loaded pitches.

2.3. Metal impregnated PAN fibers

Efforts were made to introduce metal ions into precursors for carbon fibers through solution route. 25-30 gm of PAN fibers as well as PAN-ox fibers were kept in 0.2-0.5 N silver nitrate solution for 24 hrs.

2.4. Coke Formation

Small samples of pitch as such as well as after different modifications (heat treatments) were further heated to temperature of 400-600°C in nitrogen atmosphere to obtain cokes

2.5. PAN-ox Fiber Based Carbon-Silver Complex Composite

Carbon-silver complex composites were prepared using metal loaded PAN-ox fibers as reinforcement and cokes as matrix. The silver impregnated fibers were co-milled with sinterable coke for different interval of time. During milling elliptical/spheroid shape beads of 3 mm diameter were formed. The beads were pyrolysed at 650°C in presence of nitrogen and activated with steam at different temperature from 650-950°C.

2.6. Characterization of metal incorporated Cokes and PAN-ox fiber based carbon silver Composites

The silver loaded coke and PAN-ox fiber reinforced composite were characterized for metal content, surface and physical properties. The surface characteristics e.g. surface oxygen complexes were determined. The amount of silver incorporated in the coke and PAN-ox fiber reinforced composites were determined using volhard's method.

3. Results and Discussion

3.1. Yield and softening point of pitches modified by heat treatment in air and N_2

Yield % and softening point of pitches modified by heat treatment in air and N_2 for different times (2-5 hrs) are shown in Fig. 1. The yield of pitch after treatment is found to be dependent on processing temperature and time. For mild conditions, *i.e.* at 300°C for 2 hrs., the yield is found to be same when treated in air or nitrogen. However, at higher treatment temperatures or higher times, the yield is found to decrease. This may be due to volatilization of unreacted low molecular weight species. Further, yield is found to be lower when treated in air than when treated in nitrogen. One would had expected increase in yield during air blowing due to uptake of oxygen. The fact that the yield is lower suggest that the oxidation of pitch is exothermic reaction resulting in volatilization of certain species. Softening point is also found to increase with treatment temperature and time. Environment is found to have pronounced effect on the softening point. Nitrogen blowing results in a small increase of softening point only after treatment at temperature 400°C, while heating in air exhibits this effect even at lower temperature of 300°C. The treatment in blowing air at 350°C for two hours produces pitch with sufficiently high softening point

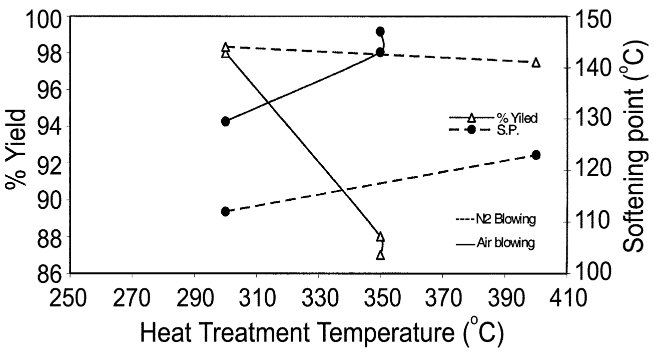

Fig. 1. Yield and softening point of modified pitches, modified by air blowing and N_2 Blowing.

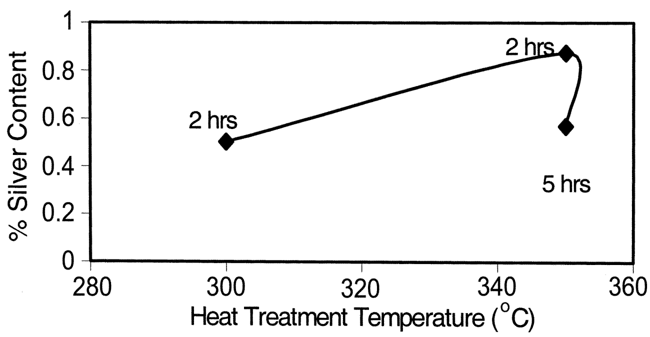

Fig. 2. Silver content in different pitches modified by air blowing.

properties required to transform these into carbon products.

3.2. Effect of Pitch Modification on Intake of Metal ions

Fig. 2 shows silver content in different pitches modified by air blowing. It shows that silver uptake by pitch is dependent on chemical constitution of pitch. Silver uptake is found to increase with modification of pitches. This increase is marginal and is observed for pitches treated under mild conditions of temperature and time. However, if the pitch is modified at higher temperature for long time, silver uptake decreases. On modification of pitch at higher temperature, the amount of aliphatic and low molecular weight component decrease. Low molecular weight fraction of the pitch undergo polymerization to form long chain aromatic compounds and therefore less sites are available for chemical bonding with silver compounds. Therefore silver pick-up decreases with severe treatment conditions in blowing air.

3.2. Composites using Metal Impregnated PAN-ox Fibers and Cokes

Efforts were made to develop metal impregnated PAN based carbon fibers in which metal was impregnated at precursor level (PAN fibers as such and stabilized PAN fibers) or in carbon fibers. It was found that metal intake is more in PAN-ox (stabilized PAN) fibers as compared to PAN fibers. No metal intake was observed in carbon fibers. Carbon-based products were also made by using sinterable coke as matrix and silver impregnated PAN fiber and PAN-ox fiber as reinforcement. These composites were first pyrolysed at 650°C in presence of nitrogen. Subsequently, these were activated at 650°C, 800°C and 950°C. in presence of steam. The results for PAN-ox based composite are shown in Table 1. The results show that impregnation of silver is enhanced considerably by using PAN-ox fiber and also intake of silver depends on the concentration of silver nitrate solutions. The

Table 1. Metal content in Composites using Metal Impregnated PAN-ox Fibers and its Characteristics

Obs. No.	Sample	Silver Content %	Ash Content %	Specific Gravity
1	PAN-ox fiber + 0.2 N $AgNO_3$ + Coke	4.11	–	1.487
	APFAC 650°C	4.87	6.35	1.644
	APFAC 800°C	5.28	6.93	1.682
	APFAC 950°C	5.33	7.02	1.723
2	PAN-ox fiber + 0.5 N $AgNO_3$ + Coke	9.11	11.00	1.558
	APFAC 650°C	9.54	13.68	1.611
	APFAC 800°C	10.04	13.92	1.707
	APFAC 950°C	10.77	14.12	1.750

(Where APFAC is activated PAN-ox fiber + $AgNO_3$ solution + coke)

Table 2. Surface characteristics of metal carbon coke and composites

Obs. No.	Sample	Surface Oxygen Complexes Meq/100 gm			
		Carboxylic group	Lactonic Group	Phenolic group	Total
1	CT300°C	192	88	123	403
	SC600°C	192	20	102.5	314.5
	ASC600°C	108.5	198	40	346.6
2	CT400°C	625	104	39	768
	SC600°C	354	52	19	426
	ASC600°C	181	220	80	441
3	PAN-ox fiber + 0.2 N $AgNO_3$ + Coke	98	116	126	340
	APFAC 650°C	77	69	101	192
	APFAC 800°C	68	62	88	169
	APFAC 950°C	61	43	60	143
4	PAN-ox fiber + 0.5 N $AgNO_3$ + Coke	92	110	120	322
	APFAC 650°C	61	53	108	220
	APFAC 800°C	83	38	71	192
	APFAC 950°C	31	53	73	157

(Where, CT is heat treated pitch in N_2, SC coke prepared by silver incorporated at 600°C, ASC activated coke prepared by silver incorporated at 600°C, APFAC is activated PAN-ox fiber + $AgNO_3$ solution + coke)

silver intake is more from 0.5 N solution than from 0.2 N solution of silver nitrate.

3.3. Surface Characteristics of Metal Impregnated Coke and Composites

Table 2 shows the results of surface oxygen complexes on metal impregnated coke and composites. The surface oxygen complexes developed on the surface depend on the surface characteristics, *i.e*. on the chemical nature of the surface of solid. In case of modified pitches, the number of total surface oxygen complexes have been found to increase with increase in the air stabilization of the pitch. It suggests that heat treatment of pitch as such result in evolution of low molecular weight compounds which might be resulting in some unpaired species. These are than the center of oxygen complexes. Since these reactions are dependent on heat treatment temperature, the formation of surface oxygen complexes increases with stabilization temperature. On converting these stabilized pitches to coke at 600°C, the amount of these oxygen complexes decreases since these break down during pyrolysis. However, a small increases in the groups is noticed on activation in steam. But surface oxygen complexes on composites have been found to be about 10-15% lower than on the coke alone. This may be due to incorporation of metal ions.

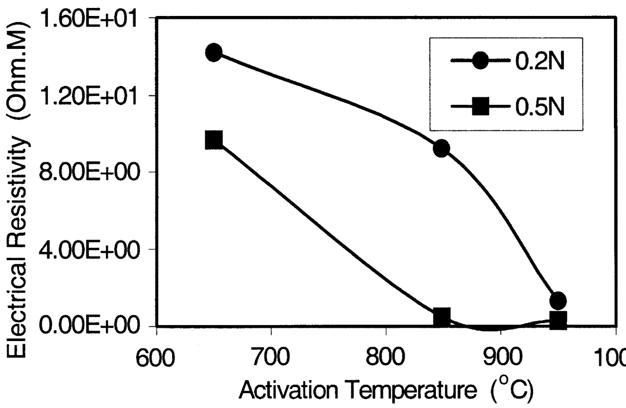

Fig. 3. Electrical Resistivity of PAN-ox fiber Based Carbon-silver composites.

3.4. Electrical Resistivity of PAN-ox fiber Based Carbon-silver composites

The electrical resistivity of these composites is given in Fig. 3. It has been found that the electrical resistivity of cokes decreases on incorporation of silver. The electrical resistivity decreases and conductivity increases with intake of silver which obviously depends on strength of silver solution. Electrical resistivity is found to decreases further with activation. Since silver is a good conductor of electricity. Therefore by controlling the amount of silver in the carbon matrix, the electrical conductivity can be tailor-made.

4. Conclusions

Modification of coal-tar pitch through heat treatment result in chemical crosslinking. The reaction is faster in air than in nitrogen. On treatment with silver salt solution, heat treated pitch under mild conditions exhibit higher silver uptake than those treated at higher temperature for long times through latter exhibit higher softening point. By controlling the amount of silver and method of modification, tailor made carbon products such as metal loaded cokes and metal loaded PAN-ox fiber-reinforced composites with desired electrical and adsorption characteristics can be developed.

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