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INFLUENCE OF CROSSLINKING ON SURFACE HARDNESS OF POLY(METHYL METHACRYLATE)

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Key Words: Poly(methyl methacrylate); Crosslinked copolymers; Diamine crosslinking; Surface hardness; TG analyses

ABSTRACT

The influence of crosslinking on the surface hardness of poly(methyl methacrylate) sheets examined by means of damping of standard pendulum oscillations as well as on the nonisothermal mass loss is discussed in this paper. Crosslinked poly(methyl methacrylate)s with different crosslink densities were prepared by copolymerization of methyl methacrylate with polyfunctional comonomers of the allyl and vinyl type and by additional crosslinking of poly(methyl methacrylate) by transamination with aliphatic α,ω -diamines. The highest increase in surface hardness, up to 52% of its value for a silicate plate glass standard, was observed for (PMMA-*co*-DAIP) sheets with 17 to 25 wt% of comonomer. For commercial noncrosslinked PMMA cast sheets, this value is only 27% of the above standard. Comonomers of the allylic type are more suitable than the methacrylic multifunctional crosslinkers. A large portion of the double bonds remains unreacted if a high concentration of multifunctional agent is copolymerized with MMA. A similar effect

on PMMA surface hardness was achieved using substantially lower concentrations of α,ω -diamines as transamination crosslinking agents. Diamine crosslinked PMMA is also a thermally more stable material compared to copolymer networks and noncrosslinked PMMA. Volatilization of the main portion (> 80 wt%) of PMMA crosslinked with 5 wt% of 1,3-DAP is shifted to a higher temperature compared to the standard PMMA by 200 K. The shape of the TG curves and thermal stability of MMA-*co*-multimethacrylates copolymers differ only slightly from the noncrosslinked PMMA.

INTRODUCTION

Transparent polymers are widely used in practical applications. In this connection, PMMA belongs to the most resistant organic glasses regarding surface damage by abrasion and scratching. However, its hardness does not attain the hardness of an inorganic glass. Efforts to increase the hardness of PMMA are directed in two directions. The first involves coating the PMMA surface by transparent films of some oxides (SiO_2 , TiO_2). This method is based on soluble alkoxysilanes or alkoxytitanates, the hydrogels of which sinter at much lower temperatures when compared to inorganic sol-gel materials (100–120°C) [1, 2]. The second method of modification consists of crosslinking PMMA. In this case the starting point is the knowledge that structures of macromolecules containing backbone bonds with high dissociation energies, or showing intense intermolecular interactions, exhibit a high resistance to mechanical and thermal stress. These strong interactions are also represented by covalent crosslinks between macromolecules [3–5].

The crosslinking of macromolecules of thermoplastic polymers gives new properties to these materials even if the application takes place at temperatures below their T_g . The fixation of the geometry of elementary chains allows modification of the physical and mechanical properties of polymer materials. For instance, the crosslinks between macromolecules reduce the plastic deformation of material, increase the yield point in stress, and make the polymer more resistant to crack formation. The hardness of polymer material increases with the density of the polymer network; however, the brittleness also rapidly increases, the fracture properties change, and the material is no longer tough but becomes brittle. The change in properties, however, is dependent on different intensities of crosslinking density which stimulate the search for the optimum topology of macromolecules in order to improve the required property without significant impairment of other material properties. It appears that crosslinking of macromolecules of PMMA can bring about an increase in hardness and surface resistance to abrasion for PMMA products as well. Therefore we attempted to influence the surface hardness of PMMA sheets by varying the density of polymer networks by

1. Copolymerization of MMA with polyfunctional allyl and vinyl comonomers
2. Crosslinking PMMA using transamination with aliphatic α,ω -diamines

The study of nonisothermal weight loss of selected samples was also performed to demonstrate the contribution of crosslinking to the higher thermal stability of PMMA networks.

EXPERIMENTAL

The PMMA sheets were cast in the form of silicate glass plates ($120 \times 150 \times 2$ mm). The radical polymerization of monomers was initiated by 0.1 wt% benzoyl peroxide. The conditions of polymerization were $55^\circ\text{C}/18$ hours and $110^\circ\text{C}/1$ hour in a hot-air thermostat with air circulation. The multifunctional comonomers used were diallylphalate (DAIP), diallylmaleate (DAIM), triallylcyanurate (TAIC), allyl methacrylate (AIMA), and ethylene glycol dimethacrylate (GDM). In the second case the polymerization batch contained the diamine instead of the crosslinking comonomer. After the polymerization of MMA the polymerization block formed was annealed for 90 minutes at 180°C . α,ω -Diamines used were 1,3-diaminopropane (1,3-DAP), 1,6-diaminohexane (1,6-DAH), and 1,12-diaminododecane (1,12-DAD). All crosslinking agents were Fluka chemicals used without further purification.

The density of the polymer network was determined from the degree of swelling after equilibrium was reached in an excess of acetone (360 hours; the maximum mass increase occurred after 200 hours). The solvent was changed twice during swelling. In all cases the soluble portion of the sample was smaller than 5 wt%. The Flory-Rehner equation was used for calculating the molecular mass (M_c) of the PMMA chain between the crosslinks of a network [6].

The hardness of the prepared PMMA samples were measured with a pendulum hardness tester (ASTM D 4366, ISO 1522). The amplitude of oscillations of a pendulum resting on a sample decreases more rapidly the softer the surface of the sample. The number of oscillations for pendulum deflection up to 50% of the initial standard amplitude is taken as the hardness value of the sample. It is only a relative quantity with respect to a chosen standard. Silicate glass usually serves as the hardness standard (100%). The instrument used was a Pendel-Härteprüfer, BYK-Mallinckrodt, Germany. The standard deviation of damping time is $\pm 2.4\%$. The accuracy of our measurements with PMMA samples did not exceed this limit.

The residual double bonds and the glass transition temperatures T_{gI} and T_{gII} of the crosslinked polymer were determined by DSC by two repeated temperature scans within the 60 – 210°C interval using a DSC-2 Perkin-Elmer calorimeter. The nonisothermal TG experiments were carried out in nitrogen using a Hungarian Derivatograph Q-1500 D at a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The mechanism of formation of a polymer network in radical copolymerization of mono- and polyfunctional monomers shows some differences when com-

pared to polycondensation or vulcanization. At present there is no satisfactory method which could enable us to predict the relationships between parameters of the copolymerization system and the network structure or network properties. The more complicated the systems are, the more we are dependent on experimental estimation [7].

Crosslinking during Copolymerization of MMA

In the radical copolymerization of MMA with DAIP we obtained polymer sheets with the surface hardness, internodal molecular mass M_c , temperature of glass transition T_g , and exothermic effect after additional curing given in Table 1. Data on the hardness of sheets of MMA copolymers with other crosslinking comonomers are correlated with M_c in Table 2.

The increase in density of the polymer network is consistent with increasing content of DAIP in the batch. Nevertheless, the surface hardness reaches the maximum at a DAIP content of 17–25%. The fact that the glass transition temperature T_{g1} as determined in the first DSC scan decreases in spite of increasing density of the polymer network indicates a softening effect of DAIP on the prepared copolymer. Even after an additional heating of the sample to 210°C, T_{g11} is lower than it is in the case of samples with a lower DAIP content. This means that the use of a very high DAIP concentration is unfavorable for increasing the hardness of PMMA.

TABLE 1. The Hardness of Methyl Methacrylate–Diallylphthalate Copolymer Sheets as a Function of the Concentration of Crosslinking Agent. Polymerization: 55°C/18 hours; 110°C/1 hour; dibenzoyl peroxide, 0.1 wt%

Sample	Crosslinking agent DAIP $\times 10^3$ (mol fraction)	Pendulum oscillations ^a		M_c , g/mol		T_g , °C		DSC exotherm, cal/g
		No.	%	Calculated	Measured	I	II	
21	8	192	43.3	6050	2170	114	114	2.3
22	21	213	48.0	2375	2490	110	114	3.7
23	43	207	46.7	1125	1480	103	114	5.1
27	77	229	51.7	600	1020	100	114	5.4
28	119	232	52.4	370	970	98	107	5.5
29	213	205	46.2	185	770	76	108	5.9
Akrylon ^b	0	121	27.3	—	∞	—	—	—
M_2^c	0	161	36.3	—	∞	79	93	6.9
00 ^c	0	180	40.6	—	∞	103		2.4
Akrylon ^b	53 GDM	190	43.0	1180	330	112		3.2
Hesaflex ^d	Unknown	241	54.4	—	730	107	106	6.8

^aPercent from reference plate glass surface; average from three measurements.

^bPMMA commercial product, PCHZ Žilina, Slovak Republic. GDM = ethyleneglycol dimethacrylate.

^cLaboratory prepared PMMA sheet; M_2 = heated to 100°C/1 h.; 00, 110°C/1 h.

^dCommercial PMMA, Bally CTU, Schönenwerd, Switzerland.

TABLE 2. The Hardness of Methyl Methacrylate Copolymers with Various Crosslinking Comonomers with Different Concentrations. Polymerization: 55°C, 18 hours, 110°C/1 hour; dibenzoyl peroxide, 0.1 wt%

Sample	Crosslinking agent ^b × 10 ³ (mol fraction)	Pendulum oscillations ^a		<i>M_v</i> , g/mol		
		No.	%	Calculated	Measured	
11	DAIM	10	212	47.8	4800	4200
12		25	206	46.5	1860	2170
13		51	208	46.9	880	1710
42	TAIC	21	210	47.4	1580	1430
43		43	216	48.8	700	980
31	AIMA	16	190	43.0	3060	1710
32		40	174	39.3	1190	920
33		81	197	44.5	570	720
34		254	190	43.0	150	300
52	GDM	26	205	46.3	1880	530
55		37	189	42.7	1330	480
53		53	192	43.3	1180	340
54		178	—	—	230	180

^aAverage from three measurements; percent from reference plate glass surface.

^bDAIM = diallyl maleate; TAIC = triallyl cyanurate; AIMA = allyl methacrylate; GDM = ethylene glycol dimethacrylate.

By a DSC scan in the 60–210°C interval we observed a transition point corresponding to the T_g temperature of MMA-co-DAIP (T_{g1}). Moreover, we found that an exothermic process starts above 130°C and exhibits maximum heat release in the 165–175°C interval. This process fades at 200–210°C for a sample heating rate equal to 10°C/min (Table 1). We assume that the released heat is due to the reaction of dangling $-\text{CH}=\text{CH}_2$ groups of DAIP incorporated in the main chain of the copolymer. The concentration of the nonconsumed double bonds rapidly increases up to 10% of DAP concentration in the batch. At higher DAIP content the number of the nonconsumed groups increases only a little (Fig. 1). The existence of residual $-\text{CH}=\text{CH}_2$ groups in cured vinyl-divinyl copolymers is a common phenomenon, and these double bonds are not able to react even by a postcuring [8]. From repeated DSC measurements in the 60–210°C interval for MMA-co-DAIP, it was observed that T_g increased (T_{g11}) but the exothermic peak observed in the first measurement no longer appeared. However, the absence of the exothermic effect does not rule out that some double bonds which are sterically effectively blocked may remain even after additional heating of the substance. As a matter of fact, this result points out the usefulness of postcuring the polymers and especially the crosslinked copolymers at temperatures above T_g . Postcuring is also an efficient method of

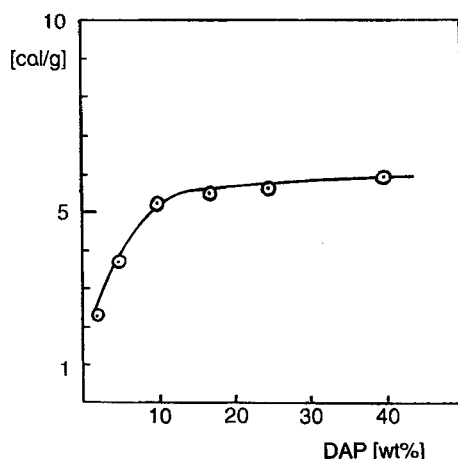


FIG. 1. Amount of heat evolved during a DSC temperature scan ($10^{\circ}\text{C}/\text{min}$, interval $60\text{--}210^{\circ}\text{C}$) for MMA-co-DAIP copolymer.

increasing the hardness for noncrosslinked PMMA. Noncrosslinked Akrylon is a commercial polymer which is very soft. In this case a 50% decrease in amplitude appeared after 121 oscillations while laboratory PMMA containing 4 wt% of dibutyl phthalate and annealed after polymerization for 1 hour at 100°C dampened the amplitude of the pendulum to 50% after 161 oscillations (sample M_2). The pendulum requires 180 oscillations before reaching 50% damping on the PMMA sheet without plasticizer and curing for 1 hour at 110°C (sample 00).

PMMA copolymers with other comonomers (DAIM, TAIC, AIMA, GDM; Table 2) show higher values of the surface hardness at the lowest concentrations in copolymer (2 wt%) compared to noncrosslinked PMMA. An increasing concentration of these comonomers above the critical value and an increase of the polymer network density have no significant influence on the surface hardness of PMMA sheets. The critical concentration occurs mostly below 2 wt% of a crosslinking agent in the polymerization batch and depends on the comonomer chemical structure and reactivity. For the DAIP comonomer (Table 1), the critical concentration shifts to 17 wt%.

The chain length between crosslinks as determined from the swelling deviates systematically in some samples using the calculated from $[\text{MMA}]/[\text{comonomer}]$ ratio. The known features of network formation mechanisms by chain crosslinking copolymerization [7] can be used to explain the observed differences.

The crosslinked polymer prepared by radical copolymerization forms very complicated polymer network structures which change in the course of conversion. The inter- and intramolecular cyclization and the apparent change in reactivity of the side $\text{C}=\text{C}$ bonds due to steric hindrances bring about inhomogeneities in the polymerization system.

At low concentrations of crosslinking comonomer the chain cyclization and entanglements increase the network density. The calculated values of M_c are higher than those determined by swelling experiments. As the concentration of multifunc-

tional comonomer increases, the crosslinker is less efficient in the network formation and the calculated M_c is shorter compared with the determined value.

The M_c s determined in the PMMA networks with GDM and diamines are lower in a whole concentration range of crosslinking agent in the batch. In these systems we can anticipate a very effective crosslinking which predominates over the side polymerization reactions of the multifunctional comonomer.

Crosslinking of PMMA with Diamines

Crosslinking of PMMA by transaminations with aliphatic α,ω -diamines can serve as an example of another mechanism of PMMA crosslinking which is not affected by so many variables as the case of radical MMA copolymerization with crosslinking comonomers.

The chemical modification of methacrylate esters and their polymers by polymer analogous reactions is most frequently accomplished by reactions involving the ester groups. The transesterification of MMA is used for preparing other esters and modifying the main PMMA chain by functional groups of different reactivities [9–11]. Our intention was to use bifunctional aliphatic diamines for crosslinking PMMA, and for this reason we investigated the course of the reaction of PMMA with amines in small concentrations at temperatures exceeding the T_g of PMMA without any additives, catalysts, and solvents [12]. We found that the amine groups of the diamine molecules used are three to five times more reactive in transamination of PMMA than the amine groups bonded to the polymer chain in the PMMA crosslinking reaction. In the period before the gel point, which can be observed only after consumption of 2/3 of the diamine present, the bonding of amine with PMMA is realized predominantly through one amine group. The formation of macroscopic PMMA gel with α,ω -diamines is thus characterized by an induction period and rapid transformation of polymer into an insoluble network. The extension of the methylene bridge in α,ω -diamines improves the reactivity of the amine groups in both reaction stages which comprise the bonding and the crosslinking of PMMA.

The hardness of PMMA sheets crosslinked with diamines is given in Table 3. The concentrations of the crosslinking agent used vary only between 1/3 and 1/10 of the concentrations of polyfunctional comonomers used for crosslinking by copolymerization. The network formed shows a molecular mass between crosslinks of M_c which is comparable with the molecular mass of the polymers crosslinked with DAIP. The surface hardness also approaches that of the MMA copolymers with DAIP and DAIM. DSC investigation of the thermal effects showed $T_g > 110^\circ\text{C}$ at the first scan, and after heating to 200°C the value of T_g increased by 5 or even 8°C . The observed exothermic effect amounts to about 1 cal/g. The heat released might be produced by polymerization of the residual MMA. From the viewpoint of the concentration of diamines necessary, the crosslinking is more effective than by copolymerization.

A homogeneous dispersion of the crosslinking agent in PMMA sheets requires an addition of the amine to the polymerization charge before starting the reaction. The course of MMA polymerization in the first stage of sheet formation is affected to some extent by the chain transfer reactions. The PMMA molecular weight is cut down, and from the determined values of degree of polymerization in dependence on diamine concentration the estimated chain transfer constant of PMMA radicals

TABLE 3. The Hardness of Poly(Methyl Methacrylate) Sheets Crosslinked with Aliphatic α,ω -Diamines. Polymerization: 55°C/18 hours; 110°C/1 hour; dibenzoyl peroxide, 0.1 wt% Crosslinking: 180°C/90 minutes in a Polymerization Casting Glass Form Inserted between Press Plates

Sample	Crosslinking agent $\times 10^3$ (mol fraction)	Pendulum oscillations ^a		M_c , g/mol		T_g , °C		DSC exotherm, cal/g
		No.	%	Calculated	Measured	I	II	
04 DAH	6.5	196	44.2	7630	1850	—	—	—
05 DAD	7.5	193	43.6	6570	1480	110	115	<1
03 DAH	13	203	45.8	3820	1100	114	122	<1
01 DAP	20	207	46.7	2430	1320	112	118	1.1
02 DAH	26	213	48.1	1880	860	112	120	1.9
00 (PMMA)	0	180	40.6	—	—	103	109	2.4

^aAverage from three measurements; percent from reference plate glass surface.

to 1,3-DAP is 7.2×10^{-4} at 50°C. This value corresponds well with the chain transfer of PMMA to aniline: 4.2×10^{-4} at 60°C [13]. On the other hand, this drawback does not appear if some other alternative method for diamine dispersion in PMMA is used. The diffusion to small PMMA particles [12] or a mixing in the PMMA melt [14] can serve as examples for preparation homogeneous mixtures with diamines.

Influence of Crosslinking on Thermal Stability of PMMA

Crosslinks introduced into polymers increase the T_g and reduce the plastic deformation of materials. They also open up the possibility of a greater heat load of such modified polymers. These alterations in PMMA structure influence the chemical depolymerization stability of crosslinked samples [15]. Nonisothermal measurements of the weight loss of selected crosslinked PMMA samples (Fig. 2) show that the 1,3-DAP crosslinker shifts the depolymerization of the more stable part of a polymer by 60°C to a higher temperature compared with standard PMMA. Comonomers of the allyl type are less efficient as retarders of depolymerization than are diamine. The polyfunctional methacrylate esters as a component of a PMMA chain are an even smaller barrier for zip depolymerization. The character of the TG curves is only slightly different from that of noncrosslinked PMMA.

A recently accepted mechanism of thermodegradation of PMMA was proved by many authors [16–18]. Radically prepared PMMA thermally decomposes in two main stages. Radical chain depolymerization is first initiated on unsaturated chain ends (the less stable part of a polymer). The rest of the sample undergoes depolymerization initiated at random polymer chain scission (the more stable part of polymer). In spite of a comprehensive list of other possible sources influencing the weight loss of PMMA, the effects of the two types of depolymerization reactions mentioned predominate. A possible mathematical analyses of TG records was used in our previous paper [15]. On the basis of results presented there, the maximum

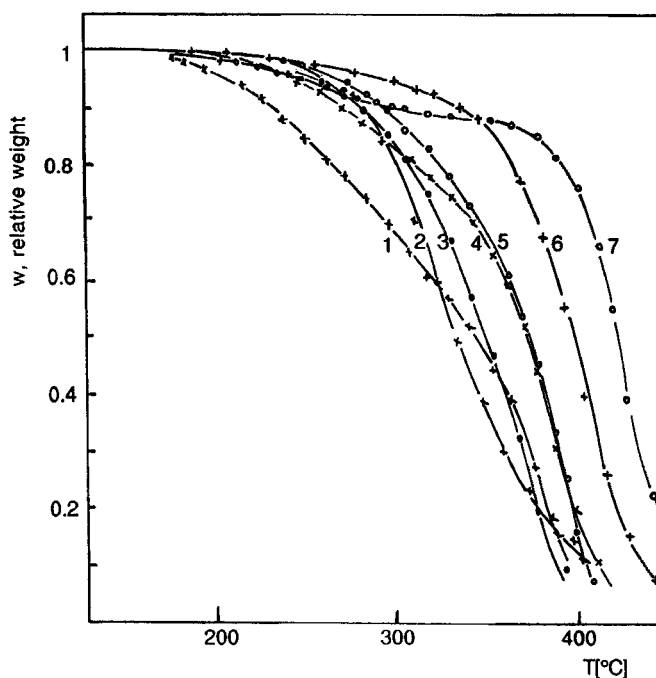


FIG. 2. Nonisothermal TG curves ($10^{\circ}\text{C}/\text{min}$) for samples of PMMA crosslinked with various multifunctional comonomers and 1,3-DAP. 1: PMMA (M_2). 2: 10% AIMA. 3: 10% GDM (Akrylon-TOS), (commercial PMMA, PCHZ Žilina, Slovak Republic). 4: Crosslinked (Hesaflex) (commercial PMMA, Bally CTU, Schönenwerd, Switzerland). 5: 7% DAIP. 6: 10% DAIM. 7: 5% 1,3-DAP.

rate of weight loss of a crosslinked PMMA depends on the type and quantity of crosslinking agent. The intensive depolymerization shifts to higher temperatures with increasing density of the polymer network due to the decrease in molecular weight of PMMA chains between the crosslinks (M_c), and consequently the depolymerized chain segment becomes shorter. As can be seen from Fig. 2, all the crosslinked PMMA samples show higher stability than the PMMA standard. This is consistent with the proposed mechanism of stopping the depolymerization zip on the branching points of PMMA chains. On the other hand, it is obvious that crosslinkers are not equally effective in suppressing depolymerization. The higher stability of PMMA when it is crosslinked with 1,3-DAP and DAIM is predominantly attributed to randomly initiated depolymerization due to PMMA chains splitting. The unzipping reaction of PMMA networks prepared by copolymerization starts at the network crosslinks [15]. It is therefore concluded that in methacrylate copolymer networks the branching points not only stop chain depolymerization but serve also as weak bonds in thermal PMMA chain scission and as initiation points of PMMA thermal volatilization.

There are clearly two separate degradation stages on the TG curve for 1,3-DAP crosslinked PMMA. In analogy to the accepted mechanism of PMMA degradation, the first stage can be associated with the less stable (about 10 wt%) and the second stage with the more stable part of the polymer. A similar separation of

differently sensitive parts of PMMA to thermodegradation, but not as sharp, can be seen on the TG curve for sample 4 (Hesaflex).

CONCLUSIONS

Crosslinking PMMA with polyfunctional monomers as well as by transamination reactions involving diamines increases the surface hardness. The result obtained is affected by the density of crosslinks and the character of bridging units between macromolecules. An optimum in the dependence of surface hardness on network density exists. A convenient selection of crosslinking agent brings about an increase in the thermal stability of PMMA.

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