

Atomic Force Microscopy Studies of Poly(methyl methacrylate) Doped with Photoinitiator

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ABSTRACT: Atomic force microscopy has been applied for measuring the nanomechanical characteristics of poly (methyl methacrylate) thin films containing 5% photoinitiator (Irgacure 651). The nanohardness, Young's modulus, and adhesion to AFM tip have been evaluated for the unexposed samples and after UV-irradiation. Additionally, FTIR spectroscopy and differential scanning calorimetry (DSC) have been applied to explain the observed changes in nanomechanical properties. It was found that the exposure to ultraviolet changed the nanomechanical properties of polymer because of photo-oxidative degradation and

relaxation processes. These studies lead to the conclusion that the applied photoinitiator has no noticeable effect on nanohardness and Young modulus during PMMA irradiation, but efficiently participates in polymer photo-oxidation increasing the surface hydrophilicity and adhesion to Si_3N_4 . Moreover, the initiator hampers the relaxation of PMMA macromolecules, what was proved by DSC. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2458–2466, 2012

Key words: atomic force microscopy; PMMA; irradiation; surface modification; initiator

INTRODUCTION

Atomic Force Microscopy (AFM) method, based on the experiences of the scanning tunneling microscope (STM), was invented by Binnig et al. in 1986.^{1,2} The AFM is a versatile, nondestructive technique which is currently applied for imaging of both conductive and insulating materials with atomic resolution. AFM, STM or combination of both methods provide the data on the arrangement of molecules or atoms at the top of the specimen layer, on the sample topography, roughness, and heterogeneity. Other physical surface phenomena such as molecular or atomic interactions and mechanical properties at the nanoscale are also studied by AFM.^{3–6} An important information on the changes at the surface exposed to external factors (temperature, pressure, radiation, chemical agents, etc.) can be also achieved.^{7–10} Moreover, AFM is an excellent research tool for the study of single biological macromolecules, molecular systems and whole cells in aqueous medium and physiological conditions. Studies of inter- and intra-molecular forces between synthetic and biological molecules by AFM supply the knowledge on the mechanisms of processes occurring in nature.

Recently, the great progress has been done in the estimation of mechanical properties of polymers in micro- and nanoscale using indentation tests.^{11–15} The correlation between microhardness and structure was found for numerous polymeric systems. The effect of thermal history, physical aging, lamellar morphology, glass transition, presence, and structure of fillers on the hardness of different polymers has been described in details. Moreover, the nanoindentation measurements allow for the mapping of the surface mechanical properties in the case of heterogeneous materials.

Poly(methyl methacrylate), PMMA, is a rigid, transparent thermoplastic material characterized by hardness, fragility, and excellent optical properties. PMMA has a good mechanical strength as well as acceptable chemical and weathering resistance. It can be modified by addition of pigments, UV-absorbers and other aid compounds. Due to its advantages, low cost and easy processing, PMMA is applied widely, for example, in manufacturing of complex optical devices.^{16–21} PMMA does not affect the human organism, and therefore finds many biomedical applications for its poor immune response. Currently, new derivatives of acrylates, methacrylates, and dimethacrylates are applied as biomedical cements in orthopedic prostheses, dental fillings, and soft contact lenses.^{22,23}

Our main interest was to expose PMMA films to ultraviolet radiation to observe modification of surface properties, which can be assessed by AFM. It was also interesting to verify if small amount of photosensitive compound introduced to PMMA

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matrix changes its nanomechanical properties and adhesion to AFM probe. The growing and promising applications of PMMA in nanotechnology are recently observed, thus this work focuses on the fast estimation of nanomechanical properties after physical or photochemical modification.

EXPERIMENTAL

Materials

Samples of poly(methyl methacrylate), PMMA, and Irgacure 651 (chemical name: 2,2-dimethoxy-1,2-diphenylethanone) initiator were supplied by Sigma-Aldrich (USA) and Ciba (Basel, Switzerland), respectively. Polymeric films about 20- μm thick have been prepared by casting of 2 wt % solutions in tetrahydrofuran (THF, pure per analysis, ζ -Aldrich) onto clean glass plates and solvent evaporation. Both types of films (PMMA and PMMA containing 5% initiator) were dried initially at air and then in vacuum.

Subsequently, the specimens have been exposed to low-pressure mercury vapor lamp (TUV30W, Philips) in air atmosphere at 20°C. The intensity of emitted radiation measured at the sample position was 32.2 W/m².

Atomic force microscopy

MultiMode NanoScope IIIa (Veeco, USA) microscope with NanoScope IIIa controller in contact mode has been applied for studies of nanomechanical properties of modified PMMA. The nanoindentation tests were performed using commercial diamond tip (DNISP, made by Bruker, spring constant equals 859 N/m), while for the adhesion measurement, the silicon nitride (Si₃N₄) probes NP-1 have been used. An accurate spring constant of cantilever was calculated on the base of direct measurements of the cantilever movement (i.e., thermal oscillations) in the function of time.^{24,25} In both types of experiments the load-displacement curves were recorded. Tip velocity was kept constant—it equals 6.0 $\mu\text{m/s}$ in indentation test and 7.88 $\mu\text{m/s}$ in adhesion studies.

The measurements of nanoindentation and adhesion were repeated 8–20 times for each sample and then the obtained values were averaged.

The manner of calculations of hardness (H) and Young's modulus (E_r) have been described elsewhere.^{26–30} The formulae applied are given below:

$$H = \frac{F_{\max}}{A_c}$$

where F_{\max} is the maximum load applied, $A_c = f(h_c)$ is the contact area between tip and surface of sample, dependent on the contact depth (h_c),

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_c}} S$$

where S is the contact stiffness (slope of the unloading curve at the initial point of unloading).

FTIR spectroscopy

FTIR spectra of PMMA and PMMA with Irgacure 651 have been recorded using Genesis II FTIR spectrophotometer, Mattson, USA. For more distinct presentation of spectral changes after various irradiation times, the difference spectra were obtained using WinFirst software.

Differential scanning calorimetry

DSC measurements were carried out in the temperature range 30–180°C using Diamond DSC power compensation type (Perkin-Elmer) and the indium for calibration. The following conditions were applied: helium atmosphere, flow rate of 20 mL/min, heating rate of 50°C/min, and sample weight of ~ 8 mg. The glass transition temperature (T_g) was obtained from the first heating run as the midpoint of the change in a heat flow versus temperature curve. The peak area corresponding to enthalpy of relaxation (ΔH_r) was also determined from DSC curve.

RESULTS AND DISCUSSION

Nanoindentation tests

The obtained polymer solutions and solid films were transparent, what indicates the good dispersion of initiator in the polymer matrix. Although Irgacure 651 contains two aromatic rings in the molecule structure, which can make the mixing with linear aliphatic chain difficult, probably its low molecular weight (256 g/mol) and relatively small content in PMMA matrix (5 wt %) allow for the good penetration into macromolecules. Also microscopic observation does not reveal the separated domains.

The nanoindentation tests have been applied for evaluation of the local surface hardness and Young's modulus at nanoscale. The dents of diamond probe into polymer have been done using the same load force and speed for the elimination of different experimental conditions. The cantilever deflection versus displacement in the Z-direction was recorded for each repeated dent. Recorded curves were transformed into classical force-distance curves using calculated cantilever sensitivity. Typical AFM image for unexposed PMMA sample with photoinitiator after nanoindentation tests is shown in Figure 1. As it can be seen, the triangular trace is surrounded by the

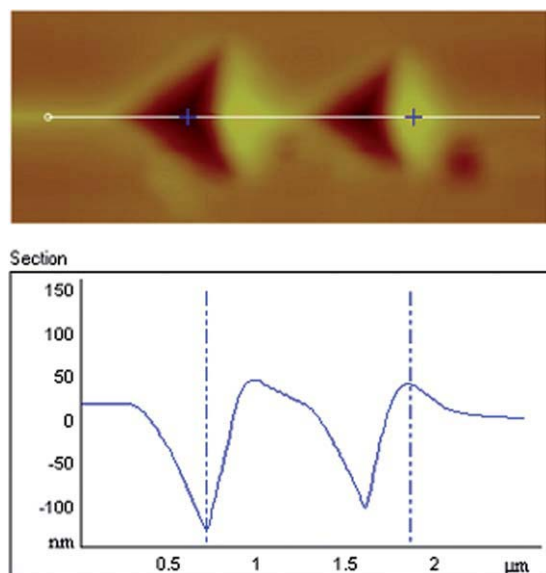


Figure 1 AFM image of PMMA sample with photoinitiator after indentation test (top) and cross section of the dents (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bulge of material (so-called buckling effect), which is caused by the film plasticity. The indentation depth is about 100 nm (see cross section).

An example of force distance curves of both unexposed polymer samples (PMMA and PMMA + Irgacure) is presented in Figure 2. Simultaneous recording of loading and unloading curve allows for observation of the hysteresis supplying an information on the sample hardness as well as on its plastic (γ) and elastic (δ) deformation.

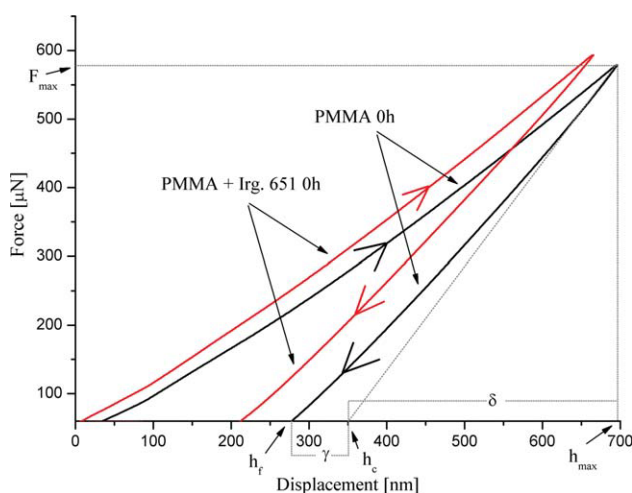


Figure 2 An example of the force-displacement curve for PMMA and modified PMMA sample; F_{\max} is maximum loading force, h_{\max} is the maximum tip displacement, h_c is the contact depth, h_f is the final depth after complete unloading, γ is the plastic deformation, and δ is an elastic deformation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hardness (H) of sample is expressed as a ratio of maximum applied load (F_{\max}) to the contact area (A_c) between tip and sample, which is a function of the contact depth (h_c). The tip geometry, which is necessary for hardness calculation, was known (three-sided pyramid). All other needed parameters were obtained from the unloading curve (Fig. 2): final indentation depth (h_f), which is the distance between the loading curve start and the unloading curve end; h_c , plastic depth taken from the intersection of the tangent to the unloading curve with the zero load line; and h_{\max} , maximum tip displacement.

The obtained values of hardness (Table I) indicate that an addition of Irgacure 651 to PMMA slightly increases the initial H for unexposed PMMA. It is not a typical behavior of low molecular weight organic compound added to polymer matrix. In numerous cases small molecules penetrate into polymer chains and exhibit rather plasticizing effect.

Such tendency—small increase of H in doped PMMA respecting to virgin polymer—is also observed after 1–8 h exposure to UV.

UV-irradiation of both types of samples leads to the significant increase of surface hardness. The changes are the highest during 1–4 h of UV treatment, which is presented on the plot of the H percentage changes versus irradiation time (Fig. 3). After that, the plateau is reached. As can be seen from Figure 3, the initiator used exhibits slightly stabilizing effect on PMMA surface.

The results of Young's modulus (E_r) calculations, based on the formula described somewhere else,³¹ are listed in Table II. The parameters needed for E_r calculation (i.e., Poisson ratios of the polymer and tip material) were taken from previously published works.^{32,33} Small increase of E_r can be noticed for PMMA containing photoinitiator. UV-irradiation causes the raise of E_r in both samples—the largest changes have been found after 1–4 h of exposure. The differences of E_r in PMMA and PMMA with Irgacure are rather insignificant—the curves

TABLE I
Hardness (H , GPa) Values of PMMA and PMMA with 5% of Photoinitiator Samples and Percentage Changes of Hardness (ΔH , %) in Doped PMMA with Respect to Hardness of Virgin PMMA After Different Exposure Time

Time of irradiation	H (GPa)		ΔH (%)
	PMMA	PMMA + Irg.	PMMA + Irg. vs. PMMA
0 h	1.47 ± 0.02	1.60 ± 0.01	+8
1 h	1.85 ± 0.05	1.97 ± 0.06	+6
2 h	2.12 ± 0.07	2.28 ± 0.06	+7
4 h	2.80 ± 0.02	2.83 ± 0.03	+1
8 h	2.81 ± 0.07	2.88 ± 0.06	+2

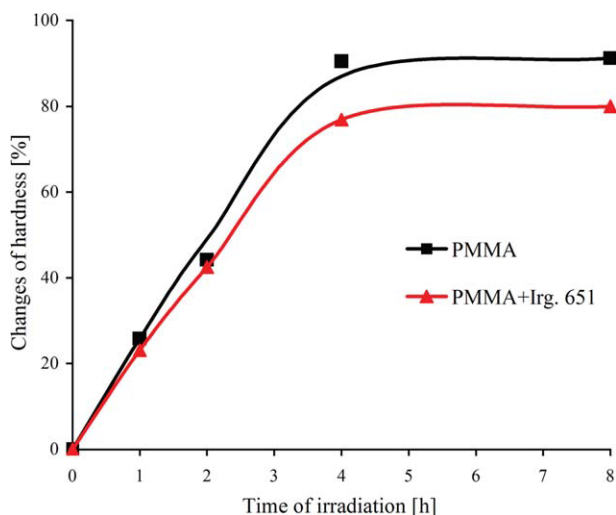


Figure 3 Percentage changes of hardness of PMMA and PMMA with Irgacure 651 versus irradiation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

illustrating the dependence of percentage changes on exposure time overlap (Fig. 4). An exception is the result obtained after 1 h UV, where the 14% increase of E_r for doped PMMA respecting to virgin PMMA has been detected (Table II).

The little increase of PMMA hardness and Young's modulus in the presence of initiator (in the case of unexposed samples) can be explained by the interactions between components, for example, dipole-dipole (Scheme 1). Both PMMA and initiator contain polar chemical bonds (C—O, C=O) in their structure, thus, the following possibility can be taken into account:

Such interactions probably reinforce the surface structure, which is reflected by the modification of nanomechanical properties.

UV-irradiation caused the raise of both nanohardness as well as Young's modulus in studied samples. It can be explained by the effect of the photochemical and photophysical processes occurring

TABLE II
Young Modulus (E_r , GPa) of PMAA and PMMA with 5% of Photoinitiator and Percentage Changes of Young Modulus (ΔE_r , %) in Doped PMMA with Respect to Young Modulus of Virgin PMMA After Different Exposure Time

Time of irradiation	E_r (GPa)		ΔE_r (%)
	PMMA	PMMA + Irg.	PMMA + Irg. vs. PMMA
0 h	1.77 ± 0.03	1.86 ± 0.04	+5
1 h	1.97 ± 0.03	2.26 ± 0.02	+14
2 h	2.40 ± 0.03	2.44 ± 0.04	+2
4 h	2.66 ± 0.04	2.96 ± 0.03	+11
8 h	2.89 ± 0.03	2.90 ± 0.04	+1

predominantly at the polymer surface. The main reactions taking place in PMMA upon UV are depolymerization and random chain scission. On the base of observed changes in nanomechanical properties one can conclude, that the formed monomer or other low-molecular weight degradation products are immediately evaporated and the surface becomes harder and stronger. The depolymerization has no significant effect on the mechanical properties because usually the end units are eliminated from macromolecules but the internal part of chains remains untouched.

The strengthening of exposed film can be induced by the relaxation process leading to the more compact organization of the top layer. There is no thermodynamic equilibrium in the films obtained by casting method from a strongly volatile solvent as THF. It is obvious that the excited macromolecules formed as a result of UV-irradiation are characterized not only by the altered chemical reactivity but also by the different geometry and mobility, particularly at the thin top layer. Thus, the gradual reorganization of macromolecules in time, which is more efficient upon UV action, is the reason of the observed hardness increase. During the relaxation processes, the points of macromolecule entanglements can play a role of physical crosslinks. Similar explanation has been presented by Flores et al. for physically aged poly(ethylene terephthalate).¹¹ Moreover, such effect appears in the polymers under loading, which is described in the literature as a strain hardening.^{34,35}

Finally it should be added that H and E_r values for virgin PMMA vary to some extent from previously reported.³⁰ There are several reasons of this discrepancy: different type, molecular weight and polydispersity of PMMA, presence of impurities,

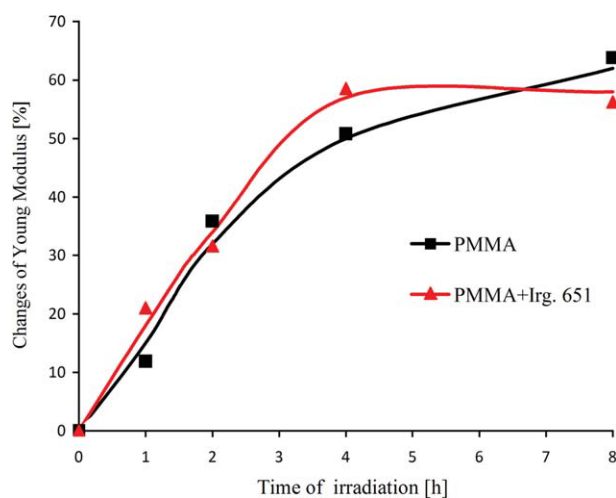
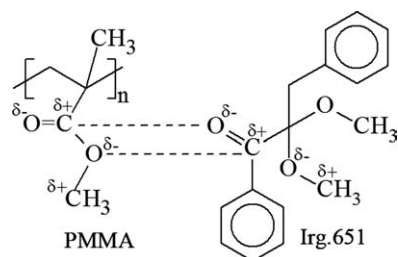


Figure 4 Percentage changes of Young's modulus of PMMA and PMMA with 5% photoinitiator versus irradiation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1 An example of possible interactions between PMMA and photoinitiator.

thermal history, diverse method of sample preparation, and finally other conditions of measurements (including type of AFM, cantilever, and method of calibration).

Adhesion forces measurements

The second set of experiments has been done for the estimation of adhesion between polymer and tip made from silicon nitride. The adhesion force was calculated from force-distance curve (Fig. 5). Initiator added to PMMA negligibly modifies the adhesion ($\sim 5\%$ decrease, Table III), which also suggests some weak interactions between components occurring at the surface.

UV-irradiation causes irregular increase of measured adhesive forces in pure PMMA and PMMA containing photoinitiator. Silicon nitride, which is a hydrophilic substance,³⁶ interacts stronger with both exposed samples in comparison to the unexposed ones. Therefore, it clearly indicates the increase of polymer polarity upon UV. It is caused by the photo-oxidation of polymer surface, which is more efficient in the case of PMMA modified by Irgacure 651 (Fig. 6). The observed decrease of adhesion after 8 h exposure can be explained by the decomposition

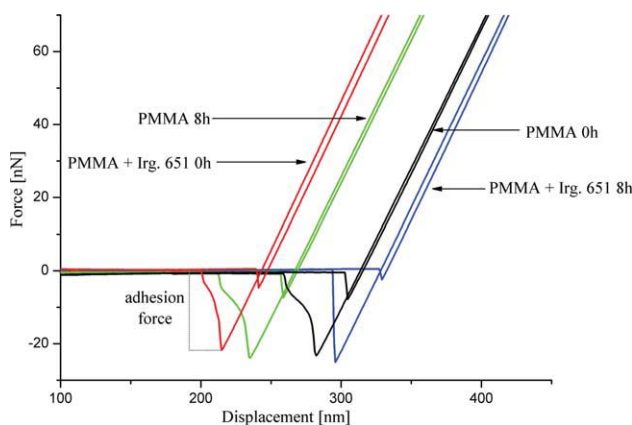


Figure 5 An example of force-distance curve for unirradiated and 8 h UV-irradiated PMMA and modified PMMA samples applied for adhesive forces calculations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Adhesion Force of PMAA and PMMA with 5% of Photoinitiator Samples to AFM Tip and Percentage Changes of Adhesion (Δ adhesion, %) in Doped PMMA with Respect to Adhesion of Virgin PMMA After Different Exposure Time

Time of irradiation	Adhesion (nN)		Δ adhesion (%)
	PMMA	PMMA + Irg.	PMMA + Irg. vs. PMMA
0 h	23.6 \pm 0.4	22.3 \pm 0.5	-5
1 h	24.2 \pm 0.5	25.5 \pm 0.4	+5
2 h	26.0 \pm 0.5	24.9 \pm 0.6	-4
4 h	27.5 \pm 0.6	26.6 \pm 0.5	-3
8 h	24.6 \pm 0.8	25.1 \pm 0.7	+2

of oxidized products formed at the first stage of irradiation. Particularly, photounstable are hydroperoxides, which undergo photolysis with formation of secondary degradation products (e.g., new carbonyls detected by FTIR).

Mechanism of photo-oxidation of PMMA in the presence of photoinitiator is proposed below.

The initiator undergoes a photolysis. As a result, the active radicals are formed (R_1 – R_3). All of them can abstract hydrogen atom from macromolecules and created macroradicals react subsequently with atmospheric oxygen. In consequence, the various oxidation product containing hydroxyl/hydroperoxide or carbonyl groups appear (some of them are shown in Scheme 2). Once initiated, reaction can propagate until complete consumption of free radicals in recombination or disproportionation process.

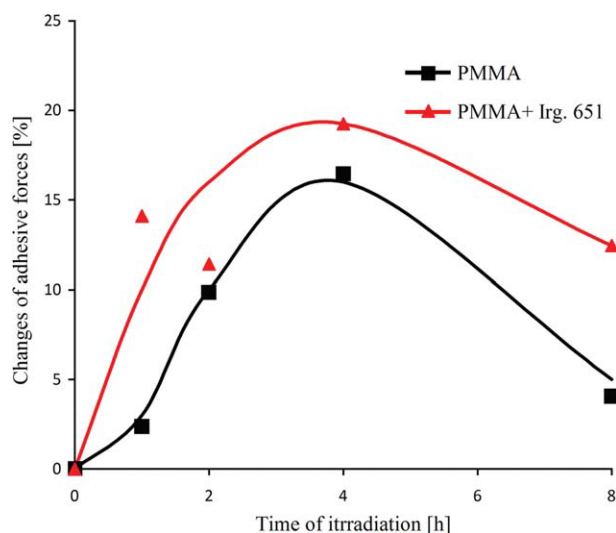
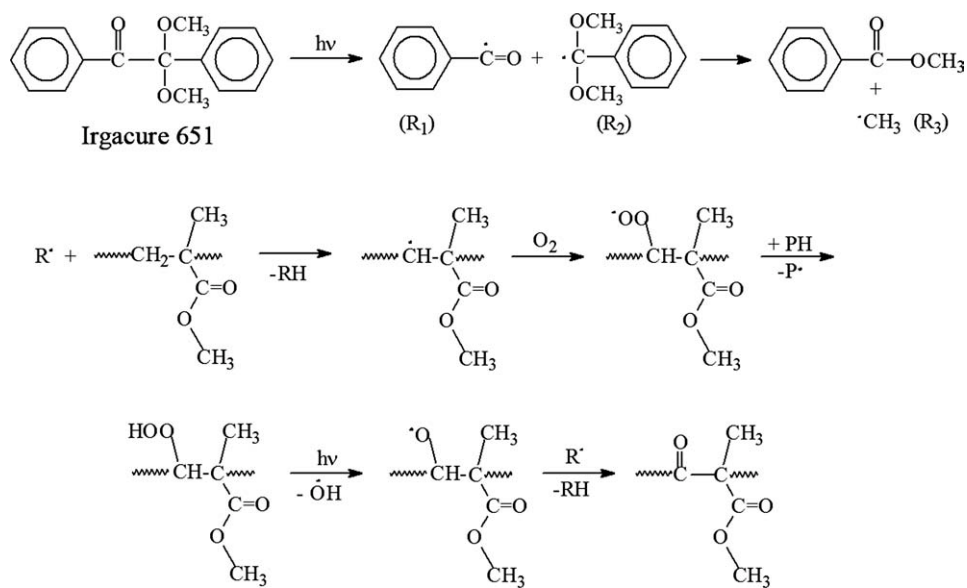


Figure 6 Percentage changes of adhesive forces of PMMA and PMMA with 5% photoinitiator versus irradiation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2 Photo-oxidation of PMMA in the presence of Irgacure 651 (R, any radical; PH, any organic molecule).

FTIR spectroscopy

The formation of new products of polymer photo-oxidation are detected by FTIR spectroscopy. The largest changes in infrared spectra of UV-irradiated samples occur in the region of carbonyl band absorption. Figure 7 presents the difference spectra for pure PMMA film (a) and polymer film with the addition of photoinitiator (b) in 1600–1850 cm^{-1} range after different irradiation times. Significant decrease of absorption at 1731 cm^{-1} due to the decomposition of ester groups is accompanying by the development of new carbonyl branches (positive peaks formed below and above 1731 cm^{-1}). The shape of PMMA difference spectra varies from that for PMMA containing Irgacure. The ester band drop is predominant in pure PMMA [negative part of difference spectra, Fig. 7(a)], whereas the oxidation prevails in the sample of PMMA + Irgacure 651. In this later case, the more distinct branches at 1718, 1749, and 1774 cm^{-1} are created [Fig. 7(b)]. Those bands can be attributed to the ketonic, carboxylic and peracid moieties.³⁷

This confirms that the increase of adhesion force during UV-irradiation is associated with the creation of new functional groups that can interact with charged moieties (e.g., SiO^- , SiN^-) situated on AFM tip.

It should be added that surface free energy of polymers cannot be measured directly. AFM and its application to adhesion measurement seem to be very useful and sensible among of other indirect methods, which are more time consuming and dependent on the external conditions.

DSC measurements

DSC measurements have been performed for explanation of changes in structure of modified PMMA

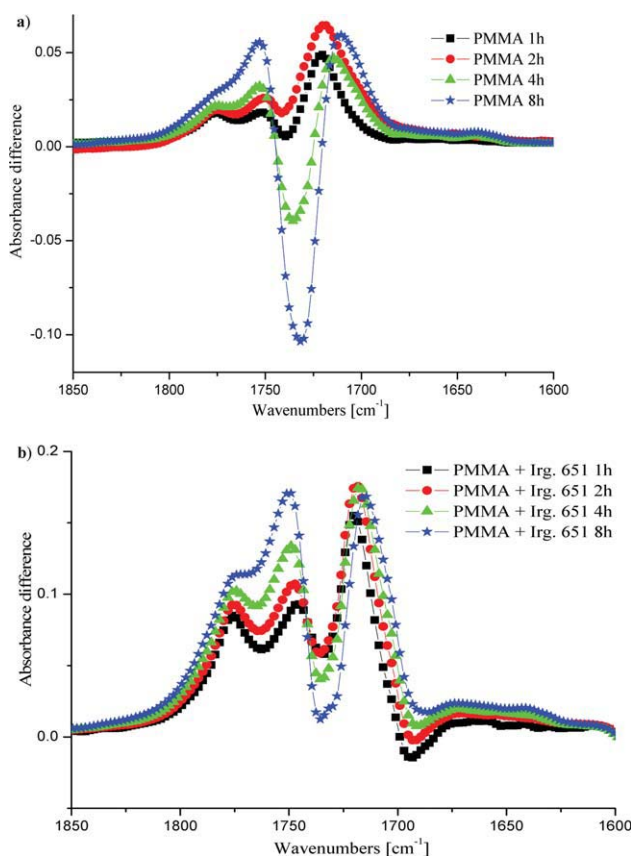


Figure 7 Difference spectra in carbonyl region for PMMA (a) and PMMA + 5% photoinitiator (b) after 1, 2, 4, and 8 h UV-irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

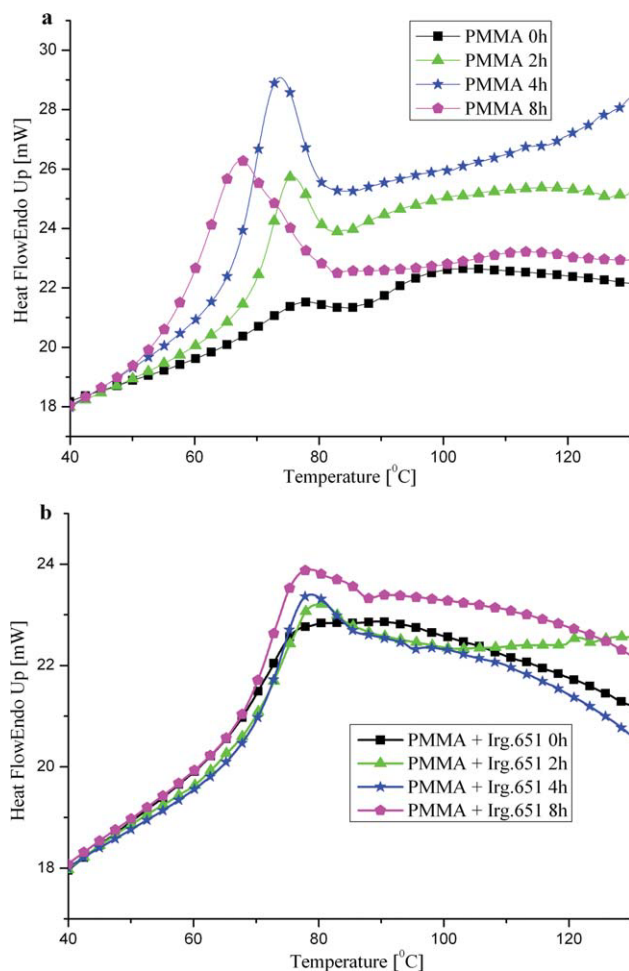


Figure 8 DSC curves of PMMA (a) and PMMA with 5% photoinitiator content (b) after various irradiation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples. The DSC curves allowed for estimation of glass transition temperature (T_g), which is a characteristic feature of polymers.

Sample of PMMA containing Irgacure exhibits somewhat higher T_g (about 3–8°C) than pure PMMA (Fig. 8, Table IV). It means that added initiator does not act as plasticizing agent in PMMA. On the

contrary, the intermolecular interactions suggested before (Scheme 1) stiffen the structure of PMMA in the presence of Irgacure. It correlates well with the observed previously higher hardness and Young's modulus of PMMA + Irgacure comparing to those values in pure PMMA.

As can be seen, T_g decreases systematically upon UV-irradiation of both PMMA samples (Table IV). It is obviously caused by photodegradation, in which monomers and other low molecular weight degradation products are formed. The decrease of glass transition temperature due to the intensive chain scission has been also reported for PMMA exposed to highly energetic gamma irradiation.³⁸

The drop of T_g is similar in both samples up to 6 h UV action but is significantly higher in PMMA after 8 h comparing to PMMA + Irgacure. However, the increase of hardness and E_r was found after photodegradation. It is necessary to remember that the properties measured by AFM concern only the thin surface layer, whereas all macromolecules participate in DSC test because the whole sample is heated.

It is worth noticing that, even in amorphous polymers such as PMMA, various random, local ordering is possible, which was discussed in literature.^{39–41} Such partial order increases the free energy of macromolecules, and simultaneously segmental motions are restricted. Most likely added initiator plays a role of crosslinking points via dipole-dipole interactions. Nevertheless, such physical binding can be easily destroyed under UV energy.

To explain more deeply the observed phenomena, the relaxation occurring about T_g have been studied. The macromolecules of glassy polymers in nonequilibrium thermodynamic state are characterized by excess of volume, enthalpy, and entropy. Physical aging involves gradual approach toward thermodynamic equilibrium, what influences the changes of physicochemical properties.

The area of endothermic peak corresponding to enthalpy change of this processes (i.e., enthalpy of

TABLE IV
Glass Transition Temperature (T_g , °C) and Specific Enthalpy of Relaxation ($\Delta H_r/m$, J/g) of PMMA and PMMA with 5% of Photoinitiator Samples and Their Changes (%) After Different Exposure Time

Time of irradiation	T_g (°C)		ΔT_g (%)	$\Delta H_r/m$ (J/g)		$\Delta dH_r/m$ (%)
	PMMA	PMMA + Irg.	PMMA + Irg. vs. PMMA	PMMA	PMMA + Irg.	PMMA + Irg. vs. PMMA
0 h	81.8	86.1	5.3	0.79	0.71	–10
1 h	80.6	84.7	5.1	1.55	1.00	–25
2 h	79.7	83.4	4.6	3.24	2.14	–34
4 h	79.5	82.6	3.9	7.29	2.50	–66
6 h	78.1	82.1	5.1	11.24	2.53	–77
8 h	73.7	81.9	11.1	11.26	3.12	–72

relaxation which is also called enthalpy of ageing⁴²⁾ was compared for both type of samples after different time of exposure (Fig. 8, Table IV). Interestingly, pure PMMA is characterized by significantly higher ΔH_r than PMMA + Irgacure. It confirms again that the interaction between polymer and initiator leads to the stiffening and hardening of the material. The changes of specific enthalpy ($\Delta H_r/m$, where m denotes the mass of the sample) in PMMA + Irgacure during UV-irradiation are much lower comparing to relatively big $\Delta H_r/m$ values for PMMA alone. The relaxation involves the segmental motions in macromolecules as well as rotations of side groups. These processes are strongly dependent on the inter/intramolecular interactions.^{43,44}

Our results indicate that free motions in PMMA macromolecules that is, their conformational changes are restricted by addition of Irgacure to PMMA matrix. Increase of hardness during exposure to UV can be explained by changes in chemical structure of polymer at the surface and alteration of molecular arrangement. Probably the residual impurities present in polymer and loosely bound groups being the structural defects are released from the surface. The direct recombination of remaining macroradicals leads to crosslinking of top layer reflected in hardening. Similar explanation has been proposed for PMMA modified by other organic initiators.⁴⁵

CONCLUSION

Our results demonstrate that physical modification of PMMA by its mixing with 5% photosensitive compound (Irgacure 651) slightly alters the nanomechanical properties. An increase of nanohardness, Young's modulus, and adhesion to Si_4N_3 tip, caused by initiator, is not so high, but indicates the presence of weak interactions between components at surface layer. The plasticizing effect has not been found. Both samples exhibited typical elastic-plastic behavior under intender load.

UV-irradiation of virgin and doped PMMA leads to noteworthy increase of hardness and Young's modulus, originating from photochemical and photophysical (i.e., relaxation) processes. Introduced photoinitiator only slightly stabilizes PMMA film.

In contrast, the adhesion of UV-irradiated PMMA containing Irgacure to AFM probe is more pronounced comparing to origin PMMA exposed at the same time. It is caused by an efficient photo-oxidation which was confirmed by FTIR spectroscopy.

Irgacure added to PMMA matrix slightly increases the glass transition temperature of polymer, which confirms the interactions between both components. It can be concluded that hindered relaxation of macromolecules in the presence of initiator

leads to higher surface hardness and Young's modulus.

AFM appeared the sensitive method allowing for the fast assessment of nanomechanical properties of modified polymers as well as their surface polarity, supermolecular structure, and component interactions. Such evaluation of surface properties in nano-scale is important in the case of practical application of PMMA as a light-weight, stable matrix for active compounds.

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