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Reflectance FTIR and SEM characterization of poly[N-vinylcarbazole-co-methylmethacrylate] electrografted carbon fiber surface: current density effect

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Electrografting of poly [N-vinylcarbazole-co-methylmethacrylate] onto high tenacity carbon fiber (TENAX HTA 5000) was carried out under preparative constant current electrolysis conditions by using anode and cathode as fiber towings. The surface morphology of the electrografted carbon fibers was determined by scanning electron microscopy (SEM). FTIR reflectance measurements (FTIR-ATR) were applied for the characterization of chemical composition on the electrografted thin film surface on carbon fiber. The efficiency of the electrocopolymerization on carbon fiber surfaces under preparative constant current electrolysis conditions were evaluated, i.e., current density (charge) vs. thickness, yield and morphology. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Carbon Fiber reinforced plastics (CFRP) offer several advantages: they have a low density and good mechanical properties in relation to weight (high stiffness and strength), which results in a lower mass inertia. So far carbon-fiber or composite carbon materials have been used mainly for individual components in aerospace and motorsport. Particularly where the material used has to withstand heavy loads whilst keeping weight to a minimum and thus offering supreme stiffness and strength, designers and construction engineers now use carbon-fiber-reinforced plastics to an increasing extent.

Carbon-fiber-reinforced plastics offer a significant potential for reducing vehicle weight also in “regular” production cars, CFRP being highly suited for body components due to its superior strength and stiffness. The body of a modern automobile, depending on the model, accounts for 15–20 percent of the overall weight of the car. Body components made of CFRP, in turn, are up to 30 percent lighter than aluminum and 50 percent or more lighter than steel. So depending on whether CFRP is used for individual components or for the entire structure of the body, this highly sophisticated material is able to reduce the overall weight of the car by up to 10 percent, without making the slightest concession in terms of stiffness and body strength. This improves the car’s performance and ability whilst reducing fuel consumption at the same time.

More recently, possible applications of fiber reinforced thermoplastics for biomedical applications, e.g., as dental implants and for bone plate applications are explored

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[1–4]. The following thermoplastic composite materials have been considered for those kinds of applications: Carbon fiber (CF)/polystyrene, CF, high-density polyethylene, CF/polypropylene, CF/Nylon, CF/PMMA and CF/polyetheretherketone (PEEK).

Carbon fiber surface interfacial adhesion with polymer matrix is a key issue for the strength of resulting CFRP. The electropolymerization procedure offers the advantage of obtaining an covalently bounded functional interfacial groups, and the thickness and functionality of such a 'reactive' coating through selective processing parameters can be controlled (i.e., the current density, monomer concentration, temperature etc.) and as a result uniform coatings could be achieved [5].

Electrochemical co polymerization of Carbazole-acrylamide (Cz-AAm) [5–8] and N-vinylcarbazole-acrylamide [9] have been performed previously on Pt and carbon fibers and highly oriented graphites (AFM and ellipsometric study). Random copolymers of poly (N-vinylcarbazole-styrene) and poly (N-Vinylcarbazole-acrylonitrile) were synthesized by free radical polymerization [10]. The resulting copolymers were electrochemically coated onto carbon fibers. At high oxidation potentials electropolymerization of N-vinylcarbazole (NVCz) could occur both through ring and vinyl group of N-vinylcarbazole, resulting a crosslinked electrografted polymeric structure which will be insoluble and stable structure.

The electrochemical initiation of MMA polymerization could be accomplished on the cathode only. More recently a cathodic electrochemical initiation mechanism on a nickel electrode in DMF and acetonitrile was discussed [11, 12].

Characterizations of conductive copolymers on carbon fibers as nanosize thin films have been developing, The development, and application of combination of such analysis techniques of conductive polymers are important for understanding the interfacial interaction between carbon surface and polymer coating. Recently we have applied the reflectance FTIR method for the characterization of electrocoated thin conductive polymeric films, i.e., poly [carbazole-co-methylthiophene] [13]. And AFM work was performed on Highly Oriented Graphite (HOPG) as a model system, and superior adhesion properties of Poly [carbazole-co-acrylamide] was determined [6, 7].

Electrocoating of conductive and nonconductive copolymers as surface functionalising materials on carbon fiber enhances the interaction of the carbon fibers as a reinforcement material in polymer matrix. Another application of these novel materials are the preparation of miniaturized chemical sensors. The use of carbon fiber homogeneously coated by conductive polymers with well-defined surface functionalities will be suitable for the miniaturization of electrode system for a particular analyte. Several copolymer and polymer coated (anodic) electrodes were shown to be an effective electrode system for the determination of p-aminophenol at low detection limits [14]. The nature of copolymeric films, their structure and compositions plays an important role on the final properties of modified carbon surface and the interest on the characterization of these functionalised thin films is increasing [15–17] and recently electropolymerization (anodic coating), and morphological studies of thiophene oligomers on carbon fiber were reported [18, 19].

Electrocoated Poly (N-vinylcarbazole-co-methylthiophene) (P[NVCz-co-MeTh], poly [N-vinylcarbazole-co-p-vinylbenzene sulfonic acid] (P[NVCz-co-VBSA]), polycarbazole and poly [carbazole-co-methylthiophene] onto carbon fiber (CF) micron sized electrodes were previously characterized by Atomic Force Microscopy (AFM), Raman, FTIR-ATR and XPS spectroscopy [20, 21]. Results show that the coating properties depends mainly on the initial feed ratio and the reactivity of monomers and electrolyte.

The reflectance FTIR spectroscopy could be successfully applied to thin film of polymer (in the range of tenth nm) on the micron size carbon fiber. High quality surface spectra can be obtained relatively easy without problems of background fluorescence, light scattering and problems related with the film thickness. Sensitivity of devices are now available that subcomponents can be distinguished easily which they overlap in the spectra of copolymers. These facts have made practical polymeric thin film coating systems amenable to studies by Reflectance FTIR spectroscopy.

In this study the current density effect on the electrografting of P[NVCz-co-MMA] onto TENAX HTA 5000 (12000 single fiber) carbon fiber was investigated comparatively with homopolymer coatings, and nondestructive characterization of surface structure of electrocoated nano-to-micron-sized thin polymeric and copolymeric coatings on carbon fibers are performed by reflectance FTIR and SEM technique. Reflectance FTIR analysis was carried out on single fiber (a diameter is $\sim 7\ \mu$). For the morphological features of the copolymer SEM was used.

2. Experimental

Polyacrylonitrile (PAN) based carbon fiber was used for this study, high tenacity (HT) TENAX HTA5000 carbon fibers (Sigri Carbon, Meitingen, Germany) having 12000 single filaments in a roving, The monomers Methyl methacrylate (MMA), N-vinylcarbazole (NVCz) were supplied from Merck (synthesis grade). Methyl methacrylate (MMA) was distillated under vacum before use.

Sodium nitrate (pro analysi), and lithium perchlorate was from Merck and DMF and Tetramethylammonium perchlorate (TMAPF$_6$) was from Fluka. All these chemicals were used without further purification.

The electrochemical cell used for the preparative electrocopolymerization procedure was a cylindirical shaped glass cell (50 mm diamater 70 mm height sized) with an effective volume of about 100 ml. This cell contained one counter electrode (CE) made of stainless steel (V2A) [except the experiments between 15–18, both electrodes were the same size of carbon fibers]. The carbon fibers were placed in a glass tube against stainless-steel plate (V2A) or against another row of C-fiber in such a way that the carbon fibers dipped into electrolyte either 60 mm to adjust the current density, while keeping the applied current constant. The area of the fiber electrodes was 160 cm^2 (dipped into the liquid 60 mm in the cell). The electrolyte solution was not stirred during the electropolymerization process. As power supply, a galvanometer was used (Statron, type 3218, VEB Statron Fürstenwalde, Germany) with an adjustable current between 0–4 A and a voltage ranging form 0–75 V. Constant current electrolysis was applied by keeping the current density ($i = \mathrm{I/A}$ [mA/cm^2]) constant by calculating the geometric surface area of the carbon fibers (fiber diameter $d_f \approx 7\ \mu$m). After the electrolysis the carbon fibers were washed thoroughly with water and distilled acetone and with THF, and afterwards the fibers were dried overnight in a vacuum oven at 1 m bar at a temperature of 50°C or in some cases in air.

Both polymers and copolymers electrografted onto carbon fiber surface (with few single grafted C-Fiber) were analyzed by FTIR reflectance spectrometry (Perkin Elmer, Spectrum One, Überlingen, Germany with an ATR attachment Universal ATR- with a diamond and ZnSe crystal).

3. Results and discussions

3.1. Weight% increase and decrease in thickness by current density

Table I summarizes the experimental parameters for electrografting of PNVCZ and P [NVCz-co-MMA] on carbon fiber (anodically) in DMF at different current density. Due to low reactivity of MMA monomer ten times higher initial MMA monomer concentration relative to initial NVCz monomer concentration was used generally.

Fig. 1 shows the weight% increase of electrografted carbon fiber with P [NVCz-co-MMA] and PNVCz against charge. The increase in diameter of electrografted Carbon fiber with P [NVCz-co-MMA] coating against current density is not in parallel line with weight% increase, due to inhomogeneous coating distribution of some fibers. The presence of MMA decreased the yield about 2.15 times (compare to #3 and 17). This explains the involvement of MMA into copolymeric structure which slow down the rate of polymerization of NVCz, it is quite faster than MMA polymerization. Going from low current density to high current density (i.e.,0.33 mA/cm^2 to 1.56 mA/cm^2) results an increase in the yield (i.e., about eight times increase (see Table I). Compare 18a and 17a), the change of supporting electrolyte ($LiClO_4$ and $TMAPF_6$) and MMA monomer feed concentration is also effective on the yield.

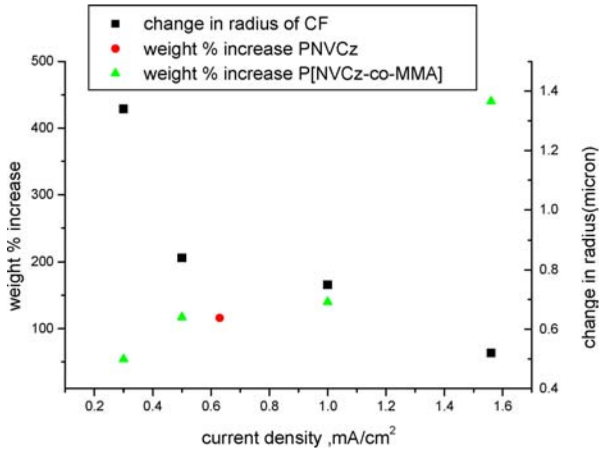


Figure 1 Weight (%) increase in electrografted carbon fiber (TENAX HTA 5000) with P[NVCz-co-MMA] and PNVCz against current density, and vs. change in radiusof grafted carbon fiber in 100 ml DMF/0.1 M NVCz-1.0 M MMA 0.1 M $TMABF_6$.

3.2. Reflectance FTIR (FTIRATR) of electrografted P [NVCz-co-MMA] onto carbon fiber

Table II, summarizes the assignments of the reflectance FTIR absorption peaks for the copolymers which are prepared at different initial concentrations of each monomers and the individual homopolymers. The FTIR ATR of copolymer formed on the carbon fiber surface shows the presence of characteristic peaks of PNVCz in addition to PMMA peaks. XPS data was also confirmed the incorporation of monomers into the structure of the copolymer

TABLE I Experimental parameters for electrografting at different current density, PNVCZ and P [NVCz-co-MMA] electrografting on carbon fiber (anodically) in DMF [1]

Sample #	$[\mathrm{NVCz}]_0$, M	$[\mathrm{MMA}]_0$, M	Current density $i = \mathrm{I/A}$ (mA/cm^2)	Electrolyte	Weight% increase
3	0.1	–	0.63	0.1 M $TMAPF_6$	116
17a	0.1	1.0	0.31	0.1 M $TMAPF_6$	54
15a	0.1	1.0	0.50	0.1 M $TMAPF_6$	117
16a	0.1	1.0	1.00	0.1 M $TMAPF_6$	140
18a	0.1	1.0	1.56	0.1 M $TMAPF_6$	440
1	0.11	9.4	1.00	0.35 M $LiClO_4$	132
2	0.11	9.4	1.56	0.22 M $LiClO_4$	58
CFMMA VIII[2] (cathodic)	–	8.0	1.56	0.40 M $LiClO_4$	117

[1] Counter electrode (CE) was also a carbon fiber roving of the same size (Xa = anode) (experiment #15a to 18a).

[2] Counter electrode was a stainless steel V2A (experiment #1 to 3).

TABLE II Assignments for the reflectance FTIR absorption frequencies observed for electrografted copolymers on carbon fiber with respect to functional groups of copolymer

Wavenumbers/cm^{-1} PNVCz	cm^{-1} P[NVCz-MMA]	cm^{-1} PMMA	Assignments	
2400–3600 (b)	3045		γ (C-H)	Asymmetric str. of aromatic structure, and N-H
2094	2285, 2650		γ (C-C)$_{\text{ring}}$	Aromatic ring of NVCz
1649			γ (C=C)ring	NVCz
	1659, 1665 (m)		γ (C=O)	MMA
1450	1450		γ (C=C)ring γ (C-C)$_{\text{ring}}$	Ring vibration of NVCz moiety
		1438(s)–1561(s)(v)	γ (C=O)	MMA
1226	1370, 1226(s), 1149		γ (C-N)	NVCz
	1310 (m)		γ (C-O)	
	1149			
		924–993(m)		
745	805, 750(s)	–		Subst.aromatic ring of NVCz
		837–860(bending)	C-H	Phenyl ring substitution bands
		631		

γ represents stretching, v — variable, m — medium, s — strong, br — broad, w — weak.

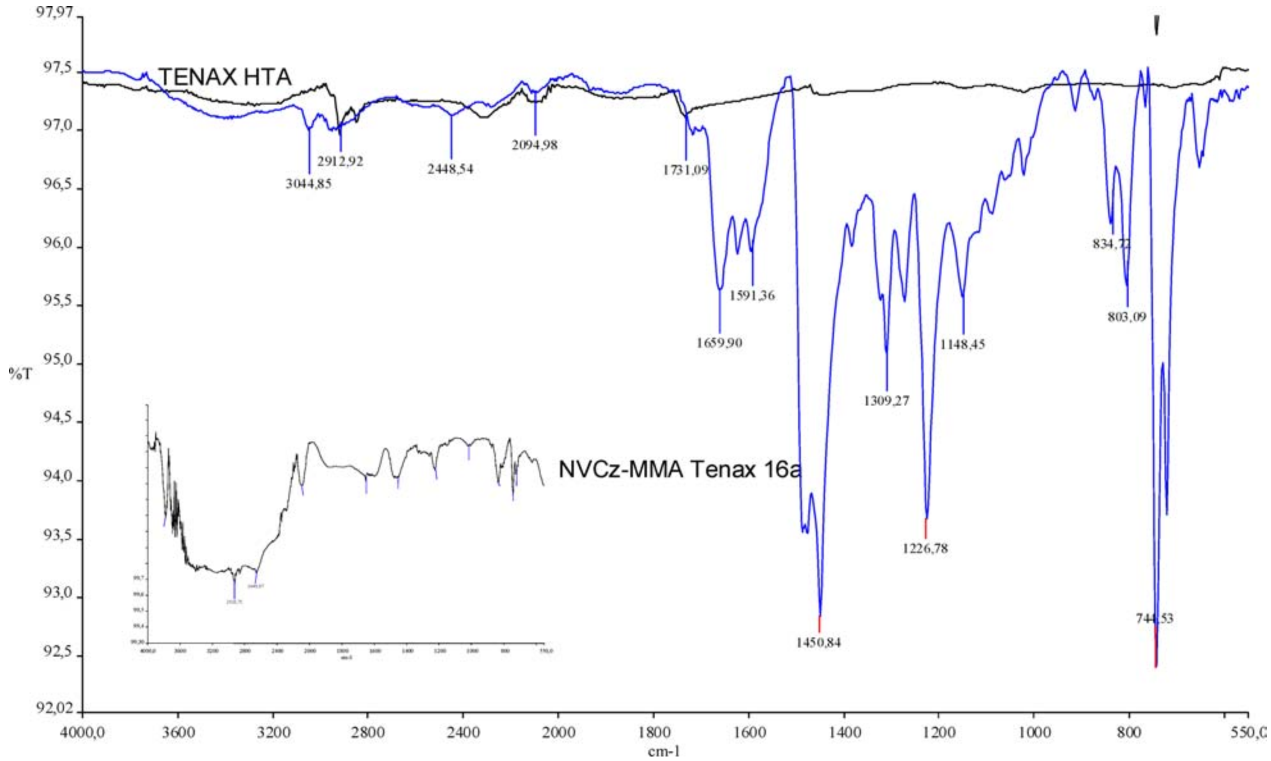


Figure 2 FTIRATR of ungrafted (Tenax HTA) and P [NVCz-co-MMA] grafted carbon fiber (16a) compared with PNVCz grafted CF, Insert picture represents the FTIRATR of PNVCz on the same carbon fiber.

coating and supporting electrolyte. [XPS results will be published separately].

Fig. 2 shows the FTIRATR of ungrafted carbon fiber and P [NVCz-co-MMA] grafted carbon fiber, and comparison with PNVCz coating on the same fiber (insert picture) indicates the inclusion of MMA into electrocoating of polymer onto carbon fiber. Comparison of electrografted copolymer and MMA homopolymer on carbon fiber surface indicates that whether new peaks appeared or peaks are shifted in the case of copolymer by comparison to corresponding homopolymers, i.e., peak at about 1560 cm^{-1} was shifted to 1591 and 1659 cm^{-1} and new peaks at 1310 and at 1226 cm^{-1} etc. was appeared in the case of P[NVCz-MMA.] (Fig. 3)

Comparison of FTIR ATR of electrografted P[NVCz-co-MMA], and PMMA (CFMMA VIII in LiClO$_4$) on carbon fiber indicates the shifts of the peaks of copolymer (Fig. 4).

The appearance of peaks at 1226, and 1149 cm^{-1} in the copolymer (NVCz-MMA – 16a vs. CFMMA VIII) compared to MMA homopolymer which is absent in that case,

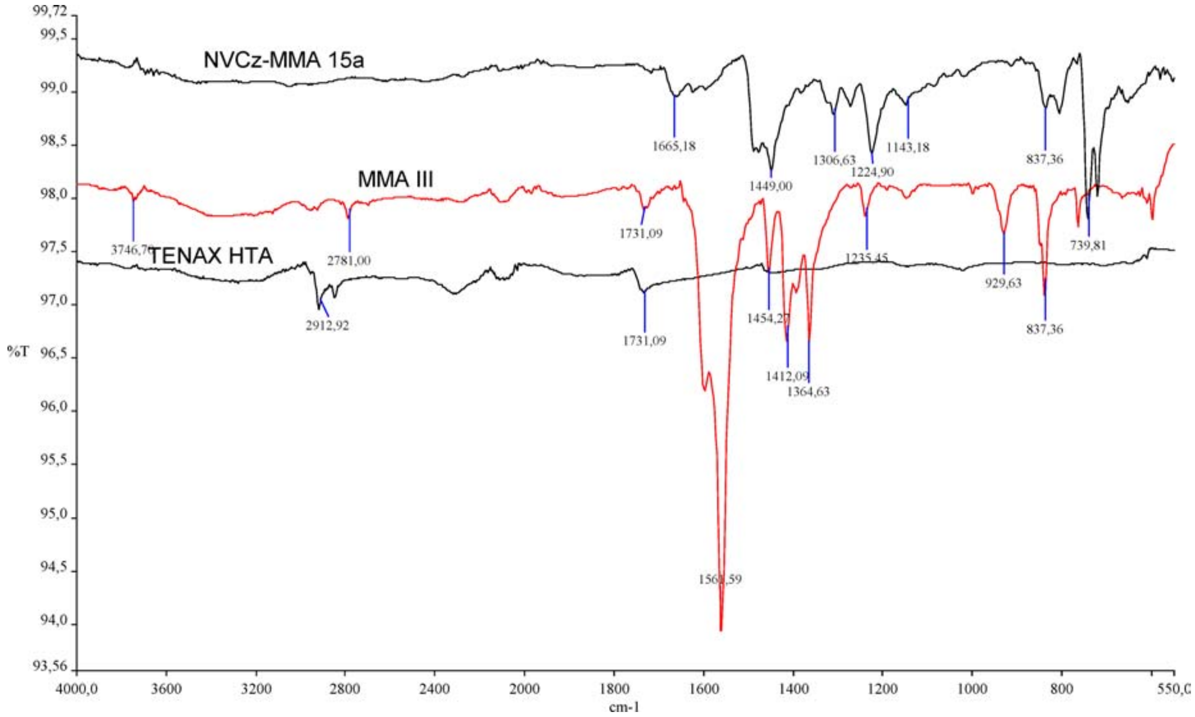


Figure 3 Comparison of FTIR ATR of electrografted P [NVCz-co-MMA], PMMA on carbon fiber and ungrafted carbon fiber (TENAX HTA).

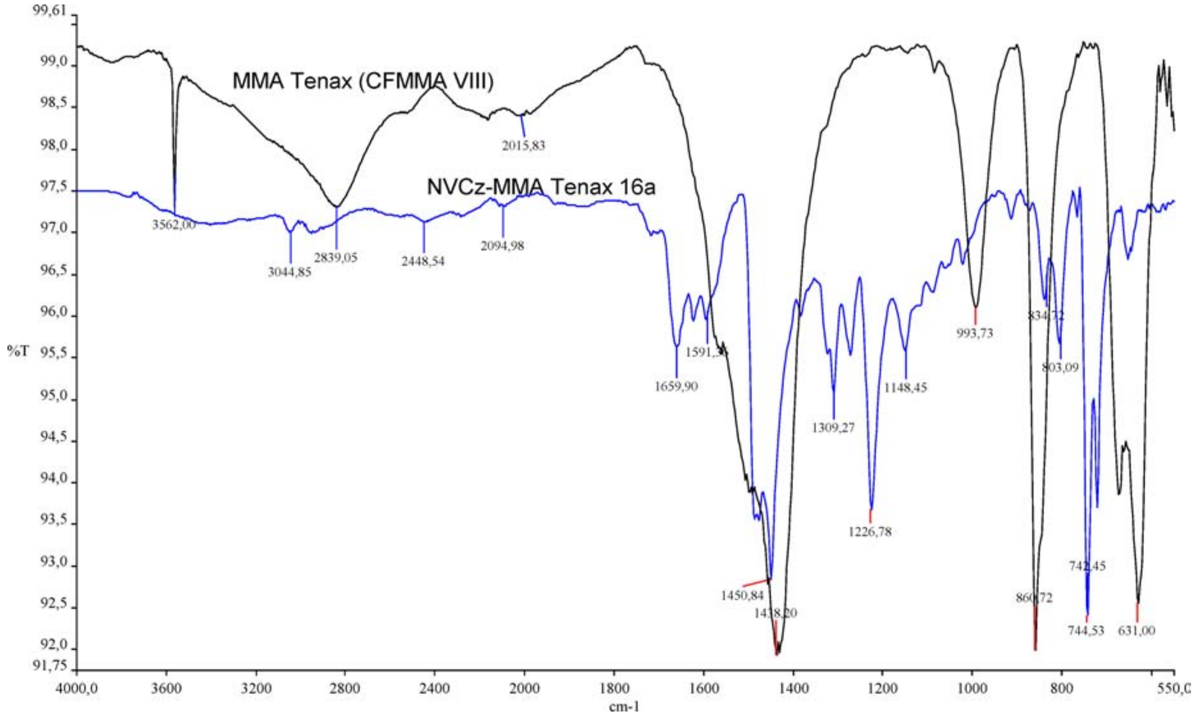
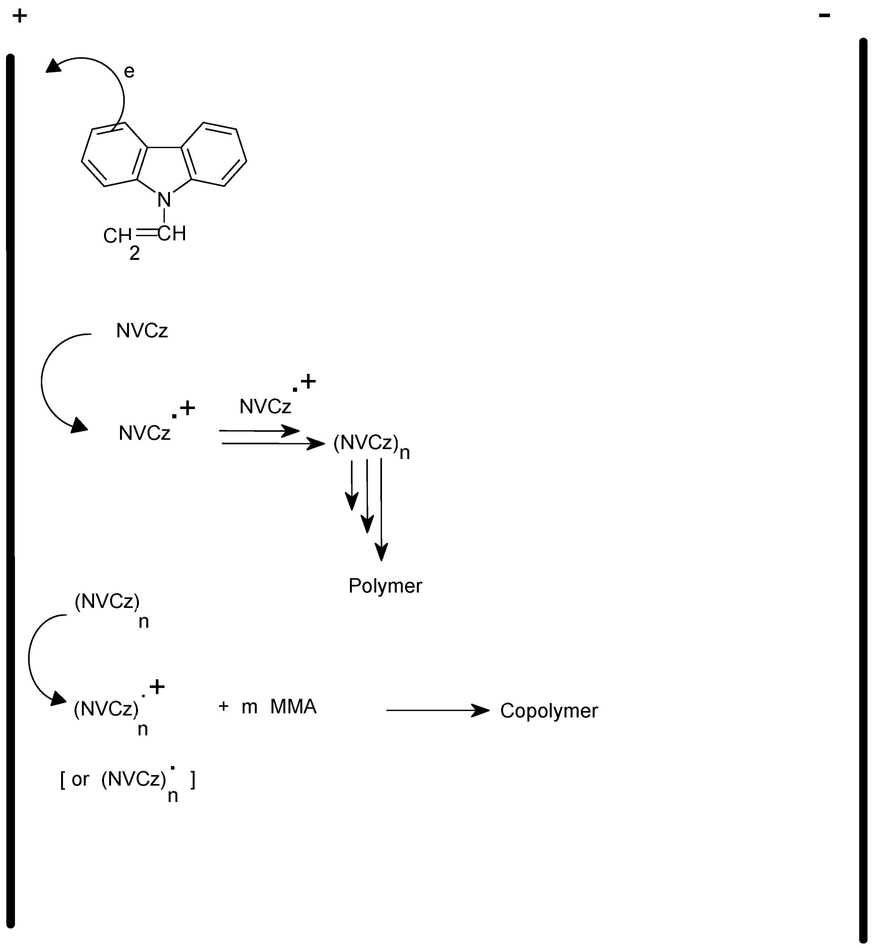


Figure 4 Comparison of FTIR ATR of electrografted P[NVCz-co-MMA], PMMA (CFMMA VIII in $LiClO_4$) on carbon fiber.

endorsed the incorporation of PNVCz in the copolymer structure. Also, the copolymer FTIR shows the presence of characteristic peaks of PMMA. Thus, FTIRATR data confirmed the incorporation of either moieties in the structure of the copolymer.

Weak FTIR-ATR intensities were observed for cathodically electrografted P[NVCz-co-MMA] copolymer on carbon fiber where thin films obtained. This can be explained by known reduction of MMA at cathode followed by radical copolymerization of NVCz. On the other hand under the same conditions thicker films and higher yields obtained at anode compared to cathodic coatings. This could be explained by ease of oxidation of carbazole ring and known fast coupling reactions (Scheme I) at anode and forming radicalic or radical cationic oligomers of NVCz which further reacts with MMA resulting a copolymer



Scheme 1 Electrogrowth mechanism of NVCz and MMA on carbon fiber.

grafting on carbon fiber anode (Fig. 5) (cathodic PMMA coating was also included in the figure for the comparison –CFMMA VIII cathodic).

Ratios of absorbances of the peaks (1450 cm^{-1}/1220 cm^{-1}) of FTIR ATR of resulting copolymer composition, for current densities of i = 0.3 and 0.5 mA/cm^2 (15a, 17a) was not much. But the change was more pronounced in the case of high current densities i.e., 1.0 and 1.5 mA/cm^2 (16a, 18a) (Fig. 6).

Ratio of peak areas of ~1450 cm^{-1}/1225 cm^{-1} were plotted against current density for the samples of P[NVCz-MMA] grafted carbon fibers (Fig. 6) corresponding to the ratio of N-C/ and C-O stretch respectively (Fig. 7).

So, carbonyl group intensities at about 1450 and 1650 cm^{-1} was increased by increasing current densities (16a and 18a) indicating that increase of MMA content of copolymer structure by current density.

The peaks in the range of 750–900 cm^{-1} corresponds to substituted benzene rings. Peaks corresponding to substituted benzene ring of carbazole was shifted (CFMMA VIII and 16a) and peaks (medium) corresponding to C–O and C=O stretching of PMMA was observed in the copolymer which are a strong peak in homopolymer of MMA, and they are absent in PNVCz.

NVCz content of copolymer (corresponding intensity of N-C increases) on the electrografted carbon fiber surface, increases by the increase of current density, [or methylmethacrylate content of copoymer decreases linearly by the increase of current density] (Fig. 7).

3.3. Surface morphology of copolymer electrografted onto carbon fiber

All electro-grafted fibers were analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 scanning electron microscope (Nissei Sangyo GmbH, Rathingen, Germany), which was connected to an energy dispersive X-ray micro analyzer (EDX) (Kevex type delta V, Foster City, CA, USA). The excitation energy was 10 keV at a beam current of 0.5 nA.

All SEM images of P[NVCz-co-MMA]-coatings deposited on carbon fiber were taken, including ungrafted carbon fiber and PNVCz grafted carbon fiber (Figs 8 and 9) in order to understand the coating morphology (i.e., their appearance) as function of the electrochemical deposition parameters. The thicknesses were determined for the deposited coatings. But due to inhomogeneous coating distribution of some fibers, increase in yield% and change

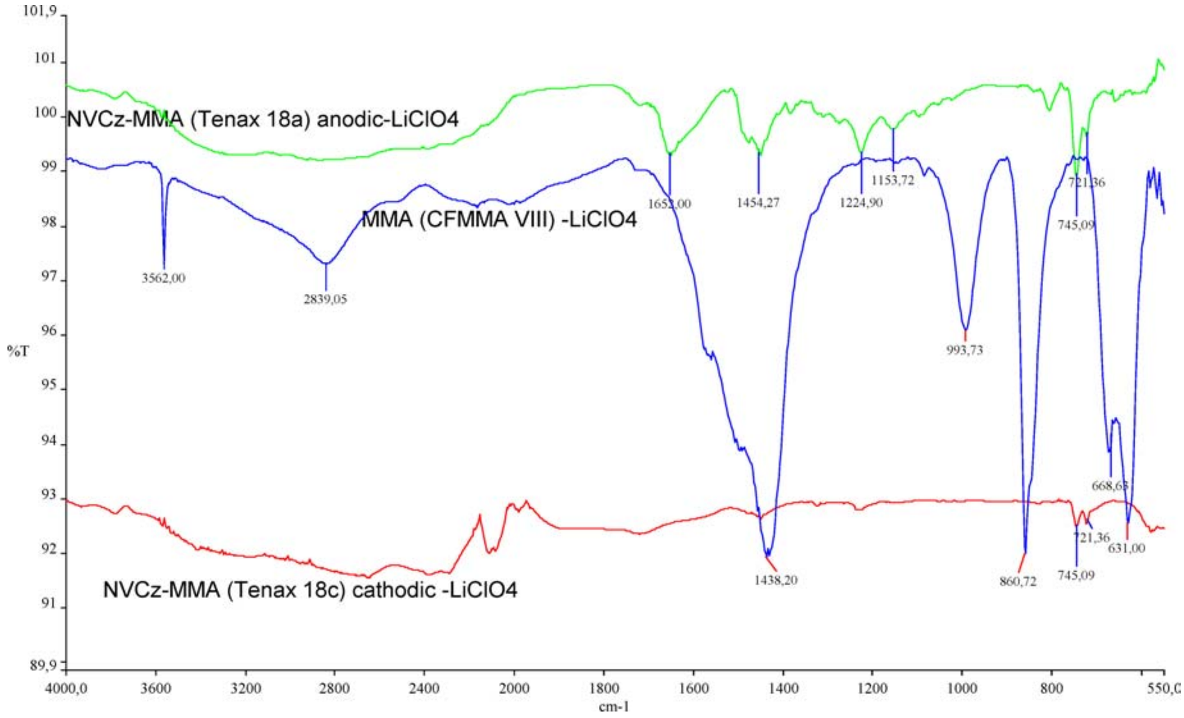


Figure 5 Comparison of FTIR ATR of electrografted P[NVCz-co-MMA] (anodic and cathodic) and PMMA onto carbon fiber in $LiClO_4$.

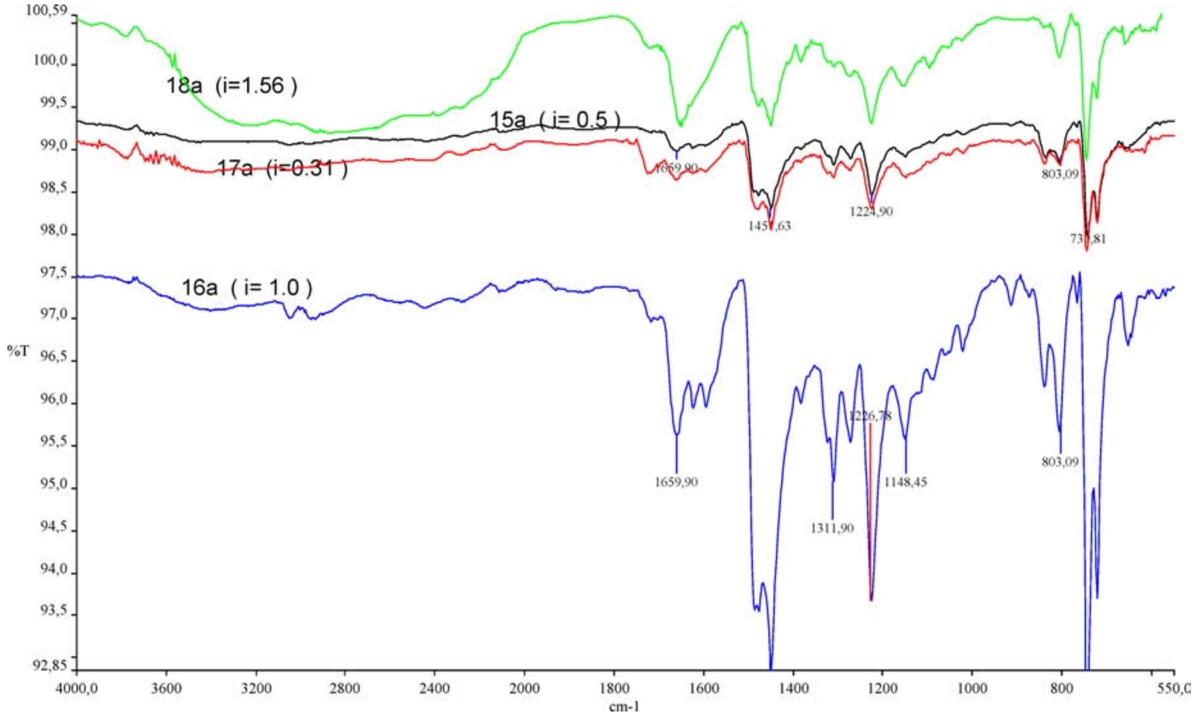


Figure 6 FTIR ATR of electrografted P[NVCz-co-MMA] onto carbon fiber in $TMAPF_6$ anodically at various current densities.

in radius of electrografted carbon fiber was not in parallel line (Fig. 1)

The SEM images of electrografted polymers in $TMAPF_6$, have a rather smooth appearance the P[NVCz-co-MMA]-coatings deposited in a supporting electrolyte $LiClO_4$ under high current densities of 1.0 mA/cm^2 and 1.56 mA/cm^2 were not good adhered and smooth coatings (Figs 10 and 11), the current density of 0.3 mA/cm^2 resulted the thick coatings (Fig. 12).

The formation of discrete lumps of irregular shapes and sizes was not observed at low current densities. The micrograph for the P[NVC-co-MMA] copolymer on carbon fiber revealed dense aggregate formation—with the tendency to form globular particles. The densely packed

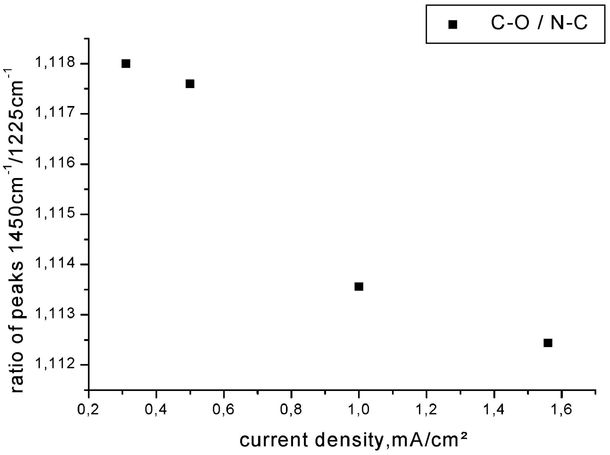


Figure 7 Ratio of peak areas of ~1450 cm^{-1}/1225 cm^{-1} (Peak areas between 1100–1252 cm^{-1}, 1354–1524 cm^{-1} corresponding to N-C, and C-O stretch.respectively) [Samples P [NVCz-MMA] on Tenax 15a, 16a, 17a, 18a].

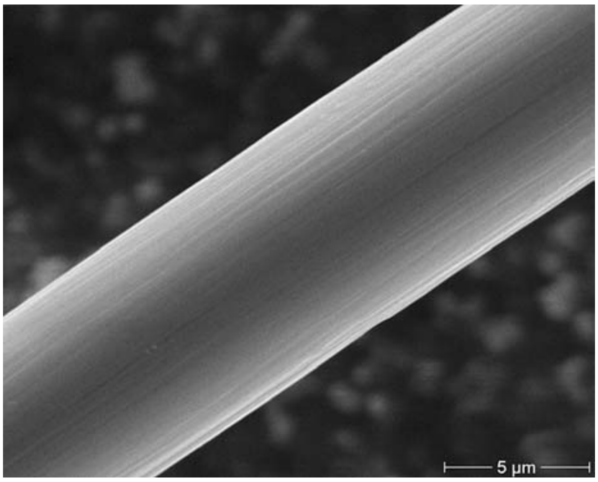


Figure 8 Ungrafted TENAX HTA 5000 carbon fiber.

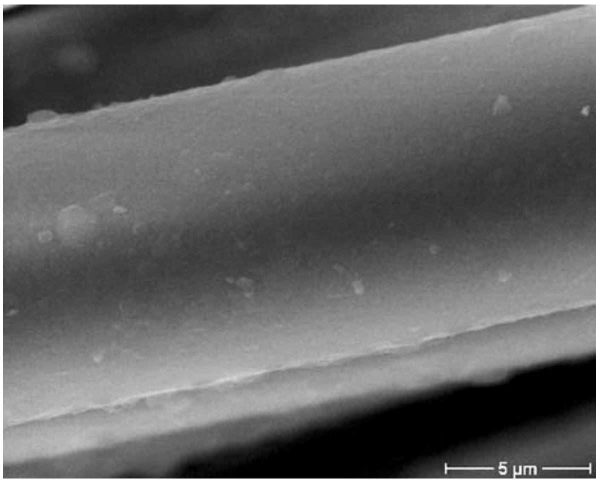


Figure 9 SEM image of PNVCz on Tenax HTA 5000 CF (#3) [0.1 M NVCz -/0.1 M TMAPF$_6$- DMF (W.E. Anode) $i = 0.63$ mA/cm^2].

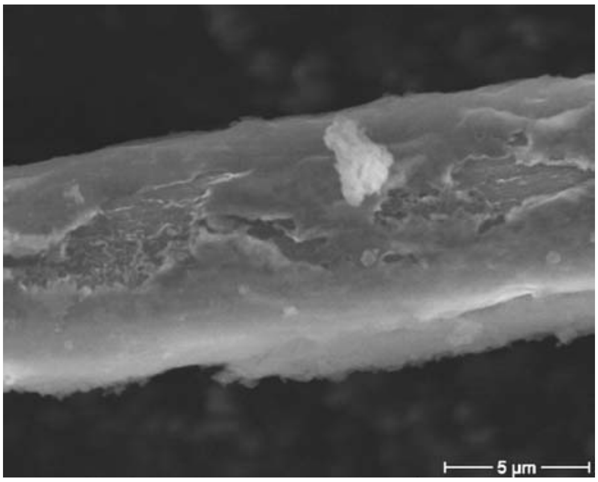


Figure 10 P[MMA-NVCz] #2 $i = 1.56$ mA/cm^2 in LiClO$_4$.

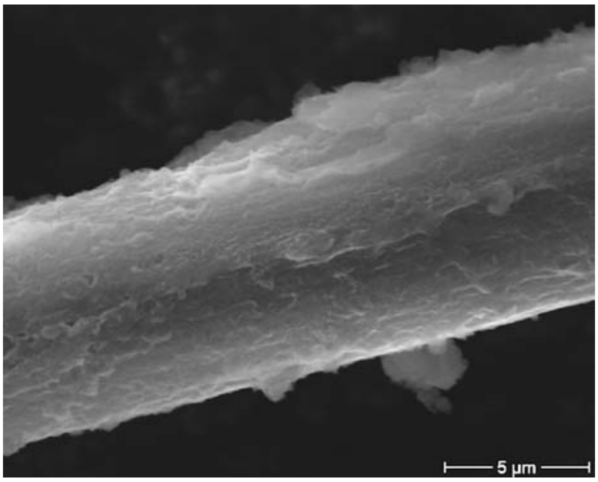


Figure 11 P[MMA-NVCz] #1 $i = 1.0$ mA/cm^2 in LiClO$_4$.

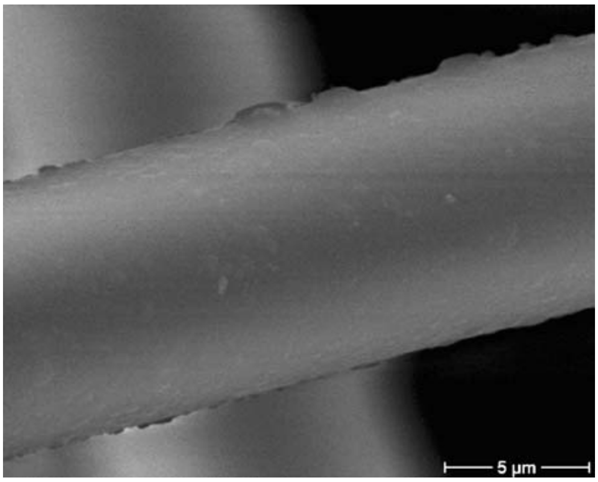


Figure 12 SEM image of P[NVCz-co-MMA] on Tenax HTA 5000 CF, $i = 0.31$ mA/cm^2 #17a.

copolymer structure was more prominently displayed in Fig. 12.

SEM-micrographs of the electrocoated carbon fibers in Figs 14 and 15 reveal a fairly uniform P [NVCz-co-MMA] coating for the current density of 1.0 and 1.56 mA/cm^2. The original (unsized and unmodified) carbon fiber has the PAN-based carbon fibers typical striations along the fiber axis (Fig. 8). After electrocoating these striations are partly disappeared in thin film coatings and a range of polymer lumps became visible 'attached' (either adhering or grafted) to the fibers. Except for the current density of 1.56 mA/cm^2, where coating was fast resulting a thin film. For fibers electrocoated using $LiClO_4$ as the supporting electrolyte the 'P[MMA-co-NVCz]-coating' was more heterogeneous and the polymer deposited as lumps simply adhering to the fibers.

In general in $TMAPF_6$, thin and homogeneous coatings were obtained for the cathodically grafted samples.

For anodically grafted samples an optimum current density (and charge) for thick and homogeneous coating was obtained at current density of 0.31 mA/cm^2 or (charge density of 2.23 C/cm^2) (#17a).

In $TMAPF_6$ electrolyte coatings are homogeneous, except current density of $i = 0.5$ mA/cm^2 (#15a) (Fig. 13), as can be seen from the observed SEM-pictures deposited coatings are relatively smooth in PNVCz coating, and grafted copolymer at current density of 0.5 mA/cm^2 is similar to the grafting in $LiClO_4$.

Although it was qualitative results from EDX measurements, the resulting electrografted fibers have included the corresponding elements of supporting electrolyte which is used in electrografting process and doped during the oxidation process.

SEM has also provided insights into the growth of bulk polymeric deposits. It can be used to distinguish the surface sites where electrochemical copolymeric nuclei form, and to follow the shape and structure as the nuclei grow from few hundred-nanometre size to μm thick films.

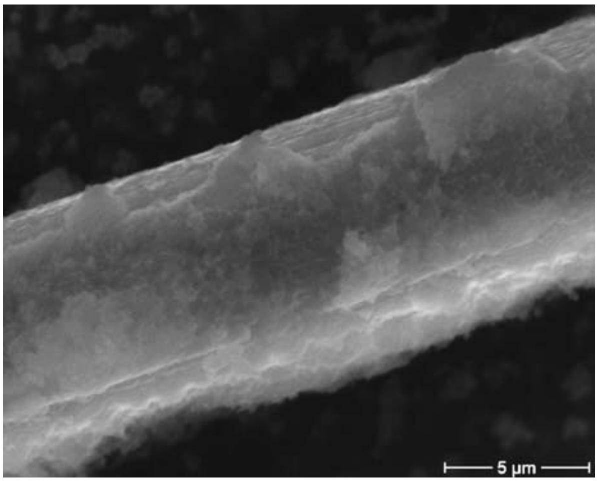


Figure 13 SEM image of P[NVCz-co-MMA] on Tenax HTA 5000 CF, $i =$ 0.5 mA/cm^2 #15a.

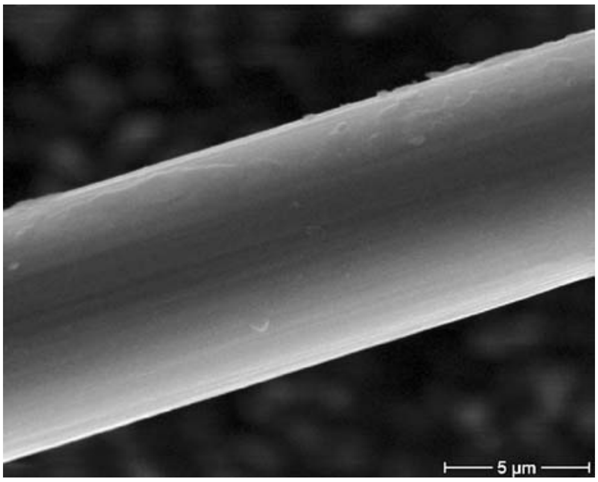


Figure 14 SEM image of P[NVCz-co-MMA] on Tenax HTA 5000 CF, $i =$ 1.0 mA/cm^2 #16a.

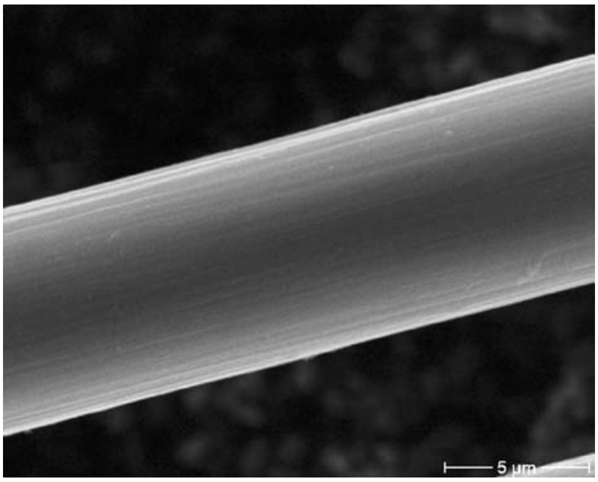


Figure 15 SEM image of P[NVCz-co-MMA] on Tenax HTA 5000 CF, $i =$ 1.56 mA/cm^2 #18a.

The thermal behavior of the polymer coatings was solely investigated using the DSC-7 apparatus (Perkin Elmer, Überlingen, Germany) between 25°C and 400°C, at 10°C/min heating rate (four heating step). The DSC was calibrated using an indium standard**,** DSC measurements performed between 25–400°C at a heating and cooling rate of 10°K.

Peaks at about 50 and 170°C both for anodic and cathodically grafted fibers in the first cycles of heatings were observed for electrografted carbon fibers by DSC. T_g (glass transition temp) for PMMA was about 120°C, and T_m (melting point) observation at about 170°C could be an explanation of depression of T_g value of PNVCz which is known as thermally stable up to high degrees and partial crystalline character of electrografted copolymer. Low melting point could attributed to doped ion of supporting electrolyte.

Since the polymer coatings formed during the electrocoating procedure on carbon fibers were extremely thin the resultant heat differences were small complicating

DSC analysis. Despite this difficulty a number of new heat changes were observed associated with P[MMA-co-NVCz] formation. The corresponding peak temperatures are consistent with the formation of P[MMA-co-NVCz] coatings in agreement with our FTIRATR measurements. For amorphous polymers (or the amorphous portion of semicrystalline polymers) the heat capacity change (ΔC_p) at the glass transition temperature, T_g, is proportional to the weight fraction of amorphous material present. Although positive endothermic effects usually indicate disordering, the precision of our measurements precludes detailed interpretation.

4. Conclusions

Surface characterizations even on single fiber by reflectance FTIR enables nondestructive determination of the surface composition. Comparison of these with corresponding SEM images help to understand the tribology of such electrografted surfaces. These results indicated that bounded polymer on the surface of carbon fiber have additional surface functional groups, i.e., carbonyl group of methylmethacrylate, and N-vinyl group of carbazole ring etc., which can be used as an interfacial functional surface groups for further interactions and applications. Presence of such functional groups will improve the surface for further applications, i.e., reinforcement of polymer matrix, modified biosensor microelectrodes.

The changes of intensities of corresponding peaks of each monomer functional groups, by changing current density shows that the composition of copolymeric electrografting is affected by current densities.

Weak intensities of FTIR-ATR of cathodically electrografted NVCz-MMA copolymer emphasizes that for the anodic electrografting of same copolymer (under same conditions results thicker film- due to ease of oxidation of carbazole ring and known fast coupling reactions) bonding may proceed through carbazole ring resulting probably a stronger bonding.

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