

## Morphology control and mechanical properties of monoacrylates polymers prepared by UV and Electron Beam photopolymerization

Amaar Elqidrea <sup>(1)</sup> and Ulrich Maschke <sup>(2)</sup>

<sup>(1)</sup>Scientific Research Department, Israa University, Gaza, Palestine

<sup>(2)</sup>Unité Matériaux et des Transformations, Université des Sciences et Technologies de Lille, Bâtiment C6, 59655 Villeneuve d'Ascq Cedex, France

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### Abstract

*The morphology and the mechanical properties of the polymer networks have been investigated under UV and electron beam irradiation based on the molecular weight distribution of the polymer chains. It has been observed that the molar mass and the length of the polymer chain have a major effect in determining the morphology and mechanical properties of the polymer. The morphology and the architecture of the polymer chains can be controlled by varying the intensity of the UV and electron beam doses during the photopolymerization.*

**Keywords:** Photopolymerization; electron beam; irradiation dose; gel fraction; molecular weight distribution; dynamic properties.

[aqidra@israa.edu.ps](mailto:aqidra@israa.edu.ps)

### 1. Introduction

Radiation curing based on free radical photopolymerization has found increasing interest in the industrial applications of preparing polymer composites due to the ease of control the reaction rate (Reiser, 1989 & Fouassier, 1995), the morphology and the final properties of the polymer matrix. The rapid development of radiation curing technology is due to its distinct commercial, technical and environmental advantages (Mehnert & Pincus, 1998).

The acrylic polymers have increasing interest ranging from simple adhesives to sophisticated industrial applications in the field of automotive and electronic devices. Poly(2-ethylhexyl acrylate) in particular have been a briefly studied due to its unique properties ranging from optical clarity, high conversion, and oxidation stability, low toxicity, low cost and ease of control (Tobing, 2001 & Jovanovic, 2004).

The molecular architecture of the polymer is the major factor that determines the polymer properties and the industrial applications; this will affect the glass transition temperature  $T_g$  of the polymer. The molecular weight distribution MWD of polymer chains during free-radical polymerization can lead to the formation of highly branched polymers with significant consequences on the its final properties (Burchard, 1999). The presence of

intramolecular has an effect on the melting point, glass-transition temperature and hardness as well as the degree of crystallinity of polymers. In contrast, intermolecular branching affects rheological properties such as sedimentation behavior, intrinsic viscosity, and the viscosity and elasticity of polymer melt. Long chain branching may also directly affect the final application properties such as the adhesive nature of pressure-sensitive adhesives (Filipe, 2008). However, in the free radical photopolymerization of acrylic monomers the molecular weight distribution and the gel fraction are related to each other based on polymerization condition (Plessis, 2001). The gel fraction is defined as the non-soluble fractions of polymer called and is usually formed by a highly branched or cross-linked polymer and largely affect the properties and applications acrylic of polymer.

The intermolecular chain transfer to polymer with termination by combination may lead to gel formation (Ahmad et al, 2009). The level of branching increasing for free radical polymerization than for controlled radical polymerization (Lovell, 1991 & Heatley, 2001). Generally, characterization and understanding the polymer structure can be obtained by characterizing the physical properties of polymer, kinetics analysis and molecular distribution of polymer chains.

The main methods commonly discussed in the literature to determine the degree of branching are  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC) and infrared (IR) spectroscopy (Helmstedt, 2000).

The use of  $^{13}\text{C}$  NMR spectroscopy for quantification the level branching and the intermolecular chain transfer is well developed for some polymers, such as polyolefins. Whereas NMR spectra For poly(alkylacrylates) are more complex and thus only the total degree of branching quantified (Heatley & Lovell, 2001). In contrast, GPC and rheology are more sensitive to low chain branching (Vittorias & Wilhelm, 2007). Thus in order to fully describe the molecular architecture information from spectroscopic, chromatographic and rheological techniques must be combined (Vittorias & Parkinson, 2007).

The main objective of this work is to perform a comparative study about the effect of preparation condition under ultraviolet UV and electron beam EB curing on the molecular structure of the polymer matrix. We focus on understanding the effect of radiation dose, reaction rate and the concentration of photoinitiator on the chain structure and the molecular weight distribution in polymer matrix. This knowledge can be exploited to fabricate new highly selective polymer composites for industrial applications.

## 2. Experiment

### 2.1 Materials

The monoacrylate monomer used in this study was 2-ethylhexyl acrylate 2EHA provided by (Aldrich). The polymerization process was induced by a photoinitiator 2-hydroxy-2-methyl-1-phenylpropan-1-one photoinitiator also known as Darocur1173 obtained from (CIBA Rueil Malmaison, France).

### 3. Sample preparation

To prepare polymer samples, mixtures of 2EHA, photoinitiator (Darocure1173) were prepared with different photoinitiator concentrations and stirred mechanically until they became homogeneous. Few drops of the reactive mixture were placed on a glass slide and rolled to a uniform thickness using wire rod and then covered with a polyester flat films (PET 50  $\mu\text{m}$  thick). The slide is then exposed to UV or EB beam using. The ultraviolet irradiation device is Minicure MC4-300 Primarc UV Technology. The intensity of the UV dose on the sample has been adjusted by controlling the speed of the conveyor belt of the UV device. The UV doses used in this study have been varied between 60, 120, 240, 300, 400  $\text{mJ}/\text{cm}^2$  to cover wide range of the irradiation intensity. UV doses were measured using UV radiometer. The UV curing was induced by a photoinitiator at a concentrations varied between 0.5 to 6 wt % with respect to the amount of monomer. The EB curing has been performed by high voltage electron accelerator Electrocurtain Model CB 150 (Energy Sciences Inc.) with a voltage of 175 kV. The electron beam dose was controlled by varying the conveyer speed and the current intensity. The polymerization for all samples has been carried out under normalized conditions for the monomer mixtures under UV or EB irradiation. The reactive mixture has been uniformly placed on glass plates with about 100  $\mu\text{m}$  film thickness. The maximum monomer conversion has been confirmed by infrared IR spectroscopy analysis based on the disappearance of the acrylate double bond.

### 4. Analysis by gel permeation chromatography GPC

The GPC analysis was carried out at room temperature in tetrahydrofuran (THF) as solvent using a Waters apparatus including a Waters 515 pump, a Waters 717 plus autosampler, a differential refractometer Waters 410 and Styragel columns HR3 and HR 3E (5  $\mu\text{m}$  particles). The polymer samples were purified and dissolved in THF and characterized at flow rate of 1 $\text{mL}/\text{min}$ . The different peaks obtained from the GPC measurements appear as a function of the retention time of the sample components, the molar mass of each polymer sample and the polydispersity of the polymer chains have been estimated based on the polynomial equation extracted from the calibration curve of the device.

### 5. Dynamic mechanical properties analysis

The dynamic mechanical properties of the UV and EB curable films were conducted using Rheometrics dynamic mechanical analyzer type Physica MCR 301 instruments. The temperature dependence of the viscoelastic properties such extension storage moduli  $E' = 3G'$  or shear storage moduli  $G'$ , extension loss moduli  $E'' = 3G''$  or shear loss moduli  $G''$ , and dynamic loss tangent  $\tan\delta$  were measured at 1 Hz and 5 $^{\circ}\text{C}/\text{min}$  heating rate. An amount of 0.5g polymer sample was used to perform the analysis. Measurements were performed at a temperature between 25 $^{\circ}\text{C}$  and 100 $^{\circ}\text{C}$ .

## 6. Differential scanning calorimetry DSC analysis

DSC measurements were performed using a SEIKO DSC-220C type instrument Perkin Elmer Pyris Diamond calorimeter equipped with nitrogen at a rate of 50ml/min at a heating rate of 10°C with a temperature range between -72°C to 100°C the same heating and cooling ramps during the measurements. The reproducibility of the results has been confirmed by repeating the analysis for at least three samples using a program consists of three heating and cooling cycles for each sample.

## 7. Gel fraction

The free radical polymerization of alkyl acrylate may produce a polymer containing a significant gel fraction [9 10]. The fraction content was measured by soaking the samples in tetrahydrofuran THF for 1 day at room temperature. The sample amount was about 50 mg in 20mL THF. The soluble part was removed by filtration and dried at 60°C to a constant weight. The gel fraction was calculated using the following equation:

$$\text{Gel fraction (\%)} = (W1/W0) \times 100 \quad (1)$$

where W0 is the weight before filtration and W1 is the weight after filtration.

## 8. Results and Discussion

### 8.1 Molecular weight

#### 8.1.1 distribution

The effect of the UV irradiation dose on the molar mass of polymer is presented in figure 1. A series of samples with the same monomer concentration were exposed to different UV doses ranging from low to high irradiation doses. The obtained polymer films were analyzed by GPC and the results of the retention time and the molecular weight distribution were compared for the selected doses. The molar mass of the polymer in terms of weight average molecular weight Mw and number average molecular weight Mn have a sharp drop when the irradiation doses increases. This results means that the at low UV dose, the propagation step continuous at the same polymer chain than at higher doses at which the probability of more radical sites increasing in the mixture which results in low molar mass of polymer.

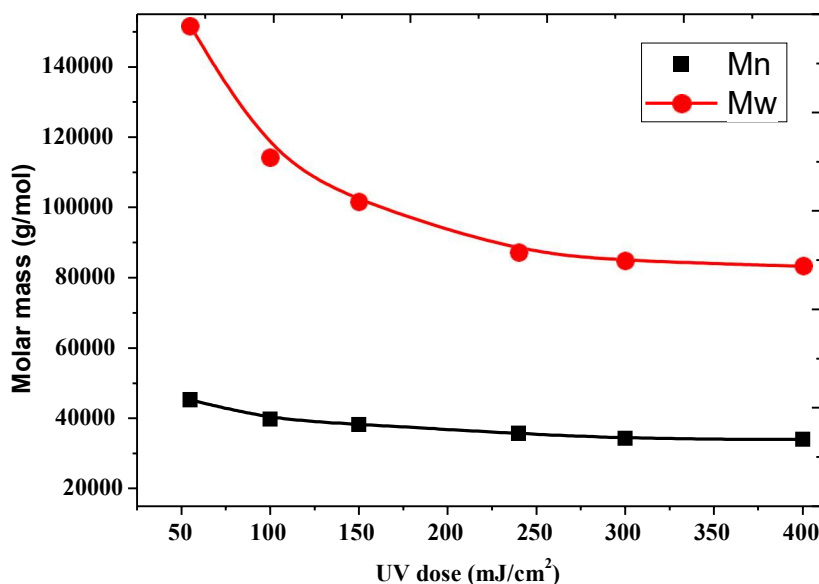


Figure 1: Variation of the molar mass of PEHA as a function of UV curing dose.

In (figure 2) the presented the variation of the molecular weight distribution with concentration of the photoinitiator. By increasing the weight percents of the photoinitiator in the reactive mixture result in sharp decrease of the polymer molar mass. The presence of larger amounts of the photoinitiator raise the probability of formation more free radicals in the mixture, which result in propagation reaction on larger amount of radicals, and low molar mass chains are formed.

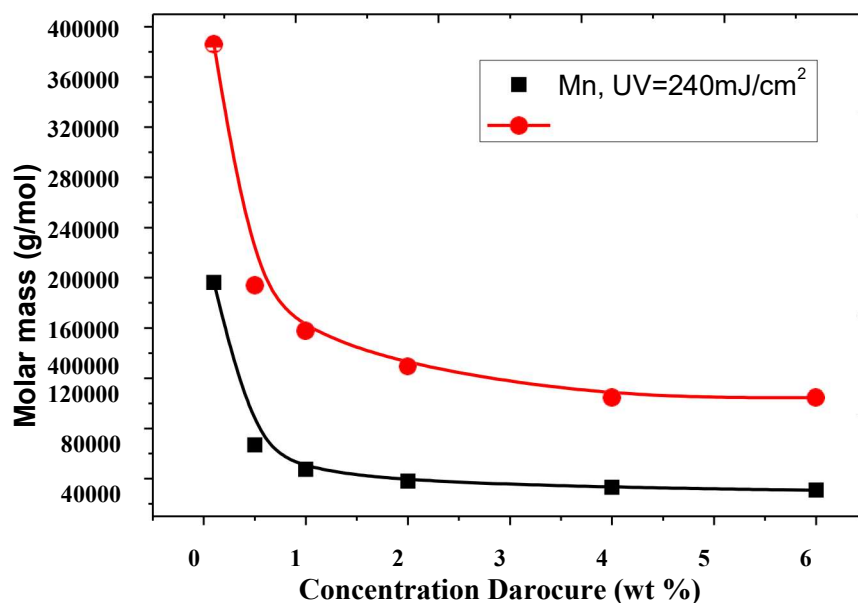


Figure 2: Variation of the molar mass of PEHA as a function of concentration of the photoinitiator.

The effect of electron beam dose on the molar mass of polymer is shown in figure 3. In this work, the reactive mixture is exposed to EB irradiation until maximum conversion and the GPC has been conducted, the same samples were exposed again to the same irradiation dose and the GPC analysis has been made for those samples with double dose. The weight average molecular weight  $M_w$  for the samples of double doses show a sharp drop of  $M_w$  of polymer by more than half the  $M_w$  of the samples with normal doses at maximum conversion. The drop in the molar mass of the polymer at higher dose can be due to the degradation at the polymer chains and formation of new radical sites.

Furthermore,  $M_w$  for the polymer prepared by EB irradiation much lower the previous results in figure 1 for the polymer films prepared by UV irradiation. This result can be explained by the presence of photoinitiator in the UV curing photopolymerization, that increase the probability of the propagation step on the same polymer chain than in the EB irradiation in which large amount of initiating radicals may exist and the propagation step proceed at those site

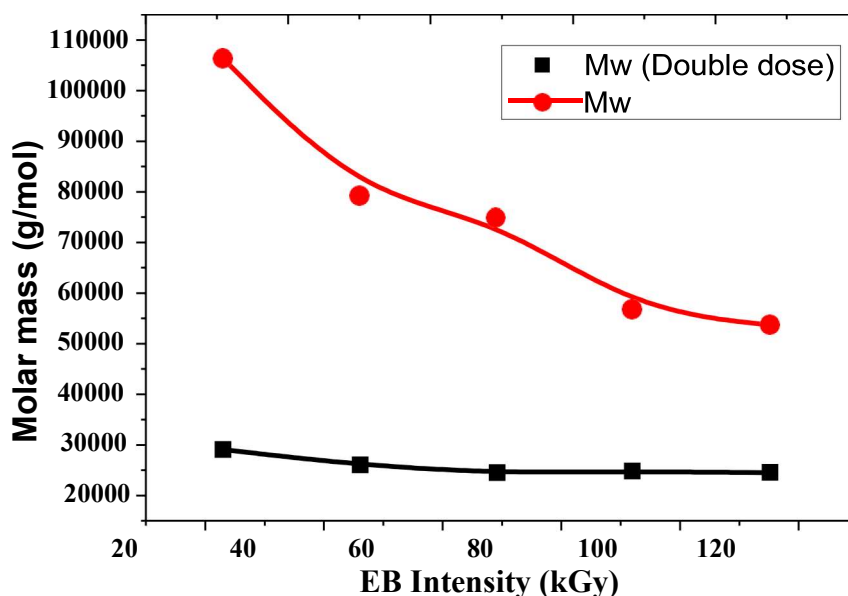


Figure 3: Variation of the molar mass of PEHA as a function of EB curing dose.

## 9. Dynamic mechanical properties

The dynamic mechanical analysis was performed to investigate the dynamic mechanical behavior of the UV and EB cured films of PEHA and study the crosslinking density of a polymer based on the behavior of elastic modulus in its rubbery state. The relationship between the concentration of the photoinitiator and the dynamic mechanical properties such as storage moduli  $G'$  and dynamic loss tangent  $\tan\delta$  are shown in figures 4. From the investigated experiments it can be observed that the increase of amount of the photoinitiator corresponds with the decreasing the storage moduli  $G'$ , while on the other hand it shows a considerable increase in the dynamic loss tangent  $\tan\delta$ . The storage moduli  $G'$  is decreasing by increasing the temperature. While the  $\tan\delta$  temperature curve shift to higher temperature range for the UV curing of PEHA with remarkable decrease with increasing the concentration of photoinitiator. For the UV cured PEHA, by increasing the weight percent of the photoinitiator in the reactive mixture, we clearly observe the increase of the viscoelastic properties of the polymer film which can be explained by decreasing the molar mass of the polymer chains by UV irradiation. At 25°C, the  $G'$  value for 0.1wt-% photoinitiator is about 17·103 Pa and decreases to about 103 Pa at 4 wt-% photoinitiator.



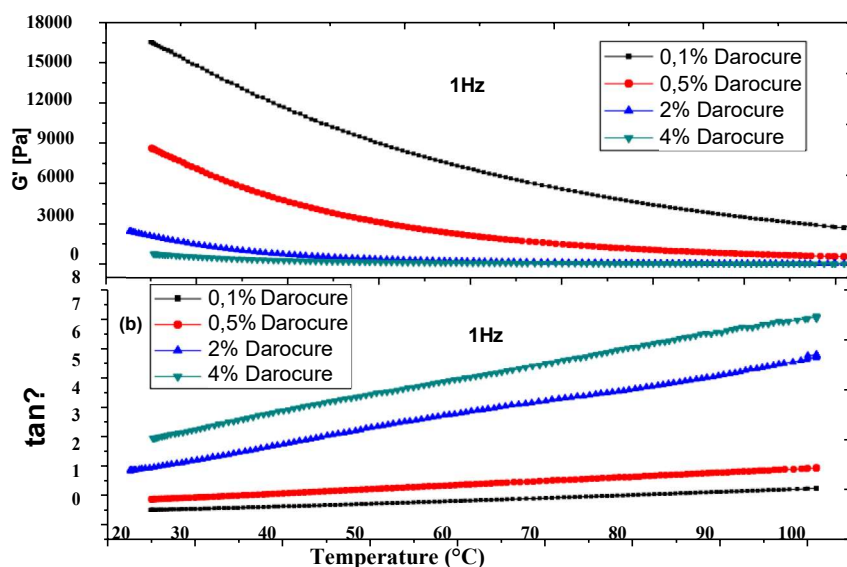


Figure 4: The temperature dependence of (a) storage moduli  $G'$  and (b) dynamic loss

Tangent  $\tan \delta$  for the UV curing of PEHA at 240mJ/cm<sup>2</sup> irradiation dose with different wt-% of the photoinitiator.

In the system of photopolymerization of 2EHA with fixed weight percents of photoinitiator at different UV irradiation doses is presented in figure 5, it is observed that the viscoelastic properties of the polymer films decrease with increasing the UV irradiation doses. The value of storage moduli  $G'$  drop from  $4 \cdot 10^3$  at UV dose of 90mJ/cm<sup>2</sup> to about  $2 \cdot 10^3$  at dose of 400mJ/cm<sup>2</sup>. The peak of  $\tan \delta$  increases with increasing the UV irradiation dose, which indicates that the Polymer networks for the samples at higher dose are of low molar mass.

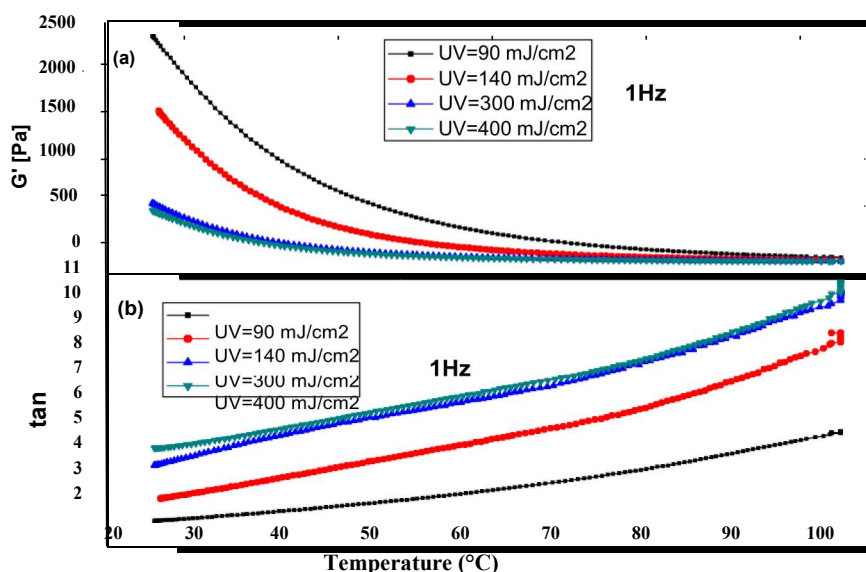
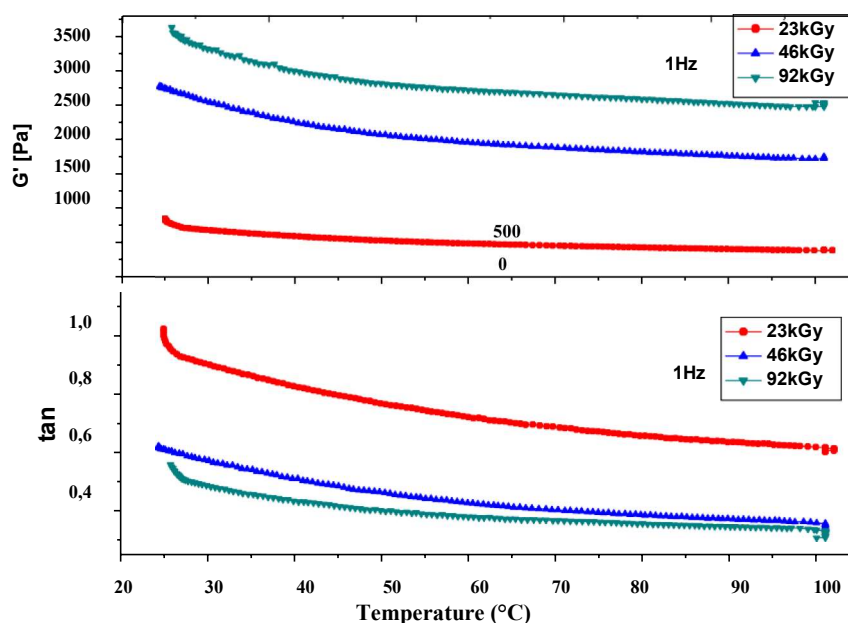


Figure 5: The temperature dependence of (a) storage moduli  $G'$  and (b) dynamic loss tangent  $\tan \delta$  for the UV curing of PEHA at prepared at different UV irradiation doses with 2 wt-% photoinitiator.



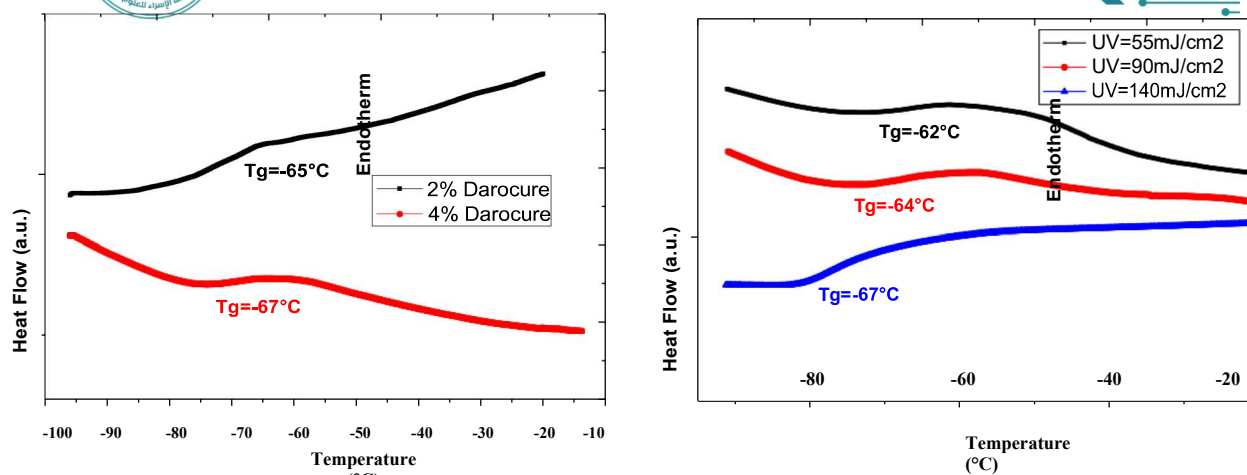
The behavior of the electron beam curing of 2EHA is presented in (figure 6); it shows that the viscoelastic properties of the polymer films decrease with increasing the EB irradiation dose. The storage moduli  $G'$  drops sharply from  $2 \cdot 10^3$  Pa at EB dose of 11kGy to about 400 Pa at a dose of 92kGy. Furthermore, the dynamic loss tangent  $\tan\delta$  which represents the material damping for the EB curing shows a different behavior from UV curing. In the EB curing  $\tan\delta$  decreases with increasing the temperature in contrast to the UV curing case which shows an increase of  $\tan\delta$  with increasing the temperature. In addition,  $\tan\delta$  have lower values ranging between 0,5 and 2 in average. This can be explained by the highly branched polymer chains of the EB curing film compared to low branching in the UV system.

It is hard to compare directly the properties of the EB and UV films. However, a remarkable drop of the viscoelastic properties is observed between the polymer films prepared by EB curing compared to the EB curing polymer. This behavior can be explained by the considerable difference of the molecular weight distribution of polymers prepared by UV and EB irradiation. In general, the UV curing mechanism allows higher molecular weight distribution during the propagation step, while the EB mechanism accelerates the termination and combination step for lower molecular weight polymers. It is expected that the differences in the viscoelastic properties and the glass transition temperatures of the polymers have direct correlation the internal structure of the polymer chains in terms of its molecular weight distribution.



**Figure 6:** The temperature dependence of (a) storage moduli  $G'$  and (b) dynamic loss tangent  $\tan\delta$  for the EB curing of PEHA prepared at different EB irradiation doses.

For the system of PEHA, the effect of the irradiation dose and weight percents of the photoinitiator on the glass transition temperature  $T_g$  can be elaborated by the DSC analysis. Figure7 shows the DSC thermograms of PEHA films prepared at different irradiation doses and weight percents of the photoinitiator



**Figure7: DSC thermogram of PEHA prepared by (a) different weight percent of the photoinitiator (b) different UV irradiation doses.**

Figures 7a shows that the glass transition temperature  $T_g$  of PEHA decreases from  $-65^{\circ}\text{C}$  to  $-67^{\circ}\text{C}$  with increasing the weight percent of the photoinitiator from 2 wt-% to 4 wt-% in the initial mixture. On the other hand, increasing the UV irradiation dose during the photo polymerization process resulted in a remarkable decrease in the glass transition temperature. The drop in the glass transition temperature can be explained by the formation of lower molecular weight polymer chains, which have more mobility segment than the higher molecular weight polymer chains.

## Conclusion and Future Work

The effect of the UV and EB irradiation doses on the degree of branching, gel fraction and molecular weight distribution MWD was investigated

The molar mass of polymer was found to decrease with increasing the irradiation doses for both films prepared by UV and EB curing. A comparison have been made between the molar mass of polymer in both methods shows the formation of low molar mass of polymer prepared by EB compared to UV curing.

The viscoelastic properties of acrylic polymer PEHA were investigated. The dynamic storage moduli  $G'$  is decreasing dramatically with temperature, while the value of the material damping  $\tan\delta$  increasing with temperature in the UV curing polymer. On the other hand,  $\tan\delta$  decreasing gradually in the EB curing systems. Further investigations on the glass transition temperature of the polymer films have been performed for the UV and EB curing polymer films. The glass transition temperature  $T_g$  decreases with increasing the irradiation dose for both EB and UV curing and decreases with increasing the weight percent of the photoinitiator due to the formation of low molar mass polymer chains.

UV and EB irradiation rate and the weight percent of the photoinitiator have a considerable influence on the mechanical and physical properties of the polymer films. The change of the mechanical and physical properties can be explained by the change of the molecular weight distribution of the polymer chains. Finally, the molecular weight distribution of the polymer can be largely controlled by varying the weight of photoinitiator and the irradiation rate. Further investigation will be made to study the behavior of diacrylate polymer system and compare the molecular weight distribution with the monoacrylate polymer films.

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