A literature review of the research on ferroelectric polymers

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Abstract. In this work, the research and development of ferroelectric polymers has been reviewed. The main focus is on properties of different types of ferroelectric polymers. Ferroelectrics of ceramic and thin film nature, are widely known for their use in several electronic devices. But the existence of ferroelectricity in polymers has made the ferroelectric polymers to be used in different electrical applications such as sensors, actuators, etc. The main theme of this paper is to report only the existing literature on ferroelectric-polymeric materials.

Keywords: Ferroelectrics; Polymers; Electrical Properties;

1. Introduction

Since the last 100 years, the synthesis and development of polymers has been really a wow! Because, the growth and use of polymers has surpassed the growth of metals for nearly two decades. It has been identified that, the foundation for the separate science and technology of polymers, has been evolved from plastics, rubbers, fibers, etc. Engineering the polymers chemically helps to develop the compounds of following properties [1]:

- Thinner in nature but relatively contain large mechanical strength
- Good resilience
- Capable of being resistive to corrosion
- Low magnitude of thermal conductivity
- Low magnitude of electrical conductivity
- Optically transparent

The main advantage of producing polymers include the low cost processing. As per the American Council of Plastics, in 2001, the production of thermosets in United States is nearly 3638 x 10^6 kg. The total production of thermoplastics is around 36571 x 10^6 kg. It almost covered the 78% total production of polymers [1]. Also, the polymers called as polyblends, have been developed by combining more than one plastic.
Examples include polycarbonate-acrylonitrile, polycarbonate-polybutylene terephthalate, etc. They possess good resistance to heat and chemicals, and exhibit high toughness. The applications of polymers include the industries of computers, aerospace, automobiles, and others. The polymers reinforced with glass, fibers, etc. have also been developed for the use in applications of above mentioned industries. The early usage of polymers was mainly for the electrical and thermal insulation. Because they exhibit low electrical and thermal conductivity. Hence, they were widely used as insulated electrical cables. In recent years, the research focus is mainly on the development of polymers that are ferroelectric in nature [1].

Based on the existing literature of polar polymers that are amorphous in nature, it has been identified that they exhibit large values of energy density and low values of loss (below their glass transition temperature). In the case of liquid polymers that are crystalline in nature, dipoles respond at relatively low electric fields resulting in the saturation of dipoles orientation [2]. This shows that, the electrical energy that can be stored could be less. Majorly, ferroelectric polymers are divided into three different types (as shown figure 1)

![Figure 1: Classification of ferroelectric polymers](image)

For the first kind of polymers i.e. normal polar polymers, the values of polarization are very high resulting in the large ferroelectric hysteresis loops. For the paraelectric kind of polymers, dipoles can orient them along the field when applied, but their reversibility was found to be difficult. Hence, paraelectric polymers does not suit high energy density and relatively low loss applications. The third kind of polar polymers is novel ferroelectric polymers. They are further divided into relaxor and non-relaxor ferroelectric polymers. To obtain relaxor behavior for ferroelectric polymers, bulky comonomers (i.e. a structural defect) can be created such that the lattice structure would expand. This results in the increase of dimensions of unit cells. Also, the reversibility of the dipoles become fast. So, these kind of polymers can be made useful for the applications of high energy density and low loss. It has been identified that the polymers of anti-ferroelectric nature are yet to be made [2].

2. Literature Discussion

Due to the extensive use of polymers as electrical insulators, polymers prepared through synthetic routes are considered as the materials that are passive electrically. Also, electrically active polymers have also been developed for use in electric circuits. But most of these polymers are found to be piezoelectric in nature. Then polar (non-centrosymmetric) and non-polar (centrosymmetric) polymers have been synthesized. Polyvinylidene fluoride is one of the famous ferroelectric polymer [3].

2.1. About Ferroelectricity in Polyvinylidene fluoride

Initially, presence of piezoelectricity was discovered in Polyvinylidene fluoride. Later, it has been established as a versatile ferroelectric material. To support the ferroelectric nature of Polyvinylidene fluoride, ferroelectric phase transitions and hysteresis loops were observed. The Curie temperature ($T_c$) was found to be 205 °C. It means that the transition of phase from ferroelectric to paraelectric occurs at the temperature that is above the melting point. The value of $T_c$ was not confined to 205 °C, but fluctuates
around ± 30 °C. Another polymer, polyfluoro carbon, exhibit the same structure of Polyvinylidene fluoride, but no data is shown in the literature indicating the ferroelectricity [3].

2.2. Literature on Ferroelectric Polymers

In one of the work by P. Gljthner and K. Dransfeld [4] poly(vinylidene fluoride trifluoroethylene), {P(VDF-TrFE)} was locally polarized by using a SFM and a bottom electrode for the polymeric film of P(VDF-TrFE). A phase transition of first order was observed for crystalline films of P(VDF-TrFE) and was found to be of similar value as compared to bulkby V. Bune et. al [5] for a monolayer film. A well-studied ferroelectric polymer, poly(vinylidene fluoride trifluoroethylene) [P(VDF-TrFE)] was studied for its electrocaloric effect (ECE) by Brez Neese et. Al [6], and was found large above Tc. This happens because this polymer induced a big change in its dipolar ordering because of applied field. Chang-Chun Wang et.al [7] used conductive (Polyaniline) to modify P(VDF-TrFE) and found that the electrical properties, such as $\varepsilon$ increased 50 times and requirement of field for switching of spontaneous polarization decreased.

In another work, [8] the ferroelectric polymer, P(VDF-TrFE) was modified by Junjun Li et. al, with TiO2nano fillers andter trifluoroethyleneter. It was found that both modifications gave similar $\varepsilon$ of 42 and 47. Both modified polymers showed changes in microstructure and a significant increase polarization values at high fields.

The polarization reversal mechanism of PVDF-TrFE was investigated by Pankaj Sharma et. al. [9] and they observed a different behavior of domain switching from solid state ferroelectrics. Lianyun Yang et. al [10] showed formation of nano domains using e-beam radiation by pinning of polymer chains. Solution casting was used by Hamed Sharif Dehsariet. al. [11] to produce cost-effective flexible memory devices made of P(VDF-TrFE), but the devices were of low-yield. Yang Liu et. al. [12] in their work on ferroelectric polymer P(VDF-TrFE) found intramolecular conformational issues between 3/1 helical phases and trans planar of P(VDF-TrFE) for the purpose of MPB formation.

| S.No. | Year | Description | Reference |
|-------|------|-------------|-----------|
| 1.    | 1983 | Piezoelectric Polymers have received appreciable importance in electric circuits. | 3         |
| 2.    | 1983 | Polyvinylidene fluoride was found to be a suitable piezoelectric polymer for electronic applications | 3         |
| 3.    | 1983 | Ferroelectric phase transition has been observed in Polyvinylidene fluoride | 3         |
| 4.    | 1983 | Piezoelectric polymer, polyfluoro carbon, has been synthesized. But no sign of ferroelectricity was identified! | 3         |
| 5.    | 2008 | Electrocaloric properties were investigated for poly(vinylidene fluoride trifluoroethylene) | 6         |
| 6.    | 2008 | A conductive (Polyaniline) has been used to modify the dielectric properties of poly(vinylidene fluoride trifluoroethylene). It is found that the dielectric constant has been increased by 50 times | 7         |
| 7.    | 2009 | Poly(vinylidene fluoride trifluoroethylene) was modified by TiO2nano fillers andter trifluoroethyleneter, to see the changes in dielectric constant values of the polymers | 8         |
Nan Menget al [13] explained that since domain walls are not responsive to high frequencies, the dielectric constant of extruded films at very high frequencies will be very low. This work was done on (PVDF-TrFE). In this work along with terahertz time-domain spectroscopy, impedance analysis was done to understand electric polarization of polymers at different length scales. Another ferroelectric polymer, PVDF, was reviewed by Xin Chen et al. [14] and found it to be highly biocompatible, with multifunctional capabilities and was easy to process!! In a review on poly(vinylidene fluoride) (PVF2) as a polymeric ferroelectric by MICHAEL A. MARCUS [15] shows its classification based on many transduction mechanisms such as electrical to mechanical and vice versa; thermal to mechanical, etc. of polymeric ferroelectrics. Yang Liu et al. [16] showed the difference between ferroelectric polymer and perovskite relaxors. The classic relaxors are characterized by chemical disorder whereas polymer’s relaxors behavior comes from the conformational disorder. The relaxor properties of polymers arises from chain chirality, which leads to the disordered (helix) confirmation. A perspective, on the orientational polarization of polymeric materials, has been discussed very well [17]. Based on the existing literature of polar polymers that are amorphous in nature, it has been identified that they exhibit large values of energy density and low values of loss (below their glass transition temperature). For first time, it was shown by J Sch¨utrumpf et.al [18], that the IFM (inhomogeneous field mechanism) can be used for both semi-crystalline polymers and ferroelectric ceramics. Even though the IFM model was primarily developed for PZT. Saleem Anwar and Kamal Asadi [19] showed that δ-PVDF can be a suited for microelectronic applications because of its fast switching dynamics and low voltage operation. This is possible because of high domain wall mobility in δ-PVDF when compared to aconventional ferroelectric and β-PVDF. Junjun Li et.al [20] studied the modification by BaTiO3 nanoparticles of polymer matrix for energy storage application of ferroelectric polymers. Lewis F. Brown [21] recommended advance studies in developing technology for ferroelectric polymer device fabrication in a review article [21]. Some of these techniques can be direct polymer deposition and multi-layer film fabrication. He also reviewed high frequency ultra sound applications of ferroelectric polymers in applications such as structural nondestructive testing, medical ultrasound and health monitoring.

3. Conclusions

• Large ferroelectric hysteresis loops can be observed for normal ferroelectric polymers
• Defects should be introduced into the polymers, for achieving relaxor behavior.
• Dielectric constant of magnitude 42, is achieved for ferroelectric poly(vinylidene fluoridetritrifluoroethyleneter-chlorotritfluoroethylene)
• The electrical properties of poly(vinylidene fluoride-tertrifluoroethyleneter can be altered by conductive (Polyaniline) nanofibers
• It is recommended to carry out intense investigations on paraelectric polymers.
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