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# Development of carbon fibres from pitches modified with polymers

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Polymethylmethacrylate (PMMA), polystyrene (PS) and polycarbonate (PC) were incorporated into the pitch with an objective to increase the tensile strength and tensile modulus of the pitch fibres (green) and to retain or to improve the mechanical properties of the carbonised fibres. It was found PMMA addition to the pitch increases the strength or flexibility of the green fibres but results in the formation of highly porous carbon fibres. The incorporation of PS and PC improves the tensile strength and tensile modulus both at the green and carbonised levels. The enhancement of mechanical properties is better in the case of carbon fibres derived from PC modified pitches.

## 1. Introduction

Carbon fibres and carbon fibre-reinforced carbon composites find applications in various high tech and commercial fields due to their unique properties like light weight, stiffness, high thermal conductivity, high strength and thermal stability up to 3000°C in an inert atmosphere [1]. The versatile nature of the carbon fibres led to extensive research on the development of the different precursor materials from which carbon fibres could be processed. As a result, technology for the manufacture of carbon fibres from viscose rayon, polyacrylonitrile (PAN) and pitch-based precursor materials were reported [2–12]. However, very little data is available on the developmental aspects of carbon fibre derived from pitch materials. Efforts are made in this communication to develop suitable isotropic pitch precursor and to spin the fibres therefrom. The present authors have recently reported from studies on the pitches that a pitch having a softening point (SP) of 200–250°C, quinoline insolubles (QI) of <0.5%, toluene insolubles (TI) of 45–60%, coking value (CV) of 75–80% with an isotropic microstructure could serve as a suitable precursor for the development of pitch-based isotropic carbon fibres [13, 14]. Such a precursor could be conveniently obtained by the treatment of coal tar and petroleum pitch mixture [13]. It was also noticed that though carbon fibres of diameter 18 $\mu$m developed from the blended pitches possessed good mechanical strength, having tensile strength (TS) of 1690 MPa, tensile modulus (TM) of 160 GPa, pitch fibres (green) are difficult to handle for subsequent processing into carbon fibres due to their poor mechanical properties showing TS of 3 MPa and TM of 1.4 GPa. To overcome this problem, Mochida *et al.* reported the addition of polypropylene oxide (PPO) to the precursor pitch to increase the strength of the green fibres but it was noticed that the mechanical properties of the resulting carbon fibres got deteriorated [15]. Based on this report of Mochida and his coworkers, the authors developed and reported the improvement on the mechanical properties of the green pitch fibres as well as carbon fibres with improved mechanical properties by incorporating polycarbonate to the precursor pitch [14]. More recently, Oya *et al.* employed polymer blend technique to prepare fine carbon material including carbon nano-fibres and nanotubes [16–18]. These research reports and the results obtained with polycarbonate modified pitches inspired the investigators to continue their efforts to improve the strength of green and carbonised fibres by incorporating polymers which exhibit good flexibility and strength in the fibrous form into the precursor pitch. This paper explains the development of carbon fibres made from pitches modified with polymethylmethacrylate (PMMA), polystyrene (PS), which have been compared with those made from polycarbonate (PC) modified pitches.

## 2. Experimental

High softening point QI-free pitch was prepared by blending and suitable heat treatment of petroleum and coal tar pitches, which were characterised with respect to SP, QI, TI and CV, melt spun, oxidised and carbonised to get the carbon fibres having a diameter ~30 $\mu$m. by following the conditions reported earlier [13, 14]. The PMMA, PS and PC were also melt spun to get the respective fibres.

The precursor pitches mixed in different lots with varying amounts of PMMA (2.5, 5 and 10% by weight) as well as PS (10, 20 and 30% by weight) were dissolved in coal tar oil (boiling point 210–270°C) and mixed under constant stirring and the solvents were later distilled under reduced atmospheric pressure to obtain the modified pitches. These pitches were melt spun to get the fibres. The preparative details of PC modified pitches are given elsewhere [14].

All the polymers were characterised for their pyrolysis behaviour using TGA (Mettler Thermal Analyser System, TA–4000) and all the polymer modified pitches were characterised with respect to SP, QI, TI, CV and for their spinnability. The fibres developed from the original and modified pitches were stabilised in air upto 280°C and carbonised to 1000°C in high purity nitrogen atmosphere to get carbon fibres. The green as well as carbonised fibres and the polymeric fibres were characterised for their mechanical properties using Instron Universal Testing Machine (Model 4411) and the surface morphology of the pitch and the modified pitch-based fibres was studied using Scanning Electron Microscope (LEO 440). All the carbonised fibres reported in this communication have the diameter around 30 $\mu$m. In the case of PC modified pitches, results obtained with fibres having a diameter of 30 $\mu$m are only reported here since mechanical properties of the PC-modified fine fibres having the diameter range 16–20 $\mu$m was already reported in our earlier paper [14].

## 3. Results and discussion

### 3.1. Polymeric fibres

The pyrolysis behavior of PMMA, PS and PC are illustrated in Table I. It is seen from the values that PC alone leaves a carbon residue after carbonization at 1000°C while PS and PMMA are completely decomposed around 500°C. Based on the structural aspects PC which has a carbonate group can give flexibility coupled with 26% carbon content and PS possessing a —CH$_2$—CH— group linked to reactive phenyl ring and less shrinkage [19] seems to be the suitable polymers that can enhance the mechanical properties of the pitch (green) fibres. Even though PMMA is an aliphatic compound with zero coking yield it is used as an additive in this investigation since it is tougher than PS and is a well known polymer used in making many appliances which possess both flexibility and strength.

The mechanical properties of the polymeric fibres are given in Table II. It is seen from the values that the PC has highest flexibility (strain-to-failure of 4.6%) followed by PMMA (2.5%) and PS (1.3%). The tensile strength of these fibres shows the reverse trend with PS, PMMA and PC having TS of 1040, 780 and 430 MPa respectively. It appears from these observations that PC which also possess coking value of 26% could help in increasing the strain-to-failure which should in turn lead to good fibres. After considering the structure and mechanical properties of the above polymeric fibres, all these polymers were used as additives in the development of carbon fibres.

TABLE I Thermogravimetric analysis of PMMA, PS, and PC

| Temperature (°C) | Pyrolysis yield (%) PMMA | PS | PC |
|---|---|---|---|
| 100 | 99.9 | 99.8 | 99.8 |
| 200 | 99.7 | 99.8 | 99.2 |
| 300 | 99.2 | 99.3 | 93.3 |
| 400 | 75.3 | 83.5 | 90.2 |
| 500 | 2.9 | 0.2 | 38.0 |
| 600 | 2.4 | 0.1 | 36.0 |
| 700 | 2.0 | 0.0 | 34.4 |
| 800 | 1.3 | 0.0 | 31.2 |
| 900 | 0.8 | 0.0 | 28.5 |
| 1000 | 0.0 | 0.0 | 26.2 |

TABLE II Mechanical properties of polymer fibres obtained from PS, PC and PMMA

| Sample | Mechanical properties Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) |
|---|---|---|---|---|
| PS | 24 | 1040 | 82 | 1.3 |
| PMMA | 15 | 780 | 31 | 2.5 |
| PC | 18 | 430 | 9.3 | 4.6 |

### 3.2. PMMA modified fibres

The characteristics of PMMA modified pitches are given in Table III. It is seen that the coking value of the pitches decrease with increase in PMMA content. The coking values obtained experimentally are in close agreement with those calculated on the basis of blending ratios. This implies that the polymer simply gets added to the pitch and does not form a new product either by condensation or by reaction with a pitch molecule. It is further observed that the handling strength of the green fibres was found to be excellent only with the 10% addition of PMMA to the original pitch.

The mechanical properties of the green fibres and carbonised fibres from the pitch modified with 10% PMMA are given in Table IV. It is seen from the values that tensile strength of PMMA modified green fibres is 70 times higher than that of the fibres derived from the original pitch. There are also marked improvements (8–10) times in tensile modulus (from 1.3 GPa to 10 GPa) and strain-to-failure ratio (from 0.2 to 2.2%). This may be attributed to the fairly good strength coupled with the good strain to failure of the PMMA

TABLE III Characteristics of the pitch—PMMA mixtures

| Characteristics | Ratios of polymethylmethacrylate with respect to pitch (wt%) 0 | 2.5 | 5 | 10 |
|---|---|---|---|---|
| Softening point (°C) | 210 | 212 | 217 | 225 |
| Quinoline insolubles (%) | 0.0 | 0.0 | 0.0 | 0.0 |
| Toluene insolubles (%) | 45.0 | 45.0 | 45.2 | 46.0 |
| Coking value (%) | 79.0 | 78.0 | 76.3 | 72.7 |
| Spinnability | Good | Good | Good | Good |
| Spinning temperature (°C) | 220–235 | 220–240 | 225–245 | 235–250 |
| Handleability | Poor | Poor | Poor | Excellent |

TABLE IV Mechanical properties of pitch and carbonised pitch filaments based on original and 10% PMMA modified pitches

| | Mechanical properties | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Green pitch filaments | | | | Carbonised pitch filaments | | | |
| Sample | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) |
| Original pitch | 55 | 2.9 | 1.3 | 0.2 | 30 | 690 | 50 | 1.4 |
| Modified pitch (with 10% PMMA) | 60 | 220 | 10 | 2.2 | 36 | 5 | 1.4 | 0.4 |

TABLE V Characteristics of pitch-polystyrene mixtures

| | Ratios of polystyrene with respect to pitch (wt%) | | | |
|---|---|---|---|---|
| Characteristics | 0 | 10 | 20 | 30 |
| Softening point (°C) | 250.4 | 256.5 | 262.1 | 273.9 |
| Quinoline insolubles (%) | 0.0 | 0.1 | 0.2 | 0.4 |
| Toluene insolubles (%) | 60.3 | 58.3 | 56.0 | 45.6 |
| Coking value (%) | 79.0 | 75.0 | 69.1 | 60.8 |
| Spinnability | Good | Good | Good | Good |
| Spinning temperature (°C) | 265–275 | 270–280 | 275–290 | 280–290 |
| Handleability | Poor | Poor | Poor | Good |

polymer. These properties are expected to be transmitted to the pitch fibres developed from the modified pitch. The scanning electron micrograph given in Fig. 1 shows two different phases which indicate that PMMA forms a mixture with the pitch and probably a portion of PMMA comes out as a separate phase on spinning imparting its mechanical properties to the pitch fibres.

It is also seen from Table IV that same trend in mechanical properties is not observed in the case of carbonised fibres derived from PMMA-modified pitches. The tensile strength, tensile modulus and strain-to-failure of the green fibres decrease drastically to 5 MPa, 1.4 GPa and 0.4%, from 220 MPa, 10 GPa and 2.2% respectively, which is nearly same as the values observed in the case of green fibres derived from original pitch. This may be attributed to the porous nature of the carbon fibres, resulting from the decomposition of PMMA from the green fibres upon carbonisation, which is confirmed by SEM photograph illustrated in Fig. 2, which shows large cracks and voids.

### 3.3. PS modified fibres

Polystyrene has $-CH_2-CH-$ group bonded to reactive phenyl ring and high melt strength [19–21]. Further, the short chain ($-CH_2-CH-$) of PS can get added to the pitch or can get occluded in the pitch since PS is known to form high impact strength PS with rubber through this phenomenon [22, 23]. Based on these reports, PS was added in varying amounts (10, 20 and 30% by wt) to the original pitch. The characteristics of the PS-modified pitches given in Table V show an increase in the SP and the increase is around 6°C on the addition of 10 and 20% PS and about 14°C on incorporating 30% PS into the original pitch. The QI also increases from 0.0 to 0.1, 0.2 and 0.4%, respectively, which is in the required limit for the development of

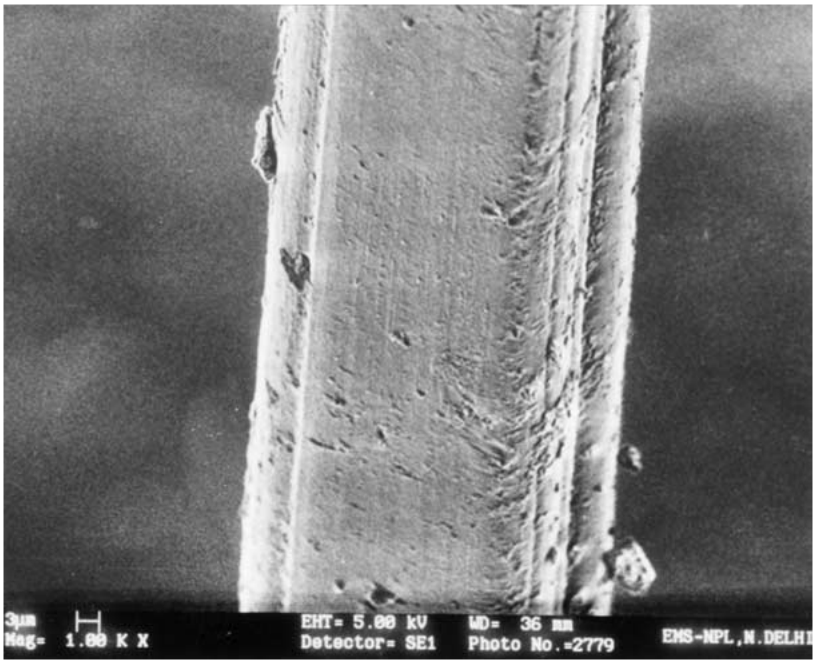


*Figure 1* Scanning electron micrograph of green fibres developed from pitch-10% PMMA blend.

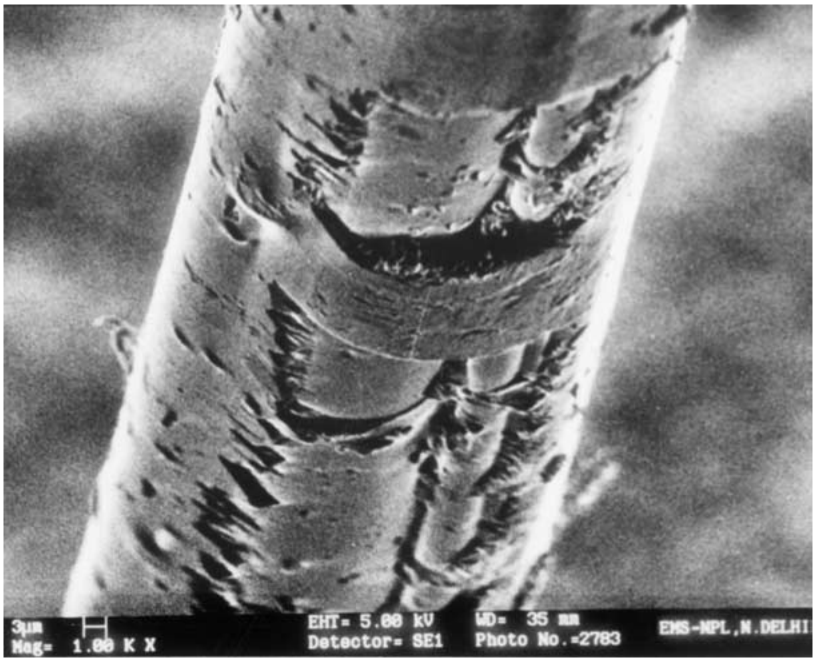


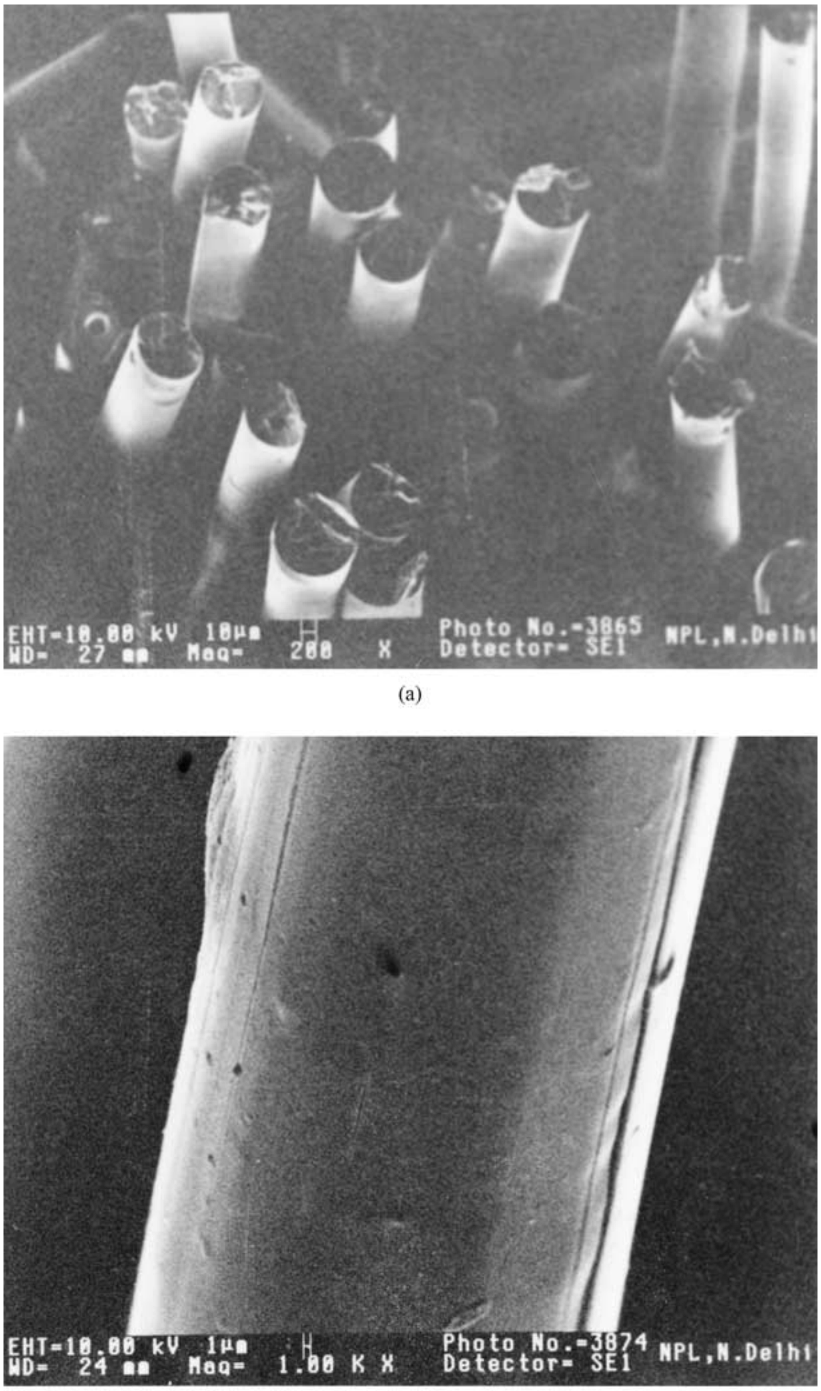
*Figure 2* Scanning electron micrograph of carbonised fibres developed from pitch-10% PMMA blend.

pitch-based isotropic carbon fibres [13]. The coking value was found to decrease gradually from 79 to 60.8% as PS content is increased to 30%. It is also observed that the CV is higher than the value calculated on the basis of mixing ratio, which indicates that probably an adduct (inclusion compound) is formed through the short styrene side chain or by occlusion of PS in the pitch molecules.

The mechanical properties of the fibres developed from PS modified pitches are given in Table VI. It is seen from the values that the tensile strength of the green fibres is slightly increased with the 10 and 20% PS additions (from 3 MPa to 4 and 7 MPa), while it increases to 70 MPa with 30% PS addition. This may be attributed to the formation of an adduct between PS and pitch molecules. This adduct during spinning temperatures (270–290°C) remains intact as seen from Table I (0.2–0.7% weight loss at 200–300°C) and thus shows an increase in the mechanical properties. The tensile modulus of the green fibres also shows the similar pattern. The strain-to-failure shows an increase only with green fibres developed from 30% PS-modified pitch and thus shows better flexibility when compared to those developed from original pitch and 10 and 20% PS modified pitches. It is also seen that there is a marginal increase in the mechanical properties of the carbonised fibres when compared to that of the carbon fibres of the original pitch. The modulus of these modified fibres also increase and follow the same trend. The increase in the mechanical properties of the carbon fibres in spite of the expected decomposition of PS upto 1000°C may be due to the retention of the melt strength of the PS fibres, which was transferred to the modified pitch fibres and finally to the carbonised fibres. The strain-to-failure values of the PS modified carbon fibres show them to be less flexible (or more brittle) when compared to the carbon fibres derived from the original pitch. The SEM micrographs of the PS-added green pitch fibres are given in Fig. 3. It is seen from these micrographs that the PS is included homogenously in the pitch unlike PMMA addition and on carbonisation the unreacted PS in the modified pitch containing 30% PS tries to escape from the interior of the fibre, which shows probably PS is occluded in the pitch forming core sheath structure as seen in the SEM micrographs of the carbonised fibres (Fig. 4). This observation also indicates that probably pitch can accommodate only up to less than 30% PS.

TABLE VI Mechanical properties of green and carbonised pitch monofilaments based on original and PS-modified pitches

| | Mechanical properties | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Green pitch filaments | | | | Carbonised pitch filaments | | | |
| Sample | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) |
| Original pitch | 50 | 3 | 1.4 | 0.2 | 30 | 690 | 50 | 1.4 |
| Modified pitch (with 10% PS) | 50 | 4 | 1.7 | 0.2 | 31 | 750 | 57 | 1.3 |
| Modified pitch (with 20% PS) | 48 | 7 | 2.9 | 0.2 | 33 | 760 | 78 | 1.0 |
| Modified pitch (with 30% PS) | 46 | 70 | 12 | 0.6 | 32 | 830 | 98 | 0.9 |



(a)

(b)

*Figure 3* Scanning electron micrographs of green fibres developed from (a) pitch modified with 20% PS (b) pitch modified with 30% PS.

### 3.4. PC modified fibres

The characteristics of the PC-modified pitches along with the mechanical properties of the carbonised fibres in the diameter range 16–20 $\mu$m were already reported [14]. For comparison purposes, fibres of 30 $\mu$m were drawn from the PC modified pitches and their mechanical properties determined are listed in Table VII. It is seen from these values that the PC modified carbonised fibres show marked increase in the tensile strength when compared to the carbon fibres developed from original pitch (from 690 MPa to 870 and 950 MPa). The increase in the tensile strength is more in the case of carbonised fibres derived from 10 and 20% PC modified pitches as compared to the values obtained with carbonised fibre derived from 10, 20 and 30% PS modified pitches. The values of strain to failure also indicate that the flexibility of the carbonised fibres is not adversely affected by the addition of PC. As mentioned in our earlier publication that the addition of PC leads to a reaction between pitch and polymer which not only results in an increase in the CV (CV was found to be more than the values calculated on the basis of mixing ratio) but also forms a single phase both in the green and carbonised levels as shown in the already reported SEM photographs which accounts for their improved mechanical properties [14].

TABLE VII Mechanical properties of green and carbonised monofilaments based on original and PC-modified pitches

| | Mechanical properties | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Green pitch filaments | | | | Carbonised pitch filaments | | | |
| Sample | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) | Diameter ($\mu$m) | Tensile strength (MPa) | Tensile modulus (GPa) | Strain-to-failure (%) |
| Original pitch | 50 | 3 | 1.4 | 0.2 | 30 | 690 | 50 | 1.4 |
| Modified pitch (with 10% PC) | 52 | 30 | 7.7 | 0.4 | 30 | 870 | 65 | 1.3 |
| Modified pitch (with 20% PC) | 58 | 43 | 13.6 | 0.3 | 30 | 950 | 76 | 1.3 |

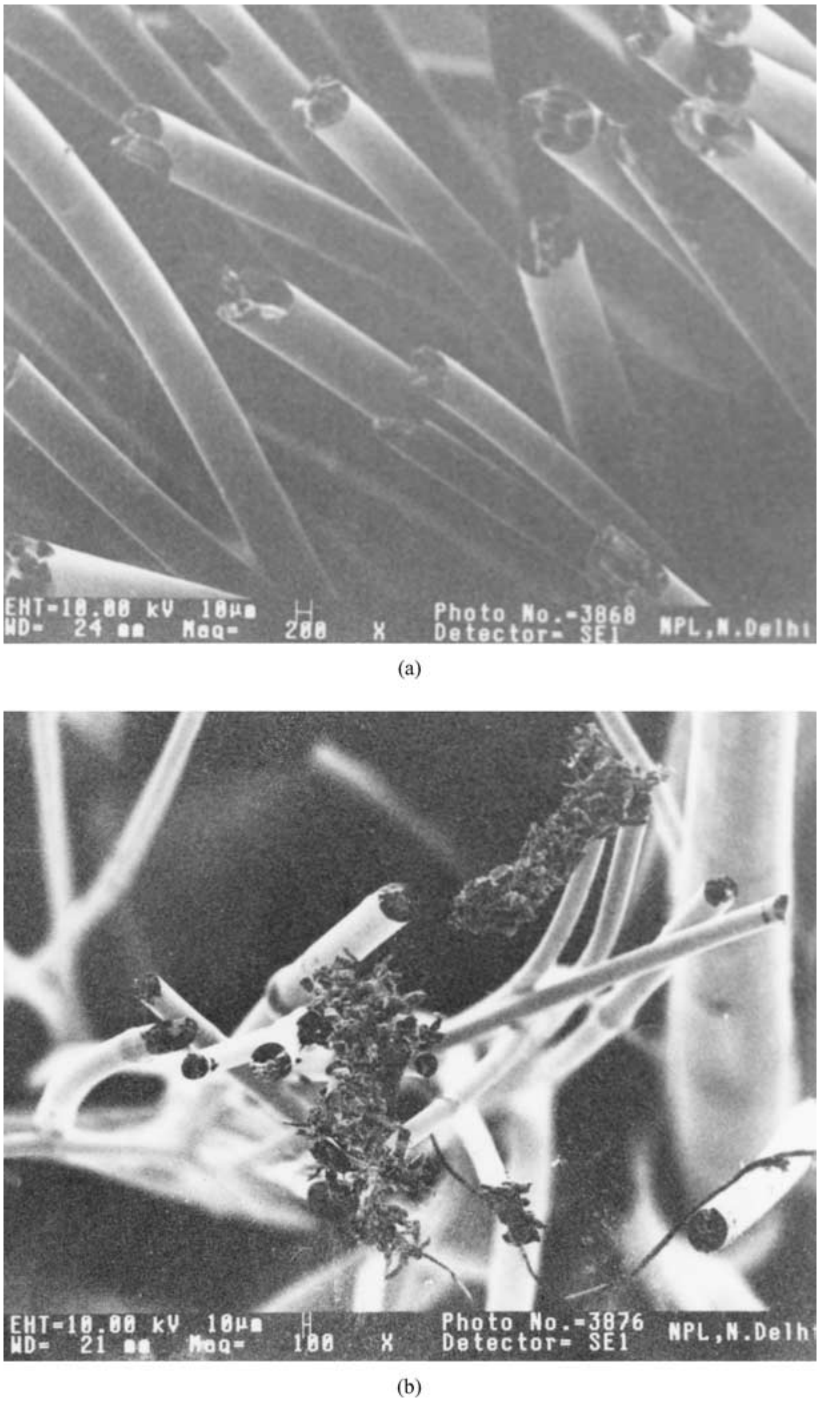


*Figure 4* Scanning electron micrographs of carbonised fibres developed from (a) pitch modified with 20% PS (b) pitch modified with 30% PS.

## 4. Conclusions

PMMA, PS and PC were incorporated into the pitch with an objective to increase the tensile strength of the pitch fibres (green) and to retain or to improve the mechanical properties of the carbonised fibres. It was found even though PMMA addition to the pitch increases the strength or flexibility of the green fibres, it results in the formation of highly porous carbonised fibres whose tensile strength is same as that of the green fibres derived from the original pitch. The incorporation of PS and PC improves the tensile strength and tensile modulus both at the green and carbonised levels. The enhancement of mechanical properties is better in the case of carbon fibres derived from PC modified pitches.

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