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ARTICLE TYPE

Poly(vinylidene fluoride)-graft-poly(2-hydroxyethyl methacrylate): a novel material for high energy density capacitors

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We report the graft copolymerization synthesis of novel high dielectric constant HEMA (2-hydroxyethylmethacrylate)-graft-poly(vinylidene fluoride) (PVDF) copolymers for potential applications in high energy density capacitors. In the present study the graft copolymerization reaction was introduced by irradiation (electron beam) treatment of the PVDF polymer powder. The chemical changes in the PVDF polymers after HEMA grafting were monitored and the results were evaluated by FTIR, DSC, TGA and contact angle measurement. An analysis is presented on the effectiveness of this approach as a function of electron beam operating variables including radiation dose, reaction time, reaction temperature, monomer concentration and effect of solvent. The PHEMA-g-PVDF copolymers demonstrate improved dielectric properties such as high dielectric constant, lower leakage and low dielectric loss as compared to pristine PVDF. Correlation of dielectric properties with the graft copolymerization reaction mechanism was discussed.

Introduction

During the last few years, great advancement has been made in the field of capacitor technology.^{1–4} The improvements were made possible by the introduction of new class of dielectric materials such as polymeric materials.^{5–7} Among various polymeric materials, poly(vinylidene fluoride) (PVDF) and its respective copolymers have often been used as dielectric materials in engineering capacitors because of their combination of remarkable properties, such as reasonable dielectric permittivity (7–13 at 10 Hz), high dielectric breakdown strength, low dielectric loss, high volume resistivity, high stability, low shrinking rate and excellent thermal stability.^{8–11} Together with its excellent mechanical properties and biocompatibility, these ferroelectric and electrical properties make PVDF a suitable material for potential applications in power-storage devices.^{1,12–14} However, it has some limitations due to its low dielectric constant, chemical inertness and hydrophobic nature which prohibit composite formation; it could not satisfy the need of emerging capacitors requirements. To overcome these shortcomings, bulk-modified or chain-modified PVDF copolymers are of interest for its potential as capacitor dielectric material. Various approaches, such as grafting techniques and coating have been developed to bestow the conventional hydrophobic polymers with hydrophilic properties.^{15–18} Modification of polymers by graft copolymerization of functional monomers is a well-known method to impart

favorable chemical and physical properties to given polymers. The grafted materials frequently possess the superimposition of properties related to the backbone and the grafted chains.^{19–22} The grafting technique is of particular interest for the modification of fluoropolymers, because these polymers are difficult to modify by purely chemical methods.^{22–25} Several methods have been proposed for initiating graft copolymerization including ionizing radiation, ultraviolet light, decomposition of chemical initiators, plasma treatment, and oxidation of polymers. Among these methods, radiation-induced graft copolymerization is advantageous due to its extensive penetration in the polymer matrix and its rapid and uniform formation of radicals for initiating grafting in many kinds of polymers.^{26–29} The interaction of high-energy radiation with PVDF and other fluoro copolymers causes various chemical and physical changes depending on the type of radiation, *e.g.*, electron, plasma, γ irradiation, and swift heavy ions (SHI).^{30–35} The radiation mainly results in chain scission, cross-linking, and the formation of volatile products depending upon radiation dose. The grafting can be initiated by ionizing radiation, such as γ -rays and high energy electrons, using the pre-irradiation method or the simultaneous radiation grafting. The pre-irradiation grafting method consists of two steps. In the first step, the base polymer is exposed to ionizing radiation to generate reactive sites. In the second step, which may be performed hours or days after irradiation, the pre-irradiated polymer is brought into contact with the vinyl monomer at elevated temperature and the grafting starts from the reactive sites.

To the best of our knowledge, no detailed study has been reported on the radiation-induced graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) onto PVDF polymer. In the

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present work, pre-radiation induced grafting of functional hydrophilic monomer HEMA onto PVDF powder was designed as an alternative route to increase the dielectric properties of the polymer for capacitor applications. A hydrophilic monomer graft copolymerization of HEMA will result in the incorporation of hydroxyl groups into PVDF polymer. Due to the high dipole and the high polarizability of the O–H bond, an enhancement in the dielectric constant is anticipated. The effects of grafting conditions such as monomer concentration, irradiation dose, reaction time, temperature, solvent, *etc.* were investigated in correlation with the degree of grafting. The thermal stability of the HEMA-modified PVDF (PVDF-g-PHEMA) was investigated by thermogravimetric analysis (TGA), and differential scanning calorimetric (DSC) analysis. The complex formation of the modified polymer was ascertained by Fourier transform infrared spectroscopy (FTIR). The improved dielectric properties will be reported.

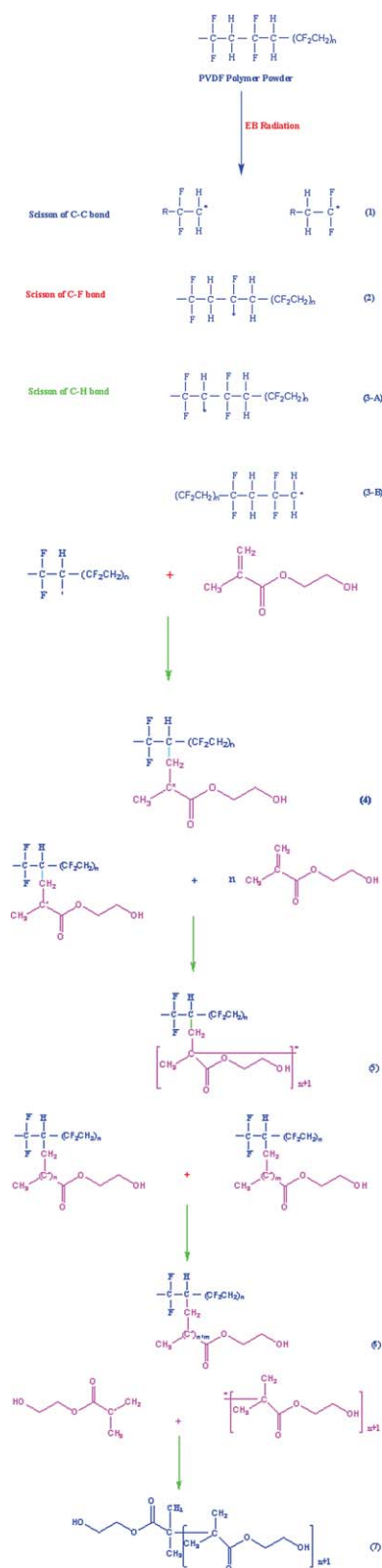
Results and discussion

Grafting conditions play an important role when determining the degree of grafting and the structure built up inside the grafted polymer. For example, contamination from initiators has been found to occur in grafted polymers prepared by chemical treatment.^{30,31} Recently, the radiation chemistry of fluoropolymers has been reviewed by a number of researchers.^{32–37} The electron beam can break the chemical bonds of the fluoropolymers and produce free radicals depending upon the radiation dose.

In the case of PVDF polymer, C–C, C–H and C–F are susceptible to cleavage, and bond strengths alone do not control the radiolysis. Since we have used a low radiation dose, there is a high possibility of abstraction of H from C–H bond as this bond is much weaker compared to C–F. The radiation chemistry is not explored here, and we have focused on the effects of irradiation as a result from the grafting reaction on the properties of the grafted polymers. In brief, irradiation of PVDF powder in vacuum forms hydrogen-free radical groups on the backbone polymer because of the abstraction of H from C–H bonds. In PVDF the active sites able to initiate the polymerization are the alkyl radical: (i) mid-chain $-\text{CF}_2-\text{C}^*\text{H}-\text{CF}_2-$ (ii) and end chain $-\text{CF}_2-\text{C}^*\text{H}_2-$.

The grafting of HEMA to pre-irradiated PVDF powder is expected to proceed by a front mechanism: grafts form first on the surface of the powder. The monomer then diffuses through the grafted portion and reacts with more radicals. Subsequently the grafting fronts meet, and the PHEMA grafts prevail throughout the bulk of the polymer. As discussed above there are two principle possibilities for the generation of free radical sites on the PVDF polymer backbone through two different routes of hydrogen abstraction; in the present discussion we are taking one possibility, that is, hydrogen abstraction from the mid-chain $-\text{CF}_2-\text{C}^*\text{H}-\text{CF}_2-$, as the initiation site. These hydrogen free radical groups serve to initiate polymerization of the monomer upon heating.

The grafting and cross-linking have been generally considered to involve three steps: firstly, initiation, which is shown in Scheme 1(1) to Scheme 1(3-B). This involves the generation of free radicals and thus the initiation of reactive sites on the substrate polymer through hydrogen abstraction from the



Scheme 1 Mechanism for graft copolymerization of HEMA onto PVDF polymer. Scheme 1(1) to 1(3-B) depicts chain initiation, Scheme 1(4) to 1(5) depicts chain propagation, and Scheme 1(6) to 1(7) depicts chain termination.

polymer backbone; secondly, propagation, which is shown in Scheme 1(4) and Scheme 1(5). This involves the addition of monomer to the substrate reactive sites and further propagation of that monomer thus the formation of macroradicals; and thirdly, termination, in which polymeric macroradicals may combine to give a final product. The growing polymeric chains thus produced can either attach to the polymer backbone to give the graft copolymer as shown in Scheme 1(6), or terminate to give the homopolymer as shown in Scheme 1(7).

Optimization of different reaction parameters for grafting of 2-hydroxyethylmethacrylate (HEMA) onto PVDF polymers

The effect of various reaction parameters on the percentage of grafting of HEMA has been studied and the results are discussed in the light of above-proposed mechanism. The irradiated PVDF powder containing the initiating radicals was immersed in the HEMA/water solution. The optimization of various reaction parameters such as the amount of solvent, reaction time, temperature, radiation dose and concentration of the monomer were carried out for the graft copolymerization of HEMA onto PVDF polymer.

Effect of radiation dose

Percentage of grafting of HEMA has been studied as a function of total radiation dose and the results are presented in Fig. 1. It is observed from the figure that the percentage of grafting of HEMA increases rather slowly with increasing total dose and reaches maximum (20%) grafting at an optimum total dose of 1.6 Mrad, beyond which it decreases. This can be attributed to (i) dose saturation in the formation of substrate radicals and (ii) an increase in the probability of monomer radical termination reactions at higher doses/higher graft yields.

Effect of temperature on grafting

As shown in Fig. 2, the percentage of grafting increases with the initial increase in temperature. The grafted yield reaches the

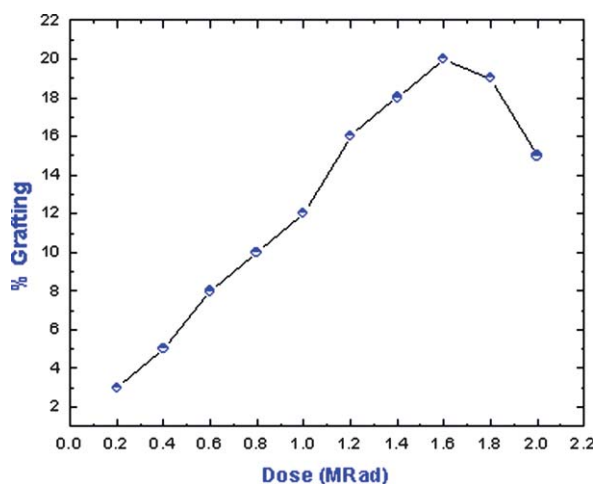


Fig. 1 Effect of total radiation dose on grafting reaction: PVDF powder – 200 mg; HEMA – 30%; reaction time – 4 h; solvent – 14 mL; temperature – 45 °C.

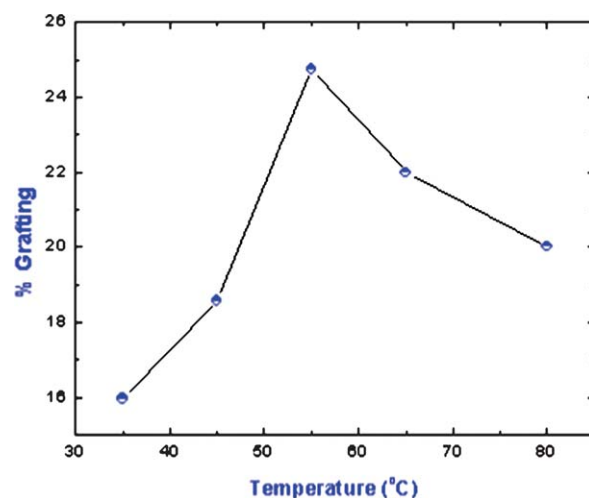


Fig. 2 Effect of reaction temperature on grafting reaction: PVDF powder – 200 mg; HEMA – 30%; reaction time – 4 h; solvent – 14 mL; radiation dose – 1.6 Mrad.

optimum value at 55 °C and decreases with a further rise in temperature. With the initial rise in temperature, as the kinetic energy of the molecules increases, more radicals drifted at faster rate onto the backbone, resulting in the increase in graft yield. However, after reaching the optimum temperature, a considerable amount of homopolymer is formed, which results in an increase in the viscosity of the reaction mixture. It provides a hindrance for the radicals to move towards the active sites of the polymeric backbone, resulting in the decrease in percentage of grafting. Furthermore disintegration of graft copolymers may take place at higher temperature.

Effect of solvent

The addition of solvent to a monomer/polymer backbone combination can enhance the percentage of grafting in the radiation induced grafting and determine the specific nature of the graft copolymer. The presence of water as a reaction medium in the grafting reactions has been found to have a very important effect on the percentage of grafting of vinyl monomers on fluoro polymers. To study the effect of water during grafting of HEMA, graft copolymerization has been carried out as a function of amount of water and the results are presented in Fig. 3. It has been observed that percentage of grafting of HEMA shows an initial jump with increasing amount of water from 4 to 8 mL, giving maximum (27.00%) grafting in 8 mL and then decreases sharply on further increase in the amount of water and becomes almost constant. The decreased percentage of grafting may be due to the dilution of reaction medium and various side reactions which lower the concentration of monomer radical per unit volume and hence less grafting takes place.

Effect of reaction time

The optimum reaction time has been found to be 5 h for graft copolymerization reaction. With the initial increase in reaction time, percentage of grafting reaches an optimum value at 5 h, and decreases with further increase in reaction time (Fig. 4).

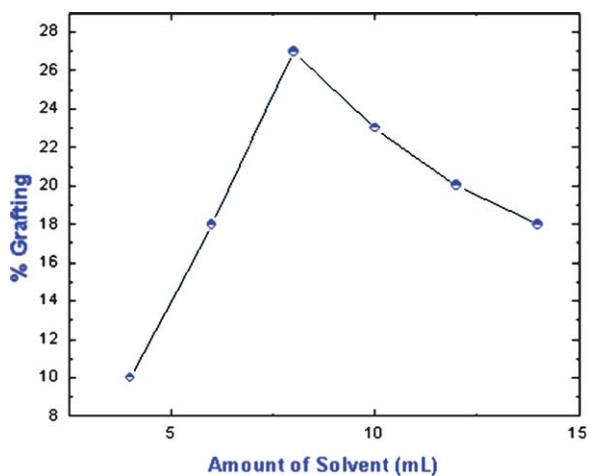


Fig. 3 Effect of solvent on grafting reaction: PVDF powder – 200 mg; radiation dose – 1.6 Mrad, HEMA – 30%; reaction time – 4 h; temperature – 55 °C.

This variation of percentage of grafting with time can be explained on the basis that as the reaction time increases, more and more radicals move onto the backbone, resulting in the increased graft yield. After reaching the optimal value (31% grafting at 5 h) with further increase in reaction time, most of the active sites on the backbone are occupied by the radicals and the formation of the homopolymer dominates the graft copolymerization. Similar behavior was previously found.^{30,31} Moreover, viscosity of the reaction medium increases with time, creating hindrance for radicals to move onto active sites of the backbone and results in the decreased percentage of grafting.

Effect of monomer concentration

It is clear from Fig. 5 that the percentage of grafting increases continuously with the increase in monomer concentration of HEMA and reaches a maximum value (35.27%) at 40% concentration. At higher monomer concentrations, more

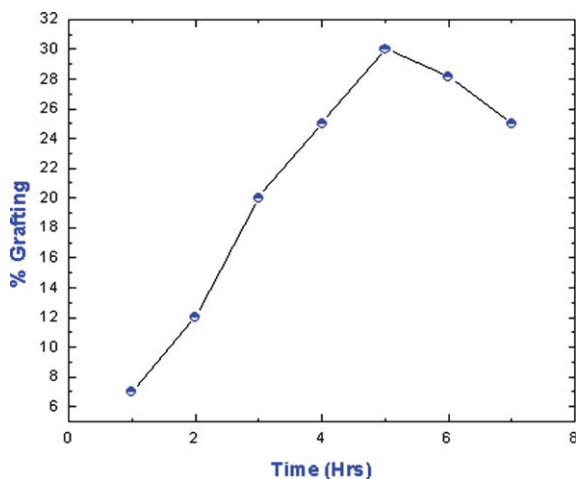


Fig. 4 Effect of reaction time on grafting reaction: PVDF powder – 200 mg; radiation dose – 1.6 Mrad; solvent – 8 mL; HEMA – 30%; temperature – 55 °C.

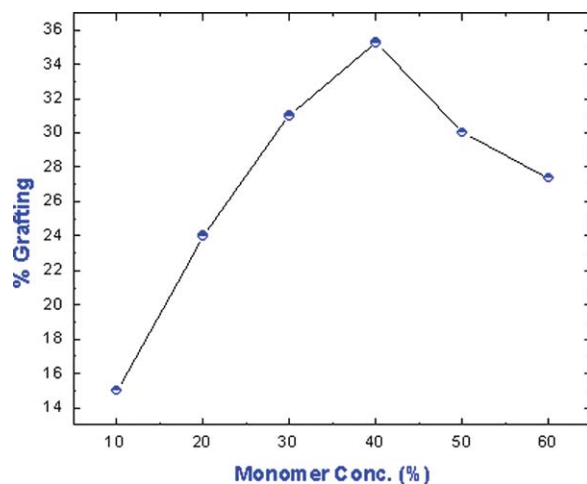


Fig. 5 Effect of monomer concentration on percentage grafting of HEMA: PVDF powder – 200 mg; radiation dose – 1.6 Mrad; solvent – 8 mL; reaction time – 5 h; temperature – 55 °C.

monomer would be available in the polymer medium for reaction with PVDF powder thereby enhancing the percentage of grafting. Beyond the optimum monomer concentration of HEMA, formation of homopolymer in preference to grafting takes place leading to decrease in percentage of grafting. Furthermore, formation of more homopolymer may lead to an increase in viscosity of the reaction medium thereby restricting the mobility of the growing polymeric chains to the active sites, and hence a decrease in percentage of grafting is observed.

Evidence of HEMA grafting

FTIR spectra of polymeric networks have been recorded to study the modification of PVDF polymer powder and incorporation of HEMA monomer chains into the polymeric backbone. In the spectrum of pristine PVDF powder, the characteristic peaks in the base polymer (Fig. 6) were those near to 3000 cm⁻¹ representing C–H stretching vibration. The characteristic absorption bands at 1191 cm⁻¹ and 1408 cm⁻¹ were due to the absorption

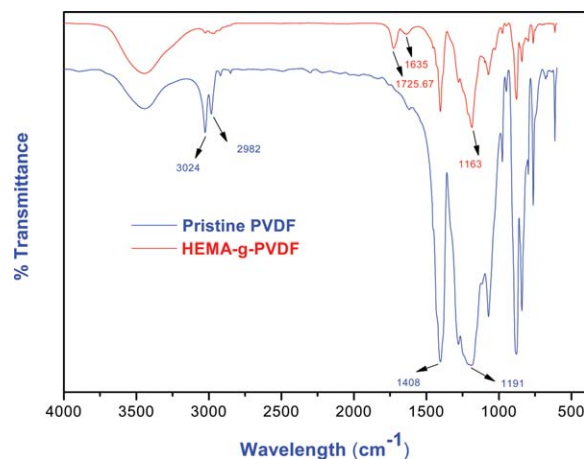


Fig. 6 FTIR spectra of pristine PVDF and PHEMA-g-PVDF polymer powder.

peaks of CF_2 stretching and CH_2 stretching modes respectively. The asymmetric and symmetric stretching vibrations of the CH_2 group in the pristine PVDF are located, respectively, at 3024 cm^{-1} and 2982 cm^{-1} . The grafting of HEMA onto PVDF was ascertained by the presence of the characteristic absorption peak of the carbonyl group at 1725.67 cm^{-1} of the PHEMA chains which was absent in pure PVDF. A typical spectrum of pure and grafted PVDF is given in Fig. 6. The spectrum for HEMA grafted PVDF clearly shows the existence of vibration modes corresponding to $\text{C}=\text{O}$ bands at 1725.67 cm^{-1} and $\text{C}=\text{C}$ band stretch at around 1635.02 cm^{-1} . The $\text{C}=\text{C}$ stretch mode at 1635.02 cm^{-1} can be attributed to the HEMA monomer, which is present on the surface of the PVDF. The peaks at 1456 cm^{-1} and 1163 cm^{-1} correspond to CH_2 and $\text{C}-\text{O}$ groups in the grafted poly-HEMA chains. Meanwhile, the $\text{C}-\text{H}$ stretching of the PVDF structure located at 2921 cm^{-1} and 2852 cm^{-1} weakened with grafting of PHEMA graft chains in the modified PVDF powder. The above results have provided evidences for grafting of HEMA onto the PVDF through covalent bonds.

The DSC curves of the pristine PVDF powder, poly-HEMA and PHEMA-g-PVDF powder are shown in Fig. 7. It is well known that the pristine PVDF is a partially crystalline polymer arising from its highly symmetrical structure. The melting point (T_m) of PVDF and poly-HEMA has been found to be $158.56\text{ }^\circ\text{C}$ and $106.68\text{ }^\circ\text{C}$, respectively. After graft polymerization with HEMA, the structural symmetry of PVDF is partially destroyed, resulting in the lowering of the melting point to $157.21\text{ }^\circ\text{C}$. This phenomenon is probably associated with the decreasing proportion of the PVDF crystalline phase in the grafted polymer possibly indicating mixing of poly-HEMA grafts into the crystallizable part of the PVDF melt. The melting enthalpy (ΔH_m) of pristine PVDF and HEMA-grafted PVDF has been found to be $53.97\text{ (J g}^{-1}\text{)}$ and $32.64\text{ (J g}^{-1}\text{)}$, respectively. The overall percentage crystallinity (X_C) of the pristine PVDF and the HEMA grafted PVDF was evaluated from the heat of fusion and has been found to be 51.51 and 42.17, respectively. It has been observed that the crystallinity of the PVDF matrix is considerably affected by the grafting process and the decrease in

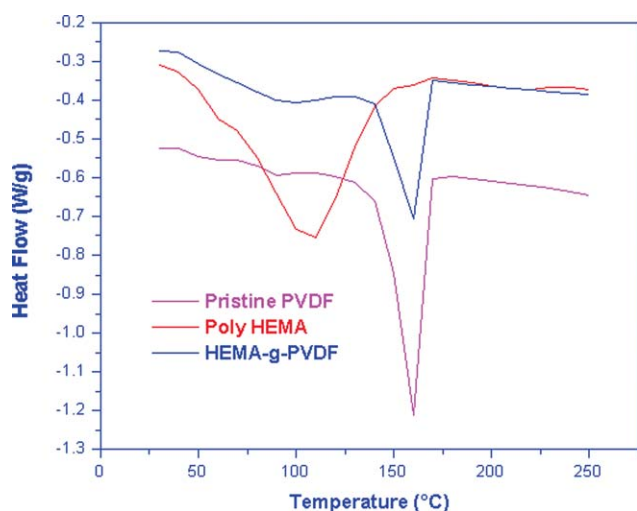


Fig. 7 DSC analyses of pristine PVDF, poly-HEMA and HEMA-g-PVDF polymer powder.

crystallinity at optimum percentage of grafting is quiet adequate. We can conclude that the small changes in melting point and percentage crystallinity (T_m and X_C) in the grafted PVDF are functions of the concentration of HEMA. In fact the graft produces irregularities that make crystallization more difficult.

Fig. 8 shows the TGA curves of the pristine PVDF powder, PHEMA-g-PVDF polymer and PHEMA homopolymer, respectively. For pristine PVDF, the weight loss is confined to a single-step degradation pattern. The PVDF homopolymer is stable up to about $357.79\text{ }^\circ\text{C}$ and suffers a weight loss of less than 4% around $450\text{ }^\circ\text{C}$ and can be attributed to the degradation of the PVDF matrix. The HEMA homo polymer is thermally stable up to about $170\text{ }^\circ\text{C}$. The last weight loss step at above $220\text{ }^\circ\text{C}$ corresponds to the bulk decomposition of the polymer residue. The PHEMA-g-PVDF powder shows intermediate weight loss behavior in comparison to that of the pristine PVDF powder. A distinct two step degradation process is observed for the PHEMA-g-PVDF sample. The onset of the first major weight loss at about $302\text{ }^\circ\text{C}$ corresponds to the decomposition of the grafted PHEMA polymer component. The second major weight loss commences at about $443\text{ }^\circ\text{C}$, corresponding to the decomposition of the PVDF main chains.

Fig. 9 shows the contact angles of pristine and grafted PVDF films. PVDF is one of the most highly hydrophobic polymers and the contact angle of the corresponding polymer film with water was 98° . PHEMA grafts are hydrophilic due to the existence of carboxylic acid and hydroxyl groups. Therefore, grafted polymer films are relatively hydrophilic. From Fig. 9, it is obvious that the contact angle of grafted PVDF films decreased with increasing percentage of grafting. This means the surface hydrophilicity of those grafted films was improved to a significant extent. The smallest contact angle of 64° was obtained for the polymer film cast from PHEMA-g-PVDF powder with a percentage of grafting of 35.27%.

Dielectric properties of the grafted and ungrafted films

Fig. 10 (a)–10 (c) displays the dielectric properties of pristine PVDF and PHEMA-g-PVDF polymer films as a function of

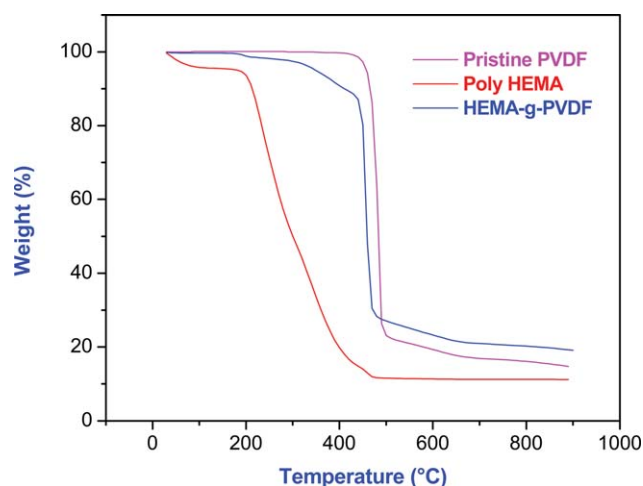


Fig. 8 TGA analyses of pristine PVDF, poly-HEMA and PHEMA-g-PVDF polymer powder.

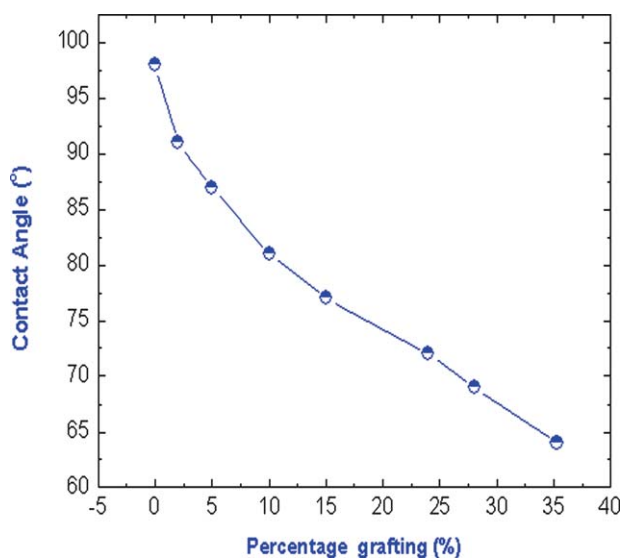


Fig. 9 Water contact angles of PVDF films as a function of percentage of grafting.

frequency from 100 Hz to 1 MHz at room temperature. The variation of dielectric constant with frequency for grafted and ungrafted polymer films is shown in Fig. 10 (a).

It can be observed that the dielectric constant of the grafted polymer substantially increased as compared to the pure PVDF. This behaviour can be explained on the basis that graft copolymerization results in the incorporation of hydroxyl groups into PVDF polymers which in turn enhances the dielectric constant due to the high dipole and the high polarizability of the O–H bond. The grafted film shows a dielectric constant of more than 40 at 1 kHz, meanwhile, the dielectric constant of pristine PVDF is around 11 at the same frequency. The dielectric constant attains high value at low frequency and decreases slightly with increasing frequency. The decreasing values with increasing frequency can be attributed to the fact that the motion and rotation of dipoles in the PVDF phase cannot keep up with the change in the frequency of the electrical field.³⁸ In other words, at higher frequency, the electric field changes at a rate too fast to sustain the polarization effects resulting in the reduction of the dielectric constant. It is interesting to find that even at the frequency of 1 MHz the dielectric constant of the grafted films still remains higher than pristine PVDF, which satisfies the dielectric requirement for high frequency applications, such as in high frequency capacitor.

Indeed the dielectric behavior of PVDF can be explained by the interactions of the grafted chains of PHEMA with the polymer matrix that interferes with the segmental motion or alters the semi-crystalline structure of the PVDF polymer.^{39,40} A decrease in crystallinity (refer DSC, Fig. 7) as a result of graft copolymerization provides a greater chance for the amorphous chains to achieve random disorder and isolation; hence, a higher dielectric constant can be attained. This can be explained by assuming that the dielectric constant of grafted PVDF films is that of a two-component system: the ordered and the disordered fraction. The disordered fraction contains the accessible OH groups responsible for the dielectric behavior. A decrease in the degree of crystallinity or an extension and the formation of

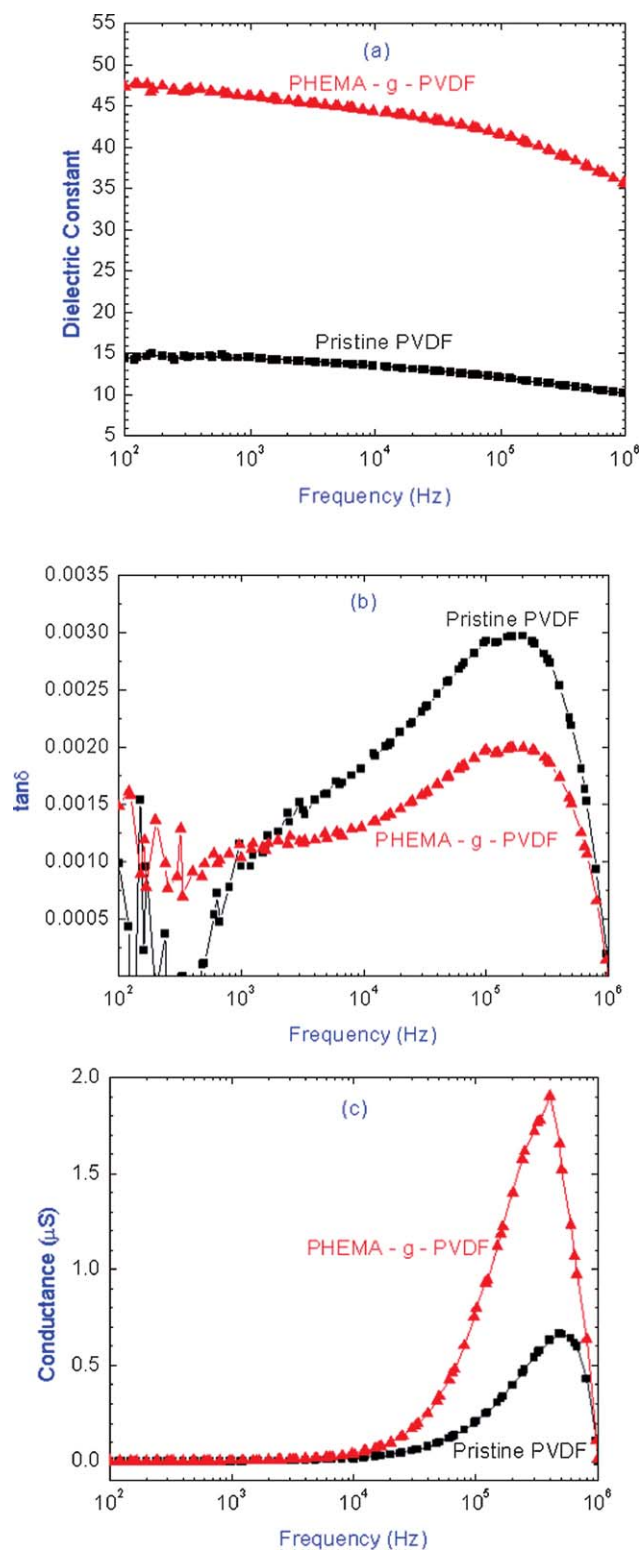


Fig. 10 Dependence of the (a) dielectric constant, (b) dielectric loss and (c) conductance on the frequency at room temperature.

disordered regions in the crystalline PVDF region results in an increased freedom of movement of the OH groups and portions of the PVDF molecule. This is because in the disordered regions, the dipolar or molecular polarization is influenced by the

proximity and configuration of adjacent molecules; consequently, a decrease in crystallinity results in a greater chance for the disordered chain to achieve random disorder and therefore results in a higher dielectric constant. In crystalline portions of the PVDF structure such movement is restricted, and the polarizations would consist, primarily, of electronic and atomic polarization.

The frequency dependencies of the dielectric loss for the pristine and PHEMA-g-PVDF film samples are presented in Fig. 10(b). From the figure, it is clear that the dielectric loss is lower for the grafted polymers. We observed loss peaks at ~400 kHz for both samples, which is a result of dielectric relaxation. At this stage, the exact polarization mechanisms over the entire frequency range could not be clearly made. However the measurement results of dielectric losses are helpful in the study of the mechanism. Fig. 10(c) shows the variation of conductance of the pristine PVDF as well as the grafted films as a function of frequency at room temperature. It is well known that conductance depends on the temperature and frequency range of the applied electrical field. It can be seen that the grafted copolymers exhibit conductance approximately two times higher than that of pristine PVDF films at room temperature. The increase of conductance for PVDF grafted with HEMA may be due to the free mobility of hydroxyl groups (OH) of the grafted chains. In addition, polymer dipolar structures present in both PVDF and poly HEMA are possible causes for the increase of the conductance in the grafted film.

The plot of current density is shown in Fig. 11. It has been observed that curve exhibits non-linear behaviour which is obvious for the polymers with polar character. The behaviour is the same for both the grafted and pristine films indicating that there is no degradation in leakage current.

Taking the above-mentioned discussion into account, we conclude that the improved dielectric properties of our grafted films mainly originate from the following effects: (1) incorporation of OH group into PVDF which reduces crystallization and creates disorder regions for segmental motion; (2) interactions between the polymer matrix and the embedded OH which enhances the molecular polarization in the disordered regions.

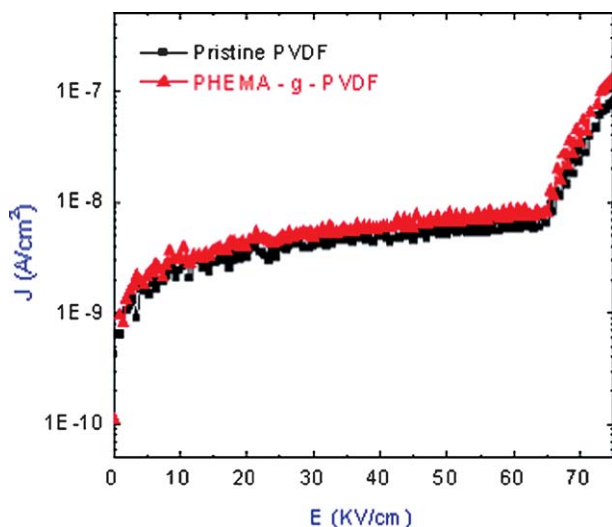


Fig. 11 The plot of current density at room temperature.

The result also shows that the graft copolymerization can improve the dielectric properties of PVDF through modified microstructure; that is, the use of PHEMA-g-PVDF leads to good interfacial interactions between PVDF and polar OH groups. This can be attributed to the polar hydroxyl and carbonyl groups in PHEMA because they can interact with the strong polar fluoride group in PVDF and therefore decrease the heterogeneity of the systems. In this case, the polarization of all dipoles is effective in improving the dielectric properties of the pristine PVDF.

Experimental

PVDF ($M = 420\,000$) powder with a diameter of 0.1 mm was purchased from Solvay Solexis Inc. 2-Hydroxyethylmethacrylate (HEMA) and methanol were supplied by (Sigma-Aldrich Chemie GmbH, Germany). All the materials mentioned above were purified wherever necessary.

PVDF powder samples were dried in an oven before irradiation at room temperature under N_2 . Samples were placed in plastic bags and purged with nitrogen for 10 min to remove oxygen and the bags were then filled with nitrogen and sealed. The irradiation process was performed in vacuum using the Energy Sciences Inc. (ESI) Electron Beam Accelerator at room temperature ($25\text{ }^\circ\text{C}$) in vacuum. The maximum accelerating voltage used was 175 kV, with the radiation dose ranging from 0.2 to 2.0 Mrad by means of a conveyor, whose speed was fixed at 18 m min^{-1} in order to have maximum exposure of radiation to the polymer. The beam current was 0.1 mA. The dose per pass was set as 0.1 Mrad. After irradiation, unless otherwise stated, the samples were immediately used for grafting with HEMA.

Irradiated PVDF (200 mg) was suspended in a known amount of distilled water in a flask. A definite amount of the HEMA monomer was added. Subsequently, nitrogen was purged through the solution for 30 min to remove oxygen. After that, the graft polymerization was performed at a particular temperature for a definite time period under stirring in a heating mantle fitted with a reflux condenser which was sealed. After the completion of reaction, the grafted powder (PHEMA-g-PVDF) was filtered and washed with hot water, then extracted for 72 h by methanol in Soxhlet apparatus to remove residual HEMA monomer and possible homopolymer that was formed. Finally, the PHEMA-g-PVDF powder was dried to constant weight in vacuum oven at $50\text{ }^\circ\text{C}$. Percentage of grafting of HEMA was calculated from the initial increase in the weight of the original polymer powder as described in eqn (1):

$$P_g = \frac{W_g - W}{W} \times 100 \quad (1)$$

where P_g is the percent grafting, W is the weight of the parent polymer, and W_g is the weight of the grafted polymer.

A customized laboratory-scale tape caster was used to prepare the polymer film. The slurry was prepared by using 60 mg ml^{-1} of the PVDF/PHEMA-g-PVDF polymer powder with DMF as the solvent. The solution was then mixed at $60\text{ }^\circ\text{C}$ for six hours in order to have uniform mixing. The slurries were subsequently cast onto a glass carrier and dried in air at $60\text{ }^\circ\text{C}$ for 3 h and in vacuum at $50\text{ }^\circ\text{C}$ for 12 h to remove DMF. The thickness of the tape was measured using a micrometre accurate to 0.001 mm; the

weight of the samples was measured using a laboratory scale accurate to 0.01 mg.

Electrical measurements were performed using a Keithley 4200 semiconductor parameter analyzer and a HP4284 LCR meter at the frequency range of 100 Hz to 1 MHz at room temperatures. Before the measurements, both sides of all samples were deposited with gold for electrodes. Before analyzing the samples, these were conditioned by maintaining them in a vacuum oven for three hours to 50 °C and 0.01 N cm⁻² pressure. For each sample 4 to 5 determinations were made, and their mean was considered the final result.

Changes in the thermal properties; the enthalpy of fusion and crystallization were investigated with the use of TA Instrument 2920 Modulated Differential scanning calorimetric analyzer (DSC) apparatus. The use of the Modulated DSC allows the heat capacity of the sample to be measured in one run with an error of 1% or less. To avoid oxidative degradation, the sample and reference pans were purged with nitrogen at a constant flow rate of 68 ml min⁻¹. The samples were heated from 30 °C to 250 °C at a scan rate of 10 °C min⁻¹, with approximately 2–5 mg of each sample used in the analysis.

The heat of fusion (ΔH_f) was obtained from the area under the melting thermogram. The crystallinity in sample was obtained by the eqn (2):

$$\% \text{Crystallinity} = \frac{\Delta H_f}{\Delta H_{f(\text{cryst})}} \times 100\% \quad (2)$$

where ΔH_f is the heat of fusion of the sample, and $\Delta H_{f(\text{cryst})}$ is the heat of fusion of 100% crystalline PVDF, and was taken as 104.7 J g⁻¹. For PHEMA-g-PVDF, the percentage crystallinity was calculated by correcting the recorded ΔH_f dividing by the weight fraction of PVDF in the investigated sample.

Thermogravimetric analysis (TGA) was carried out on a TA instrument mode 2950 in a temperature range of room temperature to 900 °C with a heating rate of 10 °C min⁻¹. The samples were dried under vacuum at 60 °C for 24 h and then were stored under desiccator. TGA runs were carried out on samples having typical weight of 10–20 mg.

Fourier Transform Infrared (FTIR) Spectroscopy was done using a Perkin-Elmer system 2000 FTIR to verify changes in the structure of PVDF before and after graft copolymerization. The FTIR spectra were obtained with 8 scans per sample over the range of 4000–400 cm⁻¹.

The water contact angle of the PVDF and the grafted films were determined using an optical contact angle meter system (Dataphysics, OCA-20) at ambient temperature to study the hydrophilicity of the films. The grafted PVDF films were stored for approximately 7 days after being prepared at room temperature in air prior to their contact angle analysis. This had to be done because their contact angles may initially change after irradiation due to reactions of the irradiated polymers with water vapor and oxygen. The films were then placed on glass slides and fastened on both ends using Teflon tapes. At least five independent determinations at different sites of one sample were taken.

Conclusions

PHEMA-g-PVDF copolymers can be successfully synthesized via free radical graft copolymerization technique. These grafted

polymers have high dielectric properties over wide frequency regions. The dielectric constant is about 4.5 times higher as compared to pure PVDF at room temperature. With respect to the cost, a copolymer with sufficient grafting is valuable for practical applications as capacitors for energy storage. The overall results of this work suggest that the structural changes that took place in PVDF during the preparation of these samples have a strong impact on their dielectric properties and the resultant energy storage capabilities. Graft copolymerization of HEMA onto PVDF through electron beam radiation is a promising route to synthesize high dielectric constant materials.

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