Study of Microhardness and Micro-Mechanical Properties of Electrically Untreated and Treated PI+ITO+GO Polymeric Composite Thin Films

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Abstract— This study is an attempt to understand the compatibility and the possibility of improving microhardness and micro-mechanical properties of developed PI+ITO+GO polymeric composite thin films, when, they undergo electrical stress (defined to be sever-aging). The microhardness and micromechanical properties had been studied using the measurements of Vicker's hardness number (H_v) and ASTMD-882 approach. The resultant change in the microhardness and micro-mechanical properties of electrically treated films interpreted the possibility of high dense packaging of ITO and GO oxide particle within the PI chain matrix along with the inter and intra molecular interaction, when, films were electrically stressed.

Keywords: Polyimide, ITO, Graphene Oxide, Microhardness, Micro-Mechanical

I. INTRODUCTION

Day by day industrial demand was growing for the polymeric composite thin films as they reduce the weight and operating cost of the final product. Thus, metal oxide incorporated polymeric composite thin films had been studied extensively in the past decade due to their unique electrical strength, good dielectric and mechanical properties. These properties make the material to be used in wide range of application like electrical insulators. Moreover, they have also made a great contribution to the miniaturization of electrical equipments [1-4].

However, increasing demand of practical use, still very less had been known about the microhardness and micro-mechanical properties of polymeric composite thin films in different composition of utility, when, they undergo electrical stress and subjected to various severe aging effects. The investigation of the polymeric composite thin films in term of mechanical performance which changes during the electrical stress is a key issue to anticipate and detect equipment incipient faults and its average useful life span. Hence leading to changes in mechanical behavior of the polymeric composite thin films due to aging factors contribute more to the deterioration in electrical behavior during operation and gradual aging becomes severe, the leakage current tends to increase and arcing discharge may occur. This can be interpreted as an indication of an incipient fault that will eventually lead to device failure. Polyimide (PI) has been used in many important specialized applications due to outstanding performance parameters and variety of applications, such as aerospace, electrical and electronics industry, etc. PI is a type of structural material which posses excellent mechanical and other properties, when, exposed to different condition [5-7].

Indium Tin Oxide (ITO) provides excellent behaviour of compatibility and continuous dispersion with other oxide particles within the polymeric matrix along with very good optical and electrical properties in terms of wide band gap semi conductor and many other photovoltaic technologies which will be of great interest for further research work [8].

Study of Graphene Oxide (GO) as reinforcing agent in terms of micro/nano meter regime to reboot the micro-mechanical properties like stiffness elastic to 340 ± 50 Nm^{-1}, strength of 42 Nm^{-1}equal to 130 GPa, intrinsic strength and toughness of 4.0 ± 0.6 MPa. Hence all these inherent properties make it great potential oxide to be incorporated within the polymeric matrix for enhancing the work functioning of energy storage, conductive and solar cells materials properties [9].

The ITO+GO were made to disperse within the continuous poly (amic acid) (PAA) which is precursor to PI matrix using In-situ Generated Inter-chain Crosslinking Moieties (IGICM) technique. Thereafter, spin coating unit method was used and further cured for 360°C to develop PI+ITO+GO the final polymeric composite thin films. The microhardness and micro-mechanical study was carried out on electrically untreated and treated PI+ITO+GO polymeric composite thin films using Carl Zeiss Universal Research microscope (NU_2) and Universal mechanical testing machine Model No-LR 100K/LLOOYDS according to ASTMD-882 method [10]. The developed polymeric composite thin films were conditioned at 160˚C for 2 hrs in a dust free vacuumised chamber before characterization.

II. SYNTHESIS OF PI+ITO+GO POLYMERIC COMPOSITE THIN FILMS

The oxydianiline (ODA), and pyromellitic dianhydride (PMDA), analytical-grade tetrahydrofuran which were supplied by M/S Merck Chemicals, Germany as it received was used to make the 200gm of poly (amic acid) (PAA) solution. Further, ITO and GO in powder form bought by Sigma-Aldrich Chemicals, USA was blended in various wt%. Then ITO+GO powder blends was prepared and the different concentration of ITO+GO powder blend which depends upon its mass density and interaction of particles with free surface volume of the host material, i.e. PAA using In-situ Generated Inter-chain Crosslinking Moieties (IGICM) technique.

The solution cast technique was used to form the PAA+ITO+GO polymeric composite solution in which the ITO+GO powder blend with PAA were stirred for 30 min with a magnetic stirrer in a dust-free environment and left as it is for 24 hours. The solution concentrations and designations of the various samples are given in Table 1.

Further, PAA+ITO+GO composite solution were weighed onto dry and clean glass plates and spread evenly using a spin-coating unit in a dust- and moisture free chamber and cured at 360°C for 2 h. The films were heated at 360°C for 2 h then allowed to cool slowly to room

temperature. The pure PI film was also cured under identical conditions. The films were of 10 cm^2 in area and 15 µm in thickness, and the same were used for all the characterizations. The physical and optical presentations of developed composite thin films were reported in Table 2.

Thereafter, the characterizations were carried out and before characterization developed films were cured at 160°C to resist the moisture possibilities.

S. No	Solution Concentration	Value	Developed Films	Designation
1.	PAA	200 gm	PI	PI
2.	PAA+ITO+GO	200 gm + ITO 1 wt% + GO 0.05 wt%	PI+ITO+GO	PITOGO-1
3.	PAA+ITO+GO	200 gm + ITO 1 wt% + GO 0.10 wt%	PI+ITO+GO	PITOGO-2
4.	PAA+ITO+GO	200 gm + ITO 1 wt% + GO 0.15 wt%	PI+ITO+GO	PITOGO-3
5.	PAA+ITO+GO	200 gm + ITO 1 wt% + GO 0.20 wt%	PI+ITO+GO	PITOGO-4
6.	PAA+ITO+GO	200 gm + ITO 1 wt% + GO 0.25 wt%	PI+ITO+GO	PITOGO-5

Table 1: The Various Solution Concentrations and Designations

III. MICROHARDNESS AND MICROMECHANICAL CHARACTERIZATION

The microhardness characterization was performed using Carl Zeiss Universal Research microscope (NU_2) universal research microscope attached with a Vickers diamond pyramidal indenter. The H_v (Vickers Hardness number) was calculated using the relation:

$$H_v = \frac{2L\sin\theta/2}{d^2} = \frac{1.8544 \times L}{d^2}\left(kg/mm^2\right)$$

Where, L is load in kg and d is diagonal of Vicker's indentation in mm.

Designation	Color	Transparency	flexibility
PI	light yellow	Color transparent	Foldable
PITOGO-1	Very light yellow	Color transparent	Foldable
PITOGO-2	Very light yellow	Color transparent	Foldable
PITOGO-3	Very light yellow	Color transparent	Foldable
PITOGO-4	Very light yellow	Color transparent	Foldable
PITOGO-5	Very light yellow	Color transparent	Foldable

Table 2: The Physical and Optical Presentations of Developed Composite Thin Films

During the experimental procedure several indentations were obtained at various loads and the average hardness number was used for the calculation.

The strain hardening index was studied by the Meyer's law [2-3]. $L = ad^n$ (dependence of microhardness on load), where, L is load, d is the length of diagonal measured in divisions, 'a' is a constant representing load for unit dimension and 'n' is the logarithmic index number. In the present case, 1 division = 8×10^{-4} mm. By logging both sides of the above equation, we get $\log L = \log a + n \log d$.

The micro-mechanical characterization in terms of tensile strength, tensile modulus and elongation (%) of pure PI and polymeric composite thin films were measured according to ASTMD-882 method using universal testing machine Model No-LR 100K/LLOOYDS. The films were conditioned at 160°C for 2 hrs before characterization.

IV. ELECTRICAL AGING CHARACTERIZATION

To investigate the effect of electrical aging on the microhardness and micro-mechanical behavior of PI+ITO+GO polymeric composite thin films were electrically stressed by applying a voltage of 250 kV/cm at 90°C. The composite thin films were placed between the two metal electrodes of the measuring cell, which was mounted inside an oven and heated to 90°C for 1 hr. Thereafter, 250 kV/cm was applied for a time period of 45 minutes and the temperature was maintained at 90°C. The polymeric composite thin films were then slowly cooled to room temperature and during that time frame electrical field was still on. For each case the electric field was maintained at 2 hr. Thereafter, the electric field was removed and the thermally and electrically aged specimens were taken out for microhardness and micro-mechanical measurements.

V. RESULTS & DISCUSSION

The variations of (H_v) with load for electrically untreated and treated (250 kV/cm at 90°C) polymeric composite thin films were shown in figure 1 and 2. The pattern of (H_v) found to be same for electrically untreated and treated composite films as they increases with load, but beyond certain load, (H_v) tends to attain saturation value. The chain-chain slipping deformation is the reason for saturation value within the polymeric composite thin films. The curvilinear trend is almost same for all the electrically untreated and treated polymeric composite films in terms of H_v-Load profile. As the load increase the value of (H_v) increases, is due to strain hardening within the polymeric composite thin films and also due to micro-modes of deformation. Moreover, large scale plastic deformation begins when sufficient number of micro-modes becomes active. The polymeric composite thin films were subjected to greater strain hardening and increase in H_v as the load is increased. Thus, H_v tends to saturate and fully strain hardened no appreciable change in the value of H_v was found. It was observed that the microhardness shows the similar trend as in case of untreated and treated composite films but value of (H_v) was found to be higher for electrically stressed samples. PI thermally flexible chains internal rotation leads to partial change within atom arrangement and there is definite value of potential energy causing interactions between atoms, electrons, nuclei etc.

The polymeric composite thin films were kept under electrical stress field at a high temperature for 2 hr for facilitating thermal movements of PI chains. The electrical stress application at this elevated temperature producing the direct action of the applied field which acts on the polarizing (moieties) results in polarization of the PI chain and this state is frozen in on cooling. It was seen that in electrically stressed polarized samples inter and intra molecular interactions are modified in such a way that steric hindrance of rotation of chain or potential rotational barrier is increased restricting kinetic flexibility of PI chain. Thus the resultant electrically stressed polymeric composite films are hard compared to the untreated one. The calculated value of (n) for electrically stressed polymeric composite thin films also support the resultant outcome as shown in Table 3 and increase in micro-mechanical strength (Figure 3, 4 and 5), which also explains the increase in the value of H_v observed for electrically stressed polymeric composite thin films in the present case. Other than that the presence of ITO and GO particles within the PI matrix get dense packaging due to hindered rotation of chain during thermal and electrical aging in micro/nano size regime contributes in strengthening the electrically treated polymeric composite thin films in compare to untreated composite film. The forgoing observation will help to correlates the increase in microhardness properties for all the polymeric composite thin films having maximum hardening in PITOGO-2 electrically treated film.

The micro-mechanical properties of polymeric composite thin films depend on the macromolecular segments and crosslinking between the macromolecular units. Tensile properties are basically characterized by measuring yield stress and corresponding elongation at break as function of polymeric composite thin films and tensile modulus is one of the most important small strain mechanical properties because it is the key indicator of the stiffness or rigidity of the material and quantifies the resistance of the specimens to mechanical deformation in the limit of infinitesimally small deformation. The results of various micro-mechanical properties of electrically untreated and treated PI+ITO+TO polymeric composite thin films are shown from figure 3, 4 and 5.

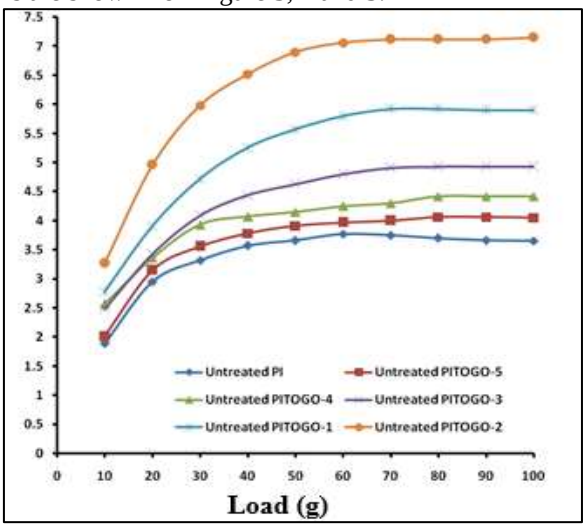

Fig. 1: Variation H_v with load for untreated PI and PITOGO polymeric composite thin films.

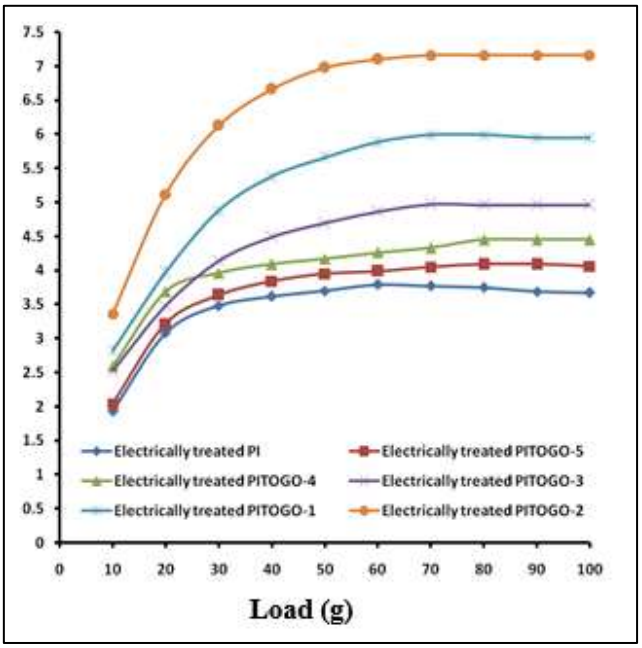

Fig. 2: Variation H_v with load for electrically treated PI and PITOGO polymeric composite thin films.

It can be inferred from the figure that incorporation of ITO and GO in calculated value per unit area significantly affected the tensile properties. However, polymeric composite thin films undergo electrical stress the tensile properties increases.

Samples Designation	Slope			
	Low load region for Untreated films	Low load region for treated films	High load region for Untreated films	High load region for treated films
PI	2.92	2.99	2.69	2.76
PITOGO-1	2.98	3.03	2.74	2.82
PITOGO-2	2.01	3.01	1.98	2.09
PITOGO-3	3.12	3.15	2.88	2.96
PITOGO-4	3.28	3.33	2.92	2.99
PITOGO-5	3.32	3.38	2.98	3.04

Table 3: For The Two Load Regions Different Calculated Values of (N) Of Electrically Untreated and Treated Pi and Pitogo Polymeric Composite Thin Films.

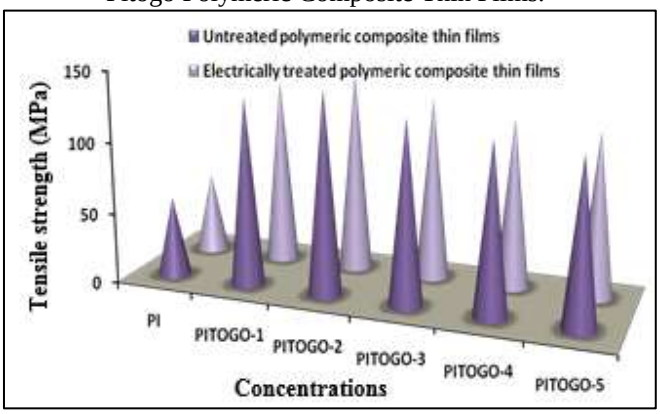

Fig. 3: Bar graph of tensile strength for untreated and electrically treated PI and PITOGO polymeric composite thin films.

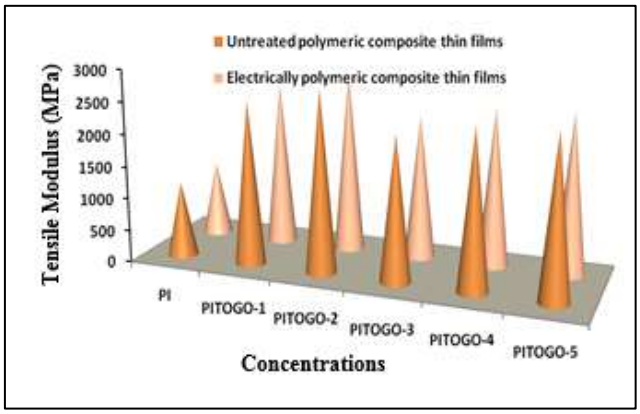

Fig. 4: Bar graph of tensile modulus for untreated and electrically treated PI and PITOGO Polymeric composite thin films.

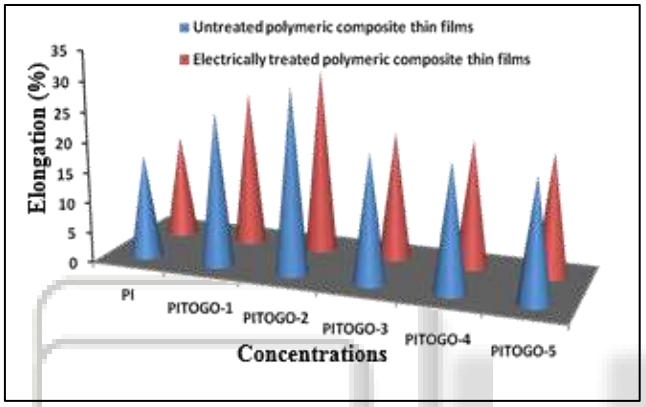

Fig. 5: Bar graph of elongation for untreated and electrically treated PI and PITOGO polymeric composite thin films.

VI. Conclusions

When ITO and GO were made to disperse in proper calculated wt% per unit area within the PI matrix, microhardness and micromechanical properties was found to be higher. The microhardness and micromechanical study on untreated and electrically treated polymeric thin films helps to understand the change in the properties due to inter and intra molecular interactions between ITO and GO oxide particle within PI matrix under electrical stress. The electrically treated PI+ITO+GO polymeric composite thin films exhibit higher level of microhardness and micro-mechanical properties as compare to untreated one. Thus developed PI+ITO+GO polymeric composite films might be a demandable material for electrical and electronic device for future.

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