TSDC studies of LASER irradiated and unirradiated PVDF composites doped with Pd(II) benzimidazole complex

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Abstract— The influence of both metal complex and laser radiation on a ferroelectric polymer PVDF is studied by means of the thermally depolarization stimulated current (TSDC) technique and fourier transformer infrared (FTIR) Dicholoro analysis. Palladium pyridyl benzimidazole is added to PVDF in a trial to form polymer-metal complex composites. Different concentrations of metal complex (1% and 3% by weight) are added to PVDF. TSDC experiment is used to study low frequency relaxations in the investigated samples. Initial rise and peak shape methods are the techniques used in determination of the activation energy followed by detection of both relaxation time and frequency for different transitions. Afterwards, different laser energies are shined on PVDF/metal complex composite of concentration 1% and TSDC analysis was applied to investigate the induced changes.

Keywords—PVDF; Benzimidazole; TSDC; Laser irradiation.

I. INTRODUCTION:

Dicholoro Palladium pyridyl benzimidazole, is one of the newest metal complexes have been discovered lately in a trial of researchers to reduce side effects of cisplatin as anticancer drug. The benefits of these complexes are reduced toxicity, increased clinical effectiveness, and larger spectrum of action, increased solubility and the ability to combine with other drugs [1]. These complexes can be added to polymer to produce a new class of polymer composite material known as; composites of polymer-metal complexes. Polymer-metal complexes composites can enhance polymer properties to achieve characteristics that cannot be achieved by a single polymer system [2]. These composites can be employed in a variety of applications including; polymer grafts, organic synthesis, pollution control, hydrometallurgy, etc. In addition, they offer a lot of advantages in terms of improving polymer properties [3], [4].

One of the unique ferroelectric polymers which can be used in these fields is Polyvinylidene fluoride (PVDF). Neat PVDF is semicrystalline thermoplastic polymer and features as a one-of a kind combination of mechanical and electrical properties (i.e., piezoelectricity). Furthermore, it is extremely Magdy M Omar <u>magdymomar@gmail.com</u> Emad Mousa <u>emad@sci.cu.edu.eg</u> Reham Osama <u>Reham31000@gmail.com</u>

pure, has low water absorption, shows high dielectric strength, displays good thermal stability, and possesses high resistance to most chemicals including; solvents, acids, and hydrocarbons [5]. PVDF comes in five different crystalline forms; alpha (generated from melt crystallization in the melting process), beta (result from mechanical deformation of the specimen via uniaxial or biaxial mechanical drawing below 70 °C), gamma (appear from crystallization at temperatures near the melting point of the alpha phase via melt casting or solution casting), delta, and epsilon. The most commonly used form is the beta phase, and together with the alpha and gamma phases they constitute the major phases [6].

In order to study the change in polymer characteristics by adding metal complexes, studying of the dielectric relaxation processes in amorphous and crystalline polymers constitutes can be used [7], [8]. The experimental method mostly retained for this analysis is the thermally stimulated depolarization current (TSDC) technique. TSDC is a flexible approach for studying material ageing effects. Because of its high sensitivity, ease of use, low equivalent frequency of roughly 10^{-3} Hz, and ability to resolve complex dielectric transitions; it is a potent technique [9]–[12]. A lot of factors are affecting TSDC process such as (i) polarizing temperature T_P, (ii) polarizing time t_p, (iii) polarizing field E_P, (iv) heating rate, and (v) electrode material [13]. In general, polymer TSDC spectra are complicated, and single peaks are usually resolved using either peak cleaning or thermal sampling techniques.

For decades, researchers have been interested in the interaction of lasers with polymer materials to produce surface modification and ablation. Polymeric materials have been employed in high-performance photonic devices and engineering applications such as micro/nanofluidics channel manufacturing, micromachining/microdrilling, splitters, waveguide gratings, and filters, as well as optical waveguide fabrication [14], [15].

In a nutshell, we aimed in the present work to study the relaxations exhibited in newly prepared PVDF/ Dicholoro Palladium pyridyl benzimidazole composite using TSDC spectra.

II. EXPERMINTAL:

MATERIALS:

PVDF (Mw = 180,000 g mol⁻¹, pellets) was purchased from Sigma Aldrich. Dicholoro Palladium pyridyl benzimidazole was synthesized as mentioned elsewhere [1]. Dimethyl sulfoxide (DMSO) was supplied by ADVENT.

FILM PREPARATION:

1 GM OF PVDF WAS DISSOLVED IN 20 ML OF WARM DMSO WITH CONTINUOUS STIRRING FOR 1 H. APPROPRIATE AMOUNTS OF METAL COMPLEX (0%, 1%, AND 3% BY WEIGHT OF PVDF) WAS DISSOLVED SEPARATELY IN 10 ML OF DMSO TILL COMPLETE DISSOLUTION, AND THEN MIXED WITH THE POLYMER SOLUTION. THE FINAL MIXTURES WAS POURED ONTO GLASS PETRI DISHES AND LEFT IN OVEN AT 80 °C FOR 72 H.

MEASUREMENT TECHNIQUE:

ATR-FTIR measurements were performed using Alpha Bruker instrument in the wavenumber region 400-4000 cm⁻¹.

A silver paste coated polymer discs was located between two electrode plates. The sample was heated by an automatically regulated electrical oven till a temperature T_p=70 °C, which is usually higher than the polymer's T_g. As the sample reached T_p, a DC field of EP=17KV/cm was applied across the plates of electrode using a DC power supply (200 V) for a period of t_p=30 min. After t_p the sample left to cool till T_r =30 °C, and then the sample was short circuited for a certain time (15 min) to get rid of any residual static charges. Finally, the sample was attached to a Keithley pico-ammeter and heated at a uniform rate of 1 °C/min. Typically, the depolarization current was monitored as a function of temperature and TSDC thermograms were extracted.

III. RESULTS AND DISCUSSION:

FTIR analysis:

Samples of pure PVDF and with metal complex loadings of 1% and 3% (by weight) were subjected to FTIR measurements as well. In Figure (1), it can be observed that at the first sight all observed peaks remain almost at the same the locations whereas their sizes are changed.





Figure 1(a-d). FTIR of PVDF loaded with (a) 0% (b) 1% (c) 3% and (d) laser irradiated 1% metal complex.

At the moment the absorbance maxima at 840 and 1276 cm⁻¹ confirm the ß-phase of the neat PVDF, the spectral lines for the neat PVDF sample (c.F. Figure 1a) are characterized by the upcoming molecular vibrations [16].

The long trans-sequence of the ferroelectric β -phase of PVDF was detected at the spectral range 1240-1400 cm⁻¹. Rocking vibration of the ρ CH2 was observed at 873 cm⁻¹ [17].

In addition, the stretching vibration of –CF2 and the twisting CH2 vibration of PVDF were observed at 973 cm-1 and 1070 cm⁻¹, respectively [18].

Moreover, the different bands in neat and composite samples are observed in Figures (1 a-d). The FTIR spectra of filled PVDF samples do not show any major changes in bands except some increase in the intensity of bands were observed. To determine the percentage of beta crystalline phase in each sample, the absorption peak of α and β phases, respectively, at wavenumbers 840 cm⁻¹ and 766 cm⁻¹ are evaluated. Using equation (1), one can calculate the percentage of β -crystalline phase R(β), where S α and S β are the absorption at 766 cm⁻¹ and 840 cm⁻¹ and C α and C β are crystalline rate of the α and β phases [19], [20].

$$R(\beta) = \frac{C\beta}{C\alpha + C\beta} x 100 = \frac{S\beta}{S\alpha + S\beta}$$
(1)

All results are tabulated in Table (1). From Figure (1a-d), one can see that with increasing metal complex particles, the percentage of ß-crystalline decreases.

Table (1): F	-TIR re	esults o	of neat	and	metal	complex	
loaded PVDF s	sample	s.				-	

Metal complex	Absorption peak		R(ß)	R(a)	
(wt%)	Sα	Sß			
0%	0.006	0.014	68.67%	30.34%	
1%	0.014	0.016	52.6%	47.38%	
3%	0.015	0.017	53.5%	46.48%	
Irradiated sample	0.016	0.018	52.9%	47.05%	

TSDC analysis:

Thermal stimulated depolarization current (TSDC) analyses of PVDF/metal complex composite samples were carried out under different experimental conditions (i.e. poling temperature, poling field, poling time, and laser exposure). Therefore TSDC results will be discussed in two different sections each for before and after laser exposure, respectively.

TSDC spectra before laser exposure:

A) Effect of poling field:

The characteristics of TSDC thermograms for PVDF polarized at constant temperature and different polarizing fields of (17, 25, and 33 kV/cm) are shown in Figure (2). Under the effect of an electric field, the alignment of dipoles and the formation of space charge or injection of charge carriers from metal electrode contribute to the polarization of PVDF.



Figure 2. TSDC spectra for pure PVDF at different poling fields 17, 25, and 33.3 kV/cm.

One can notice from Figure (2) that two TSDC peaks are observed for neat PVDF in accordance with literature [21]. The first one at 325 K (β -peak) and second one centered at 360 K (α -peak) are due to the release of charges trapped at crystalline/amorphous

boundaries [22]. With increasing the polarizing field, the magnitude of peak currents was found to be increase. Both β and α peaks shift toward lower temperature side with increasing values of polarizing field.



Figure 3. Peak current Im (α and β) of pure PVDF against the poling field.

The peak current I_m is plotted as a function of the polarizing field as shown in Figure (3) for virgin PVDF sample. This peak current is directly proportional to the polarizing field within the experimental range.

The generated thermal stimulated currents owing to the motion of the dipole during their reorganization were analyzed as a function of temperature [23].

During thermally stimulated current measurement, the current density $J_{(T)}$ at temperature T is shown in equation (2):

$$J_{(T)} = A \exp\left\{-\frac{W}{RT} - \frac{B}{q} \int_{T_{c}}^{T} \exp\left[\frac{-W}{KT}\right] dT\right\}$$
(2)

where B, A are the constant of the process, K is the Boltzmann's constant, W is the activation energy of the process, T is the temperature, T_{o} is the initial temperature and q is the heating rate. The initial rise mostly used to determine method is the characterization parameter of the process i.e. the activation energy and the relaxation time. In this method, the integral term in equation (2) is low for $T \ll T_{max}$ and so the first exponential term dominates. Therefore, the current density has an Arrhenius formula during the thermal stimulated measurement. So, from the slope of ln $(J_{(T)})$ versus $\frac{1}{T}$ plot, one can deduce the activation energy as shown in equation (3):

$$J_{(T)} = J_o \exp\left(\frac{-W}{KT}\right)$$
(3)

From the elementary spectrum, the relaxation time $\tau_{(T)}$ at temperature T can be extracted by using equation (4):

$$\tau_{(T)} = \frac{P_{(T)}}{J_{(T)}} \tag{4}$$

Where $P_{(T)}$ is the polarization at temperature T, and can be expressed as shown in equation (5):

$$P_{(T)} = \frac{1}{q} \int_0^T J(T') dT'$$
 (5)

The relaxation frequency $\alpha(T_{max})$ at the peak temperature Tmax is described in equation (6):

$$T_{\max} = \sqrt{\frac{qW}{K\alpha}}$$
(6)

The above Debye formalism in equations (2) - (6) applies only for a single relaxation process. The low temperature tail of equation (2) may be written as:

$$\ln J_{(T)} = \text{Constant} - \frac{W}{KT}$$
(7)

W may be determined from a semi-log plot of $J_{(T)}$ versus $\frac{1000}{T},$

which is the initial rise method of Garlick and Gibson [24]. By using the calculated value of W and equation (8):

$$\tau = \tau_{o} \exp \frac{W}{KT}$$
(8)

where,

$$\tau_{0} = (K T_{m}^{2})/[B W \exp(W/KT)]$$
 (9)

where ß is the heating rate, and the value of τ at T_m for both peaks may be calculated as a function of the applied poling field. The equivalent frequency of the TSDC thermograms was calculated from equation (10):

$$f_{eq} = \frac{1}{2\pi\tau}$$
(10)





Figure 4. In J versus 1000/T plot for (a) peak 1 and (b) peak 2 of pure PVDF at different poling fields (17, 25, and 33.3 kV/cm).

Figure (4) represents the ln $J_{(T)}$ versus 1000/T, for each peak, which give a straight line with slope of (-W/k). The activation energy along with the relaxation parameters at (T_P=70 °C) are summarized in Table (2) for different polarizing fields.

The activation energy could be calculated also by a peak shape method, where three parameters were used to calculate W [25].



Figure 5. Illustration of the three parameters; Y, δ and $\eta.$

$$Y = T_m - T_i$$

 $\delta = T_k - T_m$
 $\eta = T_k - T_i$

where T_m is the temperature corresponding to the maximum current, T_i and T_k are the low and high halfintensity temperature, respectively, as illustrated in Figure (5).

$$W_{\delta} = [0.97 + 7.3(\mu_g - 0.42)] K T^2 m / \delta$$
 (12)

$$W_{\eta}$$
= [2.52+10.2(μ_{g} -0.42)] KT²m/ η -2KTm (13)

where μ_g is equal to ratio δ/η .

The values of μ_g were predicted by Chen and kirch as 0.42 and 0.52 for first and second order kinetics, respectively [26].

Following the above method, average values of the obtained activation energies (W_{Υ} , W_{δ} and W_{η}) were calculated along with the corresponding relaxation parameters, for the peaks of neat PVDF at different poling fields, and tabulated in Table (2).

The activation energies obtained by peak shape method has been found to be higher than that obtained by initial rise method. This could be due to the more accuracy of the initial rise method. The activation energies estimated by the two methods are ranging from 0.3-2.6 eV (at $E_P=17kV/cm$), 0.18-2.0 eV (at $E_P=25 kV/cm$), and 0.15-1.7 eV (at $E_P=33.3 kV/cm$) for the first peak. In addition, the relaxation time for the 1st peak increases with the increase in poling field, while it decreases for the 2nd peak.

Table (2): The activation energy W, relaxation time τ , and relaxation frequency for two peaks of neat PVDF at different poling fields.

		Initial rise method			Peak shape method			
	E _p (kV/cm)	W (eV)	т (10 ³ sec)	F (10 ⁻⁴ Hz)	W (eV)	т(10 ^² sec)	f(10 ⁻³ Hz)	
	17	0.31	1.77	6	2.70	2.08	4.80	
Peak 1	25	0.18	2.78	4	1.93	2.59	3.87	
	33.3	0.15	3.35	3	1.78	2.95	3.39	
	17	0.4	1.71	5	3.62	1.89	5.29	
Peak 2	25	0.24	2.79	4	4.15	1.63	6.14	
	33.3	0.078	8.38	1	3.94	1.68	5.96	

B) Effect of metal complex addition:

The effect of dichloro palladium pyridyl benzimidazole complex as a filler at different poling fields (17, 25 and 33.3 kV/cm) and constant poling temperature (T_p =70 °C) on the TSDC spectra of PVDF composites have been recorded. Due to the presence of interface between polymer and filler, the TSDC of composites has been markedly modified.





Figure 6. TSDC spectra of PVDF doped with (a) 1% and (b) 3% of metal complex.

At the moment the TSDC curves of PVDF show two peaks at different poling fields, the PVDF/metal complex composites showed only a single peak at around (340-360 K) as shown in Figures (6 a-b). The magnitude of the TSDC peak current decreased and the peak shifted toward lower temperature side as the metal complex content in the composite was increased.

From the above results one could indicate that charge carriers tend to be captured on the upper surface of the polymer after the addition of metal complex filler [25].

The space charge formation increases if the captured charge carriers induce homocharge layers in the vicinity of the electrode. The origin of space charge polarization in tested composites is confirmed by the following:

i) The linear dependence of peak current on the poling field.

ii) The values of activation energy for this peak (Table 2) are approximately the same reported for space charge polarization in many fluoro –polymers [26].

iii) The field dependence of higher peak for composites is also suggestive of space charge depolarization [27].

By studying the dependence of T_{max} (Figures 2 and 6) on the electric field, one can explore the physical origin of the TSDC. At constant heating rate, the current peak temperature shifts in a well-defined manner with increasing electric field, T_{max} can:

a) Shift to lower temperatures when the relaxation current is associated with trapped charges.

b) Shift to higher temperatures when the physical origin of TSDC is space charge, and

c) Remain fixed when the TSDC arises from defect dipoles [28], [29].

Figures (6 a-b) showed that the single peak maximum temperature T_{max} varies with the applied poling field in the temperature range (340 - 360 K). So, T_{max} shifts to higher temperature suggesting that the origin of the TSDC depolarization peak is associated with a space charge.

To determine the activation of the TSDC three different methods were used [30].





Figure 7. InJ versus 1000/T plot of PVDF doped with (a) 1% and (b) 3% of metal complex.

In the first one, the initial rise model, the first exponential term of equation (2) controls the temperature rise of the initial current. So, In J versus 1/T gives rise to a straight line and the activation energy was determined from the slope of this line (c.f. Table 3 and Figure 7 a-b).

Table (3): The activation energy W, relaxation time τ , and relaxation frequency for PVDF composites at different poling fields.

Motol	E	Initial rise method			Peak shape method		
complex (wt%)	⊑ _p (kV/ cm)	W (eV)	т (10 ³ sec)	F (10 ⁻⁵ Hz)	W (eV)	т (10 ² sec)	f (10 ⁻³ Hz)
	17	0.05	12.1	8	1.97	3.24	3.1
1%	25	0.04	15.8	6	3.05	2.12	4.7
	33.3	0.09	6.71	1	4.11	1.53	6.5
	17	0.14	4.6	2	2.67	2.38	4.2
3%	25	0.05	12.3	8	3.19	2.02	4.9
	33.3	0.03	18.5	5	2.85	2.23	4.5

In the second method, the FWHM of TSDC peak (as mentioned before) was used to determine the activation energy (c f. Figure 6) via equation (14).

$$W=2.3 \text{ KT}^{2}_{\text{max}} / \Delta T_{1/2}$$
(14)

where $\Delta T_{1/2}$ is the FWHM of TSDC peak. All expressions in equation (14) are related to a single Debye process.

In the third method, the heating rate dependence of the TSDC peak position was used. But in our case we keep the heating rate at constant value. So this method couldn't apply here.

Important parameters of the molecular motionactivation energy and pre-exponential factor in Arrhenius equation-obtained from fitting procedure are presented in Table (4).

Table (4): Activation energy (W), temperature peaks
(Tm), and pre-exponential factor in Arrhenius equation
obtained by fitting process.

Me com (w	etal 1plex t%)	E _p (kV/cm)	T _m (K)	W (eV)	т (s)	f(10 ⁻³ Hz)
	Peak	17	330	1.95	287	3.5
	1	25	319	1.59	313	3.2
0%	•	33.3	315	1.67	313	3.2
0,0	Peak	17	364	2.38	287	3.5
	2	25	362	2.35	287	3.5
-	33.3	358	2.53	261	3.3	
		17	352	1.22	522	1.9
1	%	25	351	1.77	365	2.7
		33.3	349	2.67	235	4.3
		17	354	1.74	365	2.7
3	%	25	352	1.90	339	2.9
		33.3	351	1.87	339	2.9

TSDC spectra after laser exposure:

The TSDC technique successfully allows the understanding of the electric dipole relaxation mechanism present in polymer composites [31]. In addition, when the test sample is laser excited along with the electric field, the TSDC technique could also be used in modified way to analyze on the material relaxation.

In measurements of the laser-induced TSDC, the process is quite similar to the normal TSDC one.

After the application of the electric field at a given polarization temperature, the temperature decreased rapidly to a temperature close to room temperature. The laser beam is shined on the sample for a different given time after removing the applied electric field. Then the laser beam is removed and the temperature is increased at a constant rate. One investigates the different influence in this polarization direction with the incident of laser beam in the polymer composites.



Figure 8. TSDC spectra of PVDF doped with 1% of metal complex different incident laser energies.

The laser –induced TSDC results, for PVDF sample loaded with 1 wt% of metal complex, can be seen in Figure (8). An intense peak for normal TSDC curve with its maximum at round 350k (as detected before) is observed in Figure (8)

This band around 350k shifted to lower temperature side and becomes a broad one with increasing incident laser energy $(8x10^{-2}J, 12 x10^{-2}J, and 16 x10^{-2}J)$. Meanwhile the maximum current at Tm decrease appreciably with laser energy (Figure 9).



Figure 9. Peak current Im of PVDF doped with 1% of metal complex at different incident laser energies.

Interestingly, it can be seen in these results that TSDC bands for the test sample are less defined and less intense at the maximum temperature than for un laser induced TSDC one. So, the orientation of dipoles in T_P by the laser light is possible in opposite direction, because of the non-synergism of the laser energies together with the applied electric field. So the process of destruction of TSDC bands occurs more noticeably with increasing laser poling energy. These results are in agreement with published work by Scalvi et al. [32]. Following the above mention distinct methods that used to determine the activation of the TSDC peak by

using equation (2) and InJ versus 1/T plot, the activation energy is estimated at different incident laser energies (Figure 10) and tabulated in Table (5). The peak temperature of laser induced TSDC is lower than the dipolar peak (ß-peak) of PVDF samples. ß-peaks in PVDF mainly arise from the localized rotational fluctuations of dipoles which are hindered by laser energy [33], [34].



Figure 10. InJ versus 1000/T plot of PVDF doped with 1% of metal complex at different incident laser energies.

Table (5): The activation energy W, relaxation time T, and relaxation frequency for PVDF/metal composite (1%) exposed to different laser energies.

Laser energy (10 ⁻² J)	W (eV)	т (10 ⁴ sec)	f (10 ⁻⁵ Hz)
8	0.06	1.10	9.07
12	0.05	1.32	7.6
16	0.04	1.40	7.15

CONCLUSION:

From FT-IR spectra we indicated that, band intensity which belonging to β phase was decreased with the addition of metal complex. Furthermore, the percentage of β -crystalline phase decreases with increasing metal complex content.

From TSDC thermograms, the various noticed peaks were discussed on the basis of space charge polarization. We observed that both ß and α peaks (detected at 325 K and 360 K respectively) shift toward lower temperature side with increasing the polarizing field for neat PVDF sample. Due to the presence of interface between polymer and filler, the TSDC of composites has been markedly modified. In addition, the PVDF/metal complex composites showed a single

peak at around (340 - 360 K). The magnitude of the TSDC peak current decreased and the peak shifted toward lower temperature side as the metal complex content in the composite increased. The temperature at peak, T_{max} shifted to higher temperature suggesting that the origin of the TSDC depolarization peak is associated with a space charge. Two different methods were used to determine the activation energy. The activation energies obtained by peak shape method has been found to be higher than that obtained by initial rise method. This could be due to the higher accuracy of the initial rise method. The activation energies estimated by the two method range from 0.3 -2.6 eV at $E_P=17$ KV/cm, from 0.18-2.0 eV at $E_P=25$ KV/cm, and from 0.15 - 1.7eV at $E_P=33.3$ KV/cm for the first peak. TSDC analysis was performed after sample modification using Nd-YAG laser source, method called Laser-induced TSDC. Interestingly, it can be seen in these results that TSDC bands for the test sample are less defined and less intense at the maximum temperature than for non-laser induced TSDC one. So, the orientation of dipoles in T_P by the laser light is possible in opposite direction, because of the non-synergism of the laser energies together with the applied electric field. So the process of destruction of TSDC bands occurs more noticeably with increasing laser poling energy. ß-peaks in PVDF arise mainly from the localized rotational fluctuations of dipoles which are hindered by exposure to laser. The activation energy decreases slightly upon irradiation with laser beam.

REFERENCES:

[1] N. T. ABDEL GHANI ET AL., "MOLECULAR STRUCTURES OF ANTITUMOR ACTIVE PD(II) AND PT(II) COMPLEXES OF N,N-DONOR BENZIMIDAZOLE METHYL ESTER," JOURNAL OF MOLECULAR STRUCTURE, VOL. 631, NO. 1–3. PP. 2258–2264, 2011, DOI: 10.1016/J.MOLSTRUC.2011.02.014.

[2] L. E. NIELSEN AND R. F. LANDEL, MECHANICAL PROPERTIES OF POLYMERS AND COMPOSITES, SECOND EDITION, REVISED AND EXPANDED. 1993.

[3] J. R. LIN AND L. W. CHEN, "STUDY ON SHAPE-MEMORY BEHAVIOR OF POLYETHER-BASED POLYURETHANES . I . INFLUENCE OF THE HARD-SEGMENT CONTENT," PP. 1563–1574, 1998.

[4] L. K. LINDÉN, J. F. RABEK, AND H. KACZMAREK, "POLY(CARBOXYLIC ACIDS)-METAL SALTS COMPLEXES: FORMATION, STRUCTURE, AND APPLICATION IN DENTISTRY," MOL. CRYST. LIQ. CRYST. SCI. TECHNOL. SECT. A. MOL. CRYST. LIQ. CRYST., VOL. 240, NO. 1, PP. 143–154, 1994, DOI: 10.1080/10587259408029725.

[5] J. G. DROBNY, TECNHOLOGY OF FLUOROPOLYMERS, 2ND ED. CRC PRESS, 2009.

[6] GRAND VIEW RESEARCH, "NATURAL FIBERS MARKET SIZE, SHARE & TRENDS ANALYSIS REPORT BY APPLICATION, BY REGIONAL OUTLOOK, BY COMPETITIVE STRATEGIES, AND SEGMENT FORECASTS, 2019 TO 2025," VOL. 2025, PP. 5–9, 2019, [Online]. Available: https://www.grandviewresearch.com/industryanalysis/natural-fiber-composites-market.

[7] G. DOMÍNGUEZ-ESPINOSA, M. J. SANCHIS, R. DÍAZ-CALLEJA, C. PAGUEGUY, L. GARGALLO, AND D. RADIC, "COMPARATIVE STUDY OF LOCALIZED SIDE GROUP IN POLY(2,3 AND 4 METHYL CYCLOHEXYL METHACRYLATE)S. TSDC MEASUREMENTS," POLYMER (GUILDF)., VOL. 46, NO. 25, PP. 11351–11358, 2005, DOI: 10.1016/J.POLYMER.2005.10.023.

[8] H. P. DIOGO AND J. J. MOURA RAMOS, "SLOW MOLECULAR MOBILITY IN 4,4'-METHYLENEBIS (N,N-DIGLYCIDYLANILINE) AS STUDIED BY THERMALLY STIMULATED DEPOLARIZATION CURRENTS (TSDC)," J. MOL. LIQ., VOL. 129, NO. 3, PP. 138–146, 2006, DOI: 10.1016/J.MOLLIQ.2006.02.001.

[9] J. VAN TURNHOUT, "THERMALLY STIMULATED DISCHARGE OF POLYMER ELECTRETS," POLYM. J., VOL. 2, NO. 2, PP. 173–191, 1971, DOI: 10.1295/POLYMJ.2.173.

[10] C. BUCCI AND R. FIESCHI, "IONIC THERMOCONDUCTIVITY. METHOD FOR THE INVESTIGATION OF POLARIZATION IN INSULATORS," PHYS. REV. LETT., VOL. 12, NO. 1, PP. 16–19, 1964, DOI: 10.1103/PHYSREVLETT.12.16.

[11] J. S. SEDITA AND J. M. O'REILLY, "A THERMALLY STIMULATED DEPOLARIZATION CURRENT STUDY OF POLYMERS IN THE GLASS TRANSITION REGION," POLYM. ENG. SCI., VOL. 41, NO. 1, PP. 15–22, 2001, DOI: 10.1002/PEN.10704.

[12] C. LACABANNE, A. LAMURE, G. TEYSSEDRE, A. BERNES, AND M. MOURGUES, "STUDY OF COOPERATIVE RELAXATION MODES IN COMPLEX SYSTEMS BY THERMALLY STIMULATED CURRENT SPECTROSCOPY," J. NON. CRYST. SOLIDS, VOL. 172–174, NO. PART 2, PP. 884–890, 1994, DOI: 10.1016/0022-3093(94)90593-2.

[13] DAVID I. BOWER, AN INTRODUCTION TO POLYMER PHYSICS. CAMBRIDGE UNIVERSITY PRESS, 2003.

[14] P. E. DYER, "EXCIMER LASER POLYMER ABLATION: TWENTY YEARS ON," APPL. PHYS. A MATER. SCI. PROCESS., VOL. 77, NO. 2, PP. 167–173, 2003, DOI: 10.1007/S00339-003-2137-1.

[15] J. H. LEE, N. S. KIM, S. S. HONG, AND J. H. LEE, "ENHANCED EXTRACTION EFFICIENCY OF INGAN-BASED LIGHT-EMITTING DIODES USING 100-KHZ FEMTOSECOND-LASER-SCRIBING TECHNOLOGY," IEEE ELECTRON DEVICE LETT., VOL. 31, NO. 3, PP. 213–215, 2010, DOI: 10.1109/LED.2009.2037592.

[16] L. N. DUMITRESCU ET AL., "INDUCED HYDROPHILICITY AND IN VITRO PRELIMINARY OSTEOBLAST RESPONSE OF POLYVINYLIDENE FLUORIDE (PVDF) COATINGS OBTAINED VIA MAPLE DEPOSITION AND SUBSEQUENT THERMAL TREATMENT," MOLECULES, VOL. 25, NO. 3, 2020, DOI: 10.3390/MOLECULES25030582.

[17] L. RUAN, X. YAO, Y. CHANG, L. ZHOU, G. QIN, AND X. ZHANG, "PROPERTIES AND APPLICATIONS OF THE B PHASE POLY(VINYLIDENE FLUORIDE)," POLYMERS (BASEL)., VOL. 10, NO. 3, PP. 1–27, 2018, DOI: 10.3390/POLYM10030228.

[18] X. JIANG, X. ZHAO, G. PENG, W. LIU, K. LIU, AND Z. ZHAN, "INVESTIGATION ON CRYSTALLINE STRUCTURE AND DIELECTRIC RELAXATION BEHAVIORS OF HOT PRESSED POLY(VINYLIDENE FLUORIDE) FILM," CURR. APPL. PHYS., VOL. 17, NO. 1, PP. 15–23, 2017, DOI: 10.1016/J.CAP.2016.10.011.

[19] S. SATAPATHY, S. PAWAR, P. K. GUPTA, AND K. B. RVARMA, "EFFECT OF ANNEALING ON PHASE TRANSITION IN POLY(VINYLIDENE FLUORIDE) FILMS PREPARED USING POLAR SOLVENT," BULL. MATER. SCI., VOL. 34, NO. 4, PP. 727–733, 2011, DOI: 10.1007/s12034-011-0187-0.

[20] M. S. SORAYANI BAFQI, R. BAGHERZADEH, AND M. LATIFI, "FABRICATION OF COMPOSITE PVDF-ZNO NANOFIBER MATS BY ELECTROSPINNING FOR ENERGY SCAVENGING APPLICATION WITH ENHANCED EFFICIENCY," J. POLYM. RES., VOL. 22, NO. 7, PP. 1–9, 2015, DOI: 10.1007/s10965-015-0765-8.

[21] M. GARG AND J. K. QUAMARA, "MULTIPLE RELAXATION PROCESSES IN HIGH-ENERGY ION IRRADIATED KAPTON-H POLYIMIDE: THERMALLY STIMULATED DEPOLARIZATION CURRENT STUDY," NUCL. INSTRUMENTS METHODS PHYS. RES. SECT. B BEAM INTERACT. WITH MATER. ATOMS, VOL. 246, NO. 2, PP. 355–363, 2006, DOI: 10.1016/J.NIMB.2006.01.012.

[22] A. P. INDOLIA AND M. S. GAUR, "INVESTIGATION OF STRUCTURAL AND THERMAL CHARACTERISTICS OF PVDF/ZNO NANOCOMPOSITES," J. THERM. ANAL. CALORIM., VOL. 113, NO. 2, PP. 821–830, 2013, DOI: 10.1007/s10973-012-2834-0.

[23] I. STAVRAKAS, D. TRIANTIS, P. PHOTOPOULOS, AND A. KANAPITSAS, "THERMALLY STIMULATED DISCHARGE CURRENT (TSDC) CHARACTERISTICS IN PVDF– GRAPHENE NANOCOMPOSITES," NO. NOVEMBER, 2015.

[24] G. F. J. GARLICK AND A. F. GIBSON, "PROC. PHYS. SOC." 1948.

[25] K. H. NICHOLAS AND J. WOODS, "THE EVALUATION OF ELECTRON TRAPPING PARAMETERS FROM CONDUCTIVITY GLOW CURVES IN CADMIUM SULPHIDE," BR. J. APPL. PHYS., VOL. 15, NO. 7, PP. 783–795, 1964, DOI: 10.1088/0508-3443/15/7/302.

[26] R. CHEN AND Y. KIRSH, ANALYSIS OF THERMALLY STIMULATED PROCESSES, 1ST ED. PERGAMON PRESS, 1982.

[27] G. M. Sessler, Topics in Applied Physics: Electrets, 2nd ed., vol. 107. Springer Berlin Heidelberg, 2006.

[28] P. K. C. PILLAI, G. K. NARULA, A. K. TRIPATHI, AND R. G. MENDIRATTA, "POLARIZATION AND DEPOLARIZATION STUDIES IN POLYPROPYLENE POLYCARBONATE BLENDS," PHYS. REV. B, VOL. 27, NO. 4, PP. 2508–2514, 1983, DOI: 10.1103/PHysRevB.27.2508. [29] A. K. JONSCHER, "DIELECTRIC RELAXATION IN SOLIDS," J. PHYS. D. APPL. PHYS., VOL. 32, NO. 14, PP. R57--R70, JAN. 1999, DOI: 10.1088/0022-3727/32/14/201.

[30] B. AKKOPRU-AKGUN ET AL., THERMALLY STIMULATED DEPOLARIZATION CURRENT MEASUREMENTS ON DEGRADED LEAD ZIRCONATE TITANATE FILMS, VOL. 104, NO. 10. 2021.

[31] M. AMIN, G. M. NASR, AND S. A. MANSOUR, "STUDY OF THE THERMALLY STIMULATED DEPOLARIZATION CURRENT (TSDC) FOR COMPOSITES OF ACRYLONITRILE BUTADIENE RUBBER (NBR) LOADED WITH HAF," PP. 313–318, 2013. [32] R. M. F. SCALVI, M. S. LI, AND L. V. A. SCALVI, "THERMAL ANNEALING-INDUCED ELECTRIC DIPOLE RELAXATION IN NATURAL ALEXANDRITE," PHYS. CHEM. MINER., VOL. 31, NO. 10, PP. 733–737, 2005, DOI: 10.1007/S00269-004-0442-7.

[33] N. M. TRINDADE, A. R. BLAK, E. M. YOSHIMURA, L. V. DE ANDRADE SCALVI, AND R. M. F. SCALVI, "PHOTO-INDUCED THERMALLY STIMULATED DEPOLARIZATION CURRENT (TSDC) IN NATURAL AND SYNTHETIC ALEXANDRITE," MATER. SCI. APPL., VOL. 07, NO. 12, PP. 881–894, 2016, DOI: 10.4236/MSA.2016.712067.

[34] K. TORIZUKA AND M. YAMASHITA, "THERMAL EFFECT IN A LAMP-PUMPED CONTINUOUS-WAVE ALEXANDRITE LASER," JPN. J. APPL. PHYS., VOL. 33, NO. 4R, PP. 1899–1904, 1994, DOI: 10.1143/JJAP.33.1899.