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Dielectric spectroscopy of hydrophilic polymers–montmorillonite clay nanocomposite aqueous colloidal suspension

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ABSTRACT

Frequency-dependent complex dielectric function, loss tangent, electric modulus, alternating current electrical conductivity, and impedance spectra of poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), poly(ethylene glycol) (PEG), and blends of PVA–PVP and PVA–PEG, loaded with polymer grade montmorillonite (MMT) clay upto 5 wt% of solute (polymer + clay) in aqueous colloidal suspensions, have been investigated in the frequency range 20 Hz to 1 MHz at 27 °C. These materials show the dielectric dispersion corresponding to ionic conduction and electrode polarization phenomena in the experimental frequency range. The loss tangent peak frequency which separates the contribution of the bulk material and the electrode polarization phenomenon was used to evaluate the electrode polarization relaxation time corresponding to the dynamics of electric double layers. The dielectric and electrical conductivity spectra were interpreted as a result of these material complex structures formed by constituents H-bonding interactions, and the clay intercalation and exfoliation that alter the conduction pathways. Results show that the dielectric/electrical properties of the polymer–clay nanocomposites aqueous colloidal suspension have good resemblance to their structural properties, which were explored from other spectroscopic and morphological techniques. A close look on the dielectric parameters of the investigated materials proves the suitability for the synthesis of new materials with desirable and predicted properties.

1. Introduction

Organic polymers, loaded with small amount of montmorillonite (MMT) clay result in polymer–clay nanocomposites (PCNs). In last two decades, PCNs have evoked an intense industrial and academic research, due to their outstanding mechanical, thermal, chemical and electrical properties over pure polymers [1–8]. The MMT clay which is also called inorganic polymer has a laminar structure and excellent hydrophilic and cation exchange properties [8]. Its sheet dimensions in the length and width can be in hundreds of nanometers but thickness is only one nanometer. The MMT clay is composed of units made of two silica tetrahedral sheets centered with an alumina octahedral sheet, which is called 2:1 phyllosilicate and chemically it is a metal silicate. Its layers are stacked by weak dipolar or van der Waals forces, and it has both surface and edge charges. The charges on edges are easily accessible to modification, but they do not accomplish much improvement in interlaminar separation. These sites represent an opportunity for attachment of functional group of polymers during the synthesis of PCN materials [8,9]. In water or polar organic solvents, the MMT clay has excellent swelling properties owing to the intercalation (absorption) of solvent molecules in the clay galleries and also the adsorption of solvent molecules on its external surfaces of the sheets.

Three methods commonly used for the synthesis of PCNs are in situ polymerization [10], solvent intercalation [11] and polymer melt intercalation [12]. In case of hydrophilic polymers and clay, the PCNs films are frequently prepared by casting solution intercalated nanocomposite material directly onto a glass plate. In PCNs aqueous solutions, intercalation and exfoliation are two extremes for the clay structures. In intercalated, polymer is located in the clay galleries, expanding the clay structures but retaining some long distance register between the platelets or sheets. Whereas, in case of exfoliated, the original face-to-face structure of the clay platelets is destroyed and single clay sheets are randomly dispersed in the polymeric solution. Complete exfoliation of all the individual platelets is very difficult to achieve and most PCNs solutions contain region of both intercalated and exfoliated structures and their ratio depends on the polymer and clay interaction in the solutions. The structural morphology and polymer intercalation properties of the PCNs films are widely characterized by SEM and TEM micrographs, and XRD and FTIR spectroscopy. The characterization of dielectric properties of PCNs films have their significant applications in integrated circuits, microelectronics and insulating devices, and membrane technology [7,13,14]. The PCNs aqueous colloidal suspension and

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gels are widely used as electrolyte [15–18] for improving barrier coating efficiency due to colloidally stable of clay sheets in suspension [19,20], and effective wound dressing [21]. In order to realize the macroscopic properties of nanocomposites from molecular concepts, one must understand the molecular motions or dynamics of these materials in response to various applied fields, which is currently an important issue in condensed matter physics to underlying physics on molecular level. When nanocomposites are placed in an electric field they subject to ionic, interfacial, and dipole polarization at different time scales and length scales, making dielectric relaxation spectroscopy (DRS), which is uniquely suited for the study of nanocomposite dynamics.

Poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), and poly(ethylene glycol) (PEG) are highly water soluble hydrophilic polymers and have wide range of applications in pharmaceutical, optical, electrical, and technological industries. The solubility of these polymers in water is due to the formation of H-bonding complexation between water molecules and polar group of the polymer molecules. In these hydrophilic polymers the MMT clay can be incorporated without the need for being pre-treated but by simply dispersing the polymer and clay components in water, which results the colloidal suspension of the solute. Besides the polymer and water H-bonding interaction, the hydroxyl (–OH) group of PVA monomer units and the carbonyl (C=O) group of PVP monomer units have the ability to form hydrogen bonding with –OH groups on the surfaces of clay sheets in clay loaded colloidal suspension. That might be the main cause why PVA/PVP exfoliates the MMT clay sheets and their nanocomposites show the enhanced mechanical and thermal properties. Literature survey shows that the PVA–clay [22–25], PVP–clay [26,27], and PEG–clay [28] nanocomposites have been successfully prepared by aqueous solution intercalation, and these are structurally established by repeatedly characterization using the XRD and FTIR spectroscopy and their morphology by the SEM and TEM micrographs. Recently, film forming PCNs aqueous suspension have come into use in many on-machine or off-machine coating for improving water and moisture barrier coating, because of their environment friendly process and easy to usage ([19], and references cited therein). For improving barrier resistance, the nano-clay particles must be colloidally stable in the aqueous suspension and the clay particles must be exfoliated in the final polymer matrix. For this purpose, high hydrophilic properties of the clay surfaces and their strong affinity to hydrophilic polymer are needed, so that the polymer chain can stick to the organo-clay surface forming clay–polymer micro-aggregates. The PVA, PVP and PEG polymers, and Na^+–MMT clay fulfill the requirements for their stable colloidal suspension. Further, these liquid nanocomposites consisting of non-toxic polymers could find their application in food technology for moisture barrier coating to prevent the food product for longer duration.

The survey of literature exhibits that so far low frequency dielectric dispersion (LFDD) spectroscopy, i.e., electrokinetics of the above mentioned hydrophilic polymers–clay nanocomposite aqueous colloidal suspension have not been attempted, although these are parent materials for casting the PCNs films by solution intercalation techniques. The structure of the PCNs films prepared by solution cast technique is strongly governed by the complex structure of polymer and clay in the solution [22,29,30]. Therefore, in view of current wide interest on the solution intercalation grown PCNs films, there is need from academic and application point of view, to investigate a comparative dielectric behaviour of the PCNs aqueous colloidal suspension containing PVA, PVP, PEG, and blends of these polymers with MMT clay. In low frequency range, the polymeric solutions show large dielectric dispersion due to the polymer chain segmental dynamics, ionic conduction and electrode polarization phenomena [31–37], and these properties are governed by the solute and solvent interactions. The dielectric relaxation spectroscopy confirms the molecular dynamics in relation to morphology of the PCN films [38–42]. Bur et al. [43,44] have successfully employed the dielectric spectroscopy to yield quantitative information about the extent of clay exfoliation and possible control on it in the polymer matrix in on-line melt PCN process. The electrical/dielectric properties of a material are represented in terms of intensive quantities, namely, complex dielectric function $\varepsilon^*(\omega)$, electrical modulus $M^*(\omega)$ and electrical conductivity $\sigma^*(\omega)$, and extensive quantities, i.e., complex admittance $Y^*(\omega)$ or complex impedance $Z^*(\omega)$. The Maxwell–Wagner–Sillars (MWS) polarization is manifest in all three formalism; it appears as a shoulder in the dielectric spectrum and in the conductivity spectra, and a part of broad peak in the dielectric modulus [42]. In the present study, all of these representations are used to best describe and interpret the effect of heterogeneity on dielectric response. The effect of clay concentration, polymer chain length, and chain dynamics on the ion conduction and electrode polarization phenomena in the PVA, PVP, PEG, and blends of these polymers aqueous colloidal suspension is explored by comparative dielectric spectra over the frequency range 20 Hz to 1 MHz.

2. Experimental

2.1. Materials

The PVA of average molecular weight 77,000 g mol^{-1} and the PEG of average molecular weight 4000 g mol^{-1} of the laboratory grade were obtained from Loba Chemie, India. The PVP of average molecular weight 24,000 g mol^{-1} of laboratory grade was obtained from S.D. Fine-Chem, India. Polymer grade hydrophilic montmorillonite (MMT) clay (Nanoclay, PGV), a product of Nanocor® was purchased from Sigma–Aldrich. The MMT clay is white in colour, and have 145 mequiv./100 g cation exchange capacity (CEC), 150–200 aspect ratio (length/width), 2.6 g/cc specific gravity, and 9–10 pH value (5% dispersion), which is best recommended clay for the preparation of PCNs with hydrophilic polymers.

2.2. Preparation of polymer–clay nanocomposite aqueous colloidal suspension

For preparation of all the colloidal suspension materials, 5 wt% (weight fraction) of solute (polymer/polymer–clay/polymer blend/polymer blend–clay) was added in double distilled deionized water. For aqueous polymeric solutions, 1.5 g amount of PVA/PVP/PEG was dissolved in 28.5 g (∼30 ml) water. The PVA was dissolved in hot water of about 90 °C. For the preparation of PVA–PVP and PVA–PEG blends, 3:1 weight ratio of PVA to PVP or PEG was used. For the preparation of polymer–clay blends of varying clay concentration 0.015 g, 0.03 g, 0.045 g, 0.06 g and 0.075 g amount of MMT clay was introduced for 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of clay, respectively, with respect to the 1.5 g weight of total solute (clay + polymer) in 28.5 g water. For PCNs aqueous solutions, the amount of polymer/polymer blend is dissolved in 25 ml water for preparation of polymeric aqueous solution and the corresponding clay amount was dispersed in 5 ml water for clay suspension in separate beakers. The colloidal dispersion of clay, i.e., clay suspension was made in water at room temperature by magnetic stirring vigorously for 2 h. The polymer aqueous solution and the colloidal dispersed clay solution were mixed after 12 h, and the same mixture was then magnetically stirred for 2 h to get the PCNs aqueous colloidal suspension for the low-frequency dielectric characterization. Same procedure was followed to prepare all the PCNs aqueous colloidal suspension of varying clay concentration.