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STUDY OF GLASS TRANSITION TEMPERATURE OF PMMA AND CdS-PMMA COMPOSITE

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The present study investigates the effect of dispersed CdS on the α- and β- relaxation processes of Poly (methyl methacrylate) (PMMA). Dynamic Mechanical Analyser (DMA) have been employed at fixed frequency 1Hz at temperatures from –80 °C to 150 °C to study the dynamics of films of thickness ~ 0.05 mm of PMMA and CdS-PMMA composite. Amorphous PMMA polymer exhibits two relaxation processes. A primary (glass, or α-) relaxation process commonly referred as glass transition or α-relaxation process and a low-temperature relaxation process associated with the hindered rotation of the side group usually referred to as the β-relaxation process. CdS dispersed PMMA composite also shows α and β relaxation process and are observed at higher values of temperature as compared to pure PMMA. The higher values of glass transition temperatures are attributed to the more rigid structure of the CdS- PMMA system over the pure PMMA.

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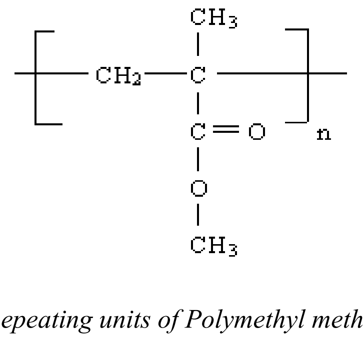
Keywords: Dynamic Mechanical Analyser, Glass transition temperature, PMMA, CdS nanocomposite.

1. Introduction

Poly (methyl methacrylate) or PMMA is the most commonly used polymer among the methacrylate family and has found tremendous application in automotive and home appliances [1]. The chemical structure of PMMA is shown in Fig. 1.



$$\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)-O-CH_3}{C}}- \right]_n$$

Fig.1 Repeating units of Polymethyl methacrylate

Nanoparticles used as fillers in polymer matrix has also proved to be useful and added much bulk to their applications. Polymer/nanoparticle composite films are used in different fields of technology such as solar cell device [2], catalysis [3, 4], lithium battery devices [5] and maganetic storage devices [6, 7]. The addition of nanoscale fillers to polymers can have a dramatic

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effect on the mechanical properties [8, 9] compared to micron scale fillers. This may be in large part due to the small size of the filler and the large surface area of nanoscale fillers. When the filler particles are added into the polymer matrix, they may or may not have interaction with the polymer. It has been reported [10] that even in the absence of specific interactions with the polymer, filler behaves as highly functional physical crosslinks and hence reducing the overall mobility of the polymer chains.

Both PMMA and CdS-PMMA exhibits a β-relaxation characterized by a transition temperature (T_β) in the neighbourhood of the α-relaxation, or glass transition temperature (T_α). The β-relaxation is associated with the hindered rotation of the methacrylate side group, while the α-relaxation is due to main chain motions [11].

The mechanical properties exhibited by the polymethacrylates family of polymers are significantly influenced in end-use applications by the presence of glass transition temperature. In this work, the effect of dispersed CdS, on the glass transition temperature of Poly (methyl methacrylate) (PMMA) has been investigated using DMA.

2. Experimental

2.1. Material preparation

CdS nanoparticle preparation: In order to prepare Polymer / nanocomposite samples, firstly CdS nano-particles have been prepared by simple chemical method using $CdCl_2$ and H_2S gas produced from thiourea [12]. The nanostructure of the CdS particles has been ascertained through X-ray Diffraction (XRD). The wide angle X-ray diffraction pattern has been recorded using a Philips 1840. The nanocrystallites powder was pressed inside the sample holder and, and the X-ray diffraction data was collected in the step scan mode. Transmission.

Fig.2 shows the XRD pattern of CdS nanoparticle. The presence of broad peaks confirms the nano size of the prepared nanoparticles. The average particle size obtained from Debye Scherrerr formula [13] is 3 nm.

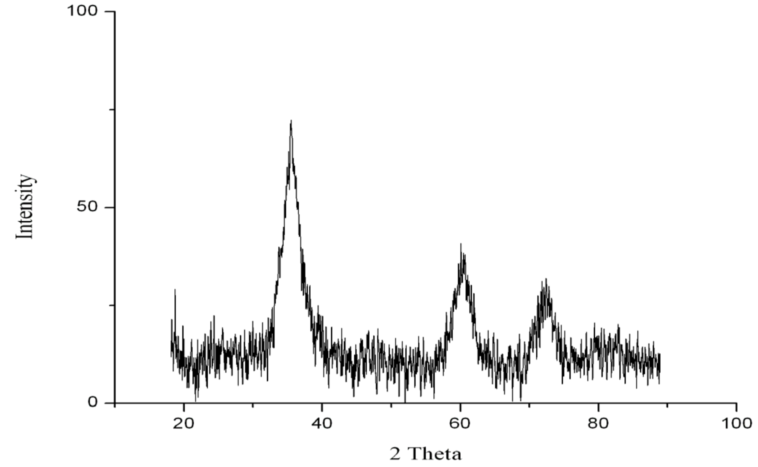


Fig.2 The XRD pattern of CdS nanoparticle

CdS-PMMA Nanocoposite preparation: Now for the preparation of CdS-PMMA composite, PMMA of laboratory grade was dissolved in Tetra hydrofurane (THF) solvent and 10 % of PMMA chalcogenide CdS nanoparticles was dispersed in this PMMA solution. This solution was then stirred with the help of magnetic stirrer and then poured into flat-bottomed petri dishes to form film with a thickness of ~ 0.05 mm. The solvent is allowed to evaporate slowly over a period of 24 hours in dry atmosphere. The so obtained film was then peeled off and dried in vacuum at 50 °C, well below the boiling point of solvent to avoid bubbling, for 24 hours in order to ensure the removal of the solvent [14, 15].

2.2. Measurement technique

Dynamic Mechanical Analyzer (DMA) is a sensitive technique that characterizes the mechanical response of materials by monitoring property change with respect to the temperature and frequency of applied sinusoidal stress. In this instrument, a force is applied to a sample and the amplitude and phase of the resultant displacement are measured. DMA employs a linear actuator where the applied force /stress to the sample is calculated from the knowledge of the input signal to the electromagnet coils of the driver [16]. The sinusoidal stress that is applied to the sample generates a sinusoidal strain or displacement. This applied stress/force is taken to be small, so as not to alter the shape and size of the material being analyzed. By measuring both the amplitude of the deformation at the peak of sine wave and the lag between the stress and strain sine waves, quantities like the modulus, viscosity and the damping can be calculated. When the response of the material to the applied wave is perfectly elastic, the input response is in-phase with that of output i.e. phase lag (δ) = 0^0, while a viscous response gives an out of phase, i.e. $\delta = 90^0$. Viscoelastic materials fall in between these two extremes i.e. $0^0 < \delta < 90^0$ [17].

This technique separates the dynamic response of materials in to two distinct parts: an elastic part (E′) and a viscous component (E″).

$$E^* = E' + iE'' \tag{1}$$

where, complex modulus E* is defined as the instantaneous ratio of the in-phase or elastic response E′ (which is proportional to the recoverable or, stored energy) and viscous response E″ (which is proportional to the irrecoverable or, dissipated energy).

Mechanical loss factor (Tan δ) is another useful parameter, which can be very useful in order to compare viscoelastic responses of different materials

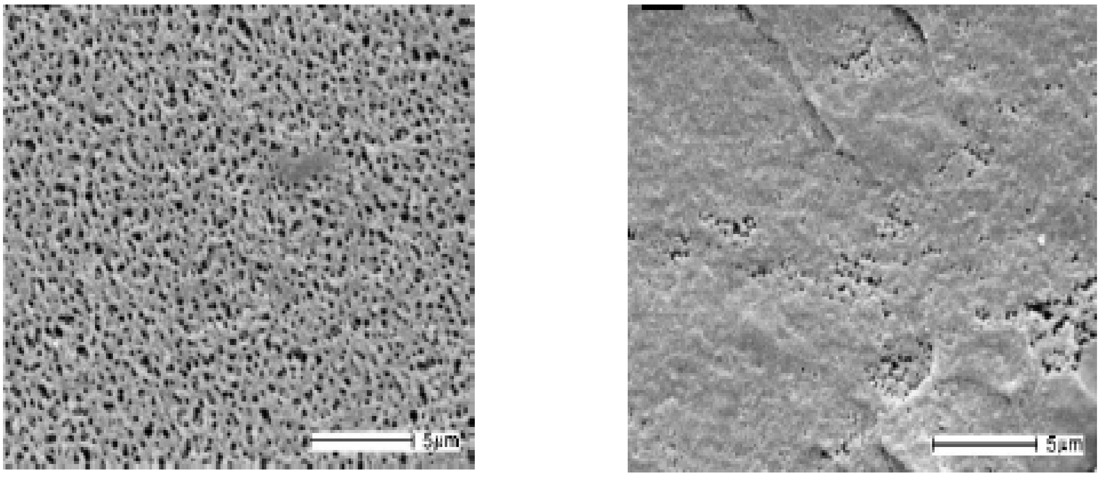
$$\mathrm{Tan}\ \delta = E'' / E' \tag{2}$$

where Tan δ (damping factor) is the ratio of energy dissipated/ energy stored. The technique has gained a great amount of popularity due to its speed and high accuracy and ability of scanning the materials over a wide range of temperature and frequency.

Film samples were cut to be between 4-6mm in width and 10mm in length for DMA measurements. After mounting the sample in tension mode, the furnace was sealed off, scanned over a temperature range from 30°C to +150 °C at fixed frequency 1 Hz. The heating/ ramp rate was 2 °C/min and strain amplitude 0.01mm within the linear viscoelastic region for all temperature scan tests. The mechanical loss factor (Tan δ) has been determined during the test as a function of increasing temperature [18].

2.3. Morphological characterization

The surface morphology of the samples have been characterized using Scanning Electron Microscopy (SEM) Quanta Fe-200 model. Fig. 3 (a) and (b) shows the micrographs of pure PMMA and CdS dispersed PMMA. From the figures it is observed that dispersed CdS filler particle creates considerable change in the morphology of the pure PMMA film.



(a) *(b)*

Fig.3 (a) SEM micrographs of pure PMMA (b) SEM micrographs of CdS-PMMA

The SEM images of the pure PMMA shows a pores and granular structure while the CdS dispersed PMMA matrix exhibits a smoother and more compact amorphous surface morphology.

3. Results and discussion

Figure 4 shows the dependency of Tan δ of PMMA and CdS-PMMA on temperature at a 1 Hz frequency.

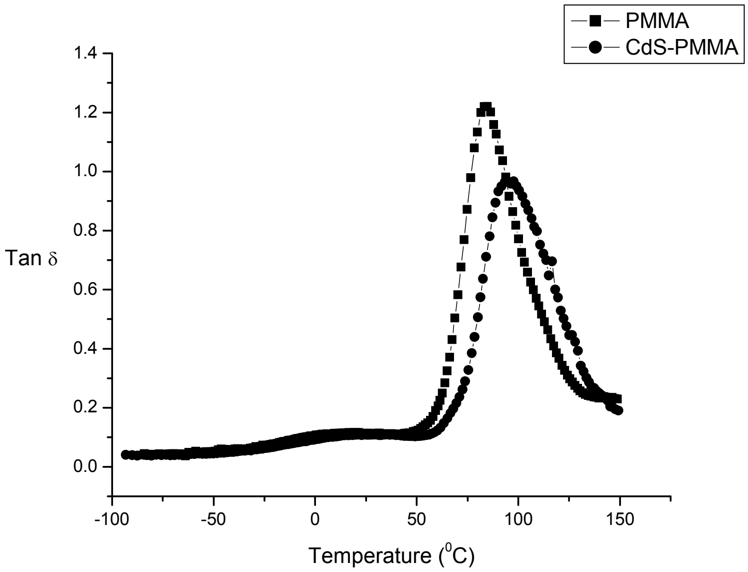


Fig. 4 Variation of Tan δ with temperature for pure PMMA and CdS dispersed PMMA

The figure clearly reveals the existence of two relaxation processes in the investigated temperature ranges. The first appearing in the higher temperature range, is attributed to the α-transition or α relaxation, while the second appearing in the lower temperature range to the β-transition or β relaxation. These two relaxations are designated as β and α process in order of increasing temperatures. The α-transition, which involves motion in long segments of the main polymer chain, is related to the glass transition temperature. The β-transition involves rotation of short-chain ester side groups attached to the polymer backbone and therefore occurs below T_g.

The variation of Tan δ showed a small peak at lower temperatures that could not be analysed due to the low amplitude of the phenomenon, but it was assumed to be a signature of a secondary relaxation or β relaxation process.

The α-process is related to the glass– rubber transition, associated with the primary relaxation involving segmental or micro-Brownian motion of molecular nature and appears at temperatures higher than the glass transition temperature, T_g. On the other hand, the β- process, appears at temperatures lower than T_g, and arises from the partial motion of side –COOR groups around the C–C bonds linking these groups to the main chain (this restricted mobility of the ester group may be due to the intermolecular H-bonding formation) [19].

The results reveal that the α and β transition peaks for CdS-PMMA composite are exhibited at higher values of temperature as compared to pure PMMA. This higher value for CdS dispersed PMMA composite can be explained on the basis of the amount of free volume in a sample. Doolittle [20] and Turnbull et al [21, 22] applied the concept of free volume to a wider class of disordered solids. The main idea behind this approach is that the probability of movement of a polymer molecule segment is related to the free volume availability in a system. The free volume is associated with the space between molecules in a sample. By dispersing the CdS nanoparticle in PMMA, the CdS particle get inside the voids present in the PMMA matrix as a result of which the free volume of the matrix decreases. The same results are also confirmed from the SEM images of PMMA and CdS-PMMA. This decrease in free volume restricts the mobility of the chains forming a compact structure and therefore more energy is required to activate the segmental motion of the chains. Hence, the CdS dispersed PMMA exhibit a higher glass transition temperature.

4. Conclusion

The investigated PMMA and CdS dispersed PMMA polymers show well resolved α and β relaxation processes. The α relaxation is attributed to the glass–rubber transition and the β process is assigned to the motion of the side ester groups. The addition of CdS nanoparticle in PMMA gives the higher value of transition temperature due to their more rigid structure.

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