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A photocrosslinkable melt processible acrylonitrile terpolymer as carbon fiber precursor

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Abstract

A novel photocrosslinkable and melt processible terpolymer precursor for carbon fiber has been successfully synthesized and characterized. The terpolymer was synthesized by an efficient emulsion polymerization route and has a typical composition of acrylonitrile/methyl acrylate/acryloyl benzophenone in the mole ratio, 85/14/1. It has been characterized by FTIR, NMR, intrinsic viscosity and GPC molecular weights. The composition of the monomer repeat units in the terpolymer was determined by NMR, and was almost identical to the molar feed ratios of the monomers used for polymerization. The T_g of the terpolymers, were somewhat a function of molecular weight, but were in the range 77–91 °C. The fibers were spun from the terpolymer melts unlike the conventional solution spinning method. The terpolymers when stabilized with boric acid afforded a stable melt for about 30 min at 200–220 °C, which was empirically found to be sufficiently long to spin fibers. The terpolymer with the highest molecular weight (M_n, ~48,000) was not melt processible, apparently because the melt viscosity was very high and the terpolymer degraded fast. However, terpolymers, which had an intrinsic viscosity <0.6 dL/g (NMP, 25 °C) were invariably melt processible. The initial carbon fibers produced from these terpolymer fibers upon complete carbonization exhibited good mechanical properties for proposed automotive applications; the tensile strength of the best fibers generated thus far was in the range 450–700 MPa with a strain to failure of ~0.4%. The diameter of the carbon fibers was of the order of 7 μm.

Keywords: Terpolymer; Acrylonitrile; Methyl acrylate

1. Introduction

Development of lightweight and high-strength polymer matrix carbon fiber composites suitable for automotive applications is one of the thrust areas of contemporary applied polymer research. Reduction in the cost of carbon fibers is required to expand their use from the current high tech applications, e.g. aerospace and military, to more high volume markets like general-purpose automotive composites [1]. It is appropriate to briefly discuss the basic chemistry involved in the currently used technology of making carbon fibers and their melt processible precursors, and how can it be amended to obtain more cost effective carbon fibers.

The commonly used precursors for making carbon fibers are the acrylic fibers used in textile applications [2]. Chemically, these fibers are copolymers of acrylonitrile (AN) with about 3 mol% of other comonomers. The comonomers include 3–4 mol% of methyl acrylate (MA), vinyl acetate, etc. which induce solubility in the commonly used fiber spinning solvents like dimethyl formamide, and 1–2 mol% of acidic comonomers like acrylic acid or itaconic acid [2,3], which help in dyeing the fibers. A carefully controlled thermal treatment in stages brings about the metamorphosis of these textile fibers into carbon fibers [3]. The important steps of this process are termed stabilization and carbonization.

In the stabilization step, the polymer fiber is typically heated at 200–250 °C for 5–10 h in the presence of air. Consequently, the polymer containing predominantly AN units is converted from a linear structure to a ladder like structure via the intramolecular cyclization of the pendant CN groups and intermolecular crosslinking. This process is believed to occur both intra- and inter-molecularly, and competes with the polymer degradation and crosslinking reactions that take place

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simultaneously [2]. Nevertheless, an acceptable yield and quality of the stabilized fibers is achieved by operating at the right temperature and amount of oxygen [2,3]. In the next step, the stabilized fibers are carefully heated in an inert atmosphere at >1000 °C for a few hours, to remove all the non-carbon elements and to obtain a carbon fiber that has at least 97% carbon content. Hence, this step is described as carbonization. The different grades of carbon fibers are characterized by their carbon content and have different mechanical properties, notably, the tensile modulus [1,2]. The textile fibers are spun from relatively dilute solutions at mild temperatures. Presence of solvent allows (i) use of low spinning temperatures that prevent premature cyclization/crosslinking (ii) formation of very fine fibers with uniform diameter of the order of 20 μm that are critical for successful stabilization and (iii) overcomes the pseudo crystallinity [4] present in these high acrylonitrile containing fibers.

For making cost effective carbon fibers, therefore, the common approach adopted by various research groups including our laboratory [5–8] is to replace the solvent spinning process by a melt spinning process. Melt spinning requires precursors of good thermal stability but the increased thermal stability may only be obtained with a decrease in certain mechanical properties [9]. The increased thermal stability may only be obtained at the price of loss of certain mechanical properties [9]. The task of reducing the cost of carbon fiber is very challenging [10] not only because of this tradeoff, but also because the chemistry of processible precursors is poorly understood. Hence, there is a need to study the design of the melt processable carbon fiber precursors, with the objective of achieving reasonable thermal stability without missing the important mechanical characteristics. However, it has been noted in studies from our laboratory [5,11] that copolymers containing >90 mol% AN do not truly melt, and hence exhibit very high melt viscosity. Copolymers containing 85–90 mol% AN have melt viscosity in the processible range of 100–1000 Pa s at 220 °C; beyond which they start to thermally degrade [12]. The much higher content of comonomer (10–15 mol%) reduces or eliminates the melting point and hinders the cyclization of the CN groups responsible for the stabilization process. The net effect is the lowering of the mechanical properties of the copolymers containing lower amounts of AN, which may undesirably promote fiber fusion during the stabilization step rather than undergoing cyclization or cross-linking. To circumvent this problem it was thought worthwhile to marginally crosslink the fibers before stabilization. This can be achieved by electron beam irradiation or UV induced cross-linking [13]. It was, therefore, proposed to use a carefully selected UV-sensitive comonomer to afford terpolymer precursors having reasonable mechanical strength prior to stabilization.

In continuation of the AN-copolymers work [14] from our laboratory, in the present study, the design and synthesis of AN terpolymers containing MA as the major comonomer and acryloyl benzophenone, ABP (<1 mol%) as the minor comonomer intended for assisting in the UV induced cross linking is discussed. The choice of the major comonomer was based on a study of the reactivity ratios of AN and MA, which showed that both these monomers make an excellent pair for copolymerization [14a]. The emulsion polymerization route was adopted for the synthesis of the terpolymer; the choice of the route was made following a systematic study of the possible methods of polymerization, in our laboratory [10,15,16]. Structural characterization and thermal analysis of the copolymers are reported. Both dynamic and steady shear viscosities have been studied to assess the suitability of these copolymers as melt-processible carbon fiber precursors.

2. Experimental

2.1. Materials

The monomers, AN and MA were obtained from Aldrich and used as received. ABP was synthesized using a reported procedure [17]. The chain transfer agent, 1-dodecanethiol and boric acid were also obtained from Aldrich. $MgSO_4$ and the initiator ammonium persulfate were obtained from EM Sciences and used as received. DOWFAX 8390 solution surfactant was obtained from The Dow Chemical Company.

2.2. Copolymer synthesis

The terpolymer synthesis was carried out in aqueous medium via an emulsion polymerization route as described below.

A 250 mL reaction flask fitted with a condenser, glass stirrer, nitrogen inlet tube and thermocouple probe was purged with nitrogen and was charged with 50 mL water containing the surfactant (2.07 g). A premix of the monomers (2.5 mL, 10% of the total) and the mercaptan (0.5 g) were added followed by the initiator (17 mg in 10 mL water). The temperature was raised to 60 °C and the remaining monomer mixture (AN, 20.5 g, MA, 5.48 g and ABP, 1.15 g) was added over a period of 2 h. At the end of addition of the monomer mixture, an extra quantity of initiator (10 mg in 10 mL water) was added through the condenser. The latex was held at 60 °C for an additional 30 min. The product was isolated by precipitation with 500 mL 1% aqueous $MgSO_4$ at 65 °C. The terpolymer was vacuum dried at 70 °C for 24 h (recovered yield, 85%).

2.3. Characterization

The IR spectrum was recorded using a Nicolet FTIR spectrometer. ^1H NMR spectrum was obtained with a Varian UNITY 400 MHz spectrometer using DMSO-d_6 as solvent. The intrinsic viscosity (IV) measurements were performed in *N*-methyl pyrrolidone (NMP) at 25 °C using a Cannon Ubbelohde viscometer. The melt viscosity was measured using a RMS 800 Dynamic Spectrometer. A steady shear frequency sweep was employed to determine the melt viscosity, and a time sweep was used to determine the stability of the polymer melt over a time of 30 min at 220 °C. Differential scanning calorimeter (DSC) was used to determine the glass transition temperature (T_g) of the copolymers with a TA instrument (model Q 1000). The scans were carried out under nitrogen, with a heating rate of 10 °C/min and with a sample mass of 5 mg. The weight-loss pattern of the tepolymer was determined using a TGA instrument (TA Instruments, model Q 500) in nitrogen atmosphere at a heating rate of 10 °C/min, using a sample mass of 10 mg.

2.4. Melt processing of precursors

Powder precursors were compacted at 25 °C to obtain 1 mm thick disks using a pelletizing die and a Carver laboratory press. Pelletized precursors were packed in the barrel of an Instron capillary rheometer 3211 fitted with a die of 250 μm diameter and an aspect ratio of ~2 for melt spinning at a temperatures ranging from 200 to 210 °C. The nominal shear rate during spinning was ~500 and ~1500 s^{-1} for low and high throughput rates of 0.04 and 0.14 cm^3/min, respectively. Spun fibers were collected on a spool at a winding speed of 125–300 m/min; the nominal draw down ratio was in the range of 40–310.

2.5. Stabilization and carbonization of melt spun fibers

The as-spun fiber tows were clamped in a metal frame to maintain a constant length and then UV irradiated in 100 W Oriel Hg arc lamp for 3 h at 110 °C. Next, the fibers were oxidatively stabilized in a forced-circulation oven (ATS 3610) at 320 °C and 30 min soak time (ramping to 320 °C at 2.5 °C/min). Oxidatively stabilized fibers were then carbonized at 1500 °C in He atmosphere in an Astro Furnace.

2.6. Characterization of fibers

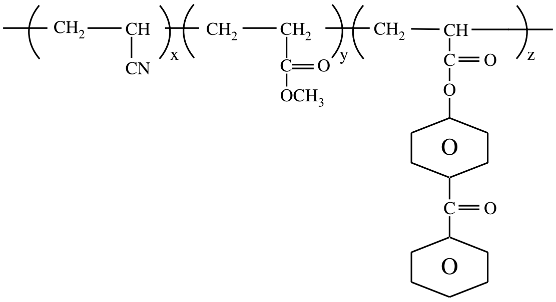
Tensile properties of the fibers at various stages of treatment were measured in a computerized MTI Phoenix tensile testing machine equipped with 500 g load cell (ASTM D 3379-75). SEM micrographs of the fibers were obtained using a Hitachi cold field emission scanning electron microscope (CFE-SEM) S-4700. Specimens were Pt sputter coated to avoid charging.

3. Results and discussion

The FTIR spectrum of the terpolymer is shown in Fig. 1. The aliphatic C–H stretching is observed at 2931 cm^{-1}, the CN stretching at 2237 cm^{-1}, the ester (of the methyl acrylate) at 1734 cm^{-1}, the keto group (of the benzophenone) at 1666 cm^{-1} and the C–O–C stretching at 1166 cm^{-1}.

The terpolymer structure was elucidated by ^{1}H NMR, which showed that the comonomer mole ratios of the feed were reasonably represented in the terpolymer structure. The spectrum of the 85/14/1 (AN/MA/ABP) terpolymer is given in Fig. 2. The aromatic protons appear at δ 7.5–8.0, –O–CH_3 at δ 3.7 and –O–CH at δ 3.15 and the –CH_2– around δ 2.0.

Based on the currently developed process, the terpolymer synthesis has been scaled up to kilogram level by Monomer–Polymer and Dajac Labs, Inc., Feasterville, PA, USA, using the reactants described earlier. The composition and properties of these terpolymers are shown in Table 1.



Chemical structure of the terpolymer

3.1. Thermal analysis

Thermal analysis of the terpolymer was carried out to determine the glass transition temperature (T_g), the degradation temperature and the weight-loss pattern during degradation. The T_g determined using DSC varied from 77 to 91 °C, depending on the molecular weight (Table 1). A typical T_g trace is shown in Fig. 3.

The polymer degradation as measured by DSC appears as a strong exotherm shown in Fig. 4. The initiation of the

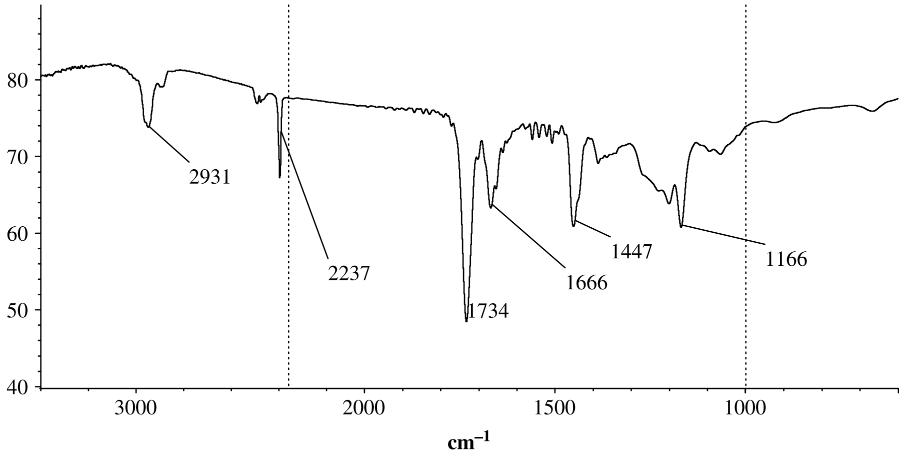


Fig. 1. FTIR spectrum of the terpolymer.

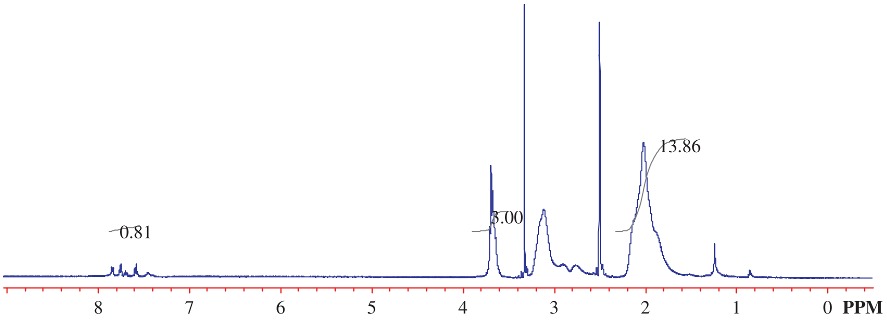


Fig. 2. ^{1}H NMR spectrum of the terpolymer.

Table 1
Composition and properties of the terpolymers

AA/MA/ABP terpolymer	Monomer feed	Composition (NMR)	IV[a] (dL/g)	T_g (°C)	M_n (g/mol)	M_w (g/mol)	PDI	Melt processible
Lab batch	85/14/1	84.3/14.5/1.2	0.50	77	–	–	–	Yes
Scale up 1	85/14/1	84.8/13.8/1.4	1.36	91	48,000	206,000	4.3	No
Scale up 2	85/14/1	84.8/14.2/1.1	0.34	72	16,000	36,500	2.2	Yes
Scale up 3	85/14/1	84.3/14.2/1.4	0.52	76	22,000	42,000	1.9	Yes

[a] NMP, 25 °C.

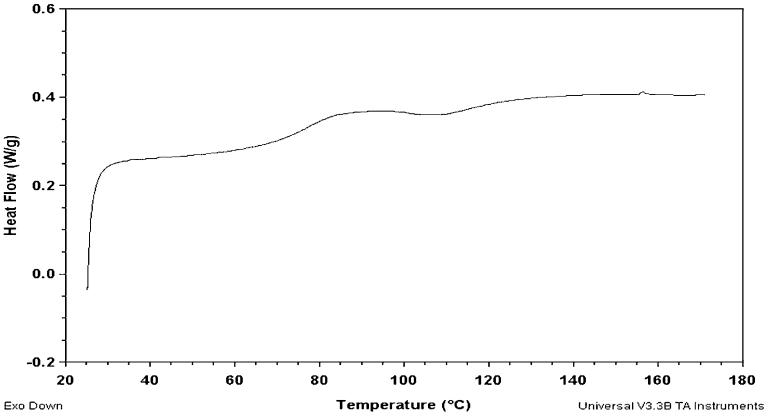


Fig. 3. DSC curve of the terpolymer depicting the T_g.

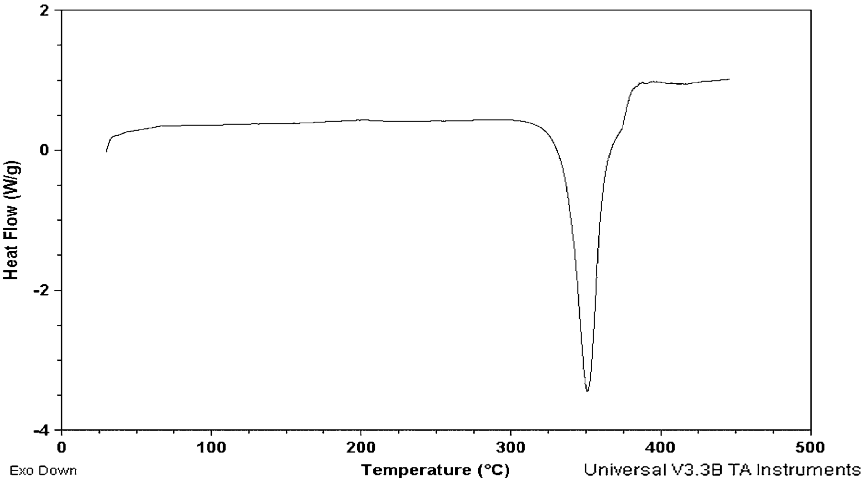


Fig. 4. DSC curve of the terpolymer depicting degradation.

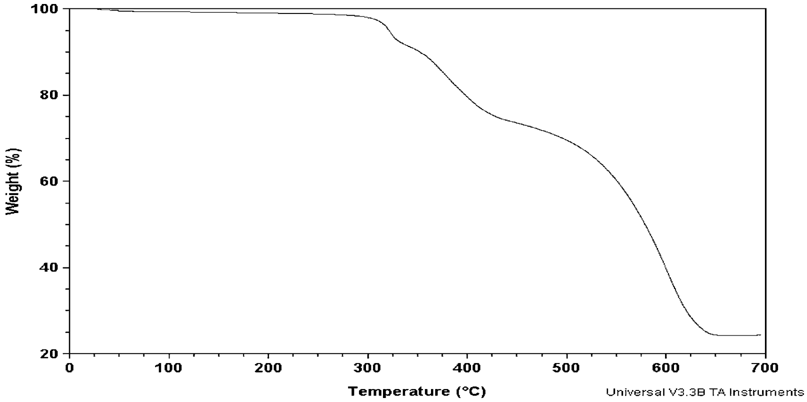
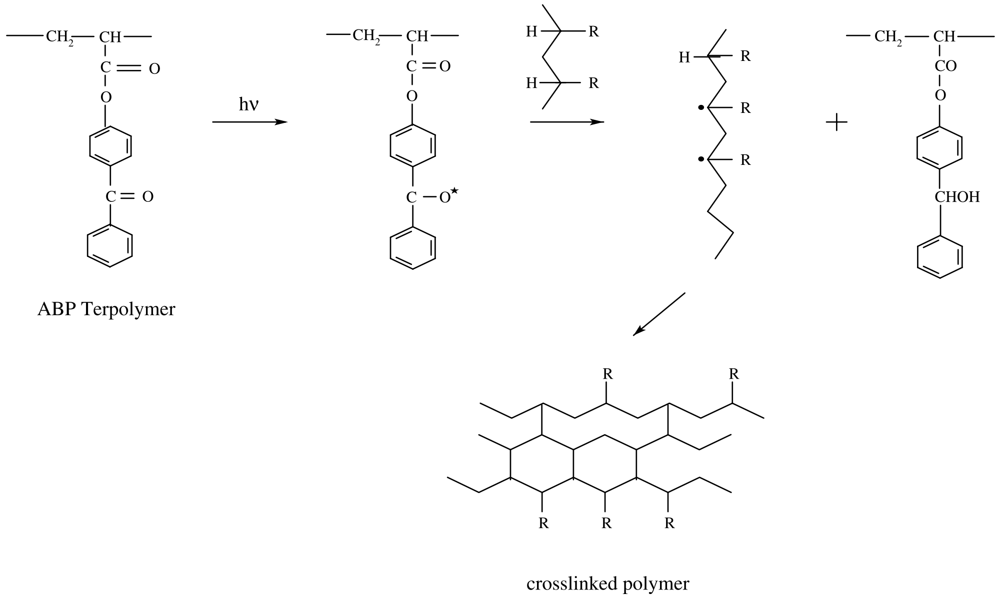


Fig. 5. TGA curve of the terpolymer.



Scheme 1. Possible photocrosslinking pathway for the terpolymers.

exotherm is at 322 °C, the peak temperature is at 353 °C and the end temperature is at 380 °C. The heat of degradation was ∼500 J/g.

The TGA curve of the terpolymer measured in air atmosphere is presented in Fig. 5. The curve shows a three-step weight loss and is similar to the weight-loss reported for the AN/MAA copolymer [18].

3.2. Melt viscosity

In the case of AN/MA copolymers, a significant dependence of dynamic melt viscosity on the copolymer composition was observed [5]. Thus, increasing the MA content from 7 to 10 mol% or more caused the melt viscosity to drop by several orders of magnitude. This observation was explained on the basis of a generally accepted view [19,20] that comonomers like MA can get incorporated in the crystal lattice of AN up to a critical comonomer content and disrupt the characteristic morphology beyond the critical limit.

The copolymer with a 90/10 molar ratio (AN/MA), builds up very high viscosity at the melt processing temperature, 220 °C, and is not processible. The 85/15 copolymer, on the other hand, exhibits a steady melt viscosity for about 30 min, during which the fibers could be drawn. This base copolymer composition was, therefore, chosen for the synthesis of the terpolymer. The strategy was to replace about 1 mol% of MA with ABP so that the AN content remained the same [14].

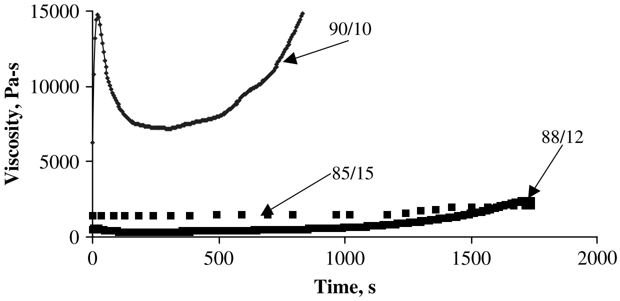


Fig. 6. Rheological behavior of the acrylonitrile copolymers.

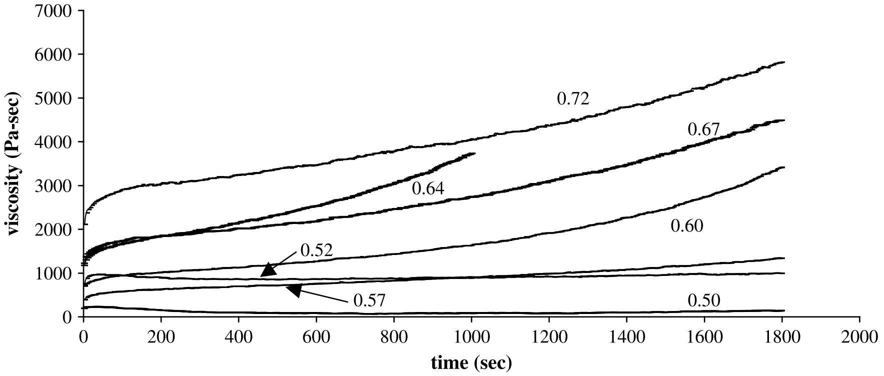


Fig. 7. Processability window for the terpolymer is a function of molecular weight.

3.3. Importance of a photosensitive comonomer in the synthesis of melt-processible precursors

The selection of the photo cross-linkable ABP comonomer was guided by the following factors. UV-sensitive monomers are very useful in solvent-free and low volatile-organic-content (VOC) coatings [21]. Several such monomers are used for these applications [21]. The present application requires a comonomer that is incorporated quantitatively and uniformly in the copolymer chain. As discussed above, acrylate monomers as a generic class seems to work well for this purpose relative to other types of monomers. Hence, acryloyl benzophenone (ABP) was selected for the synthesis of the photo-cross-linkable terpolymer AN/MA/ABP, wherein ABP is used in small amounts (1–2 mol%). The photochemistry of ABP is well documented [22] and based on this, it may be envisaged that a possible photo-cross-linking reaction to produce a gelled network may occur in the terpolymer AN/MA/ABP as shown in Scheme 1.

A preliminary study of the UV exposed thin films of the AN/MA/ABP (85/14/1) terpolymer indicated that they become insoluble in DMSO after 30 min of irradiation and completely insoluble after 2.5 h of irradiation at room temperature, when exposed to a medium pressure mercury lamp. This suggests that ABP could be effecting the desired cross-linking of the terpolymer. Furthermore, the AN/MA/ABP, 88/10/2 terpolymer has comparable melt stability as the AN/MA, 88/12 copolymer, and it also possess low enough melt viscosity to be melt processible. Thus, at least in principle, a photosensitive comonomer may help to make melt processable precursors with adequate mechanical strength prior to stabilization.

3.4. Rheology of acrylonitrile copolymers

The steady shear viscosity of the AN copolymers is composition dependent [12]. The copolymers which contain >90 mol% AN do not produce a stable melt. Even the composition AN/MA, 90/10 does not exhibit a steady shear viscosity for a period that is adequate to spin fibers out of the melt. The steady shear viscosity of the AN copolymers of different compositions are shown in Fig. 6. From the figure, it can be seen that AN/MA, 85/15 exhibits a steady melt for about 30 min, which has been empirically found long enough to spin fibers out of the melt.

The processability window of the 85/14/1 terpolymer is represented in Fig. 7. The polymer was treated with boric acid, which ensured a period of stable melt viscosity of about 30 min. The effect of molecular weight is also evident. Polymers with IV around 0.5 hold the melt stable for 30 min; a drastic increase in viscosity sets in even before 30 min for polymers with IV of 0.6 and above.

3.5. Mechanical properties of the fiber spun from the terpolymers

Mechanical properties of fibers from terpolymer precursors were tailored by choosing desired melt-processing conditions. Attempts were made to obtain oriented spin-drawn fibers at a maximum winding speed (hence, draw ratio) without breakage in thread line. For this, the winding speed was varied from 100 to 400 m/min at different throughput rates (0.14 and 0.04 cm^3/min, through a 250 μm orifice) at different spinning temperatures (200–210 °C). The present section highlights the properties of the spin-drawn fibers at different stages of processing to obtain final carbon fibers. The melt-spinning conditions of the three types of fibers, discussed in this article, are summarized in Table 2. The tensile properties of these fibers at various stages including final carbonized fibers are summarized in Table 3. The tensile stress–strain plots for the as-spun fibers obtained from two types of precursors (intrinsic viscosities 0.34, 0.52 dL/g) are displayed in Fig. 8. The low molecular weight

Table 2
As-spun fiber types and their spinning conditions

Fiber types	Precursor IV (dL/g)	Spinning temperature (°C)	Capillary throughput rate (cm^3/min)	Winding speed (m/min)	Draw down ratio
I	0.34	200	0.14	125	40
II	0.52	210	0.14	300	120
III	0.52	200	0.04	275	310

Table 3
Mechanical properties of fibers at different stages

Fiber type	Parameters	As-spun	UV-irradiated	Oxidized	Carbonized
I	No. of specimen tested	15	15	10	11
	Diameter (μm)	40.0 ± 1.7	31.7 ± 1.6	28.8 ± 1.3	23.8 ± 1.4
	Modulus (GPa)	3.35 ± 0.32	4.77 ± 0.41	5.06 ± 0.50	34.9 ± 10.4
	Yield strength (MPa)	66.4 ± 6.2	85.5 ± 4.3	–	–
	Tensile strength (MPa)	64.7 ± 7.4	81.5 ± 4.3	101.2 ± 6.9	176.7 ± 75.5
	Strain-to failure (%)	55.9 ± 13.7	2.5 ± 0.3	3.2 ± 1.0	0.47 ± 0.22
II	No. of specimen tested	15	15	14	12
	Diameter (μm)	20.7 ± 0.4	22.7 ± 0.6	17.6 ± 0.6	13.4 ± 0.5
	Modulus (GPa)	5.16 ± 0.32	4.09 ± 0.26	3.94 ± 0.57	52.9 ± 7.7
	Yield strength (MPa)	95.2 ± 5.2	78.8 ± 2.6	–	–
	Tensile strength (MPa)	155.9 ± 6.1	78.8 ± 12.6	119.6 ± 15.3	451.8 ± 162.0
	Strain-to failure (%)	22.2 ± 2.7	13.5 ± 8.2	6.9 ± 1.8	0.90 ± 0.30
III	No. of specimen tested	12	15	15	12
	Diameter (μm)	13.9 ± 0.3	14.2 ± 0.6	14.1 ± 3.1	7.3 ± 0.7
	Modulus (GPa)	6.85 ± 0.35	5.10 ± 0.89	6.02 ± 1.2	126.0 ± 15.6
	Yield strength (MPa)	111.5 ± 6.3	91.8 ± 12.2	–	–
	Tensile strength (MPa)	234.8 ± 10.7	116 ± 20.5	159.5 ± 30.2	594.1 ± 147.5
	Strain-to failure (%)	14.6 ± 0.9	16.5 ± 4.4	7.5 ± 2.1	0.42 ± 0.11

(IV, 0.34 dL/g) precursor could be drawn down only to 40 at 200 °C, hence displays a very high strain-to-failure of ~60% and a low tensile strength of ~65 MPa. The high molecular weight precursor were drawn down to 120 and 310 to get as-spun fibers of ~21 and ~14 μm, respectively. Increase in draw ratio caused increased modulus, yield and tensile strengths with lowering in ultimate elongation.

The fibers were successfully stabilized by UV irradiation at 110 °C. It was observed that the stabilization of highly oriented fibers at temperatures higher than 110 °C was difficult due to high shrinkage force, which caused fiber breakage during radiation processing and subsequent oxidative stabilization steps. Figs. 9 and 10 display the tensile stress–strain plots for the UV-irradiated and oxidatively stabilized fibers, respectively. After UV irradiation, fiber I shows very low strain-to-failure and slightly lower modulus than others. However, the tensile strengths and yield strengths for irradiated fiber II and I are comparable. Table 3 shows that after UV irradiation the tensile strength of fiber I is slightly improved but the strengths for the others lowered. Possibly, because of lower molecular weight and high segmental mobility during the UV processing the fiber I got efficiently crosslinked, which improves load sharing among chains. Highly oriented fiber III displays better

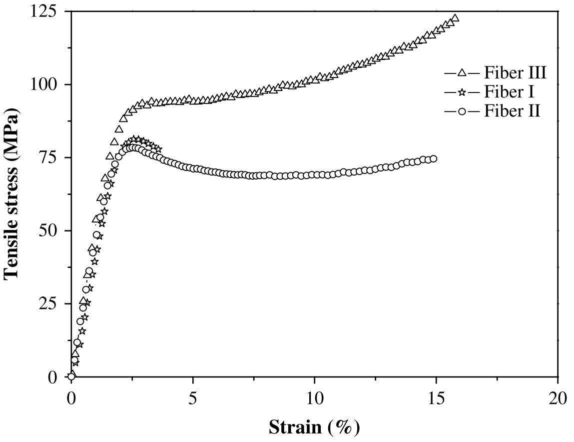


Fig. 9. Stress–strain curves of UV irradiated fibers.

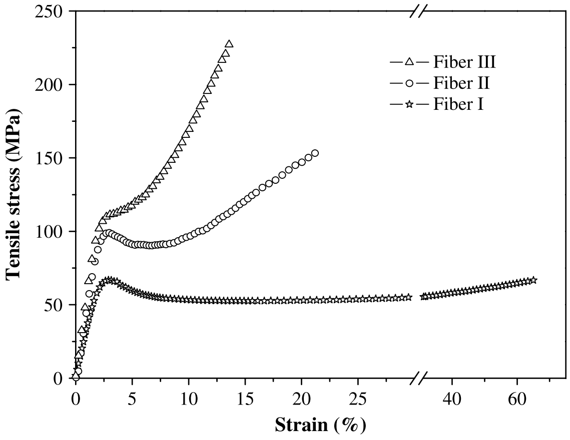


Fig. 8. Stress–strain curves of as-spun fibers.

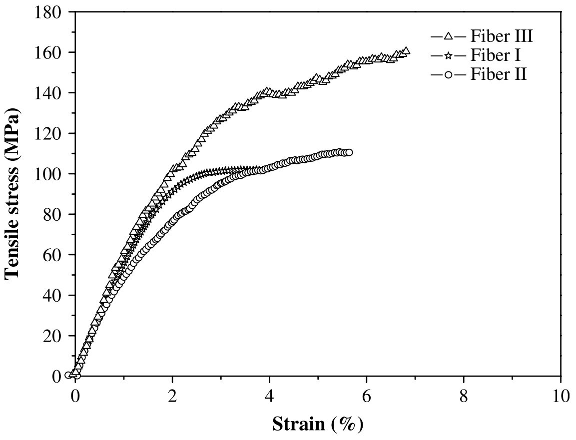


Fig. 10. Stress–strain curves of oxidized fibers.

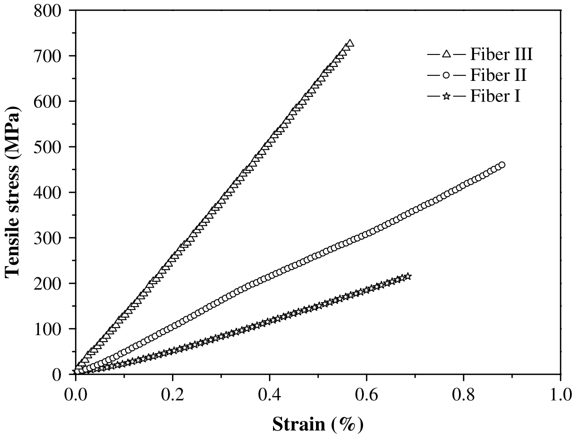


Fig. 11. Stress–strain curves of carbonized fibers.

properties than others. Similarly, after the oxidative stabilization, the fiber III displays better properties; fiber I show the least strain-to-failure but higher modulus than II, as that was crosslinked efficiently (Fig. 10 and Table 3). UV crosslinking not only prevents fiber breakage due to melting during oxidative stabilization but also retards relaxation of fiber through loss in orientation.

The tensile stress–strain plots for the carbonized fibers are displayed in Fig. 11. It can be seen from the Fig. 11 and Table 3 that the tensile strength and modulus increased with increase in draw ratio of the as-spun fibers. The carbonized fiber I being of low molecular weight and low draw ratio shows a modulus of ~35 GPa, while those of fibers II and III are ~55 and ~130 GPa, respectively. Retention of fiber orientation with minimum relaxation during stabilization is desired. A high dosage irradiation process for faster stabilization is under development for the highly drawn fibers.

Fig. 12(i)–(v) displays the SEM micrographs of fiber III at different stages of processing, i.e. as-spun, UV crosslinked, oxidatively stabilized and carbonized fibers. As-spun fibers show ductility (fibriller failure pattern), which progressively disappears by crosslinking and cyclization in the successive steps and failure pattern becomes brittle (catastrophic failure). Cross-section of failed carbon fibers (Fig. 12(iv)) shows defects inside the fiber. The lateral surface of the carbonized fiber was found to be very smooth (Fig. 12(v)), however, failed carbon fibers show pits and scales on the surface (Fig. 12(iv)). Presence of surface defects also causes fiber failure. Although the modulus of the carbonized fibers were very good, gross defects in the fiber caused failure at

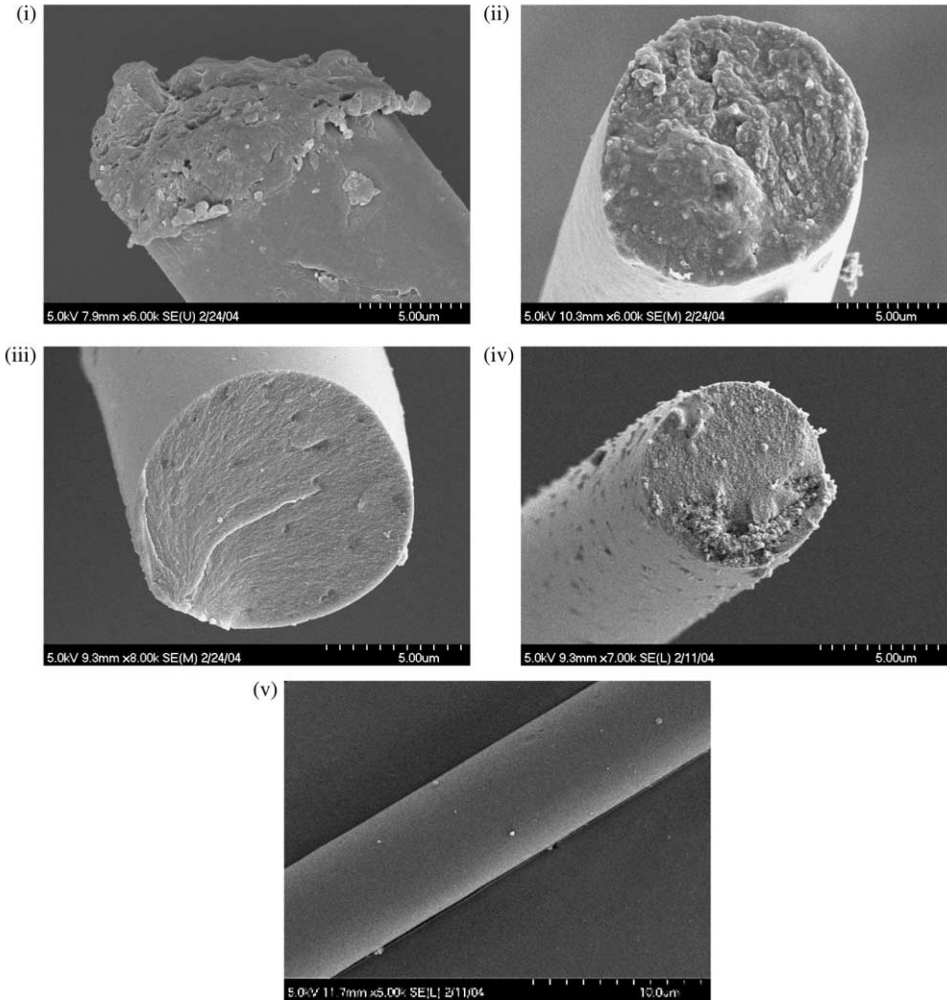


Fig. 12. SEM micrographs of (i) as-spun, (ii) UV irradiated, (iii) oxidized and (iv), (v) carbonized fiber III.

a lower strain level (~0.5%) resulting in poor tensile strength of the carbonized fiber relative to the commercial fibers. Carbonized fiber III displays a tensile strength ranging up to ~730 MPa, with a modulus ranging up to ~140 GPa, whereas, that of the commercially available fibers are in the range of ~2 and ~200 GPa, respectively. Continued studies on further investigation in properties of carbonized fibers from this novel melt processible precursor are in progress and will be reported later.

4. Conclusions

Terpolymeric melt processible carbon fiber precursors have been synthesized and characterized by IR, NMR, GPC, intrinsic viscosity and rheological tests. A general correlation between the melt viscosity and copolymer composition was observed. The study also showed that the design of melt processible copolymer precursors need to be based on the criteria such as reactivity ratios, T_g, melt viscosity and its stability as a function of time. In addition, the thermal behavior of the copolymers must also be qualitatively similar to conventional polyacrylonitrile precursors. Acrylates in general, and MA in particular, are the most suitable comonomers to synthesize AN based melt processible precursors for carbon fibers. The presence of photosensitive comonomers like ABP is desirable for photocrosslinking the fiber or film and to make precursors that will have enough mechanical strength to resist fusing during the stabilization step. The most suitable composition of the precursor appears to be AN/MA/ABP in the mole ratio range 85/14/1.

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