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DC conduction mechanism and dielectric properties of Poly (methyl methacrylate)/Poly (vinyl acetate) blends doped and undoped with malachite green

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ABSTRACT

Cast thin films of Poly (methyl methacrylate)/Poly (vinyl acetate) blends of different concentrations undoped and doped with malachite green have been prepared and subjected to both dc electrical conduction and dielectric spectroscopy measurements. The analysis of dc electrical conduction data showed that the space charge limited current mechanism has been dominant for Poly (vinyl acetate) while Schottky–Richardson conduction mechanism prevailed for the Poly (methyl methacrylate) and blended samples. The values of field lowering constant β and the thermal activation energy ΔE involved in the dc conduction were reported, which provide another support for the suggested Schottky–Richardson mechanism. The increase in current for the blend sample doped with malachite green has been attributed to the formation of charge transfer complexes inside the polyblend matrix. The dielectric constant as a function of temperature for all samples have been calculated which are affected by the composition ratio and the addition of dye. The relaxation peak that appeared in the dielectric loss curve at 347 K for the doped blend sample is related to local dipoles that are present in the dye material. The obtained relaxation process spectra present in the investigated samples were analyzed with the well-known model of Havriliak–Negami.

1. Introduction

Polymer blending is a simple method to cast materials that posses new characteristics, it has also demonstrated the importance in improving the performance of many new materials by varying the polymeric composition. It has become an economical and versatile way to obtain materials with a wide range of desirable properties [1–4]. Poly (methyl methacrylate) (PMMA) and Poly (vinyl acetate) (PVAc) are organic amorphous polymers and their blends can be used for developing useful materials that acquire some level of electrical properties. PMMA has received great attention due its optical properties and its possible use in nonlinear optics [5]. PMMA is known for its medical applications, particularly for hard tissue repair and regeneration [6]. Also PMMA beads have been developed to deliver amino glycoside antibiotics locally for the treatment of bone infections [7]. PVAc has been a base material in numerous applications but popular in the manufacture of emulsion paints, varnishes and adhesives [8]. In cosmetics, it has been applied as a binder, emulsion stabilizer and hair fixative [9]. Many investigations have been reported on the electrical properties of the PMMA and PVAc, as individual polymers and as well as in blends with other polymers [10–17].

Dye-polymer composites have received considerable attention as potential electro-optic materials [18] and solar concentrators [19]. Malachite green (MG) is a basic organic dye which dissociates into anion and colored cation. MG, when doped in a polymer, may reside at various sites of the polymer chain. Even though MG may become embed into the polymer chains and diffuse into the amorphous polymer forming charge transfer complexes (CTCs), or it may exist in the form of molecular aggregates between the polymer chains.

Electrical conduction in polymers has been studied, extensively, during the past two decades to understand the nature of charge transport in such materials. Dielectric relaxation spectroscopy reveals significant information about the chemical and physical state of polymers. In addition, it separates various dynamic processes according to the different rates of molecular orientations in a polymer.

In this study, an extensive analysis is carried out to examine the probable dc conduction mechanism and the nature of charge transport in PMMA and PVAc individual polymers and their blends. In addition, dielectric constant and dielectric loss as a function of temperature and frequency have been investigated to throw more light on the molecular origin of the dielectric

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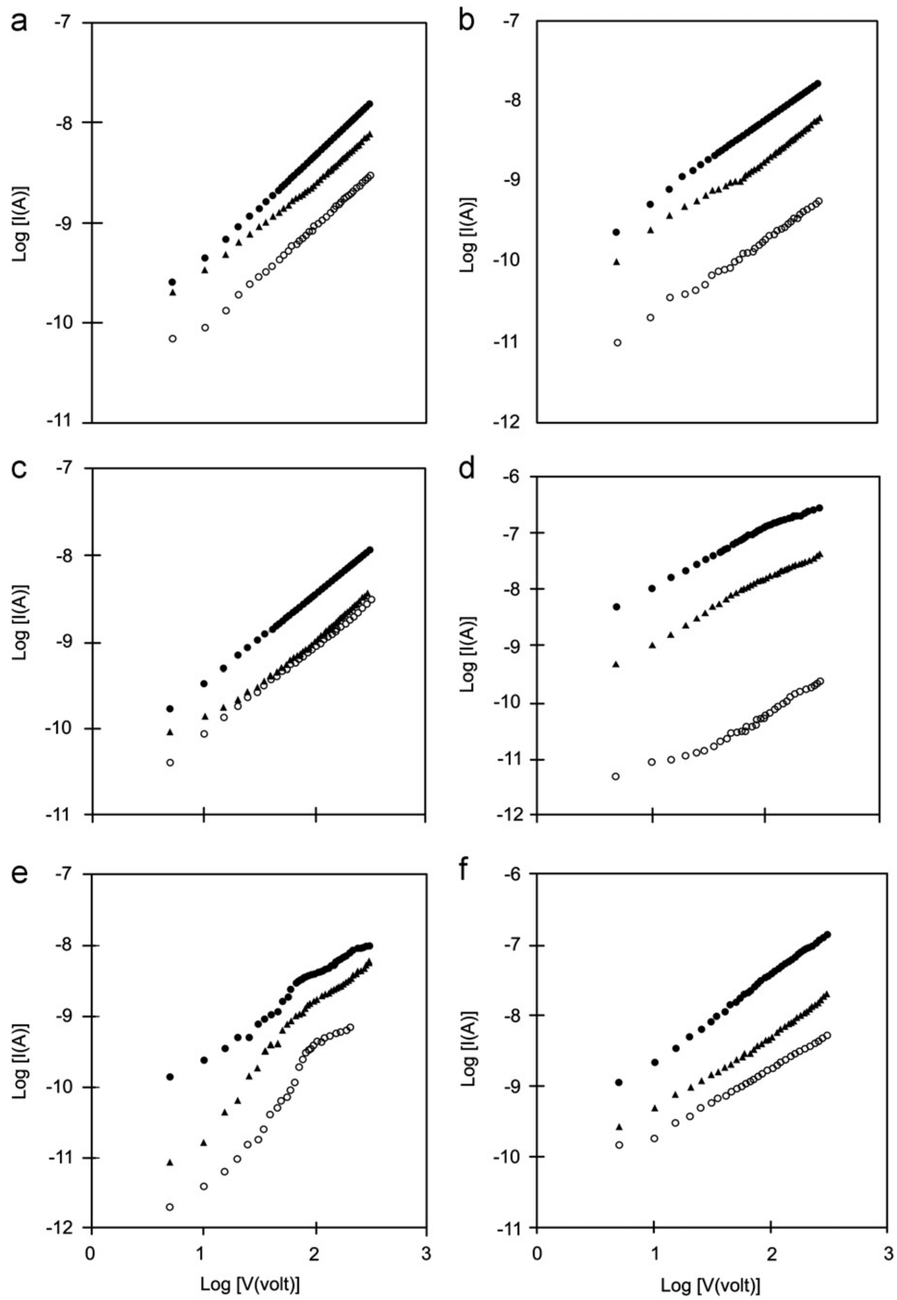

Fig. 1. Log *I* vs Log *V* for: (a) 100/0, (b)75/25, (c) 50/50, (d) 25/75 (e) 0/100 and (f) 75/25 doped with malachite green; wt/wt% PMMA/PVAc blend samples at different temperatures: (*o*)303, (▲)323 and (●)343 K.

relaxation. The general Havriliak–Negami equation was used to fit the relaxation process for all samples. Similar analysis was performed on the blend samples doped with MG.

2. Experimental

PMMA/PVAc blend samples were prepared by mixing weighed amount of PMMA, supplied by Aldrich and has a molecular weight of 120,000, and PVAc, supplied by Acros Organics, and has molecular weight of 170,000. All materials were supplied in a powder form and mixed to form the ratios 100/0, 75/25, 50/50, 25/75 and 0/100 wt/wt% PMMA/PVAc. Mixtures were then dissolved in chloroform using a magnetic stirrer for 8 h to obtain a homogeneous mixture at room temperature. MG of concentration 0.05%, in a powder form and supplied by Cambrian Chemicals, was added to the 75/25 wt/wt% PMMA/PVAc. The solutions were cast in a stainless steel Petri dish and then dried in air at room temperature for about 24 h to ensure the full evaporation of the solvent. The thickness of the films was measured with a precision digital micrometer (Digenetic Indicator, Mitutyo Corporation, Japan) to the nearest 0.001 mm at five random locations on the film. The mean value of the film thickness was used in the calculations of electrical conduction and dielectric properties. Current–voltage (*I–V*) characteristics were studied at different temperatures; 303, 323, 343 K and different voltages 10–400 V, in sandwich configurations with an effective area $\approx 1\ cm^2$. Current measurements were made by means of an electrometer (Keithley 617 Aurora Road Cleveland, Ohio, USA) which was carefully grounded to avoid extraneous electrical noise. The sample capacitance was measured using a Type PM.6304/031 programmable automatic RLC meter. The