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Thickness Dependent Dielectric Loss of Plasma Poly (Ethylene Oxide) Films

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Abstract: Dielectric properties of plasma poly (ethylene oxide) (pPEO) thin film samples were investigated at room temperature. The thin film samples with different thicknesses were deposited by plasma assisted physical vapor deposition (PAPVD) technique at 5 W plasma discharge power. The thicknesses were 20, 100, 250, 500 nm. It was observed that dielectric constant increases with increasing thickness. The relaxation times determined by dielectric loss-frequency relation, shift toward higher frequencies with increasing thickness. In addition film thickness, heating processes were defined as another parameter. By this purpose, thin film samples were heated and cooled, respectively. It was observed that maxima and minima of dielectric loss at cooling process take place at lower frequencies in comparison with frequencies at which maxima and minima were detected at heating process. These results may show the effect of dead layer at thinner films. After heating process, it was observed from behavior of dielectric constant and dielectric loss that the crosslinking density increases by heating effect. This effect may cause additional reactions between free radicals which are production of PAPVD. Moreover, dynamic glass transition temperatures were calculated. These temperatures prove the effect of dead layer approximation.

Keywords: Plasma poly (ethylene oxide), thin film, dielectric properties, dynamic glass transition temperature.

Plazma Poli(etilen oksit) Filmlerin Dielektrik Kaybının Kalınlığa Bağlılığı

Özet: Plazma poli (etilen oksit) (pPEO) ince film örneklerinin dielektrik özellikleri oda sıcaklığında incelendi. Farklı kalınlıklardaki ince film örnekleri, 5 W plazma boşaltma gücünde plazma destekli fiziksel buhar depozisyonu (PAPVD) tekniği ile elde edildi. Film kalınlıkları 20, 100, 250, 500 nm'dir. Artan film kalınlığı ile dielektrik sabitinin arttığı gözlenmiştir. Dielektrik kayıp ve frekans ilişkisi ile belirlenen relaksasyon zamanları, artan kalınlık ile daha yüksek frekanslara kaymaktadır. Film kalınlığına ilaveten, ısıtma süreçleri bir diğer parametre olarak tanımlandı. Bu amaçla, ince film örnekleri sırasıyla ısıtılmış ve soğutulmuştur. Soğutma sürecindeki dielektrik kaybın maksimum ve minimumunun, ısıtma sürecindeki maksimum ve minimumunun belirlendiği frekanslardan daha alçak frekanslarda meydana geldiği gözlenmiştir. Bu sonuçlar, daha ince filmlerde ölü tabakanın etkisini gösterebilir. Isıtma sürecinden sonra, dielektrik sabiti ve dielektrik kayıp davranışından, çapraz bağlanma yoğunluğunun ısıtma etkisiyle arttığı gözlenmiştir. Bu etki PAPVD'nin ürünü olan serbest radikaller arasında ek tepkimelere neden olabilir. Ayrıca dinamik camsı geçiş sıcaklıkları hesaplandı. Bu sıcaklıklar ölü tabaka yaklaşımı etkisini ispatlamaktadır.

Anahtar Kelimeler: Plazma poli (etilen oksit), ince film, dielektrik özellikler, dinamik camsı geçiş sıcaklığı.

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1. INTRODUCTION

In recent days, polymers became row materials in electrical and electronic devices as insulating materials [1-7]. Poly (ethylene oxide) is an attractive member of this family with its biological non-fouling properties [8]. Poly (ethylene oxide) can have developed and modified properties as homogeneity, free from pinholes, water insolubility, high electrical resistance, chemical stability, high cross-linking density, good adhesion and thermal stability by plasma polymerization [7, 9-12]. High crosslinking density is one of important reasons of good non-fouling properties. Crosslinking density can be investigated by some techniques such as differential scanning calorimetry (DSC), X-Ray photoelectron spectrometry (XPS), Fourier transformation infrared spectrometry (FTIR) and mass spectrometry (MS). Especially DSC is a useful technique to analyze the crosslinking and its result via detecting glass transition temperature. Although the technique is a good way to determine glass transition and change of crosslinking density, it unable to analyze the glass transition temperature depending on the thickness of plasma polymer thin film. Dielectric spectroscopy can be used to determine the glass transition temperature via dielectric properties [11-14]. In this work, the dielectric properties of plasma poly (ethylene oxide) thin films deposited at 5W plasma and at various thicknesses as 20, 100, 250, 500 nm were analyzed. In literature it was found that the thickness dependent dielectric properties of plasma poly (ethylene oxide) thin films were not investigated. In addition to investigation of dielectric properties, we aimed to determine the glass transition temperature and analyze the effect of dead layer which is a result of good adhesion of crosslinked surfaces onto substrates.

2. EXPERIMENTAL

Plasma PEO thin film samples were deposited between alumina (Al) thin film electrodes by plasma assisted physical vapor deposition (PAPVD) method. Al thin film electrodes were deposited by thermal evaporation method. Thin film samples were deposited on glass substrates. All samples were deposited at 5 W radio-frequency (RF) plasma power in different thickness as 20 nm, 100 nm, 250 nm, and 500 nm. Dielectric spectroscopy measurements were performed by Alpha-N high frequency Impedance analyzer (Novocontrol Co.) in frequency range between 0.1 Hz and 10^7 Hz and temperature range between 173 K and 353 K.

3. RESULTS and DISCUSSION

It is known from literature that the vapor of PEO undergoes a fragmentation under the influence of plasma discharge. This fragmentation causes production of free radicals and oligomers as CHO+, CH_3O+, C_2H_5O+, C_3H_7O+ ions and CH_3COH, CH_3 O CH_3, CH_3 CH_2OH, CO_2 groups [15, 16]. Oligomers and free radicals re deposited on substrate randomly and a new structure so called plasma polymer with high crosslinking is produced. Frequency dependence of dielectric constant (ε') for different thicknesses at first cooling process is presented in Fig. 1 a, b, c, d. For a comparison, frequency dependence of ε' for different thicknesses at second cooling process is presented in Fig.2 a, b, c, d.

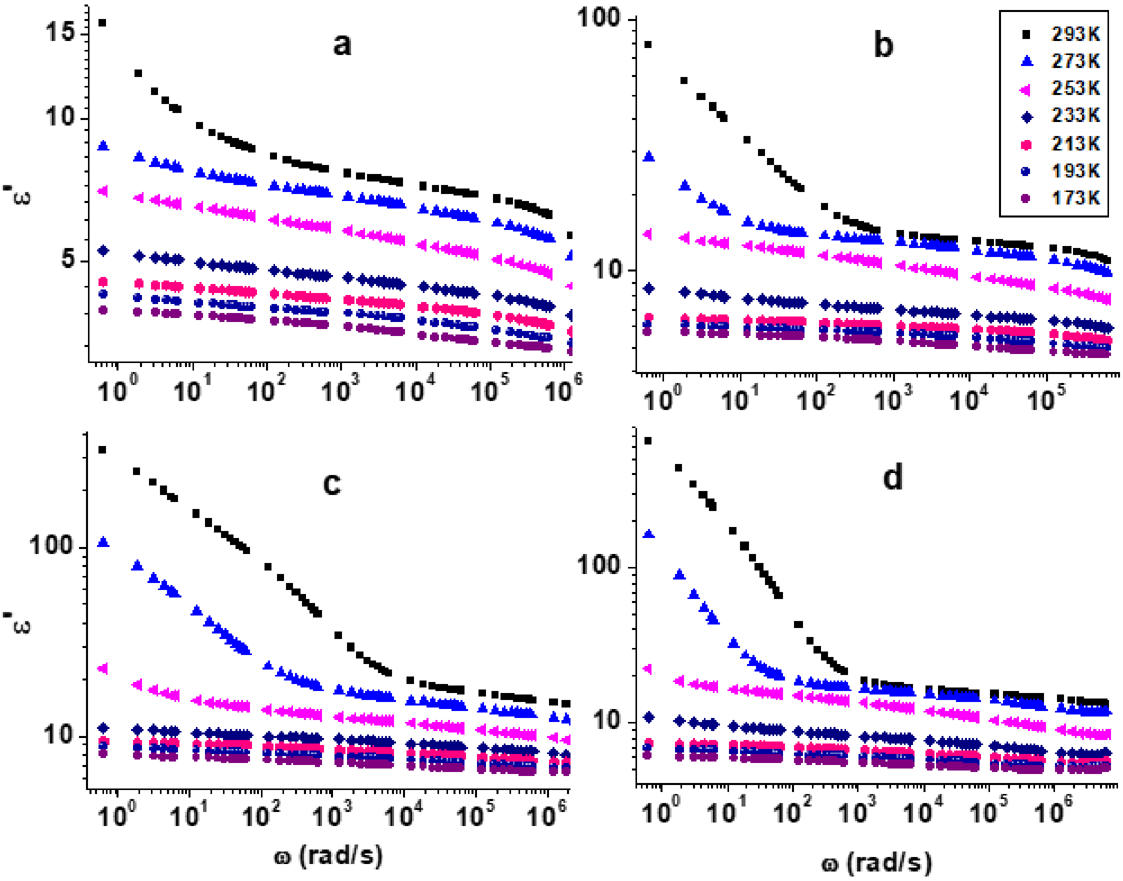


Figure 1. Frequency dependence of dielectric constant (ε') for a) 20 nm, b) 100 nm, c) 250 nm, d) 500 nm at first cooling process.

Dielectric constant decreases with increasing frequency as shown in Fig.1. This behavior can be attributed that the polymer back bone and side chains can’t follow the applied electric field toward high frequencies. Thus, the polarization in structure decreases and proportionally the dielectric constant decreases [17]. Additionally, the dielectric constant increases with increasing temperature as shown in Fig.1. Since increasing temperature may cause increase in motion of polymer back bone and side chains, the polarization increases [18]. Increasing thickness shows increasing effect on dielectric constant as shown in Fig.1. The number of dipoles increases with increasing thickness [19]. In both temperature processes it is observed that there are two relaxation regions in the investigated frequency range. The mechanism observed at low frequency side and at high temperatures is called as α-relaxation which is attributed to phase transition of structure from rubber state to glassy state. The other mechanism observed at high frequency side and at low temperatures is called as β-relaxation which is attributed to dipolar fluctuation of side chains [20-26].

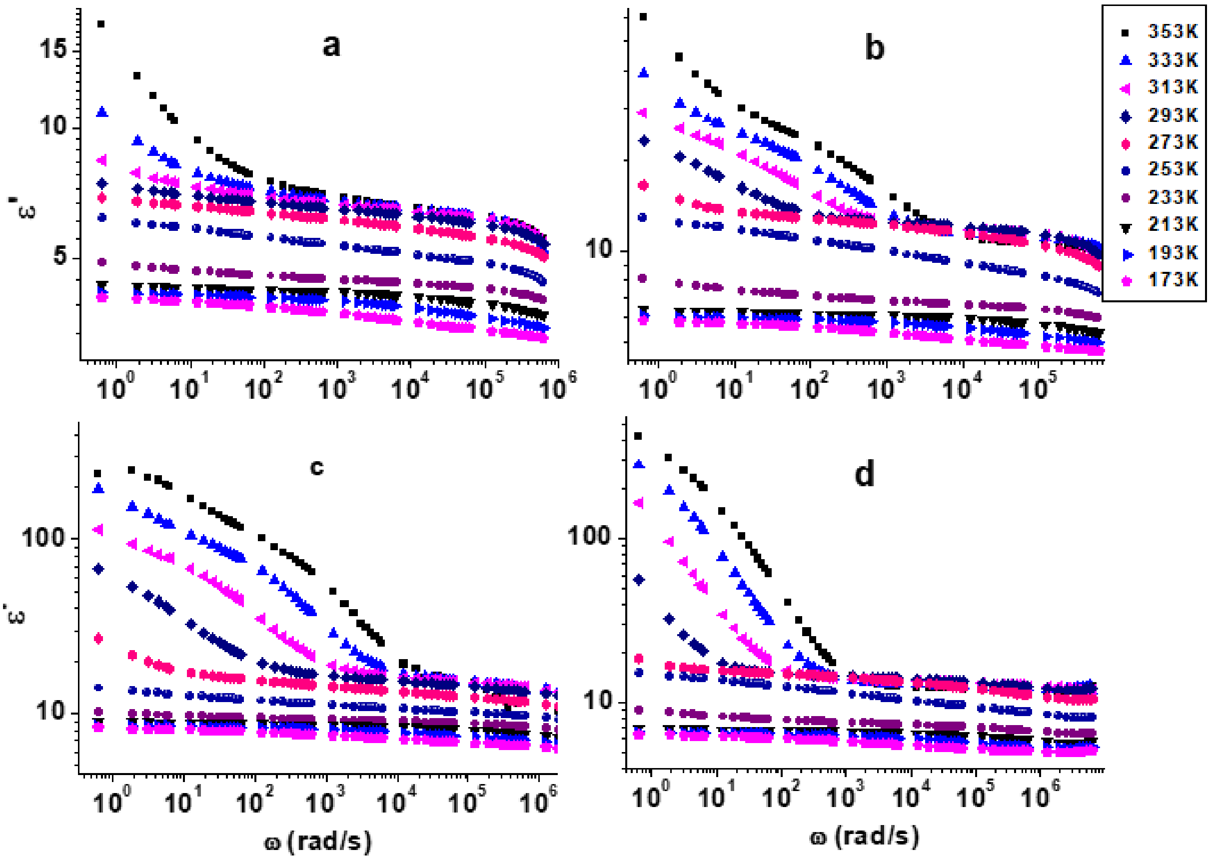
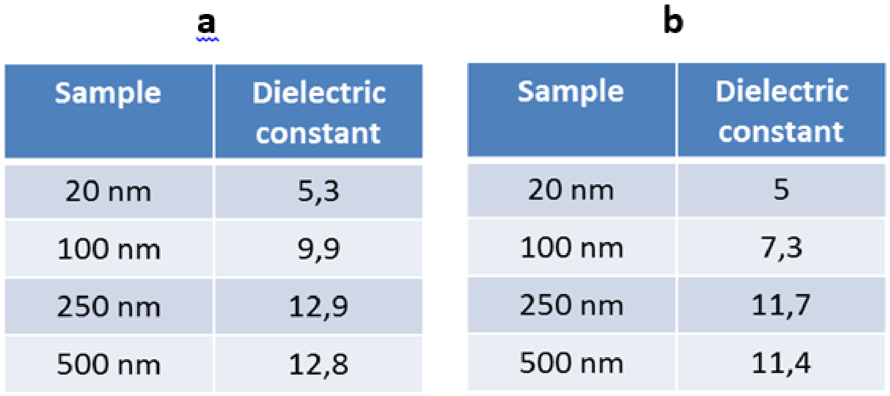


Figure 2. Frequency dependence of dielectric constant (ε') for a) 20 nm, b) 100 nm, c) 250 nm, d) 500 nm at second cooling process.

It can be detected that the dielectric constants measured at first cooling are greater than the dielectric constants measured at second cooling. It is expected that there are still some active free radicals at the end of deposition. When a heating is applied after the first cooling, it is possible of production of new crosslinking by the effect of temperature. Thus, at second cooling the crosslinking density may be more than the crosslinking density at first cooling. This difference can be clearly observed with the difference between dielectric constants as shown in Table 1 a, b.

Table 1. Dielectric constant for different thicknesses at a) first cooling, b) second cooling.



a

Sample	Dielectric constant
20 nm	5,3
100 nm	9,9
250 nm	12,9
500 nm	12,8

b

Sample	Dielectric constant
20 nm	5
100 nm	7,3
250 nm	11,7
500 nm	11,4

Dielectric loss exhibits two relaxation regions in the investigated frequency range as shown in Fig. 3 and Fig. 4. The relaxation which is observed at low frequencies so called α-relaxation can be attributed to dynamic glass transition. The other relaxation so called β-relaxation can be attributed to dipolar fluctuations [21-24]. These relaxation regions shift toward high frequencies with increasing temperature as shown in Fig. 3 a, b, c, d and Fig. 4 a, b, c, d. This behavior may be attributed that the motion of α and β-relaxations can follow the applied electric field at higher frequencies with increasing temperature [25, 26].

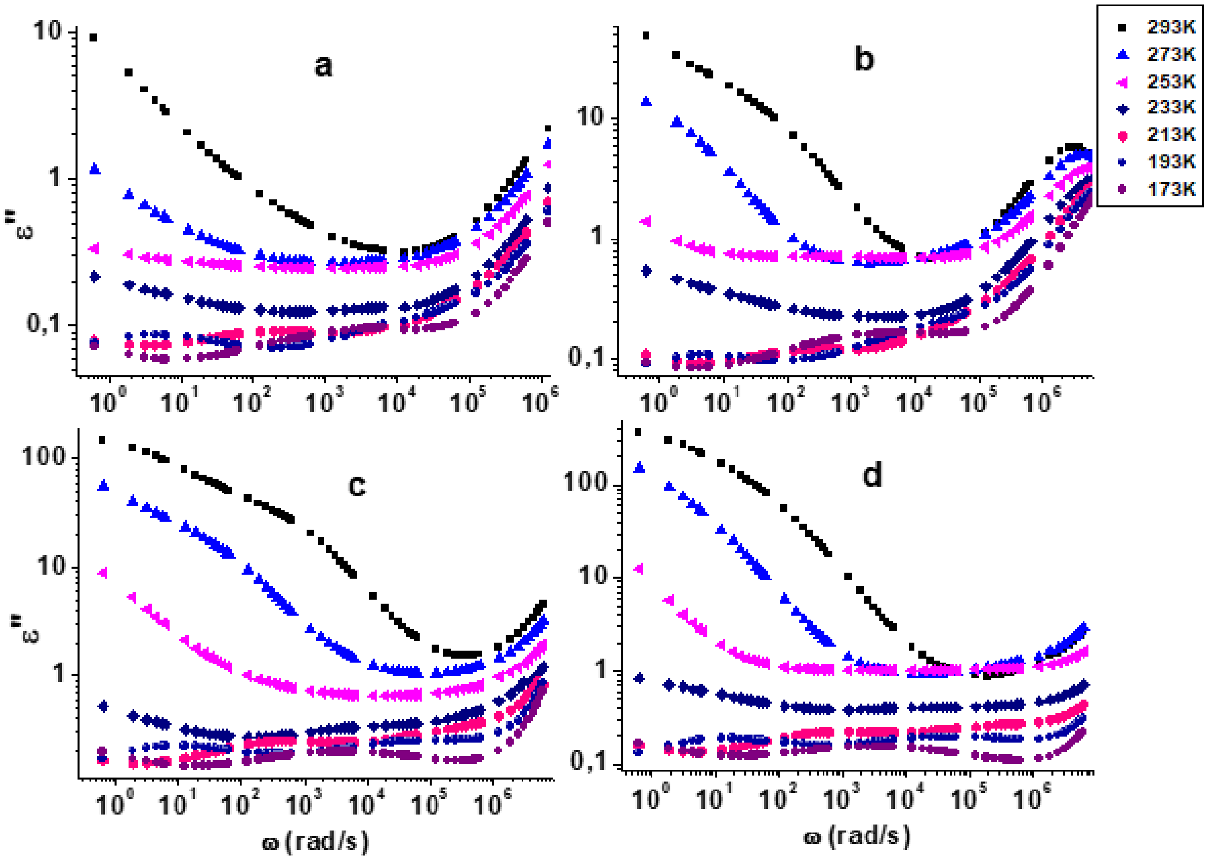


Figure 3. Frequency dependence of dielectric loss (ε´´) for a) 20 nm, b) 100 nm, c) 250 nm, d) 500 nm at first cooling process.

At second cooling process, the temperatures at which α-relaxation observed shift toward low temperatures with decreasing thickness as shown in Fig. 4 a, b, c, d. When the thickness of the samples decreases, the effect of dead layer may be pronounced and as a result of this α-relaxation can’t follow the applied field at higher frequencies.

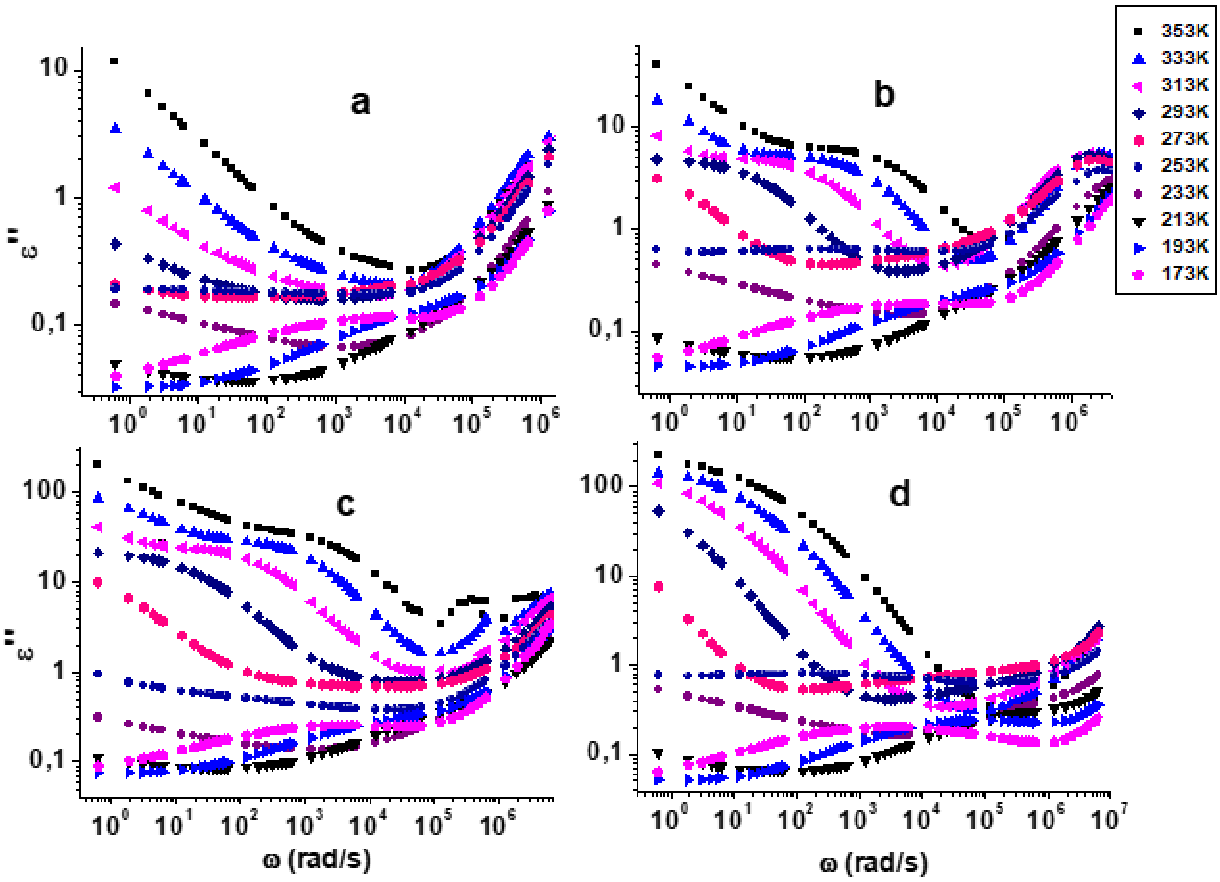


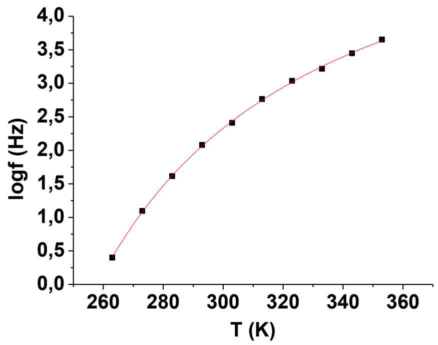
Figure 4. Frequency dependence of dielectric loss (ε”) for a) 20 nm, b) 100 nm, c) 250 nm, d) 500 nm at second cooling process.

When the frequencies at which maximum dielectric loss observed are fitted by Vogel-Fulcher-Taman equation, dynamic glass transition temperatures were calculated by equation below [1],

$$f_{p,\alpha} = f_{\infty} \exp\left[-\frac{B}{T - T_0}\right]$$

Glass transition temperature increases with decreasing thickness. The calculated glass transition temperatures and a representative graph showing the relation between peak frequencies and temperature are shown in Table 2.

Table 2. Dynamic glass transition temperatures at heating and second cooling processes.



Sample	To (Heating)	To (Second cooling)
20 nm	242 K	282K
100 nm	195 K	201 K
250 nm	196 K	200 K
500 nm	174 K	211 K

It is observed that glass transition temperature increases with decreasing thickness. Plasma polymers have adhesion ability onto substrates. The adhesion layer so called dead layer is the most adhesive layer of structure. Dead layer has more fluency on thin film if the thickness is low. The low dielectric constant for thinner films supports the presence of dead layer [27, 28].

4. CONCLUSION

Frequency, temperature and thickness dependence of dielectric properties of pPEO thin film samples at first cooling and second cooling processes. It was observed that the crosslinking density has influence on dielectric properties. At second cooling process, it was observed by decreasing dielectric constant and increasing glass transition temperatures. This change was attributed to increasing crosslinking density due to catalyzing effect of temperature on free radicals. It is thought that more free radicals reacted with each other and raised the number of crosslinking by the effect of temperature. The glass transition temperatures were calculated using the relation between peak frequencies at which maximum dielectric loss observed and temperature. The calculated glass transition temperatures exhibit a behavior associated with interpretation about dead layer approximation as mentioned in literature. This association gives us an idea that we can use dielectric spectroscopy and VFT equation to determine glass transition temperature in thin film form.

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