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Preparation and Electo-optical Characterization of Poly (N-Vinyl Carbazole) Magnetite Composites

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ABSTRACT: In this study, the magnetic particles were prepared through the chemical method, using the mixing a water solution of $FeCl_2.4H_2O$ (1.0 M) and $FeCl_3.6H_2O$ (1.5 M). Different weight percentage of magnetite (0%, 1% and 5%) and N-vinyl carbazole (NVC) were placed into 20 mL of NMP and chemical polymerization was performed by using AIBN as iniator at 70 ˚C for 24 h. These composites are characterized by methods such as SEM (Scanning Electron Microscopy, and UV-Vis (Ultraviolet-visible Spectroscopy). Thanks to these methods it can be inform about morphology and optical properties of the samples. Moreover, dielectric measurement of the samples have been done by impedance spectroscopy.

Keywords: Composite, conducting polymer, dielectric, magnetite, poly(N-vinyl carbazole).

Poli (N-Vinil Karbazol) Magnetit Kompozitlerinin Hazırlanışı ve Elektro-optik Karakterizasyonu

ÖZET: Bu çalışmada manyetik partiküller, $FeCl_2.4H_2O$ (1.0 M) ve $FeCl_3.6H_2O$ (1.5 M) sulu çözeltisinin karıştırılması ile kimyasal yöntemle sentezlendi. Farklı ağırlık yüzdesine sahip magnetit (% 0, % 1 ve % 5) ve N-vinil karbazol, 20 mL NMP içine yerleştirilerek başlatıcı olarak AIBN kullanılarak 70 °C 'de 24 saat boyunca kimyasal polimerizasyon ile yapılmıştır. Bu kompozitler, SEM (Taramalı Elektron Mikroskobu) ve UV-Vis (UV-Görünür Bölge) spektroskopisi ile karakterize edilmiş olup, bu yöntemler sayesinde örneklerin morfolojik ve optik özellikleri hakkında bilgi edinilebilmektedir. Ayrıca, kompozitlerin dielektrik karakterizasyonları, empedans spektroskopisi ile araştırılmıştır.

Anahtar Kelimeler: Kompozit, iletken polimer, dielektrik, magnetit, poli(N-vinil karbazol)

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INTRODUCTION

Poly (N-vinyl carbazole) (PNVC) has a different ability to form distinct excimers and is important in industry as it is a high sensitive photoconductive polymer. (Brar and Kaur, 2006). PNVC has wide application areas such as electrochromic materials, LEDs, and photovoltaic devices. (Morin et al., 2005; Grazulevicius et al., 2003; Iraqi and Wataru, 2004; Walkim et al., 2008; Xu et al., 2011)

Polycarbazoles are very important among various conductive polymers. Because they have charming properties such as their good electroactive and photochemical properties (Cloutet et al., 1999). Beside this, their derivatives has potential applications areas such as light emitting diodes (Siove and Adees, 1999; Taoudi et al., 2001), electroluminescent (Huang et al., 2002; Abe et al., 2002) and electrochromic displays (Donnat-Bouillud et al, 1997).

Magnetite (Fe_3O_4) is the strongest magnetic material in aspect of natural mineral; beside this, it has not only magnetic properties but also electrical properties (Phang and Kuramoto, 2010; Gu et al., 2012; Kurlyandskaya et al., 2007; Jolivet and Tronc, 1998). Moreover, magnetite has several curious applications area like magnetic storage media, printing inks, and magnetic drug delivery, microelectronic devices (Wrighton, 1986; Laranjeiras et al, 2002; Laranjeiras et al, 2002).

Conducting polymer composites have huge application areas in the aspect of organic electronics such as electronic devices, rechargeable batteries, solar cells etc because of their matchless properties (Zhong et al., 2015; Yoon, 2013; Lei et al., 2013; Yoo et al., 2014; Ravindranadh, 2013).

In this study, different weight percentage of magnetite (0%, 1% and 5%) and N-vinyl carbazole were placed into 20 mL of NMP and chemical polymerization was performed by using AIBN as iniator at 70 ˚C for 24 h. These composites are characterized by SEM (scanning electron microscopy) and UV (Ultra violet spectroscopy). Thanks to these methods it can be inform about morphology, and optical properties of the samples. Moreover, dielectric measurement of the samples have been done by impedance spectroscopy.

According to previous studies, this study presents a detailed investigation and information of dielectric properties especially at high frequencies and spectroscopic and morphological characterization of PNVC-Magnetite composites. Accordingly, it is thought that spectroscopic, morphological and dielectric characterization of PNVC-Magnetite composites synthesized for the first time in this study may be important for various technological applications.

MATERIAL AND METHODS

Materials and instruments

N-vinyl carbazole (Aldrich), azobisisobutyronitrile (AIBN) (Aldrich), $FeCl_2.4H_2O$ (Aldrich), $FeCl_3.6H_2O$ (Aldrich), and all the other chemicals used were of analytical grade and were used as received without any further purification. Measurements have been performed by SEM (Jeol 7001F), UV–VIS–NIR (Shimadzu 3600) spectrophotometer and of a dielectric analysis system (Fytronix FY-3000) in the frequency range of 100 Hz–20 GHz.

Preparation of PNVC and its composites

In this study, different weight percentage of magnetite (1% and, 5%) in 20 mL of water were placed into ultrasonic bath at 25 ˚C and sonicated for 5 h and N-vinyl carbazole were placed into 20 mL of NMP and was sonicated at 25 ˚C and then radical polymerization of NVC was performed by using AIBN as initiator in presence of magnetite at 70 ˚C and then at the end of the reaction, the mixture was transferred into ethanol to remove of the soluble monomer and initiator contaminants then the samples were dried under vacuum at 25 ˚C for 24 h.

RESULTS AND DISCUSSION

Spectroscopic characterization

Figure 1 shows that evolution of $(\alpha h\upsilon)^2$ plotted against photon energy (hυ) of PNVC, PNVC+1% magnetite and PNVC+5% magnetite. It was calculated the energy band gap value for PNVC and its composites. As the weight percentage of magnetite increases, the band gap value decreases owing to the iron ions giving metallic character to the composites.

Morphological Characterization

Morphological condition of PNVC samples were observed by scanning electron microscopy. The SEM pictures of PNVC (Figure 2a) and PNVC composites (PNVC+1% magnetite and PNVC+5% magnetite), have been shown in 2b and 2c, respectively. In Figure 2a, the morphology of PNVC is various shapes (Boddula and Srinivasan, 2014) and the magnetite in different percentages were attached with PNVC (Figure 2a and 2b). In addition, magnetite particles were observed to be well distributed in the PNVC matrix, and by adding magnetite, PNVC+5% magnetite, which is composed of smaller particles, appears to be formed [Hariani et al., 2013] (Figure 2c).

Dielectric Properties

For studying the dielectric measurements, the PNVC and PNVC composites were prepared in the circular disc form of pellets under 10 ton.cm^{-2} pressure value.

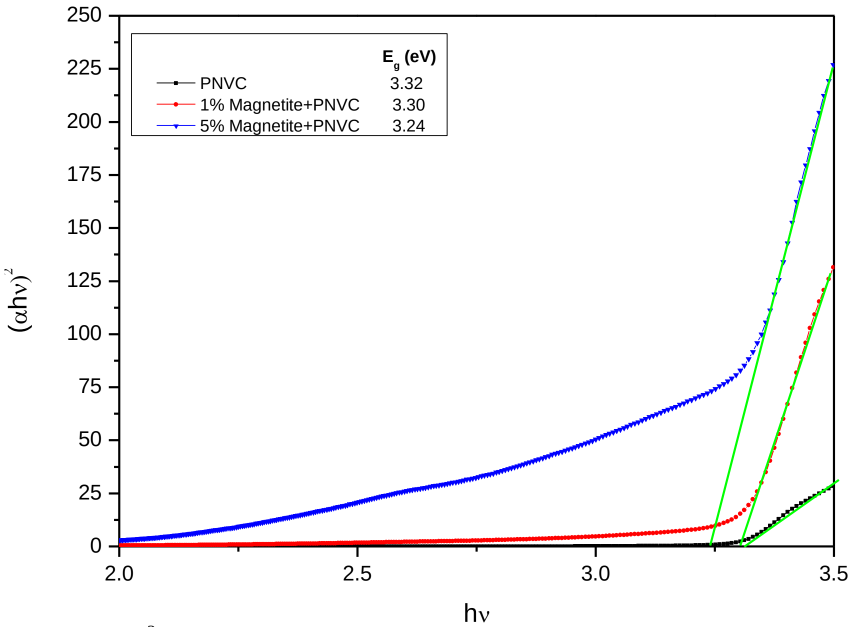

Figure 1. Plot of $(ahv)^2$ versus hv of the PNVC and PNVC with different magnetite concentrations.

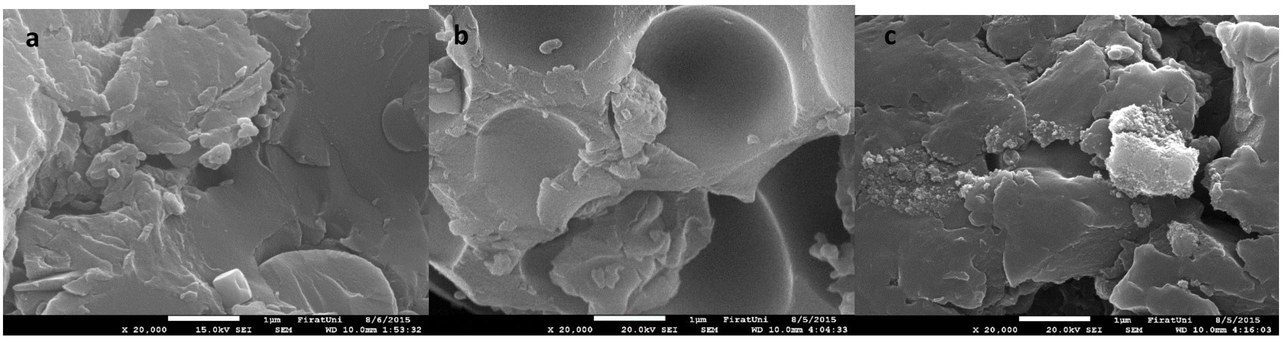

Figure 2. SEM Picture of PNVC and PNVC doped with 1%, 5% magnetite, respectively.

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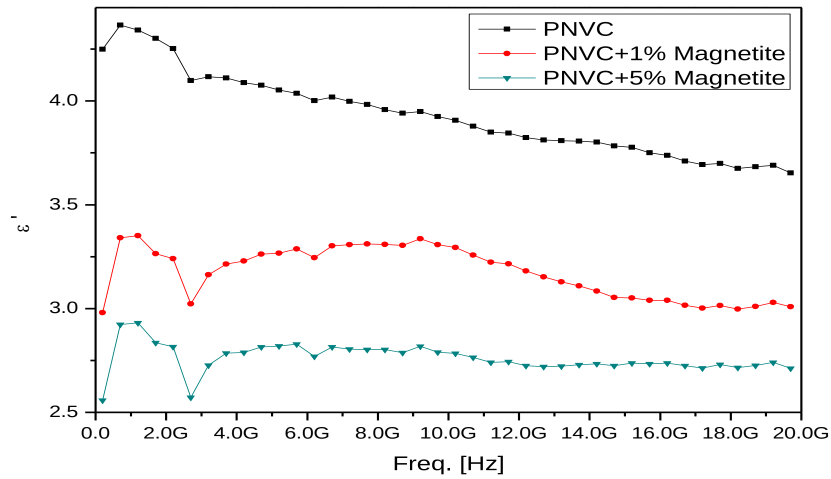

Figure 3. Plot of the real part (ε′) of dielectric constant versus frequency for PNVC and PNVC with different magnetite concentrations.

Real (ε′) part of dielectric constant decreases with increasing frequency (Figure 3). PNVC has highest value and ε′ reduces with the increasing of frequency for all of samples and also ε′ decreases by adding of magnetite. Therefore, PNVC+5% magnetite has the smallest value of real part of dielectric value.

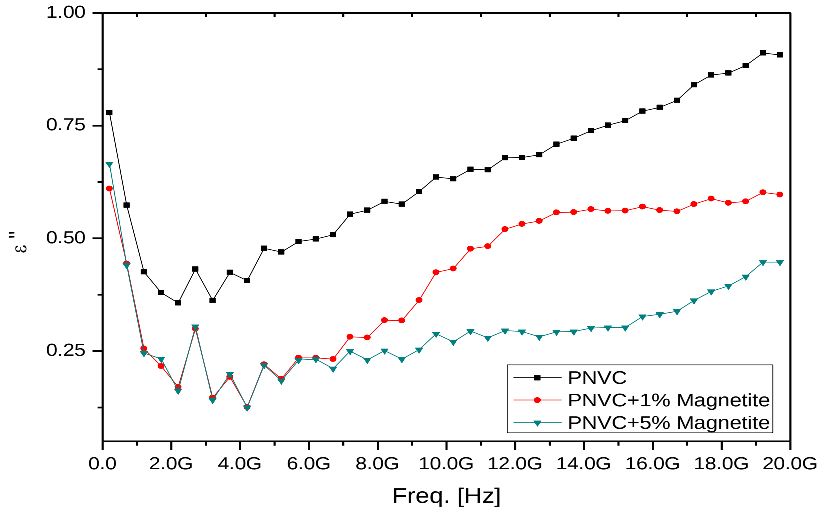

Figure 4. Plot of the imaginary part (ε″) of dielectric constant versus frequency for PNVC and PNVC with different magnetite concentrations.

Imaginary (ε″) part of dielectric constant decreases with increasing frequency (Figure 4). PNVC and PNVC+5% magnetite have highest and lowest value, respectively. In the high frequency, the atomic polarization behavior has been obtained for PNVC and PNVC doped with 1% and 5% magnetite at 25 ˚C.

The dielectric constants of composites decrease with increasing of weight percentage of magnetite. Because the composites have gained metallic properties due to iron ions.

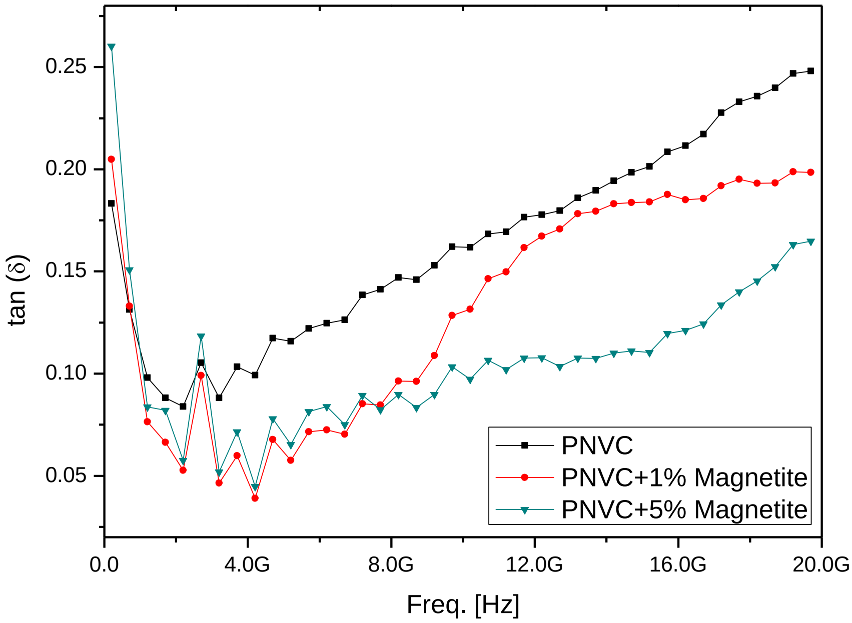

Figure 5. Plot of the loss factor versus frequency for PNVC and PNVC with different magnetite concentrations.

Up to 4 GHz, the loss factor reduces with increasing of frequency, but after 4 GHz it increases with increasing of frequency. PNVC has highest value of loss factor at high frequency, but loss factor decreases with increasing the amount of magnetite. As seen in Figure 5, The energy loss value is range between 0.05 and 0.25.

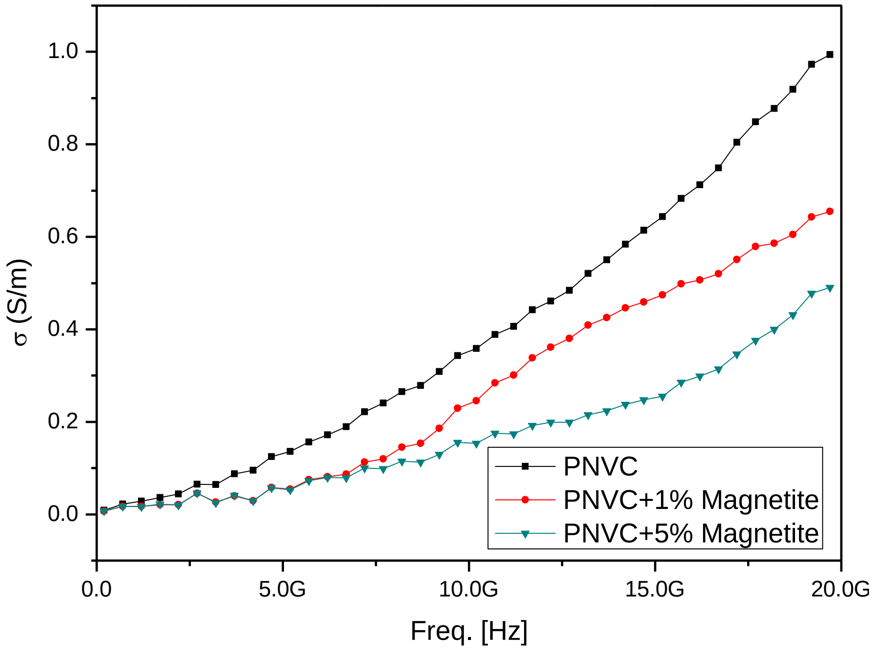

Figure 6. Frequency variation of the conductivity for PNVC and PNVC with different magnetite concentrations

The conductivity values increases with frequency for all samples (Figure 6). PNVC and PNVC+5% magnetite has highest and lowest value, respectively.

The ac conductivity dependence of frequency can be expressed by the following relation, as the empirical Jonscher's universal law (Özdemir et al., 2015),

$$\sigma_{AC}(\omega)=A\,\omega^{s} \tag{4}$$

where, A is a constant, ω is the angular frequency and s is the frequency exponent parameter which determines AC conduction mechanisms. The angular frequency exponent values *s* was calculated from the slopes of Fig. 8 (Ahlatcıoğlu Özerol et al., 2015). The variations of ln(σ_{AC}) with angular frequency have been given in Fig. 7 for PNVC and PNVC doped with magnetite. Since the frequency exponent is used to determine the electrical conduction mechanism for PNVC and PNVC doped magnetite**,** the frequency exponent values *s* have been calculated from the slopes two range of Fig. 7 for the first region and second frequency regions (Table 1).

The frequency dependence of ac conductivity (σ_{AC}) of PNVC and PNVC with magnetite composites have been investigated by means of frequency exponent “s” parameter in the three frequency regions.

The *s* parameters can be interpreted by different power laws for frequency dependent conductivity; for the original work of Jonscher, frequency exponent “s” was restricted to be 0<s<1 which is known as Jonscher Power Law (JPL).

According to the values of exponent “*s*” varying from 0.27 to 1.74 are shown in the Table 1. PNVC doped magnetite all samples composites show JPL model behaviors in the first region. The *s* parameters can be interpreted by different power laws for frequency dependent conductivity given by (Meller, 1983) super linear power law (SLPL) of the conductivity with a frequency exponent between one and two (1< s< 2). These composites also indicate SLPL in the second and third regions.

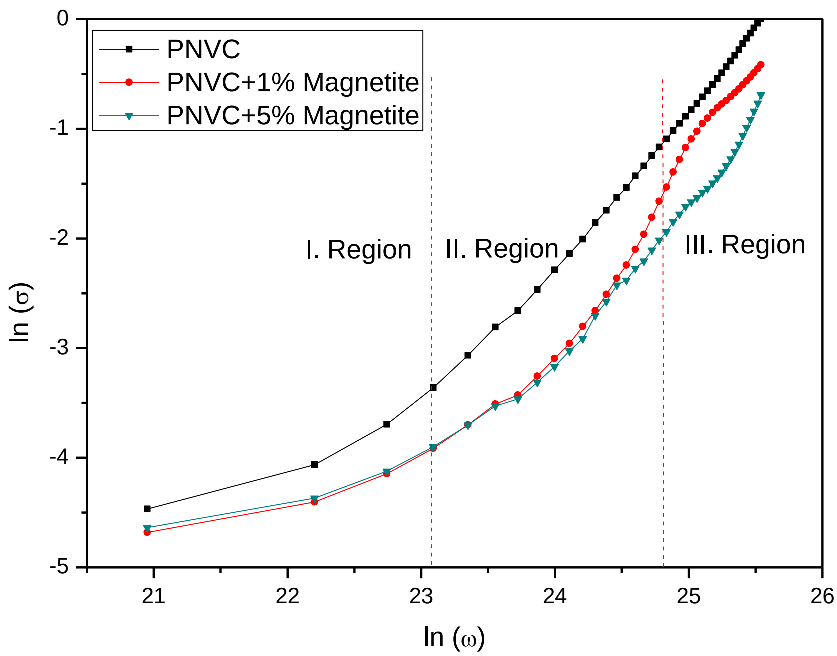

Figure 7. AC conductivity for PNVC and PNVC with different magnetite concentrations.

Table 1. s parameters of the samples.

Samples	**I. Region**	**II. Region**	**III. Region**
PVNC	0.41	1.29	1.58
PVNC+1%Magnetite	0.28	1.24	1.30
PVNC+5%Magnetite	0.27	1.12	1.74

CONCLUSION

In this work, the magnetic particles were synthesized through the chemical method, using the mixing a water solution of $FeCl_2.4H_2O$ (1.0 M) and $FeCl_3.6H_2O$ (1.5 M). Different weight percentage of magnetite (0%, 1% and 5%) and N-vinyl carbazole were placed into 20 mL of NMP and chemical polymerization was performed by using AIBN as iniator at 70 ˚C for 24 h. These prepared composites characterized using, UV, SEM and dielectric spectroscopy at high frequency. The dielectric constants of composites decreases with increasing of weight percentage of magnetite. Because the composites has gained metallic properties due to iron ions. The atomic polarization behaviors in the high frequency regions have been obtained for PNVC and PNVC doped with 1% and 5% magnetite at 25 ˚C. According to the values of exponent "*s*" varying from 0.27 to 1.74. Because of this range, the *s* parameters can be interpreted by different power laws for frequency dependent conductivity. JPL model behaviors in the first region and SLPL model behaviors in the second and third region.

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