Electrical properties of polyurethane graphite composites

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Polyurethane (PU) is one of the industrially important polymers which offers a combination of unique properties and meets a wide range of demanding application. Electrical conductivity and dielectric properties of polyurethane/graphite composites were investigated in this paper. Moisture Cured Polyurethane was prepared with varying NCO/OH ratio 2.0, 2.2 and 2.4 by polyoxytetramethylene glycol (PTMO) Mw 2000 and Toluene diisocyanate (TDI). Graphite powder of 0 to 12.5 vol% was dispersed in PU to form electro conductive composites. Percolation concentrations were determined to be as (9±1), (9±2) and (10±3) vol. % for the NCO/OH ratio of 2.0, 2.2 and 2.4 respectively. It shows that percolation concentration does not have significant change as the NCO/OH ratio increases. The dielectric properties of the composites were investigated in the frequency range of 1 KHz to 10MHz. It was found that PU composites became electro-conductive when filled with 9 to 10.0% of the filler and support well the dc conductivity results.

I. INTRODUCTION

The introduction of electrically conducting particles into a polymeric material have been the subject of numerous work and gives very interesting and useful properties to the filled composites. In general, low content of filler in composite are still an insulator because the conducting particles are well separated. As the percentage of the filler is increased the conductivity increases [1].

Graphite is used as electroconductive filler due to its good conductivity and moderate cost. It is also reported that graphite increases the mechanical and thermal properties as well as the dimensional stability of the polymeric material [2].

The properties of polymers depend upon several factors like molecular weight, chemical nature of the units composing the polymer and the morphology in solid state [3]. Polyurethanes are used as potting compounds and as cable insulation, therefore, the frequency dependence of the dielectric properties is important in practical and theoretical evaluations [4].

Dielectric spectroscopy is a useful technique to study the structure and relaxation properties of polymers [4]. Generally the dielectric properties of polymers are studied as a function of the degree of polymerization, frequency, temperature, and pressure [5-8]. This paper concentrates on the electrical properties of PU with three different NCO/OH ratios and this resin filled with different volume percentages of graphite powder. The NCO/OH ratio is varied in order to control the crosslink density of the material.

Most articles investigate the effect of NCO/OH ratio of the PU on mechanical, chemical and thermal properties and hardly on electrical properties. However, this paper concentrates solely on the electrical properties of PU and also PU graphite composites.

II. EXPERIMENTAL DETAILS

IIa. Materials

Toluene diisocyanate (TDI, Aldrich), Polyoxy-tetramethylene glycol (PTMO, Mw = 2000, Aldrich, Germany) and glycerol (Aldrich) were used as received. Xylenes (Merck, Germany), Toluene (JT Baker, USA), and Ethyl acetate (Merck, Germany) were used as solvents, stored over molecular sieve until use. PTMO was dried under vacuum at 80-85°C for 2 h and graphite fine powder (50 μm Merck) was left in the oven at 100°C for 24 h before use.

IIb. Synthesis of Polyurethanes

The polyurethane investigated in this work, was prepared by a prepolymer method and moisture cured. The prepolymer method consists of drying the PTMO and glycerol under reduced pressure. Then the prepolymerization with TDI was carried out at 75-80°C for 2 hrs. Graphite powder was dispersed in PU by vigorous mixing of the component to ensure thorough mixing and fabricated into a film by solution casting technique. For electrical conductivity measurements circular discs with diameter 15 mm and thickness about 0.2-0.5 mm were prepared. While for measurement of dielectric properties, circular discs with diameter 38 mm and a thickness about 0.2-0.5 mm were prepared.

IIc. Measurement of Electrical Conductivity

The volume electrical conductivity in polymer composites was measured according to ASTM D257. The samples were measured using a KEITHLEY 6517 Electrometer/ high resistant system with voltage level varied in the range of 0.1-150 V.

IId. Measurement of Dielectric Properties

Dielectric measurements were carried out according to ASTM D150. Dielectric measurements were performed on the PU composites in order to determine their dielectric constant ε' and dissipation factor (tan δ) as a function of frequency. These measurements were conducted over the frequency range 1 kHz to 10 MHz using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer equipped with a HP 16451B Dielectric Material Test Fixture.

III. RESULTS AND DISCUSSION

IIIa. Electrical Conductivity

The dependencies of electrical conductivity of PU/Graphite composite (NCO/OH ratios 2.0, 2.2 and 2.4) on the volume portion of filler are shown in Fig. 1. The absolute values of the electrical conductivity of the composites are summarized in Table I.

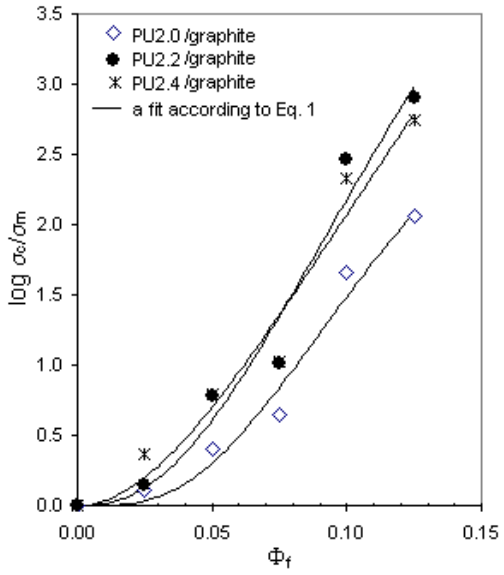

FIG. 1. Electrical conductivity of polyurethane NCO/OH ratio 2.0, 2.2, and 2.4 filled with graphite.

Percolation concentration Φ_c is the concentration of the filler when internal conductive network of particles is formed within the polymer matrix and the material becomes electro conductive. There are many contributing factors involved in the formation of conductive networks in filled polymers. Among the parameters influencing the percolation concentration, the filler distribution, filler shape, filler/matrix interactions and the processing technique are the most important ones. Therefore, prediction of percolation concentration and dependencies of electrical conductivity on the filler content becomes more complicated and difficult [16]. The most prominent models were reviewed by Lux [17]. He has concluded that currently no model exists which can explain all the different experimental results on the percolation process.

TABLE I. The absolute values of the electrical conductivity of composites.

Volume portion of the filler	σ_c (Sm^{-1})		
	2.0	2.2	2.4
0	8.09×10^{-9}	5.18×10^{-10}	4.58×10^{-10}
0.025	1.03×10^{-8}	7.19×10^{-10}	1.07×10^{-9}
0.050	2.07×10^{-8}	3.10×10^{-9}	2.82×10^{-9}
0.075	3.61×10^{-8}	5.34×10^{-9}	4.79×10^{-9}
0.100	3.69×10^{-7}	1.50×10^{-7}	9.81×10^{-8}
0.125	9.23×10^{-7}	4.10×10^{-7}	2.56×10^{-7}
ϕ_c	0.09±0.01	0.09±0.02	0.10±0.03

The summary of percolation concentration (ϕ_c) is stated in the last row.

In this paper, the percolation concentration (ϕ_c) of the filler was calculated according to model [11,12]. Experimental data of electrical conductivity were fitted by empirical function given by Eq. (1) [13,14], which appropriately fits experimental dependencies of electrical conductivity versus volume filler content.

$$\log (\sigma_c/\sigma_m) = B\,(1 - e^{-a\phi_f})^n \qquad (1)$$

B, a, n are adjustable parameters, σ_c is the electrical conductivity of the composites, σ_m is the electrical conductivity of the polymer matrix and ϕ_f is the volume portion of the filler.

The percolation concentration (ϕ_c) of the filler was calculated according to Eq. (2):

$$(\phi_i) \equiv (\phi_c) = (\ln n)/a \qquad (2)$$

where ϕ_i is an inflexion point of the dependence described by Eq. (1).

The results shown Fig. 1 which have been summarized in Table I relate to the effect of graphite concentration on the electrical conductivity of PU composites. From the figure and table, it can be noted that conductivity increases as the content of graphite increases. It is also observed that even a very small graphite amount present in the composites results in a significant conductivity increases.

Percolation concentrations were determined to be as (9±1), (9±2) and (10±3) vol% for the NCO/OH ratio of 2.0, 2.2 and 2.4 respectively. It shows that percolation concentration does not change significantly as the NCO/OH ratio increases. Chemical cross linking can be introduced into PU system by having the NCO/OH ratio greater than 1. When the polymer is highly cross linked,

the chains have higher degree of inter-chain interaction [18]. However, in this case there seems to be insignificant increase in the cross linking and the inter chain interaction between the polyurethanes. It can be suggested that a small amount of plasticizer is present in our sample and the presence of plasticizer should result in smaller experimental crosslink density than those predicted from theory.

IIIb. Dielectric Properties

The complex dielectric constant is usually defined as $\varepsilon^* = \varepsilon' - i\,\varepsilon''$, where ε' is known as real part of permittivity. It is a measure of how much energy from an electric field is stored in a material. The ε'' is the imaginary part of permittivity and is also called as loss factor. It is a measure of how dissipative or lossy a material is to an external electric field. The ratio of imaginary to the real parts ($\varepsilon''/\varepsilon'$) is tan $\tilde{\delta}$.

The relation between real dielectric permittivity and frequency for PU composites of three various NCO/OH ratios are summarized in Table II. From the table, it can be noticed that the dielectric constant decreases as the frequency increases. This phenomenon can be explained as below. PUs are segmented block copolymers consist of alternating hard and soft segments. Soft segments are the polyols and the hard segments are the diisocyanate [19-21]. The hard domains act as filler particles and as crosslinks to restrain the motion of soft segment chains. The soft segment provides elastomeric character for the polymer, while hard segment provides dimensional stability [22]. It is reported that the two incompatible nature of the segments cause Maxwell-Wagner-Sillar (MWS) effects arises when conducting phase is dispersed within a non conducting phase [23,24]. MWS polarization was reported also for commercial polyurethane elastomer, five polyurethanes by Dev [25] and three polyether polyurethanes by North [26]. MWS-relaxation mechanism is due to interfacial polarization related to the existence of soft and hard micro domains with different conductivity [27,28]. Hence, charge carriers will be trapped at the boundaries of the conducting and nonconducting matrix forming space charges. And when the electric field is applied these space charges will orient themselves along the applied field. As the frequency of the applied electric field increases, polarization decreases and therefore the dielectric constant decreases.

Another noticeable aspect is that the value of ε' increases as the graphite concentration is increased but the rate change of dielectric constant at any fixed frequency with the filler loading is not uniform. This behavior could be due to reduction of distance between filler aggregation is not uniform.

Figs. 2a, 2b and 2c show the variation of tan δ with frequency of PU/Graphite composites at three different NCO/OH ratios. For NCO/OH ratios of 2.0 and 2.2, maximum peaks are observed for tan δ of graphite above percolation threshold concentration, ϕ_c, (9±1)% for 2a and (9±2)% for 2b. The tan δ for the graphite concentration below ϕ_c have no significant peak. It is also observed that the peak position shifts to lower frequencies as NCO/OH ratio increases and there is no peak observed for PU composites of ratio 2.4. At the moment, we can not explain the reason being for this phenomenon. Future work will be concentrated on this field.

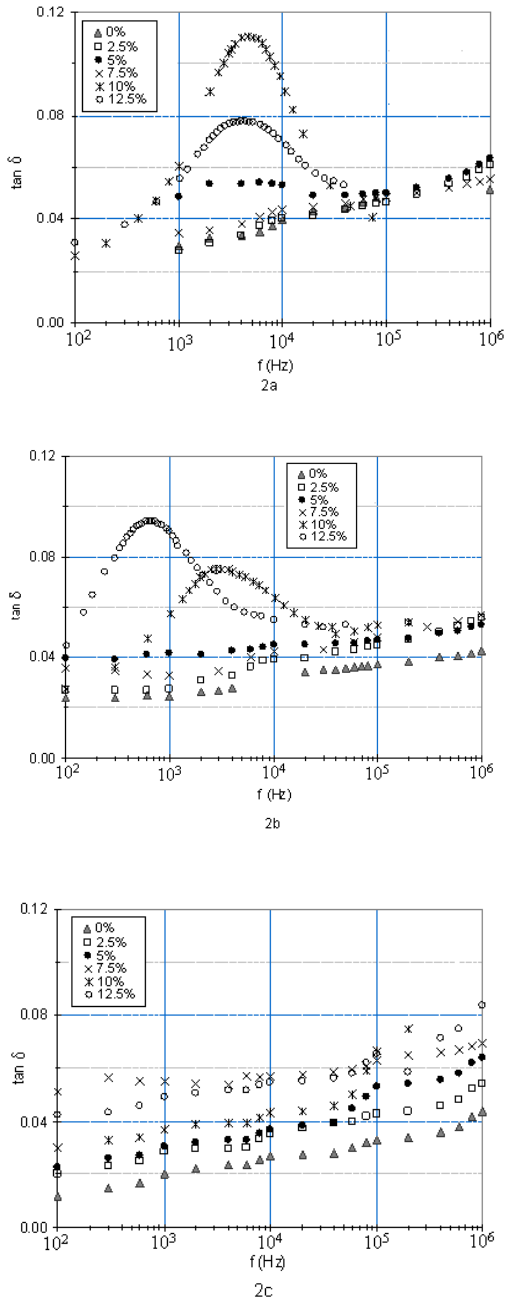

FIG. 2. tan δ versus frequency of various content of graphite powder in PU with NCO/OH ratio (a) 2.0, (b) 2.2, (c) 2.4 .

TABLE II. ε' values of six samples (0%, 2.5%, 5%, 7.5%, 10% and 12.5% graphite) of different frequencies at NCO/OH ratios of 2.0, 2.2 and 2.4.

		Dielectric constant ε'					
		Graphite (vol %)					
NCO/OH	f (kHz)	0.0	2.5	5.0	7.5	10.0	12.5
2.0	1	4.16	4.91	7.25	7.43	8.67	9.51
	10	3.97	4.67	6.66	7.04	7.49	8.40
	100	3.72	4.08	5.77	6.11	7.18	8.05
2.2	1	5.6	6.30	6.85	8.39	8.94	12.14
	10	5.14	6.00	6.02	7.94	7.97	11.65
	100	4.85	5.28	5.62	6.89	7.78	11.21
2.4	1	4.70	5.94	5.68	8.13	10.02	10.18
	10	4.24	5.76	5.47	7.74	9.07	9.49
	100	3.54	5.18	4.92	6.82	7.67	8.08

IV. CONCLUSIONS

In summary, electrical percolation thresholds of PU-graphite composites were found for NCO/OH ratio of 2.0, 2.2 and 2.4. It has been noted that NCO/OH ratio does not influence the percolation concentration of the composites.

Percolation theory has been used to explain the insulator–conductor transition occurring in composite systems when the critical percolation concentration Φ_c is reached. The dynamic electrical properties of PU-graphite compounds were studied over a wide range of frequencies. MWS relaxation mechanism was used to explain the dielectric properties of the composites.

The percolation threshold is distinct from dependences of dielectric constant and also dissipation factor on filler concentration. Peak was found at the dependence of dissipation factor on filler concentration above percolation concentration for PU composites of NCO/OH ratios 2.0 and 2.2.

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