

303
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INFLUENCE OF PROCESS VARIABLES ON PRECURSOR AND CARBON FIBRES

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Special grade acrylic fibres have been developed from PAN-co-methyl acrylate. The effect of molecular weight and distribution have been studied in relation to precursor and carbon fibre properties. The influence of process variables such as coagulation bath temperature, stretching, etc. on strength and modulus of fibres have been studied.

Acrylic fibres have been in use from early 1960 onwards and the development has been almost parallel to the nylon and polyester fibres. The special properties of acrylic fibres are its silk like and wool like appearance and hence suitable for combination with casein fibres and wool. Since there has been a lot of commercial application even from the beginning there is not much literature available on the acrylic fibre processing. All the process details have been carefully guarded by the fibre manufacturers.

From the early part of this century there has been special application of this fibre for the production of carbon fibres. Because of its chemical nature of decomposition without melting during heating, these fibres have been carbonised and graphitized in inert atmosphere to produce carbon fibres for the preparation of high performance composites. The properties of carbon or graphite fibres are dependent on the precursor properties like tensile strength, modulus, elongation, etc. These properties are in turn influenced both by the polymer properties and processing.

Although the textile grade PAN fibres have been originally used as precursors, there has been a lot of efforts to develop special grade PAN fibres. The main differences envisaged are given in Table 1.

TABLE 1
Difference between special grade and textile grade PAN

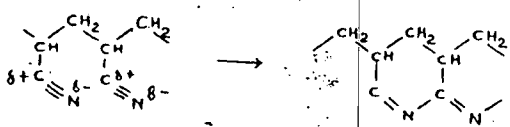
Textile grade	Special grade
1. Co-monomer content as high as 15 per cent	restricted upto 6 per cent
2. Two or three co-monomers to improve the processing and dyeing characteristics	Only one co-monomer to improve processing
3. No. of filaments as high as several thousands	No. of filaments 10,000 or less for uniform carbonisation
4. Moderate stretch and high elongation	High stretch and strength
5. —	Clean room conditions for spinning to avoid tarry by-products.

This only shows the qualitative difference. No data are available on the precursor polymer properties with respect to carbon fibre properties. Spinning of fibres in general is a complex field which involves proper choice of the polymer, spinning conditions and after treatment of fibres. The acrylic fibres have been mainly prepared by the wet spinning process and the factors which govern the fibre properties are:

- (a) Basic polymer molecular weight and distribution
- (b) Spinning conditions - wet or dry spinning and
- (c) After treatment - (i) stretching (ii) sizing and anti-static agent (iii) crimping.

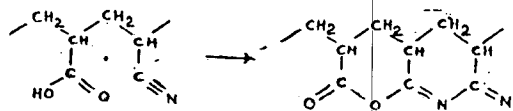
The carbonisation process involves several stages such as: (1) Oxidation under tension around 250°C - Ladder formation and cross-linking (2) Carbonisation under nitrogen around 300 - 1200°C - Graphitic structure formation and (3) Graphitization under Helium or Argon around 2000°C.

The precursor properties namely the tensile strength and elongation as well as the co-monomers influence this stage. The co-monomer acts as a catalyst in cyclization which is believed to proceed through nitrile polymerization.



The presence of co-monomer may influence this stage, in two ways.

- 1. By direct participation in the cyclisation



- 2. By lowering the t_g of the basic polymer to facilitate intra-molecular

cyclisation and inter-molecular cross-linking. Theoretically 100 per cent PAN is suitable for high strength, high modulus carbon fibres. But due to the difficulty in solubility and other processing parameters it has been reported⁴ that 3-6 per cent co-monomer is optimum for high conversion carbon fibres. The effect of various co-monomer on the carbonisation and carbon fibre properties have not been studied in detail.

We have chosen the system AN-6 per cent MA copolymers for comparison of precursor and carbon fibre under various process conditions. The first variable, namely, the basic polymer property such as molecular weight and distribution, solubility, dope viscosity and stability have been studied with respect to various polymers prepared under the following conditions:

- 1. Different polymerization temperatures 35, 45, 55, 65, 75°C; Table 2. Different catalyst/activator ratio Table 4, Table 2 and 3
- Chain transfer agent.

TABLE 2

Polymerization at different temperatures

No.	AN/MA wt. ratio	C/A wt. ratio	CTA	Water g	Temp. °C	Time hrs.	[η] dl/g
P ₁	94/6	1/1.5	—	500	35	5	3.2
P ₂	94/6	1/1.5	—	500	45	5	2.8
P ₃	94/6	1/1.5	—	500	55	5	2.2
P ₄	94/6	1/1.5	—	500	65	5	1.81
P ₅	94/6	1/1.5	—	500	75	5	1.12

Polymerization was carried out in water using K₂S₂O₈/NaHSO₃ - Fe²⁺ system at pH 2.5 - 3.0

TABLE 3

Effect of CTA on polymer properties

No.	AN/MA wt. ratio	C/A wt. ratio	CTA	Water g	Temp. °C	Time hrs.	$[\eta]$ dl/g
P ₁	94/6	1/1.5	2	500	55	5	1.4
P ₂	94/6	1/1.5	1.5	500	55	5	1.6
P ₃	94/6	1/1.5	1	500	55	5	1.72
P ₄	94/6	1/1.5	0.5	500	55	5	1.9

The GPC analysis of these polymers in DMF showed some interesting features. In the case of P₁, P₂ and P₃, more than one peak in the region 48–56 ml elution volume have been observed. This may be due to the presence of different molecular weight species or mixture of homo and co-polymers. Similar results have been reported by the Japanese workers⁸ which is attributed to the peculiarity in the suspension polymerization.

The effect of chain transfer agent on the polymer properties have been studied using certain thiols.

The GPC analysis of these copolymers show the presence of only one peak and this gives a definite proof that the molecular weight distribution has been narrowed the presence of CTA. It has also been found that the catalyst activator ratio (C/A) (Table 4.) plays an important role in determining the molecular weight and polydispersity.

Samples 10 and 3 give two peaks in GPC whereas 11 and 12 give only one single peak. This may be due to the chain transfer mechanism to the activator



TABLE 4

Effect of C/A on PAN co-polymers

No.	AN/MA wt. ratio	C/A wt. ratio	CTA	Water g	Temp. °C	Time hrs.	$[\eta]$ dl/g
P ₁₀	94/6	1/1	—	500	55	5	2.4
P ₃	94/6	1/1.5	—	500	55	5	2.2
P ₁₁	94/6	1/2	—	500	55	5	1.8
P ₁₂	94/6	1/2.5	—	500	55	5	1.6

The second important aspect governing fibre properties is the spinning conditions. In the case of wet spinning of PAN fibres, several systems have been used, namely, DMF, DMAC, Salt solutions and nitric acid. For our studies, we have chosen DMF system and the prime requisite in the dope preparation is the solubility index. This solubility index is very much influenced both by the molecular weight and distribution which again influences the dope viscosity and stability. For the various polymers we found the maximum solubility and dope viscosity (Table 5.).

TABLE 5

Solubility and bulk viscosity of PAN co-polymers

Polymer	Max. solubility g/100 ml DMF	Dope viscosity poise
P ₁	12.14	830
P ₂	18	630
P ₃	20	526
P ₄	24	320
P ₅	30	360
P ₆	26	400
P ₇	25	460
P ₈	24	510
P ₉	21	—
P ₁₀	19	560
P ₁₁	25	420

The tendency for gelation is higher for higher molecular weight species.

In the wet spinning of acrylic fibres, we have chosen PAN/COMA in DMF and aqueous DMF as coagulation bath. During coagulation a concentrated viscous polymer solution is transformed into proto fibres which require further processing before they acquire the textile fibre properties.

Because of its importance, the fibre generation step-coagulation offers a fruitful area for additional study. The influence of variation in coagulation conditions on the structure of the protofibres in its formative period are of particular interest. Inter-related with spinnability are the various parameters which are used for characterization of fibres. (1) Orientation (2) Crystallinity (3) Density (4) Porosity (5) Internal surface (6) Cross sectional shape (7) Mechanical properties.

These are very much influenced by the dope composition, coagulation bath composition and temperature and stretch ratios. Within DMF water coagulation system, it appeared that slower coagulation is better than rapid coagulation. During coagulation there is a rapid mass transfer through the solidified skin which acts as a membrane for the counter diffusion of water from coagulating bath and DMF from the gel. The fibre properties increase with increase in DMF upto 55 per cent and then decrease (Table 6). A progressive improvement in fibre diameter and internal structure as well as tensile strength were noted with reduced bath temperatures (Table 7). The mechanism by which reduced bath temperature gives improved fibre structure is probably related to coagulation rates. At low temperatures coagulation is retarded as the fibril formation is hydrophobic and endothermic in nature. At low temperatures coagulation is retarded and more time is allowed. The varia-

tion of coagulation bath temperature from 10, 20 and 30°C showed that the tensile strength is better at 10° of coagulation as seen in Table 7.

TABLE 6

Effect of bath composition on fibre properties

No.	Bath comp. per cent DMF	Temp C°	T. S.	M.	Cross section	Surface area m ² /g
			10 ³ psi	10 ⁶ psi		
P ₁	35	25	32	0.6	round	80
P ₁	45	25	55	1.1	round	120
P ₁	55	25	82	1.2	round	180
P ₁	65	25	76	1.3	round	140
P ₁	75	25	57	0.8	round	160

TABLE 7

Effect of bath temperature on precursor and C. F.

Polymer	Bath temp.	Stretch ratio	Precursor		C.F.	
			T. S.	M.	T. S.	M.
P ₁	10	1:8	85	1.4	140	18
P ₁	20	1:8	75	.9	85	14
P ₁	30	1:8	51	.87	60	—
P ₅	10	1:6	42	.87	—	—
P ₅	20	1:6	29	.60	—	—
P ₅	30	1:6	27	.60	—	—

The effect of stretch ratio on the precursor and carbon fibres have been studied and stretching is found to improve both the precursor and carbon fibre properties Table 8.

TABLE 8

Effect of stretch ratios on precursor and C. F.

Polymer	Bath temp.	Stretch ratio	Precursor		C. F.	
			T. S.	M.	T. S.	M.
P ₁	25	1:4	26	0.57	62	10.8
P ₁	25	1:5	28.9	0.61	86	10.9
P ₁	25	1:6	39.7	0.80	101	14
P ₁	25	1:8	43	0.82	106	18
P ₁	25	1:10	62	0.96	143	16

TABLE 9

Effect of molecular weight on fibre properties

Polymer	Stretch ratio	diam. μ	T. S. $\times 10^3$, psi	M. $\times 10^6$, psi	C. F.	
					$\times 10^3$ psi T. S.	$\times 10^6$ psi M.
P ₁	1:10	16	73	1.03	104	20.3
P ₂	1:8	18	66	1.12	60	14.92
P ₃	1:6	22	55	1.1	85	19.00
P ₄	1:5	25	45	0.8	100	10.00
P ₅	1:5	23	29	0.6	—	—

Comparison of the effect of molecular weight on fibres showed that the high molecular weight polymers give better fibres as seen in Table 9. The effect of polydispersity on fibre properties will be communicated in due course.

Acknowledgement

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