

## THE EFFECT OF PRESSURE ON THERMAL PROPERTIES OF POLY(PHENACYLMETHACRYLATE)

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The influence of pressure on the polyphenacilmethacrylate [poly(PAMA)] was investigated using thermal and scanning electron microscopical (SEM) methods. It is observed that the application of pressure reduces 10% of the initial glass transition temperature. A part from each of the sample was taken for thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The activation energies were calculated by Ozawa method and significant changing was observed due to this calculation justified the effect of applying pressure.

**Keywords:** activation energy, pressure effect, thermal analysis

### Introduction

Amorphous polymers show a very interesting behaviors such as two-level systems, thermal conductivity and excess of vibration density of states [1]. Non-linear optical measurements on several amorphous polymers confirmed the existence of the changing of local structures at pressures in the 1.1–1.5 kbar range [2]. The dynamic structure factor  $S(Q,E)$  of polymeric glass shows an inelastic feature that disperses with momentum transfers  $Q$  and also by increasing the hydrostatic pressure up to 4.5 kbar the energy position of this excitation linearly increases, with a change of slope around  $P_0=1.6$  kbar [3]. It was reported that the effect of pressure on the fluorescence of two flexible dye molecules (a series of para-substituted benzylidenemalononitriles dissolved in solid poly(methyl methacrylate)) exhibit a remarkable increase of intensity and slowing of excited state decay [4]. Changing of the second harmonic generation (SHG) in organic crystals is a subject of extensive investigation and some original studies of the influence of pressure on SHG in some organic crystalline compounds were reported previously [5]. In a previous study [6] we described the synthesis and spectroscopic characterization of polyphenacilmethacrylate [poly(PAMA)] monomer and its homopolymer. In this work the pressure effect on the sample was investigated by using different methods, calorimetric and SEM. It is found that poly(PAMA) is not a visible light sensitive.

### Experimental

A desiccated adequate amount of poly(PAMA) was taken and prepared as a pellet for applying proper pressure. The glass transition temperatures ( $T_g$ ), were determined by a Setaram 131 DSC. 5–8 mg samples were held and sealed in the aluminum crucibles. The heating rate was fixed to  $20^\circ\text{C min}^{-1}$ . Heating procedures were carried out under the high purity nitrogen atmosphere  $20\text{ mL min}^{-1}$ .  $T_g$  was taken as the mid-point of the transition region from the DSC measurement. Also the thermal stability of the polymers was investigated under the nitrogen atmosphere using a heating rate of  $10^\circ\text{C min}^{-1}$ . TG curves were obtained and the decomposition activation energies ( $E_d$ ) for thermal degradation of poly(PAMA) were calculated at various heating rates using the Ozawa method, which is one of the widely used methods [7]. Degradations were scanned using temperatures from 30 to  $500^\circ\text{C}$  under nitrogen flow. Heating rates  $\beta$ , were varied as 4.0, 7.0, 10.0,  $12.5^\circ\text{C min}^{-1}$ . 5.0–8.0 mg samples held in an aluminum crucibles were used and the variation of the mass with temperature was measured as a function of temperature and stored into the as a list of data of the appropriate built-in program of the processor. The TG curves were transferred to the computer and plotted for various heating rates. The microstructure of the poly(PAMA) was examined by a scanning electron microscopy (SEM), Hitachi, Model: JSM-5600 imaging mode.

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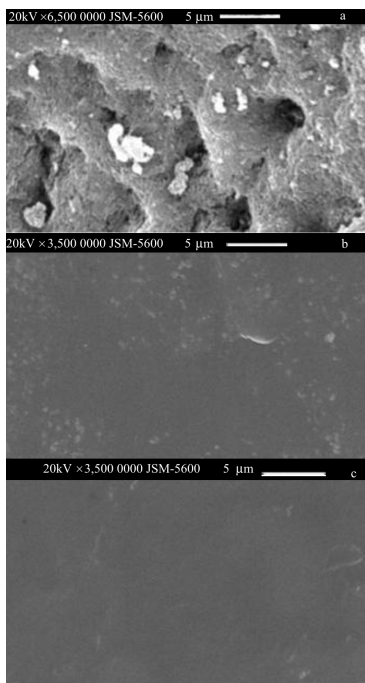
## Results and discussion

### Microstructure

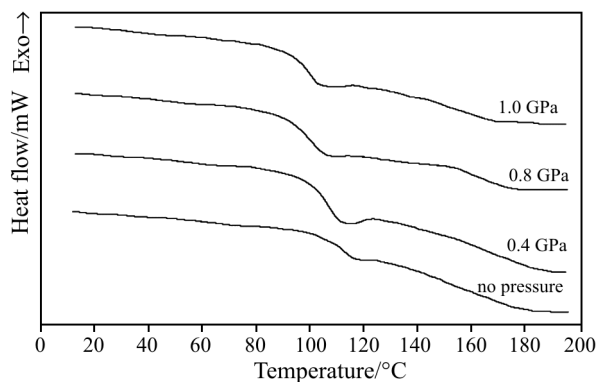
The physical effect of pressure was observed by SEM. Figures 1a–c show the micrograph of the poly(PAMA) polymer obtained from scanning electron microscope before pressure and after 0.2 and 0.6 GPa pressure. The white colour of the sample changes to opaque yellow and finally almost transparency was observed. Those pictures display a clear difference in microstructure from the powder poly(PAMA). Figure 1a shows very clear that the size of the nuclides and holes of the polymers are very clear and the distance of the molecules are wider. The size of the nucleation and structure of the polymer chains is changed as expected (Fig. 1b). More pressure caused to reduce the size of the nuclides and the gap of each chain (Fig. 1c).

### The effect of pressure on the glass transition temperature

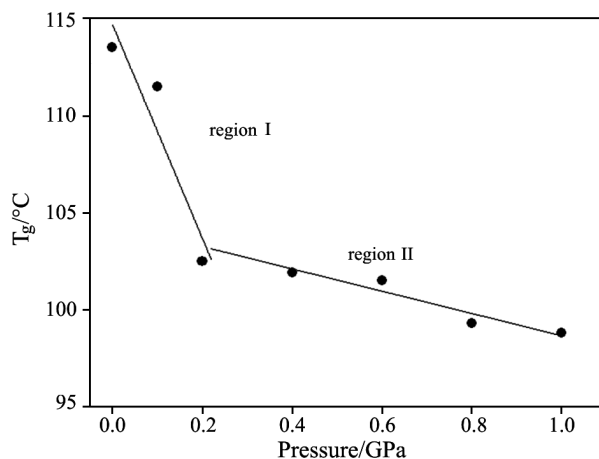
The DSC curves are shown in Fig. 2. It is observed that the glass transition temperature  $T_g$  shifted from 113.5 to 98.8°C with applied pressure. The variation is 14.7°C. It should be pointed out that the pressure tends to decrease the  $T_g$ . This implies that the plasticization and pressure effect were not cancelled out by each other. The DSC curves show an endothermic peak. It is suggested that decrease in the  $T_g$  is due to the gap of the molecules reducing when the external pressure was applied to the poly(PAMA). If the molecules are closer to



**Fig. 1** SEM micrographs of poly(PAMA) under different pressures, a – powder, b – 0.2 GPa and c – 0.6 GPa



**Fig. 2** DSC curves of poly(PAMA) under different pressures



**Fig. 3** The pressure dependence of the glass transition temperature

each other, the heating transfer becomes much easier than the molecules which are not under the pressure. The pressure dependence of the glass transition temperature is shown in Fig. 3. It is observed that the glass transition temperature decreases with increasing pressure. The figure shows that there are two regions (I and II) having different slopes. Applying the well known Clausius–Clapeyron equation, which gives the change of the temperature of the glass transition with pressure. Clausius–Clapeyron equation can be expressed as,

$$\frac{dT_g(\sigma)}{d\sigma} = \frac{\Delta V}{\Delta S} \quad (1)$$

where  $\Delta V$  is the volume and  $\Delta S$  is the entropy change. The calculated pressure derivatives ( $dT_g/dP$ ) of the polymer for both regions in Fig. 3 are  $-55$  and  $-5.75^\circ\text{C GPa}^{-1}$ .

### The effect of the pressure on decomposition kinetics

The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TG) in a nitrogen stream at a heating rate of  $10^\circ\text{C min}^{-1}$ . The TG curves of

polymer under no pressure, 0.2 and 0.6 GPa are shown in Fig. 4, it is clear that two degradation stages for poly(PAMA) were observed. For this study on the kinetics of thermal degradation of polymers we can select the isothermal thermogravimetry (ITG) or the thermogravimetry (TG) at various heating rates [8]. ITG is superior to obtain accurate activation energy for thermal degradation, although it is time-consuming. In the case of thermal degradation of polymers, in which depolymerisation is competing with crystallization or cross-linking due to the side groups, the TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in the present work TG curves at various heating rates were obtained and the activation energies ( $\Delta E_d$ ) for thermal degradation of polymers were calculated by Ozawa's plot, which is a widely used method.  $E_d$  calculated from the Ozawa method is superior to other methods for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy [9]. Degradations were performed in the scanning mode, from 30 up to 500°C, under nitrogen flow (20 mL min<sup>-1</sup>), at various heating rates ( $\beta$ : 4.0, 7.0, 10.0 and 12.5°C min<sup>-1</sup>). Samples of 5–8 mg held in alumina open crucibles, were used and their masses were measured as a function of temperature and stored in the list of data of the appropriate built-in program of the processor. The TG curves were immediately printed at the end of each experiment and the masses of the sample at various temperatures were then transferred to a PC.

According to the method of Ozawa [7], the apparent thermal decomposition activation energy,  $E_d$ , can be determined from the TG curves under various heating rates, such as in Fig. 5 [for poly(PAMA) under the 0.2 GPa pressure], and the following equation:

$$E_d = -\frac{R}{b} \left[ \frac{d \log \beta}{d(1/T)} \right] \quad (2)$$

where  $R$  – gas constant;  $b$  – a constant (0.4567); and  $\beta$  – heating rate (°C min<sup>-1</sup>). According to Eq. (2), the

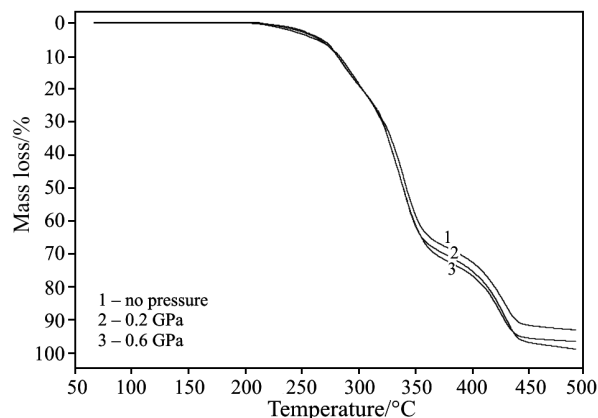


Fig. 4 TG curves with pressure and without pressure

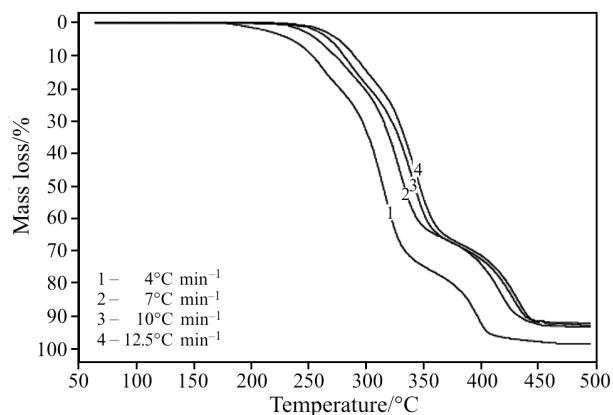


Fig. 5 TG curves with different heating rates of poly(PAMA) under 0.2 GPa pressure

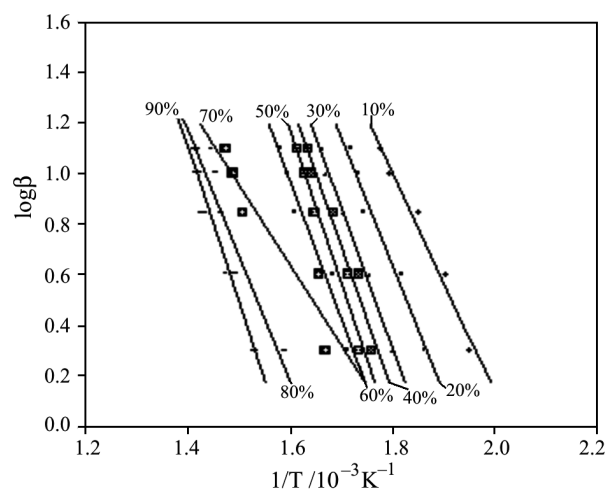


Fig. 6 Ozawa's plots of logarithm of heating rate ( $\beta$ ) vs. reciprocal temperature ( $1/T$ ) at different conversions for a poly(PAMA) under 0.2 GPa pressure

activation energy of degradation can be determined from the slope of the linear relationship between  $\log \beta$  and  $1/T$ , as shown in Fig. 6 [for poly(PAMA) under the 0.2 GPa pressure]; the apparent thermal decomposition activation energies for poly(PAMA)s under no pressure and 0.6 GPa pressure were calculated by the same methods. The  $\Delta E_d$  values for polymers are given as below: 78.1 kJ mol<sup>-1</sup> (residue: 3%, no pressure), 89.1 kJ mol<sup>-1</sup> (residue; 5% under the 0.2 GPa pressure) and 93.0 kJ mol<sup>-1</sup> (residue; 8% under the 0.6 GPa pressure), respectively. The irreversible changing of the structure caused to reduce  $T_g$  values at the DSC curves (Fig. 1).

## Conclusions

Effects of pressure on poly(PAMA) can be observed and  $T_g$  values reduced from 113.5 to 98.8°C by using thermal methods. It is evaluated that SEM diagrams agreed with the thermal analysis results. Thermal

decomposition activation energy ( $E_d$ ), was changed from 78.1 to 93.0 kJ mol<sup>-1</sup>. By applying the pressure and the residue was increased from 3 to 8%.

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