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EFFECT OF ADDITIVES ON THE MECHANICAL PROPERTIES OF POLYACRYLONITRILE FIBRES

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In spinning of synthetic fibers, several additives are used for various purposes. Some organic compounds are known to reduce viscosity and facilitate many technical operations besides increasing solid content of the dope in wet spinning process. Gelation if preceded by phase separation increases the mechanical properties of the fibres. The effect of organic additives and gelating agents (of inorganic compounds and non-solvents) on the mechanical properties of the PAN fibres have been reported here. The organic additives decreased both the modulus and the strength, the inorganic additives increase them whereas non solvent has no effect. When all the additives are added the overall strength and modulus of the fibers increase as compared to the fibres without any additive. Carbon fibers from the PAN fibers produced in the presence of all the additives have comparable mechanical properties with those of some of the industrial fibers carbonized at 1000°C.

Numerous soluble and insoluble additives are used for various purposes in most of the synthetic fibres.

Dull or semi-dull fibres are de-lustered with TiO_2. Coloured fibres may be produced by the incorporation of either insoluble pigments or soluble cationic dyes. Flame resistance of fibre is increased by additives containing chlorine, bromine or phosphorous.[1] Antimony[2,3] compounds are used for synergestic effect on flame resistance in fibres containing a halogen.

Heat stabilizers are added to minimise discolouration of the solution prior to spinning, and fibre during production and some other additives are used to improve fibre light stability.[1]

Some organic additives[4] are reported to reduce viscosity and facilitate many technical operations such as dissolution, filteration, de-areation and increase the solid content of the dope. Addition of non-solvent is known to reduce viscosity and hasten the gelation of the polymer. It is reported in literature that additives such as congo red,[5] borax or boric acid[6] stimulate gelation.

Wet spinning, as is well known, is a three component system of polymer, solvent and non-solvent in which two transitions occur – gelation and phase separation. To achieve desired dense, homogeneous fibre structure with good mechanical properties, gelation should precede phase separation or solidification. Additives in the work reported here were aimed at reducing the viscosity of the dope and effect gelation. This communication deals with the effect of these additives

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on the machanical properties of the fibres. Their effect on cross section of the fibres is reported elsewhere.[7]

Experimental

Polyacrylonitrile–co–methyl acrylate (6 per cent) was prepared in the laboratory at 69–70°C using redox catalyst system.

Dimethyl formamide (DMF) is used as a solvent for making the spin solution and DMF–H_2O (55–45 per cent) is used as the coagulation bath.

Organic additives like hydrochlorides of aryl, alkyl secondary amines of analar grade were made use of from 0.5 to 5 per cent. They were added to DMF while making the spin solution.

Inorganic additives like calcium salts, borax and boric acid etc., were used in the concentration range of 0.1 to 2.0 per cent. 0.1 to 1.0 per cent of distilled water is used as non-solvent in the preparation of the dope solution. The compositions of the spinning solution, the coagulation bath and temperature were the same for all the experiments carried out.

Fourne Laboratory model wet spinning assembly with 48 holes of diameter 0.025 mm was used to spin PAN fibres. All the spinning parameters such as the volume rate flow, temperature, the composition of the stretch baths and the stretch ratios were kept constant through all the experiments. The fibres obtained were tested in Instron testing machine.

Results and discussion

The following table shows the effect of the additives on the modulus of the PAN fibres.

TABLE 1

Effect of the additives on the modulus of PAN fibres.

Additive	*Per-centage concentration in g.*	*Modulus $\times 10^6$ psi*
Organic	0.5 – 5.0	0.6
Inorganic	0.1 – 2.0	1.2
Non-solvent	0.1 – 1.0	0.7
Without any additive	–	0.75
Mixture of organic-inorganic and non-solvent	range as given above	1.0

Without any additive added, the modulus of PAN fibres is 0.75×10^6 psi. When an organic additive is added, the modulus decreased to 0.6×10^6 psi. In the presence of non-solvent, there is not much of a change in the modulus value, whereas when an inorganic additive is added, the modulus rises to 1.2. In the presence of all the additives, the modulus is less than what is observed with inorganic additive. However, there is an over all increase from 0.75 to 1.0×10^6 psi.

Modulus values are chosen for comparison of the fibres, because modulus is measured when the fibre has not undergone a drastic change in the initial structure. Strength values are not reliable because the fibre breaks after considerable irrecoverable or permanent deformation and hence undergoes drastic change from the initial structure of the fibre.

It can be seen from Table 2 that tensile strength of PAN fibres is increased by inorganic additive, decreased by organic additive and that non-solvent does not have much effect. This comparison also reveals the presence of probable flaws in the fibre.

The stresses would concentrate at the flaws and with the decrease of gauge length the fibre breaks. Higher the strength, lower is the number of flaws

TABLE 2

Effect of additives on the strength and elongation of PAN fibres

Additive	*Elonga-tion*	*Tensile strength* $\times 10^3$ *psi*	*Breaking strain*
Organic	5.7	26.35	0.113
Inorganic	4.9	46.28	0.098
Non-solvent	5.73	34.17	0.113
Without any additive	6 62	36.66	0.132
Mixture of all additives	5.73	43.98	0.115

Note: The concentration range of the additives given above is the same as given in Table 1.

The diametres of all these fibres have been quite high and they have been stretched in a separate process.

During stretching, the fibre is heated above its glass transition temperature and so the surface flaws would be annealed and not the voids. The maximum strength and modulus of the fibres in the presence of all the additives after stretching has been 109 $\times$ 10^3 psi and 1.85 $\times$ 10^6 psi respectively.

These fibres when heated to 1000°C produced carbon fibres and their mechanical properties are compared with those of other industrial PAN fibres treated in similar way.

The rusults in table 3 reveal that PAN fibres produced in the presence of all the additives (J_{26}) possess mechanical properties higher than those of Toray (T_2) and to some extent nearer to the properties of Hercules fibres treated in similar way. However, the carbon fibres from J_{26} were found to be brittle may be due to larger diameter than those of imported PAN fibres.

TABLE 3

Comparision of the mechanical properties of PAN fibres corbonized at 1000°C

Precursor	*Primary younges modulus* $\times 10^6$ *psi*	*Strength* $\times 10^3$ *psi*	*Younges modulus* $\times 10^6$ *psi*
Courtella	1.35	300	28
Beslon	1.23	230	25
Toray (T_1)	1.08	230	23
Toray (T_2)	0.63	140	13
Hercules	0.78	210	16
J_{26} (CLRI)	0.87	188	19.18

The cross section of the PAN fibres was found to be of bean shape in the presence of organic additives and the mixture of all additive. It was round in the other cases.

The change of cross sectional shape from round to bean is dependent on the pH of the dope solution. These findings are supported by the results reported by Grobe and Gieske.[8] The detailed discussions are reported elsewhere.

To confirm the mechanistic role of the additives on the mechanical properties of the PAN fibres, detailed studies are under way.

Conclusions

The effect of the additives on the mechanical properties of PAN fibres show that viscosity modifiers like organic additives decrease the strength and the modulus, whereas when an inorganic additive is added which is supposed to promote gelation during coagulation increases both strength and modulus. The non-solvent in the concentration range employed in these experiments, however, does not show any remarkable effect. In the presence of all the additives, the strength and the modulus values are higher than found in the case of addition of organic or non-solvent or in the absence of any additive, but it is less than what has been observed in the presence of inorganic additive. Further, by the reduction of the diameter of the fibres through additional stretching process the mechanical properties of the carbon fibres may be improved.

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