

Evaluation of Activation Energy (E_a) Profiles of Nanostructured Alumina Polycarbonate Composite Insulation Materials

Sudha L. K., Sukumar Roy, and K. Uma Rao

Abstract—This paper focuses enhancement of the electrical insulation properties of commercial polycarbonate using nanostructured alumina as an additive material. Various polycarbonate composites have been prepared by varying the level of additive material and DC conductivity in presence of oxygen of the derived composite materials has been measured in which activation energy (E_a) profiles of the composites have been evaluated. Results show that the incorporation of additive significantly reduces the E_a for the DC conductivity of the composites, compared to the base polycarbonate material. Further, the decrease in the E_a in the DC conductivity is found to be dependent on the level of the additive in the composite body. As the polycarbonate polymers are used in the manufacturing of various insulating products, this study indicates the possibility of using such commercial polymers in the form of composites as a superior insulating material in the fields of electrical or electronic insulation and allied areas.

Index Terms—Activation energy, nano-structured alumina, DC conductivity, electrical insulation.

I. INTRODUCTION

A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material [1]. In case of nano-filled polymer composites, nano particulates are appropriately added to the identified polymer matrix that can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler [2]. This strategy is specifically effective in yielding high performance composites, when the dispersion of the filler is homogeneous and the properties of the nanostructured filler are substantially different or better than those of the matrix. The fillers added to the matrix are relatively small in quantity, usually upto 5 w% [3] and in some cases, a maximum filler level upto 10 w% have been reported. Nano-fillers could be amorphous in the XRD and could be associated with very low tap density (0.01 – 0.05 g/cc) besides its nanostructures in the particles [4], [5]. However,

because of high specific surface area of the fillers embedded in the matrix, the interaction of polymer matrix to that of the filler particles is expected to be significantly high, which sets the direction of the property of the composite to be achieved. Such interactions within the matrix can potentially alter various properties of the base polymers, i.e., mechanical, electrical, thermal, environmental [6] etc.

As per the transition-state theory, the activation energy, (usually represented by the symbol, E_a) is the difference in energy content between an activated or transition-state configuration to that of the corresponding initial configuration. The activation energy, as introduced by Hood about a century ago, as a purely empirical relationship and is temperature dependent. In this context, the Arrhenius conductivity equation is regarded as an experimentally determined parameter that indicates the sensitivity of the reaction rate to temperature. The E_a is a potential indicative parameter while evaluating a specific reactivity or function or property of interest of the material.

Being a good electrical insulator, polycarbonates (PC) represent an industrially important polymeric material, extensively used in electronic (PCBs) and allied insulation fields, because of its excellent durability, high impact resistance, heat resistance and flame retardant properties additionally with safety features, which are usable over a greater temperature range. It can also serve as a dielectric in high-stability capacitors. Because of the above characteristics and industrial relevance, polycarbonate materials were used in this study solely to enhance the electrical insulation properties through nano-filler incorporation. Two specific grades of the said polymer were sourced commercially and taken in this study as a base polymer material.

Under the present background, the objective of the present study is to enhance the electrical insulation properties [6], [7] of polycarbonate polymers by modifying such base polymers using nanostructured amorphous alumina as filler. Another objective is to evaluate the activation energy profile of the derived polycarbonate composites by measuring DC conductivity of individual composite material and examine the extent of lowering of activation energy, which is regarded as a proof of composite formation with enhanced electrical insulation characteristics.

II. EXPERIMENTAL

The two specific grades are (Trademark PC1100 and PC1220 polymers), which are available commercially in the form of solid crystals (manufactured by Samsung Makrolon) were used as a base material. On the other hand,

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nanostructured alumina (Al_2O_3) powder [4], [5], which is in-house synthesized by a LPG-fired spray pyrolysis system (LPG=liquid petroleum gas) was used as an additive filler material. The said alumina filler material has an amorphous structure in the XRD (x-ray diffraction) with a tap density of about 0.03 g/cc, which is further associated with primary crystallites of about 60 nm in the bulk particles of the material. The additive level in both the polycarbonate material, i.e., PC1100 (PC1) and PC1220 (PC2) was varied in the range of 1 – 5 w% and nano-modified polycarbonate composites with specific additive level of 1 w%, 3 w% and 5 w% respectively in each case were prepared and used as representative composite materials in this series.

The composites were synthesized by mixing the base polycarbonate polymers (PC1 and PC2) and the additive material (nanostructured alumina) in desired proportion using a Haake Rheo Mixer at CIPET, Chennai, India. As per the requirement of DC conductivity measurement, the composites specimens were prepared with desired dimension by punching into square shape (~ 1 cm × 1 cm with thickness about 2 cm) using the bulk composite material/s and also by maintaining uniform thickness.

DC conductivity (σ_{dc}) testing of the derived composites was carried out by employing the test set up, as shown in Fig. 1. Insulation resistances of the said composite specimens were recorded directly by varying the temperature of the sample in the aid test up from 30°C to 120°C.

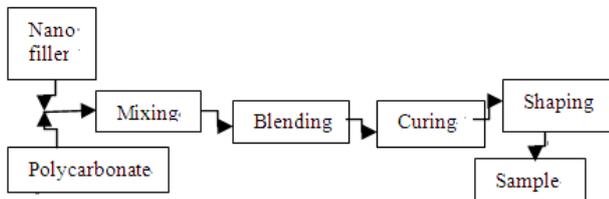


Fig. 1. The Composite processing scheme.

It has been observed that the σ_{dc} curves are linear from room temperature until a temperature up to 80°C and then σ_{dc} decreases in a small temperature range (upto a temperature of 88oC) and then further increases upto 120°C. It has been observed that the DC conductivity $\ln(\sigma_{dc})$ in S/m decreases with increase in temperature ($1/T$) in $1/^\circ$ Kelvin [8].

III. COMPOSITE MATERIAL PROCESSING AND SAMPLE PREPARATION

The scheme for the preparation and processing of composite materials is shown in Fig. 2. As mentioned in the previous section, the polycarbonate in the box (Fig. 2) represent both PC1100 (PC1) and PC1220 (PC2) grades of Samsung Macrolon Trademark, whereas the nano filler material in the box is nano structured alumina as described previously [3], [4], which is incorporated by weight percentage of 1%, 3%, and 5% respectively to each of the base PC1 & PC2 materials using Haake Rheo Mixer. Various composite materials are resulted when the said filler material with appropriate ratio is incorporated at the softening point of the polymer material at the elevated temperature ($120 \pm 5^\circ\text{C}$) by maintaining the speed of the

blades of the mixer about 120 rpm. The mixture has the provision to carry out both the blending and curing respectively. For comparison, a base material is also prepared by maintaining identical conditions and without incorporating any filler material therein. Hence, a total number of four sample specimens were prepared in each of the base polymer, which are named as i) base, PC1 (PC1100 polycarbonate and without any additive), PC1-1 (1 w% additive), PC1-3 (3 w% additive), and PC1-5 (5 w% additive) respectively. Similarly, other composite materials in the PC1220 polycarbonate series, PC2 (base polymer & without any additive), PC2-1 (1 w% additive), PC2-3 (3 w% additive) and PC2-5 (5 w% additive) respectively were prepared. The composite materials become hard when the temperature of the composite falls below 80°C or so. The composite material, upon cooling at ambient temperature, results in the form of lumps, in which sample specimens for the purpose of DC conductivity measurement could be generated into desired shape/dimension by uni-axial pressing using a suitable stainless steel die. The time taken for processing a single batch is about 60 minutes in the Haake Rheo Mixer.

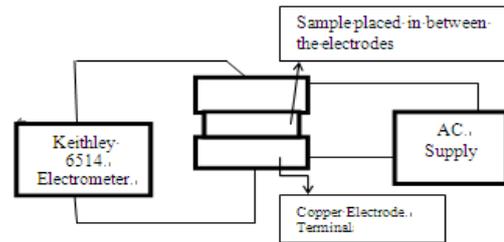


Fig. 2. Experimental set up.

IV. EXPERIMENTAL SET UP AND PROCEDURE

As any material could be specified by different properties such as conductivity [9], resistivity, dielectric constant, loss factor, insulation resistance, activation energy etc. and the specific property of interest would depend on the application for which the material is targeted [10]. Since the interest in the present work was to enhance electrical insulation properties of the composites [9], DC conductivity measurements were of primary interest in which the calculated ‘Ea’ value in the process provides the resistance of flow of current within the composite material.

The experimental set up is shown in Fig. 2. The sample is placed between the two copper electrodes in the furnace under the flow of oxygen gas. The copper electrodes are connected to the two probes of Keithley-6514 System

Electrometer, in which a $6\frac{1}{2}$ digit multi-meter enables direct measurement of current and insulation resistance (Giga ohms or Terra ohms region) as a function of temperature of the composite material. The temperature is varied in steps of 2°C from ambient temperature to 120°C.

V. COMPUTATION & EVALUATION OF ACTIVATION ENERGY (EA)

The resistivity and conductivity parameters are calculated by the following formulae.

$$R = \rho (l/A) \text{ ohm} \quad (1)$$

R is the resistance in gigaohms obtained from the Keithley-6514 System electrometer, l is the thickness of the sample in mm, and A is the area of cross section in mm^2 . The resistivity of the material ρ in $\Omega\text{-m}$ is calculated from the equation (1). ' σ ' is the conductivity [9], [10] in $\text{mho}\text{-m}^{-1}$ and is calculated using

$$\sigma = \frac{1}{\rho} \text{ mho}\text{-m}^{-1} \quad (2)$$

The Arrhenius equation plays a dominant role in classical studies of chemical kinetics [11]. It expresses the dependence of the rate constant over a wide range of temperatures in terms of only two parameters where A is the pre exponential factor; E_a is the experimental Activation Energy in joules by the following formula [12],

$$\sigma = A \exp\left(\frac{-E_a}{KbT}\right) \quad (3)$$

Kb is the Boltzmann's constant which is 1.3806×10^{-22} joules/kelvin, T is the temperature in Kelvin.

The E_a is in practice taken to be the slope of an Arrhenius plot of $\ln(\sigma)$ versus $\frac{1}{T}$ in Kelvin [12], [13]. The slope is

calculated as follows. $\left(\frac{-E_a}{KbT}\right)$ is the slope and equation (3) can be written as

$$\ln(\sigma) = \ln(A) \text{ slope}\left(\frac{1}{T}\right) \quad (4)$$

Now the value of the slope can be computed from the linear graph of $\ln(\sigma)$ vs $\frac{1}{T}$ in kelvin as follows [12]:

$$\text{Slope} = \frac{\Delta \ln(\sigma)}{\Delta \frac{1}{T}} \quad (5)$$

The activation energy (E_a) is now calculated as

$$E_a = -Kb \times \text{slope} \quad (6)$$

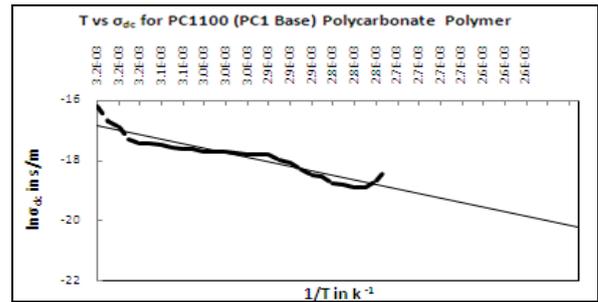
The slope being negative, a positive value of E_a is obtained.

VI. RESULTS AND DISCUSSIONS

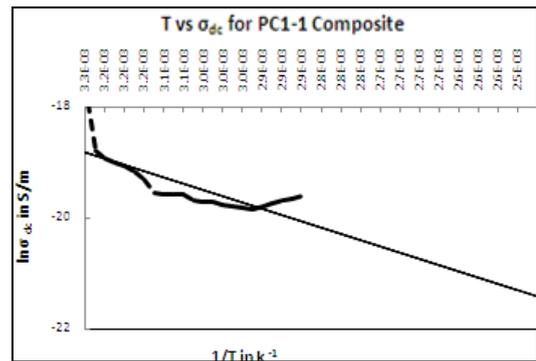
A. Variation of $\ln(\sigma_{dc})$ vs $(1/T)$ for PC1100(PC1) and PC1220(PC2) for Measuring Activation Energy

The Fig. 3(a), (b), (c), (d) indicates the variation of dc conductivity (--) shown as dotted lines as a function of temperature. It shows clearly, as the temperature increases DC conductivity decreases. The linear curves called as Arrhenius plots shown as straight line is obtained using curve fitting method. From the Arrhenius plots shown in Fig. 3(a), (b), (c), and (d) indicate that $\ln(\sigma)$ reduces gradually from the base polymer PC1 to PC1-1, PC1-3 & PC1-5 composites respectively. By using the Arrhenius plots, slope of the linear curve has been calculated by using

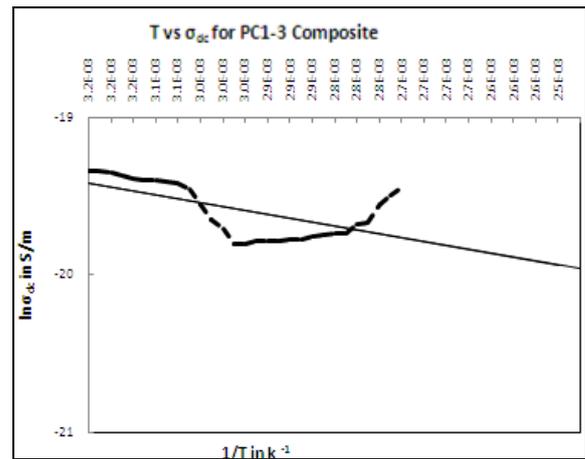
the equation (5) and E_a has been calculated by using the equation (6).



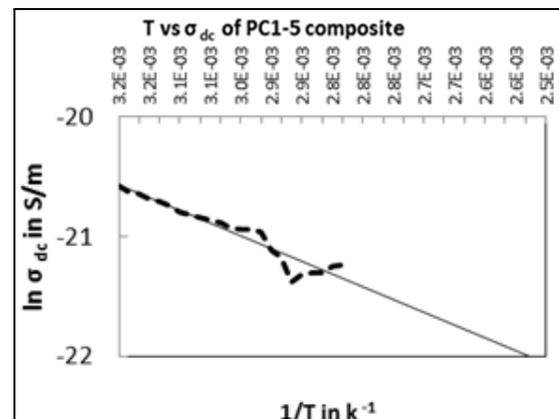
(a)



(b)



(c)

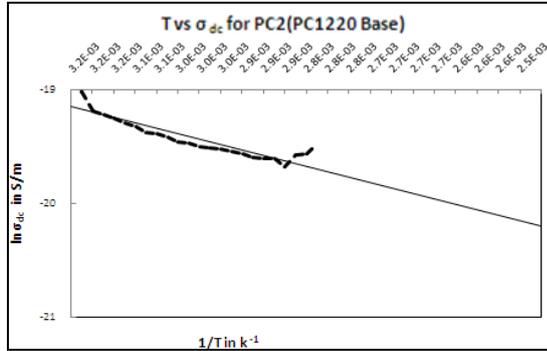


(d)

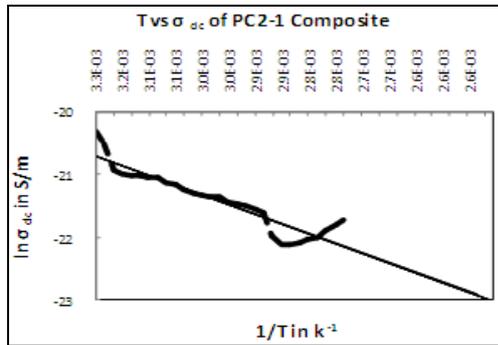
Fig. 3. $\ln(\sigma)$ vs $\frac{1}{T}$ for PC 1100 (PC1) base, 1%, 3%, and 5%.

As the above figures show that there is a gradual decrease in the $\ln(\text{dc conductivity})$ from the base polymer PC1220 to

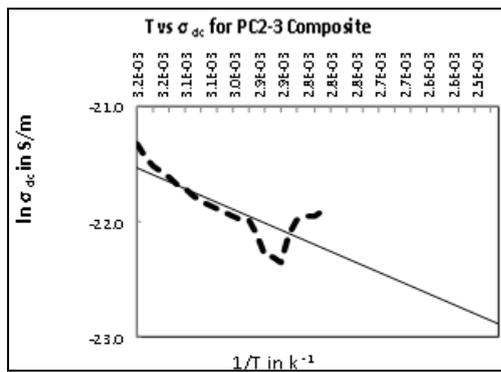
the corresponding 1 w%, 3 w%, 5 w% composites. The behavior of the Arrhenius plots in the composites belonging to both the polymer grades that is PC1100 (PC1) and PC1220 (PC2) is the same. The conductivity of PC1220 is lower as compared to PC1100. From the Arrhenius plots in the Fig. 4, the slopes and “Ea” are calculated that shows lowering of Ea in DC conductivity as function nano-filler incorporation. Hence, results show that both the polymer grades with the nano-filler modification could be used as a better insulating material [6]-[13].



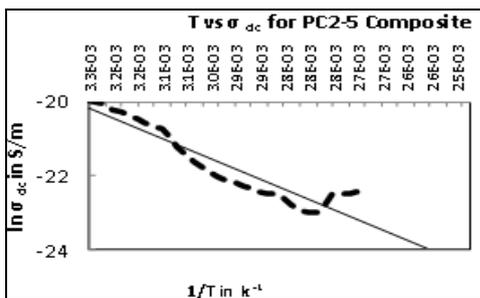
(a)



(b)



(c)



(d)

Fig. 4. $\ln(\sigma) \text{ vs } \frac{1}{T}$ for PC 1220(PC2) Base, 1%, 3%, 5% for measuring activation energy.

B. Activation Energy (Ea) Profiles

It is to be mentioned that after calculating the slope and the activation energy from the Arrhenius plots for different composites in each PC1 and PC2 series, Ea in electron volt are derived using $1\text{eV}=1.6 \times 10^{-19}\text{J}$. The decrease in the “Ea” of PC1 and PC2 composites is shown in Table I and Table II respectively. Data show that Ea of base polymer PC1100 is 0.03588 eV, which is then reduced to a value of 0.001025 eV by the incorporation of nanostructured alumina at 5 w% in PC1-5 composite. Whereas, Ea of base polymer PC2-Base is 0.041938eV, which is reduced to 0.0077eV in case of the composite PC2-5, a level of 5 w% addition of nanostructured amorphous alumina filler material.

TABLE I: ACTIVATION ENERGY (EA) OF THE BASE PC 1100 POLYMER AND THE COMPOSITES IN ELECTRON VOLT

Material	Ea (eV)
PC1	0.03588
PC1-1	0.00497
PC1-3	0.00288
PC1-5	0.001025

TABLE II: ACTIVATION ENERGY (EA) OF THE BASE PC1220 POLYMER AND COMPOSITES IN ELECTRON VOLT

Material	Ea (eV)
PC2	0.041938
PC2-1	0.01112
PC2-3	0.00816
PC2-5	0.0077

C. Comparison of Nanocomposite Material with the Base Polymer

The comparison of the “Ea” from the nano modified composites with the base polymer and in the terms of %age decrease in Ea after nanomodification is shown in the Table III and in the Fig. 5 and Fig. 6.

TABLE III: DECREASE IN “EA” IN ELECTRON VOLT FOR THE DERIVED NANOCOMPOSITES TO THAT OF BASE PC1100

Technical parameters.	Base PC1100	Nano composite with 1% nano additive	Nano composite with 3% nano additive	Nano composite with 5% nano additive
Activation Energy(eV)	0.03588	0.00497	0.00288	0.001025
%agedecrease in Ea after nano modification		-86.148	-91.97	-99.8

Thus, as the conductivity $\ln(\sigma)$ is reduced drastically from base polymer to nano-filler modified composites, the nano-structured alumina filler material, distributed in the composite matrix is creating further barrier for DC conductivity of the bulk composite material. The exact role

of the said filler is to be understood further in the course of future work. Such composite materials in both the polymeric systems provide the opportunity of using as better insulating materials in applications.

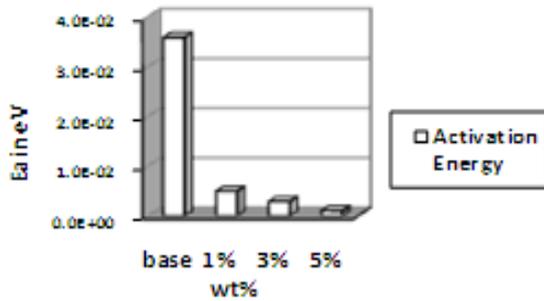


Fig. 5. Ea vs. wt% of PC1 in the composites.

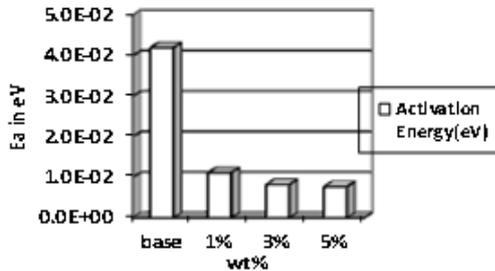


Fig. 6. Ea vs. wt% of PC2 in the composites.

VII. CONCLUSION

The work highlights the processing of nanostructured alumina modified commercial polycarbonate composite materials and its feasibility of using such composite materials as a better electrical insulation material. Experimental results indicate that a significant reduction in activation energy for the Dc conductivity in composite materials is achieved, as compared to their counter base polymers. Activation energy profile for DC conductivity of the composite specimens shows that through this nano-modification, Ea levels are drastically reduced. Such composite materials could find applications as the dielectric medium in capacitors and also as a better base insulation material for (PCB) Printed Circuit Boards.

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