

THE SYNTHESIS AND CHARACTERIZATION OF Ba-CROSSLINKED POLYMER ANTI-RADIATION MATERIALS

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ABSTRACT

Crosslinked poly(methyl methacrylate) and polystyrene with barium dimethacrylate $[Ba(MA)_2]$ as crosslinking agent have been synthesized. The relationship between X-ray absorbability and the content of $Ba(MA)_2$ in polymers was investigated. TGA and DSC results indicated that the crosslinked polymers containing barium dimethacrylate have a much better heat stability than pure PMMA or PS. The mechanical properties of the polymers containing barium are improved in comparison with the pure PMMA.

INTRODUCTION

The interest in radio-protective materials is increasing with the extensive usage of various radiation^[1]. Most radio-protective polymer materials are principally composed of polymer matrix and fillers, while the fillers, most being the heavy-metal oxide such as lead oxide, play an important role in absorbing radiation^[2-4]. Poly(methyl methacrylate) with lead oxide as a filler named lead glass has been widely used as radio-protective materials exhibiting good absorbability for X-ray and γ -ray. But during the processing, the lead oxide filler must be first dissolved in an organic acid, and then mixed with monomers and polymerized. The lead glass obtained by this method has poor strength and hardness^[5,6]. In this paper, a new kind of anti-radiation polymer material is reported, which can be obtained by using barium dimethacrylate as crosslinking agent. The barium crosslinked PMMA not only absorbs certain wavelength radiation but also improves the mechanical properties and heat stability^[7].

EXPERIMENTAL

1. Materials

Barium dimethacrylate $Ba-(OOC-\underset{\text{CH}_3}{\underset{|}{C}}=CH_2)_2 [Ba(MA)_2]$ was prepared in our lab. The commercial available reagents including MMA, styrene, ethylene glycol dimethacrylate, and AIBN are of reagent grade and are purified prior to use.

2. Synthesis of barium containing crosslinked polymers

$Ba(MA)_2$ was dissolved in an unsaturated organic acid (< 15wt %); the mixture was added to methyl methacrylate or styrene, and then polymerized at 70 °C for 40 min. using AIBN as initiator (0.002g per gram of monomer). The prepolymerized and bubble free solution was poured into a vessel which was made of two glass plates

with a 4 mm spacer between them. The edges of the vessel were sealed with Teflon tape. Polymerization was carried out at 50 °C for 24 hours, successively at 60 °, 80 °, and 110 °C each for 2 hours. Polymer samples of hard plates with thickness of 4 mm were obtained. Samples' numbers are listed in Table 1.

3. Measurements

The absorbability of the barium-containing polymers for $\lambda = 0.709 \text{ \AA}$ and $\lambda = 1.542 \text{ \AA}$ characteristic X-ray was measured by D/Max-ra rotating Anode Diffractometer. The thickness of the measured samples was strictly controlled to 4 mm. The attenuation of X-ray was measured by counts since the intensity of X-ray is in linear proportion to the counts.

Table 1 Samples' numbers of different contents of Ba salts

Main monomers	Sample No.	Ba(MA) ₂ %					
		0	0.9	1.8 *	2.7	3.6	
MMA		# 1	# 2	# 3 # 3'	# 4	# 5	
St		# 6	# 7	# 8 # 8'	# 9	# 10	# 11 **

* Ba(MA)₂ was added in samples 1—10 while barium propionate [Ba(PA)₂] was added in samples 3' and 8' as additive.

** In sample # 11, 1.8 wt% ethylene glycol dimethacrylate was used as crosslinker instead of Ba salt.

TGA was run on Shimadzu T-30 Thermogravimetric Analyser. The conditions were: sensibility 50 μ V, heating rate 10 °C/min, weight range 5 mg, nitrogen atmosphere. T_g was determined by Perkin-Elmer DSC Differential Scanning Calorimeter.

The tensile strength, elongation at break and Young's modulus were measured by Instron 1122 Universal Testing Machine. The testing rate was 5 mm/min. Barcol's hardness was determined by HBa-1 Barcol's hardness tester. The ultrathin sections for TEM observation were 500—700 $\text{\AA}$ thickness.

RESULTS AND DISCUSSIONS

1. Relationship between X-ray absorbability and Ba(MA)₂ content in polymers

The X-ray absorbability of barium containing polymers is shown in Figure 1 and Figure 2. The absorbability increases with the increasing content of Ba(MA)₂ in polymers and the polymer plates absorb X-ray of 1.542 $\text{\AA}$ more strongly than that of 0.709 $\text{\AA}$. Barium has a different mass attenuation coefficient for different wavelength X-ray, e. g. that is 40.8 cm^2/g when $\lambda = 0.7 \text{ \AA}$ and 354 cm^2/g when $\lambda = 1.5 \text{ \AA}$. Both PMMA and PS systems have stronger absorbability for $\lambda = 1.542 \text{ \AA}$ X-ray than for $\lambda = 0.709 \text{ \AA}$ X-ray as shown clearly by the experiment results. X-ray absorbability of polymer # 3' and # 8' was decreased by 5—10% compared with the crosslinked polymers with the same percentage of barium salt. It may caused by different distribution and bound barium.

2. Heat stability of the polymers

TGA results of barium containing polymers and pure polymers are given in Table 2. In both PMMA and PS systems crosslinked by Ba(MA)₂, the heat stability relative

to that of pure polymers is much improved.

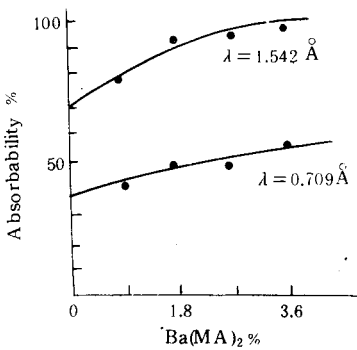


Fig. 1 Relationship between X-ray absorptivity and Ba(MA)₂ content in PMMA

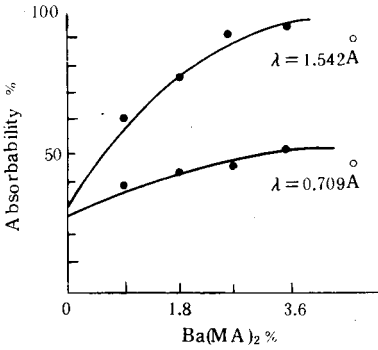


Fig. 2 Relationship between X-ray absorptivity and Ba(MA)₂ content in PS

Table 2 TGA Results of polymers

Polymers	1	2	3	4	5	6	7	8	11
$T(^{\circ}\text{C})$ (20% wt. loss)	295	346	348	346	348	345	374	380	340
$T(^{\circ}\text{C})$ (50% wt. loss)	318	390	389	388	386	405	398	406	370
$T(^{\circ}\text{C})$ (90% wt. loss)	378	440	425	510	420	428	415	495	416

From DSC results of polymers # 2, # 4 and # 11, T_g are 441. 3, 446. 8, and 438. 3 K respectively, and for pure PMMA synthesized under the same conditions T_g is 386. 8 K. With the increase of the crosslinking density, the inter-chain separation should be limited so that the molecular mobility and flexibility being reduced and the T_g rises. PMMA crosslinked by Ba(MA)₂ also has a high T_g even higher than those crosslinked by organic crosslinkers owing to the strong attraction between barium ions and the oxygen atoms in polymer chains.

3. Mechanical properties

The tensile strength, elongation at break , and elastic modulus of polymer #1, # 3, and # 11 are shown in Table 3. The Young's modulus of polymer # 3 and # 11 are higher than that of pure polymer #1. The tensile strength of metal containing crosslinked polymer # 3 is higher than that of polymer # 1 or polymer # 11.

Table 3 Mechanical Properties of Polymers

Polymer	Tensile strength (Kg/cm ²)	Young's modulus (Kg/cm ²)	Elongation at rupture (%)
# 1	620.7	8053	4.5
# 3	666.4	10231	3.8
# 11	555.0	10442	3.0

The Barcol's hardness of pure polymer #1 and barium containing polymer #5 was measured. The average Barcol's hardness of polymer #1 was 46, polymer #5 was 52, whereas for commercial lead glass it is below 20. So the hardness of crosslinked polymer containing barium salts is enhanced compared with pure polymer and lead glass.

4. Morphological observation

The TEM photographs of PMMA and PS containing barium are given in Figures 3A and 3B. Well-distributed domain can be seen from these polymer samples.

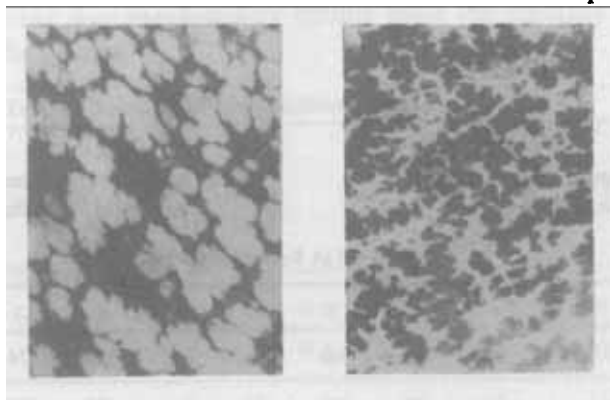


Fig. 3A TEM photograph of sample # 3($\times 5,000$)

Fig. 3B TEM photograph of sample # 7($\times 5,000$)

REFERENCES

- [1] 高南, 华家栋, 俞善庆, 夏继余编著《特种高分子》上海科技出版社, 1984
- [2] 日本公开特许公报 85, 157092 (CA: Vol. 103, 202543)
- [3] *Ger. Offen.* DE3,338, 122 (CA: Vol. 103, 105765)
- [4] 日本公开特许公报 86, 98765 (CA: Vol. 105, 154497)
- [5] *Eur. Pat. appl.* 19121(1980) (CA: Vol. 104, 140872)
- [6] *Ger. Offen* DE 2,751,487 (CA: Vol. 89, 75645)
- [7] 日本公开特许公报 80, 73713