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The investigation of conduction current characteristics of segmented PU elastomers.
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The Investigation of Conduction Current Characteristics of Segmented PU Elastomers

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Abstract: **Polyurethane elastomers (PUs) are a class of multi-phase copolymers commonly composed of polyester or polyether soft segments and urethane hard segments. Microphase separation caused by the thermodynamic incompatibility of the soft segments and the hard segments is believed as the structural basis for many unique properties of PUs, such as shape memory and self-healing. PU is one of the most promising polymers to develop into a new generation of smart self-healing polymer dielectrics due to its shape memory effect and tailor characteristics. Conduction current is not only a basic parameter of dielectrics, but also can reflect many microscopic characteristics of the carrier transport process, which is widely used to investigate the electrical behavior of dielectric materials. The aim of this paper is to report on the conduction current characteristics of segmented PUs.**

PUs with 50% hard segment content were synthesized with polyether polyol, 4, 4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) by a two-step method. The hydrogen bonding interaction of the microphase separation interface is evaluated by the deconvolution of the FT-IR spectra in the carbonyl stretching regions and the amino stretching regions. The charging and discharging behavior of the PU under the applied electrical field strength from 0.2 kV/mm to 1.4 kV/mm is investigated. The results shows that the unique microphase separation structure of PU is a significant reason of interface polarization, leading to an increase in its transient current, which is different from the continuous decay trend of transient currents in most other polymer dielectrics. Meanwhile, when the applied electrical field strength is greater than 1 kV/mm, the measured conduction current is affected by space charge injection, and the discharging current curve shows an increasing peak of heteropolar charge.

I. INTRODUCTION

Segmented polyurethane elastomers (PU) are typical multiblock copolymers that consist of alternating hard and soft segments. Very often the flexible and long soft segments (SS) are made from long chains of polyester or polyether and the polar and rigid hard segments (HS) consist of diisocyanate and chain extender [1]. The thermodynamic incompatibility of the HS and SS results in a unique microphase separated structure of PU at mesoscopic length scales. The HS form physical crosslinks arising from polar interactions, hydrogen bonding and potential crystallization in the hard domain, while the SS form a reversible phase because of molecular motion in the rubbery state [2]. The complex microphase separated structure of PU endows them with a series of versatile and seemingly contradictory properties, such as superior mechanical strength and thermal stability while retaining the shape memory effect and even self-healing capability, which make PU interesting for various applications [3]. Meanwhile, polymer and its composites are increasing used as the main insulating components in various energy applications. However, in the process of manufacture, transportation, and operation, polymer materials are inevitably subjected to long-term electrical, thermal, and mechanical stress, which may cause micro defects in the materials. Researchers are developing self-healing polymers to heal the slight damage in the materials that are traditionally considered irreparable and irreversible [4][5]. Naturally, PU is one of the most promising polymers to develop into a new generation of smart self-healing polymer dielectrics due to its shape memory effect and tailorable characteristics. Additionally, PU is easily recycled when compared to traditional cross-linked polymer, such as XLPE, silicone rubber, and epoxy resin [6]. These two features together will make PU an environmentally friendly insulation material with self-healing property when mechanically or electrically compromised. Hence, a potentially recyclable insulation material to replace that traditional insulating polymer in the longer term.

Conduction current is not only a basic parameter of dielectrics, but also can reflect many microscopic characteristics of the carrier transport process, such as carrier injection, charge trapping and de-trapping, conduction mechanism, and electrical aging threshold, etc., it is widely used to investigate the electrical behavior of semiconductor and dielectric materials [7]. In this paper, the DC conductivity properties of the 50% HS content PU were investigated by measuring the charging and discharging behavior and effective instrumental analysis.

II. EXPERIMENTAL DESCRIPTION

A. Sample Preparation

The PU with 50% hard segment content were synthesized using a bifunctional polyether polyol Arcol 1004 (MW=450, obtained from Covestro), 4,4'-methylene diphenyl diisocyanate (MDI, obtained from Covestro), and 1,4-butanediol (BDO) using a two-step polymerization method. As shown in the **Figure 1**, an NCO-terminated prepolymer was prepared firstly by carefully adding MDI to a reaction vessel containing the appropriate polyols, and BDO was subsequently added for chain extension to obtain PU. Anhydrous tetrahydrofuran (THF) was

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used as solvent to aid with viscosity in the two-step process. The solution was cast into a petri dish with covers and evaporated at 70°C for 24h to obtain thin films typically with a thickness of 700 um. The molar ratio used for this study was MDI: Polyol: BDO = 2.2: 1: 1.2, and the mass fraction of MDI and BDO, the so-called HS content, is controlled at 50%.

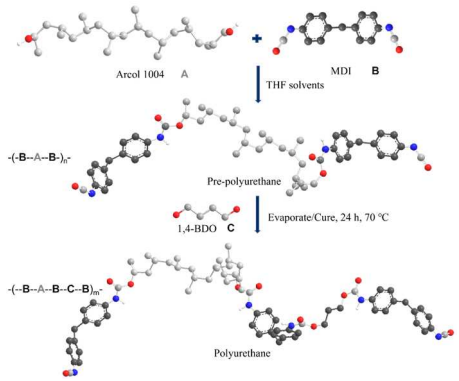

Figure 1. Synthesis route of polyurethane elastomers

B. Conduction Current Measurement

The conduction current measurement system comprises a HVDC supply, electrometer (Keithley 617), measuring electrode, shield enclosure, guard resistance, switch box, as shown in the **Figure 2**. The measuring electrode adopts a three-electrode system for shielding the surface current during measurement. The diameters of the HV electrode, the measurement electrode, and the guard electrode are 20 mm, 10 mm, and 40 mm, separately. Before testing, the sample is placed between the electrodes inside the shielding enclosure and the initial charge condition of the sample and the environmental noise of the test system is established prior to applying any voltage to the sample. There are two stages in the test. The charging current is measured for 30 minutes when the switch S1 is opened and S2 is closed. Subsequently, opening S1 and closing S2, discharging current is tested in the circuit for 30 minutes. The sampling time of the electrometer is set to 400 ms. The current measured for the last 20 mins is averaged every 12 points, since the current stabilizes after 10 mins. The experiment is carried out at room temperature (23℃) and controlled by LabVIEW-based self-programming software.

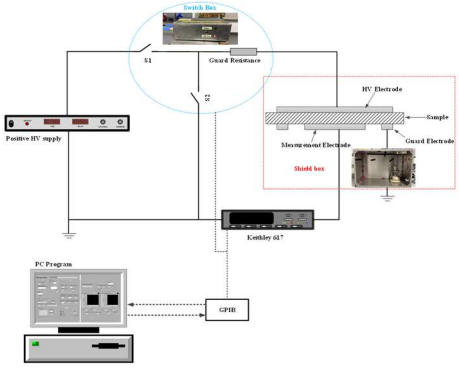

Figure 2. Configuration of conduction current measurement system

III. RESULT AND DISCUSSION

Figure 3 shows the charging current curve over 30 mins for PU with 50% HS content under an electrical field from 0.2 kV/mm to 1.4 kV/mm. The response of a polymer to an electric field is quite complicated. The transient current observed in the external circuit decays continuously in most cases with time until a steady conduction current is reached, due to a series of different dielectric and electrical processes, such as fast and slow dipole orientation, electrode polarization, charge injection etc. Unlike the continuous decay process of transient currents in most dielectrics [8][9], the time-domain characteristics of transient current of PU are different. As shown in the **Figure 3**, the transient current of PU decays sharply to the lowest value around 20 s, and then climbs quickly, reaching a quasi-steady state at about 200 s. After this point the conduction current maintains a slow upward trend with time. Generally, since the various polarizations inside the dielectric tend equilibrium states, the part of the absorption current contributed by the orientation or displacement of molecules always is in the same direction as the conduction current and will decay towards zero. However, a short period of increasing transient current may appear in some double-layered dielectrics because of certain interface polarization behaviors [10]. As a result of the unique micro-phase separation structure, such interface polarization behavior of segmented PU is possible.

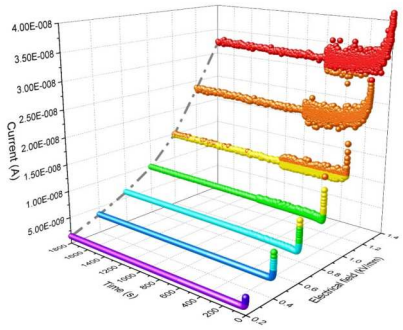

Figure 3. Charging current curve of PU under different electrical field

Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer Spectrum 400 spectrometer) is measured in the range from 3900 cm^{-1} to 1000 cm^{-1} resolution, in order to better understand the microphase separation structure of PU, and the result is shown in the **Figure 4**. The position of the urethane carbonyl absorption is sensitive to the molecular environment of the carbonyl group. Hydrogen-bonded urethanes will absorb around 1705 cm^{-1} whilst free (non-hydrogen-bonded) urethanes absorb around 1730 cm^{-1}. In our case the spectrum shows both free and hydrogen-bonded contributions and deconvolution of the carbonyl region will provide an indication of the relative contribution of each. As free carbonyls in the hard segment or phase-mixed regions, an indicative assessment of the phase morphology can be made. Accordingly, mathematical deconvolution of the carbonyl stretching peak can be used to

divide the free and hydrogen carbonyl [11]. The hydrogen bonding interaction between the carbonyl in soft segments and amino in hard domains also evaluate the degree of phase separation of PU to some extent. A hydrogen-bonded carbonyl stretching peak was found at 1705 cm^{-1} and its relative proportion is 86.63%, which proved the existence of the micro-phase separation structure of the prepared 50% HS PU samples. The abnormal rise of transient current may be due to the influence of the interface polarization behavior between hard domains and soft segments, and similar phenomenon was reported in reference [12].

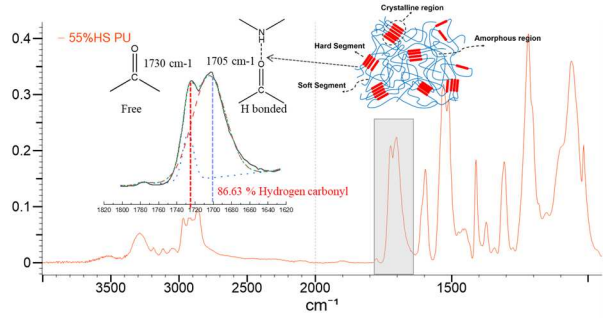

Figure 4. FTIR spectrum of 55% HS PU and deconvolution peak of C=O stretching regions

Besides that, the I-E curve displayed on the YZ plane in the Figure 3 shows obvious nonlinear characteristics. When the applied electrical field is lower than 1 kV/mm, the conductivity of the PU is ohmic, and the conductivity is 3e-11 S/mm. At this stage, the conduction current in PU is mainly composed of intramolecular conduction band transport and intermolecular hopping conduction. The conduction current increases sharply, and the conduction mechanism changes, when the applied electrical field is higher than 1 kV/mm. The injection of space charges could be responsible for the non-linear conductivity, combined with the increasing peaks of heteropolar charge appearing in the discharging current curve in the **Figure 5**. 1 kV/mm is the transition electrical field strength threshold of 50% HS PU. The injection of space charge will accumulate a large number of carriers inside the polymer, thereby, resulting in the non ohmic behavior of the conduction current, when applied electrical field strength is higher than the threshold.

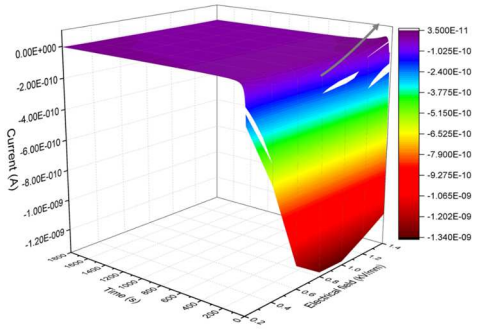

Figure 5. Discharging current curve of PU

IV. CONCLUSION

In this paper, 50% HS content PU with MDI, Arcol 1004, and BDO, is synthesized using the two-step method, and the microphase separation structure between hard and soft domains is evaluated by a detailed analysis of deconvolution FTIR in the stretching carbonyl region. The charging and discharging behavior of the PU under the applied electrical field strength from 0.2 kV/mm to 1.4 kV/mm is investigated. The unique microphase separation structure of PU is a significant cause of interface polarization, leading to an increase in its transient current, which is different from the continuous decay trend of transient currents observed most other polymer dielectrics. When the applied electrical field strength is greater than 1 kV/mm, the measured conduction current is affected by space charge injection, which shows an increasing peak of heteropolar charge in the discharging current curve. The research on the conduction current of PU is quite complicated, especially since it couples multiple polarization behaviors. Hence, the experimental study of PU's dielectric response will be carried out in the next stage.

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REFERENCES

[1] M. V Mokeev, S. A. Ostanin, N. N. Saprykina, and V. V Zuev, "Microphase structure of polyurethane-polyurea copolymers as revealed by solid-state NMR: Effect of molecular architecture," Polymer., vol. 150, pp. 72–83, 2018.

[2] A. V Menon, G. Madras, and S. Bose, "The journey of self-healing and shape memory polyurethanes from bench to translational research," Polym. Chem., vol. 10, pp. 4370–4388, 2019.

[3] C. Yuan, M. Z. Rong, and M. Q. Zhang, "Self-healing polyurethane elastomer with thermally reversible alkoxyamines as crosslinkages," Polymer (Guildf)., vol. 55, no. 7, pp. 1782–1791, 2014.

[4] Y. Yang, Z. Dang, Q. Li, and J. He, "Self-Healing of Electrical Damage in Polymers," Adv. Sci., vol. 2002131, p. 2002131, 2020.

[5] Y. Wang, Y. Li, Z. Zhang, and Y. Zhang, "Effect of doping microcapsules on typical electrical performances of self-healing polyethylene insulating composite," Appl. Sci., vol. 9, no. 15, 2019.

[6] S. Yang, S. Wang, X. Du, Z. Du, X. Cheng, and H. Wang, "Mechanically robust self-healing and recyclable flame-retarded polyurethane elastomer based on thermoreversible crosslinking network and multiple hydrogen bonds," Chem. Eng. J., vol. 391, p. 123544, 2020.

[7] M. Pope and C. E. Swenberg, Electronic processes in organic crystals and polymers. Oxford University Press on Demand, 1999.

[8] D. Das-Gupta, "Conduction mechanisms and high-field effects in synthetic insulating polymers," IEEE Trans. Dielectr. Electr. Insul., vol. 4, no. 2, pp. 149–156, 1997.

[9] S. Diaham and M.-L. Locatelli, "Time and frequency domains dc conductivity analysis in thin dielectric films at high temperature," J. Phys. D. Appl. Phys., vol. 44, no. 10, p. 105402, 2011.

[10] C. Suo, Z. Li, H. Zheng, and Y. Sun, "Dynamic characteristics analysis on interface polarization and depolarization of nonlinear double-layered

dielectrics," IEEE Trans. Dielectr. Electr. Insul., vol. 24, no. 3, pp. 1511–1526, 2017.

[11] A. W. Grzelak, P. Boinard, and J. J. Liggat, "The influence of diol chain extender on morphology and properties of thermally-triggered UV-stable self-healing polyurethane coatings," Prog. Org. Coatings, vol. 122, pp. 1–9, 2018.

[12] P. Ortiz-Serna et al., "Thermal and dielectric properties of polycarbonatediol polyurethane," J. Appl. Polym. Sci., vol. 44, no. 10, p. 105402, 2015.