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An experimental study on effect of thermal properties of PVDF Polymer

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Abstract: In this paper, the application of photoacoustic method to study the thermal properties of Polyvinylidene fluoride (PVDF) is described. PVDF is a semicrystalline polymer whose crystalline domains appear in four different forms. These forms may be interconverted by the application of heat, pressure,electrical fields,pyroelectric and optical devices. PVDF has such unique properties as flexibility, ruggedness, availability as thin films, and low acoustic impedance, but a somewhat smaller electromechanical coupling factor. The photoacoustic measurements are carried out for thermal properties on PVDF.The theoretical basis for quantitative measurements are discussed together with the advantages and limitations of these methods as compared with conventional measurements.
Keywords: Polyvinylidene fluoride (PVDF) Polymer, Photoacoustic, Thermal Conductivity, Thermal Diffusivity.

Introduction

Weight, shape-flexibility, cost effectiveness and good processability of a material are the key factors for electric power applications, so polymeric materials play an important role [1]. Polyvinylidene fluoride (PVDF) stands out amongst other polymers due to its extraordinary pyro-and piezoelectric properties and also technologies concerning the development of the passive components such as resistors, inductors, and capacitors are steadily growing in the electronic industries [2-3]. Not only the Electronic components, useful for all household components and particularly solar cell design and fabrication.

PVDF is a semicrystalline polymer consisting of long chain molecules with the repeat unit CF_2CH_2. Its molecular weight is about $l0^5$ corresponding to 2000 repeat units or an extended length of $0.5x\ 10^{-4}$ cm. Chain defects of the head to head (CF_2 followed by CF_2) and the tail to tail (CH_2 followed by CH_2) types occur in a few percent of the sequences. The material consists of about 50% lamellar crystals which are of the order of 10^{-6} cm thick and up to 10^{-5} cm long. The crystals are embedded in an amorphous phase which has super cooled liquid properties with a glass-transition temperature T_g of about -40^0C when measured at low frequencies[3]

The sound effect induced in a heated solid by an intermittent light beam was first observed by Bell in the eighteenth century [4]. This effect was understood as a photothermal (PT) phenomenon and was the origin of the so-called photoacoustic effect. Nowadays, there is a wide range of PT techniques and most of them were derived from the Photoacoustic Spectroscopy (PAS). Basically, their differences are related to the employed detection schemes. There are detection systems using: photodiodes [5], pyroelectrics [6,7], piezoelectrics [8, 9], thermopiles [10], and microphones [11,12]. Recently Pena-Rodriguez et al. [13] have determined the thermal diffusivity of low carbon steel at room temp using the photoacoustic(PA) technique in a heat transmission configuration. This technique has been widely used in the thermal characterization of any type materials because it offers several advantages over other methods such as high precision, small sample management and non destructive technique. We can measure without direct conduct and the temperature varies inside the photoacoustic cell are small [14-17].

Material

Definite amount of PVDF powder (as purchased from Alfa Aesar) was dissolved in dimethylformamide at a temp 60^{o}C. Solution is then poured on to a glass mould and allowed to evaporate nearly 6 Hours at constant temp of 60^{o}C. Membrane of size is < 1mm thickness. Like this various membranes of different thickness and concentration are prepared.

Experimental

Photoacoustics:

Photoacoustic spectroscopy(PAS) offers minimal or no sample preparation, the ability to look at opaque and scattering samples [18] and the capability to perform depth profiling experiments. In particular, depth profiling experiments are useful for the characterization of surface coated ,laminar materials and to studies the weathering, aging, curing and also the diffusion of species into or out of a polymer matrix.

When a modulated light is absorbed by the sample located in a sealed cell, the non radiative decay of the absorbed light produces a modulated transfer of heat to the surface of the sample. This modulated thermal gradient produces pressure waves in the gas inside the cell that can be detected by the attached microphone. The resulting signal depends not only on the amount of heat generated in the sample (and, hence, on the optical absorption coefficient and the light-into-heat conversion efficiency of the sample) but also, how the heat diffuses through the sample [18]. The quantity, which measures the rate of diffusion in a material, is the thermal diffusivity α. Apart from its own intrinsic importance, thermal conductivity can be directly evaluated from this thermal diffusivity.

Photo Acoustic Spectrometer

The photoacoustic spectrometer is shown in fig1. where 400 W Xe- lamp (Jobin Yvon) is used as the light source. The sample is placed in the PA cell and a microphone is placed very near to the sample. To get the modulated light, a mechanical chopper (Model number PAR 650) is used with the source. The PA signal from the sample is fed to a lock in amplifier (Model Perkin Elmer 7225 DSP). The light is allowed to fall on the sample through a monochromator (Model Triax 180, Jobin Yvon). Before doing the actual experiments, the spectrum profile of Xenon lamp was studied and proper care is taken when the spectral response of a material is studied i.e. only in the region where the spectral profile is nearly flat. [Xe lamp will have an emission peak at 480 nm].

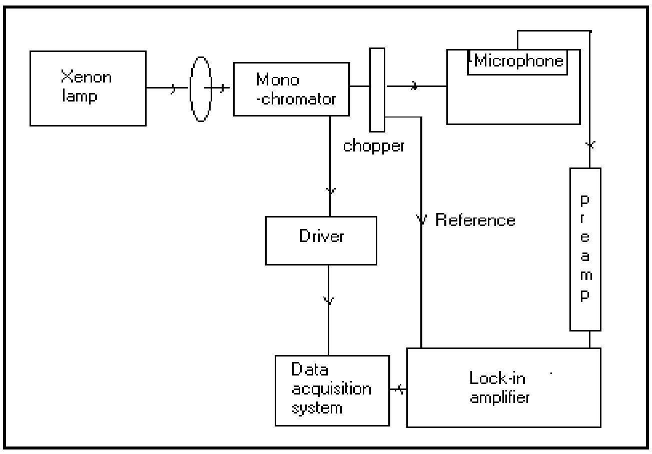

Fig. 1 Schematic diagram of the PA setup

Photo Acoustic Measurements:

The sample is taken inside the PA cell and the PA signal is observed for different chopping frequencies. The thermal diffusivity was determined from the thermal diffusion model [19] of the photoacoustic effect which states that, for an optically opaque and thermally thin sample the pressure fluctuations are given by,

$$\delta p = \gamma p_0 I_0 (\alpha_g \alpha_s)^{1/2} \exp j\left(\omega t - \frac{\pi}{2}\right) / 2\pi T_0 l_g \kappa_s f \sinh(l_s \sigma_s) \qquad (1)$$

where γ is the specific heat ratio of air, p_0 the ambient pressure, I_0 the incident light beam intensity, T_0 the room temperature, f the chopping frequency and l_i, k_i, and α_i are the thickness, thermal conductivity and thermal diffusivity of material i, respectively.

The subscript i denotes either sample (s) or gas (g) and $\sigma_i = (1+j)\, a_i$ with $a_i = \left(\frac{\pi f}{\alpha_i}\right)^{1/2}$ is the complex thermal diffusion coefficient of material 'i'. Particularly, for an optically opaque and thermally thick sample ($l_s\sigma_s$ >>1), the expression for the photoacoustic amplitude is given by,

$$S = \frac{A}{f}\exp(-af^{1/2}) \qquad (2)$$

where the constant A, apart from geometric constants, include factors such as the light intensity, room temperature, gas thermal properties and $a = \left(\frac{\pi l_s^2}{\alpha_s}\right)^{1/2}$. From the slope of ln(f. S) as a function of $\sqrt{f}$, we deduce the thermal diffusivity, α of the sample from this relation $a = \left(\frac{\pi l_s^2}{\alpha_s}\right)^{1/2}$

Thermal conductivity is,

$$\kappa = \alpha \rho C_p \ \text{Wm}^{-1}\text{K}^{-1} \qquad (3)$$

where ρ is the density and C_p is the specific heat capacity.

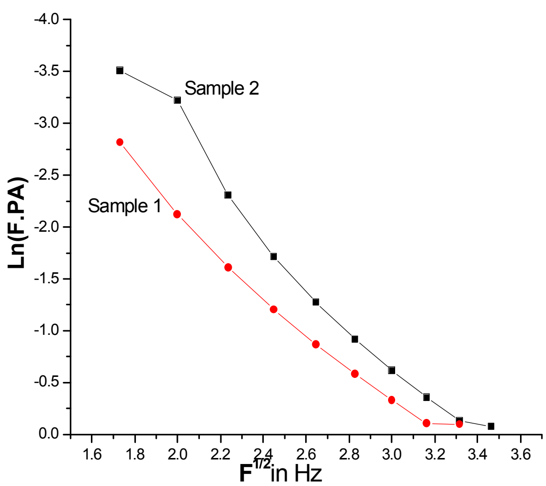

Fig.2:**Variation of PA signal with chopping frequency- PVDF**

Table 1: Thermal diffusivity and Thermal conductivity for PVDF

S.No.	At room temperature	Thermal diffusivity (mm^2/sec)	Thermal conductivity ($Wm^{-1}K^{-1}$)
1	Photoacoustic	17.3(sample1) 16.4(sample-2)	0.46 0.43
2	Literature	6.0	0.16[19]

Results and Discussion

In order to determine whether the method gives accurate results,we carried out a series of measurements on selected samples whose thermal parameters were already known. The thermal diffusivity and thermal conductivities of a number of such samples have been determined. Thermal diffusivity value obtained by employing the present technique agree very well with the ones already reported in the literature, establishing the reliability and accuracy of this technique. The values agree very well with the values reported in the literature, to within experimental limits. Fig.2 shows the plot of PA signal amplitude versus modulation frequency. The goal was to measure the thermal diffusivity of PVDF for various thickness. Thermal diffusivity values for all the samples are summarized in Table 1.The thermal diffusivity of PVDF is found to be 17.3cm^2/sec with the literature value of 6.0 cm^2/sec. and thermal conductivity of the PVDF is 0.46$Wcm^{-1}K^{-1}$ which has been shown to give good agreement between experimental and literature value. The results reveal that the thermal diffusivity is almost unaffected under heat treatment. This is very important as the material used in storage applications should withstand any drastic changes of working temperatures and other environmental conditions. For such useful PVDF, thermal diffusivity and thermal conductivity are not available in the literature for various heat treated conditions and here they are reported.

Conclusions

- Thermal diffusivity here is more compared to the literature value
- The exact number of monomers is not known in both the cases.
- This will be useful for photopyroelectric effect
- The material properties of PVDF has been greatly enhanced for the past few years Particularly x-ray and infrared transmission measurements have clarified structural details of the crystalline forms.
- Such experiments were also instrumental for the confirmation of the Thermal properties of PVDF. These findings led to a better understanding of the piezoelectric behavior of this material.

References

1. Thomas P, Varughese KT Compos Sci Technol 2010;70(3):539–45.
2. V. Ranjan, L. Yu, S. Nakhmanson, J. Bernholc and M. B. Nardelli. Acta. Cryst., A66 (2010) 553-557.
3. Y. R. Wang, J. M. Zheng, G. Y. Ren, P. H. Zhang and C. Xu. Smart Mater. Struct., 20 (2011) 045009
4. A.G. Bell, Am. J. Sci. 20 (1880) 305.
5. A.C. Boccara, D. Fournier, and J. Badoz, Applied Physics Letters, 36 (1980) 130.
6. A. Mandelis, Chemical Physics Letters, 108 (1984) 388.
7. H. Coufal, Applied Physics Letters, 44 (1984) 59.
8. W. Jackson and N.M. Amer, Journal of Applied Physics, 51 (1980) 3343.
9. J. Mura, L.C.M. Miranda, M.L. Baesso, A.C. Bento, and A.F. Rubira, J. Appl. Pol. Sci., 82 (2001) 2669.
10. S.O. Kanstad and P.E. Nordal, Powder Technology, 22 (1978) 133.
11. A. Rosencwaig and A. Gersho,Journal of Applied Physics, 47 (1976) 64.
12. M.D. da Silva, I.N. Bandeira, and L.C.M. Miranda, Journal of Physics E: Scientific Instruments, 20 (1987) 1476.
13. G. Peña-Rodríguez, O. Flores-Macías, C. Angeles-Chávez,J. A. I. Díaz Góngora, Orea, and F. Sánchez Sinencio, *Anal. Sci*. 17 (2001) s357.
14. D. Fournier, J. P Roger, A. Bellouati, C. Boué, H. Stam, and F. Lakestani. *Anal. Sci*.17 (2001) s158
15. L. F. Perondi and L. C. M. Miranda, *J. Appl. Phys*. 62, (1987) 2955.

16. A. Calderón, R. A. Muñoz Hernández, S. A. Tomás, A. Cruz Orea, and F. Sánchez Sinencio. J. Appl. Phys 84 (1998) 6327.
17. L.R.de Freitas, A.M..Manasanares and E.C.da Silva,Review of Sci.Inst 74 (2003) 735.
18. S.Mahalakshmi, P. Palanichamy and K.Ramachandran., NDT&E 9 (2004) 6.
19. A.Rosencwaig., *Phys. Today.,* 28. (1975) 23.

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