Current Applied Physics 14 (2014) 1596–1606

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Universal microstructure and conductivity relaxation of polymer-conductor composites across the percolation threshold

Maheswar Panda [a, b, *], V. Srinivas [a, c], A.K. Thakur [a, d]

[a] Department of Physics and Meteorology, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
[b] Department of Physics, Dr. Hari Singh Gour Central University, Sagar 470003, India
[c] Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India
[d] Department of Physics, Indian Institute of Technology Patna, Patna 800013, India

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form
27 July 2014
Accepted 24 August 2014
Available online 4 September 2014

Keywords:
Composites
Microstructure
Percolation in phase transition
Impedance spectroscopy
Relaxation

ABSTRACT

Micro-structural and impedance analysis of series of insulating polymer/conductor composites (PCC) as a function of frequency and volume fractions of the conductor (f_{con}) have been studied. Evidences of conductivity relaxation have been noticed with a correlation with the sample micro-structure. This has been understood and explained in terms of equivalent electrical circuit model of the material established through complex impedance spectroscopy (CIS) across the percolation threshold (f_c) for all the PCC. CIS analysis confirmed that PCC with $f_{con} \geq f_c$, exhibit conductivity/interfacial relaxation due to polarization of Maxwell–Wagner–Sillars (MWS) type at f_c and the relaxation frequency increases with increase of f_{con}. The modulus spectroscopy analysis suggests the presence of two types of relaxations in different frequency ranges; (i) dipolar relaxation associated with the flipping of dipoles present in the pure polymer for $f_{con} < f_c$ and (ii) the conductivity/interfacial relaxation due to the formation of artificial MWS dipoles at the interface of the two components. A long range dc conductivity appears at $f_{con} \geq f_c$ and Jonschers universal fractional power law is satisfied for both the regions of $f_{con} < f_c$ and $f_{con} \geq f_c$ in all PCC.

1. Introduction

High dielectric-constant materials are required for the electrical devices, such as; cellular telephones [1], for stress relief in high voltage electrical apparatus [2] and embedded capacitor applications [3–14], etc. Insulating polymer-conductor composites (PCC) loaded with conducting fillers (e.g., metal, alloy, carbon black and nano tubes, etc) [1–14] have attracted more attention for their excellent functions, such as; equalization of the electric field distribution [3], higher storage capability of the electric energy [4–12], embedded capacitor applications [12], printed circuit boards [13], etc. Further these composites are more flexible and can be easily fabricated into various shapes [14]. The interesting properties of these PCC is that they undergo an insulator to metal transition (IMT) at a critical volume fraction of the conductor (f_{con}) called percolation threshold (f_c) which is characterized by the divergence of real part of dielectric constant and abnormal increase of ac conductivity (σ_{ac}) [15]. For designing new composite materials with desirable properties, the understanding of electrical properties of these PCC is of great significance [1–14].

In spite of numerous research results reported up to now, the relationship between the microstructure and electrical properties of PCC is not complete and universal although so many results are available [11,13,16–18]. Almond et al. [19] explained theoretically that for insulator-conductor composites (ICC), the power law dispersions in permittivity and dielectric loss is characterized universally by the Cole-Davidson response function [20], for the composites with $f_{con} \geq f_c$. There are a few reports which deal experimentally the microstructure and electrical properties of ICC [21,22]. The experimental investigation of correlation between the microstructure and electrical relaxations in case of ICC/PCC across f_c using complex impedance spectroscopy (CIS) [23] may find the universalization of relaxation processes.

2. Experimental details

The polymers, polyvinyledene fluoride (PVDF), low density polyethylene (LDPE) and high purity (99.9%) metal powders, such as; Nickel (Ni), Aluminum (Al), Copper (Cu), Iron (Fe), having initial

* Corresponding author. Department of Physics, Dr. Hari Singh Gour Central University, Sagar 470003, India. Tel.: +91 7582265459.
E-mail addresses: maheswar.panda@rediffmail.com, panda.maheswar@gmail.com (M. Panda).

http://dx.doi.org/10.1016/j.cap.2014.08.019
1567-1739/

particle size of ~(10–20) μm, were purchased from Alfa Aesar. The as purchased Ni (μ-Ni) was also milled for 60 h in order to obtain nanocrystalline Ni (n-Ni) of particles size (~20 nm–30 nm). The milling has been carried out in toluene and tungsten carbide milling media by maintaining the ball to powder weight ratio at 10:1 at a milling speed of 300 rpm. The formation of well-ordered quasicrystalline $Al_{65}Cu_{23}Fe_{12}$ powders (n-QC) of particle size (~300 nm) was obtained [7]. The annealing of n-Ni at 500 °C for 6 h converts it in to a composite of Ni and nickel oxide (NiO) [10]. The details of various series of possible combinations of PCC prepared are given in Table 1. The final samples were taken in the form of pellets (diameter 13 mm& thickness ~1.8 mm). The electrical properties were measured using a high precision impedance analyzer (Agilent 4294A) in the frequency range of 40 Hz–10 MHz, with an applied voltage of 400 mV, using Agilent 16451B Dielectric Text Fixture. The various abbreviations and symbols used for different terminologies through out the manuscript are given in Table 2.

3. Results and discussion

In order to have a complete understanding regarding the microstructure and dynamics of charge carriers at/above f_c of the variety of PCC under study, the simultaneous analysis of the frequency dependent CIS data is analyzed. Various formalisms to probe the electrical behavior have been adopted are; the variation of impedance (Z), modulus (M) and σ_{ac} as a function of frequency to search for a generalized electrical relaxation behavior in a broad class of PCC across f_c.

3.1. Microstructure

Polarized optical microscopy is used in order to see the distribution of metallic filler clusters in the polymer matrix of the PCC. Some of the typical optical micrographs of the PCC corresponding to $f_{con} \ll f_c$, $f_{con} \rightarrow f_c$ and $f_{con} \geq f_c$ are given in Fig. 1. The typical morphological features for all the composites are composed of two phase components in which one component shows the brighter region and the other component being the background region. Due to the presence of metallic clusters in the polymer matrix, the reflection of the polarized light from the metallic clusters occurs and that corresponds to the brighter regions in the composites. For $f_{con} \ll f_c$, the filler clusters (brighter regions) are well isolated from each other and for $f_{con} \rightarrow f_c$ the filler clusters approach and become very close to each other. The extent of heterogeneity of the distribution of the filler particles increases with increase of f_{con} and the filler clusters are found to be overlapped with each other for $f_{con} \geq f_c$. Such a tailoring in the morphological features, controlled by dispersion of conducting fillers of variable geometrical shape, size and loading in the PCC, may be expected to modulate their physical properties and electrical response on application of an a. c. electric field across it. To confirm this CIS has been carried out on each of the seven series of samples over a wide range of frequency.

Table 2
The details of various abbreviations and symbols used through out the manuscript.

Terminology	Abbreviation/Symbol
Polymer/conductor composites	PCC
Volume fractions of the conductor	f_{con}
Percolation threshold	f_c
Complex impedance spectroscopy	CIS
Maxwell–Wagner–Sillars	MWS
Insulator-conductor composites	ICC
nickel oxide	NiO
Polyvinyledene fluoride	PVDF
Low density polyethylene	LDPE
Quasicrystalline $Al_{65}Cu_{23}Fe_{12}$ powders	n-QC
Resistive/resistance	R
Capacitive/capacitance	C
Constant phase element	CPE/Q
Exponent associated with the CPE	u
Exponent associated extent of Non-Debye ness	α
Hopping or critical frequency	ω_H
Kohlrausch–Williams–Watts	KWW
Full width at half maximum	FWHM
Real part of impedance	Z′
Imaginary part of impedance	Z″
Real part of modulus	M′
Imaginary part of modulus	M″
AC conductivity	σ_{ac}
Dielectric constant	ε
Real part of dielectric constant	ε'
Imaginary part of dielectric constant	ε''
The peak relaxation time	τ_0
Dielectric, modulus and impedance time constants	τ_ε, τ_M & τ_Z
Relaxation frequency	f_{max}/ω_{max}
Static permittivity	ε_s
Limiting permittivity	ε'□
Frequency corresponding to the loss peak position	ω_p

3.2. Impedance spectroscopy

The complex-plane impedance spectrums (Nyquist plots) for all the PCC are shown in Fig. 2. We observe that for $f_{con} < f_c$ the Nyquist plot typically displays a straight line for all the series of PCC. The straight line is attributed to the pure insulating nature of the

Table 1
The details of the components and various series of samples prepared with their process conditions and labeling.

Components	Density(g/cc)	Average particle size (μm)	DC conductivity (Ω^{-1} cm^{-1})	BET surface area (m^2/g)	% age of crystallinity	Phases of existence	Melting temperature (°C)
PVDF	1.74	0.4–0.6	~10^{-14}	–	50%–60%	α, β, γ, δ, ε	170
LDPE	0.92	400	~10^{-15}	–	30%	Single phase	130
μ-Ni	8.91	5–10	~10^{9}	0.03	–	fcc	1500
n-Ni	<8.91	0.02–0.04	~10^{6}–10^{9}	1.30	–	fcc	1500
n-QC	4.7	0.2–0.3	~10^{3}–10^{4}	–	–	Quasicrystal	>1500
n-Ni@NiO	<8.91	0.02–0.04	~10^{-5}	–	–	fcc	>1500

Sample	Label	Process conditions	f_c
PVDF/μ-Ni	A	Cold pressed at 10 MPa for 5 min	0.57
PVDF/n-Ni	B	Cold pressed at 10 MPa for 5 min	0.27
PVDF/n-QC	C	Cold pressed at 10 MPa for 5 min	0.23
PVDF/μ-Ni	D	Hot molded at 10 MPa @200 °C for 45 min	$0.25 < f_c < 0.26$
PVDF/n-Ni	E	Hot molded at 10 MPa @200 °C for 45 min	0.07
PVDF/n-Ni@NiO	F	Hot molded at 10 MPa @200 °C for 45 min	0.30
LDPE/n-Ni	G	Hot molded at 10 MPa @130 °C for 30 min	0.06