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The Influence of E-beam Irradiation on POLY(ETHER-BLOCK-AMIDE) (PEBA, Pebax)

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Medical polymers require sterilization and must be able to maintain material properties for a specified shelf life. Sterilization can be achieved by using gamma or e-beam exposure. In this study, accelerated aging tests of poly(ether-block-amide) (PEBA) copolymer samples is presented. PEBA copolymer samples with different polyether content that result in Shore hardness of 35D to 72D, were sterilized using e-beam radiation followed by accelerated aging at 55°C. E-beam sterilization effect on molecular weight and mechanical property has performed and analyzed. The average molecular weight significantly reduced as a result of ageing. The enlarged proportion of low molecular weight chains in the aged samples is consistent with the generation of degradation products produced by oxidative chain scission. Also E-beam materials have shown decreased tensile strength and elongation. Overall, this study demonstrated that the medical grade PEBA was significantly affected by radiation exposure over aging time, particularly at high irradiation doses. For medical use in case of radiation sterilization required, it is recommended to avoid Pebax material. If Pebax material must be in use for medical device, recommend to use alternate sterilization method such as Ethylene Oxide sterilization.

Key Words: Medical Polymers, e-beam Irradiation, PEBA degradation

Introduction

Poly(ether-block-amide) copolymers (PEBA) are thermoplastic elastomers sold under Arkema's trade name Pebax. PEBA is a material widely used in the medical device industry. Valued for its flexibility and thermal stability at body temperatures, its applications range from catheter bodies to angioplasty balloons. The PEBA family of copolymers[1-11] have the general chemical formula

$$HO\text{-}CO\text{-}PA\text{-}CO\text{-}O\text{-}PE\text{-}O]_n\text{-}H,$$

where PA is polyamide, and PE is polyether. By adjusting the polyamide/polyether ratio or the length of the polyamide and polyether blocks, a number of different hardness can be achieved for a particular application. The polyether block allows for a high degree of flexibility without the use of additives or plasticizers, an important advantage for the medical device industry where additive use is limited. The polyamide content influences the melting point and gives the elastomer its tensile strength and hardness. In addition to its flexibility and tensile strength, PEBA shows excellent adhesion to other materials and polymers. PEBA exhibits a semi-crystalline morphology; the degree of crystallinity depends on the polyamide content. For Arkema's 3533 (35D) Pebax grade, the polymer average crystallinity is estimated at 5%.[1] An average of 25% crystallinity is estimated for the 7033 (70D) PEBA, which has a higher polyamide content.[12] Numerous degradation studies on irradiated medical polymers have been performed although predicting room temperature degradation from higher temperature studies is not always easily accomplished.[13] Studies on the degradation of irradiated PEBA are not as common, however. An e-beam sterilization study was performed on PEBA 70D, a grade with low polyether content, approximately 10.7%. Results were

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consistent with cross-linking occurring between mobile polyether segments, although the effects were subtle, and doubling the radiation dose did not seem to significantly affect the polymer dynamics.[14] In this study, preliminary accelerated aging tests of four PEBA types are presented. The PEBA samples with different polyether content were sterilized using e-beam radiation followed by accelerated aging at 55°C. Data include Gel Permeation Chromatography (GPC), and tensile measurements from simulated oven aging tests.

Materials and Methods

Tubing was constructed with a 35D, 40D, 55D and 72D PEBAX material from Arkema Corp. The PEBA grades did not contain any antioxidants or stabilizers. E-beam sterilization was performed by Nutek in Hayward, CA, using a 10 MeV electron accelerator. Samples were irradiated in a serial fashion via a conveyance system for approximately 10 minutes per dose according to Table 1. All samples were placed in the oven for accelerated aging simulation at 55Celsius degree with 50% relative humidity. Table 1 summarized Pebax material with different hardness grade used, e-beam condition and accelerated simulated aging time. 10 weeks of accelerated aging time is equivalent to 1 year aged in actual situation.[15] The GPC system used for this work was calibrated using Agilent/Polymer Laboratories EasiVial polymethylmethacrylate calibrants. The highest molecular weight calibrant was considered to be 'excluded' and was not used in the calibration. The results are expressed as the 'PMMA equivalent' (Poly Methyl Metha Acrylate) molecular weights and it should be appreciated that there could be considerable differences between these PMMA equivalents and the true molecular weights of the polymer. All materials were evaluated by mechanical testing. A Criterion Universal Testing Systems from MTS was used to mechanically test all materials in tensile mode.

Table 1. Material and e-beam radiation dose information.

Material	E-beam condition
Pebax 35D	Control
	e-beam @ 50 kGy& aged 10 weeks
Pebax 40D	Control
	e-beam @ 35 kGy& aged 10 weeks
	e-beam @ 50 kGy& aged 10 weeks
Pebax 55D	Control
	e-beam @ 35 kGy& aged 10 weeks
	e-beam @ 50 kGy& aged 10 weeks
Pebax 72D	Control
	e-beam @ 35 kGy & aged 10 weeks
Pebax 35D	80 kGy for all samples used for tensile test, aged for 48 months.

Results and Discussion

E-beam radiation and ageing leads to changes in crystalline structure in addition to oxidative damage. A significant reduction in molecular weight due to oxidative chain scission would cause a reduction in melting temperature and mechanical property. GPC was conducted to investigate any changes in molecular weight distribution resulting from either chain scission or cross-linking. Fig. 1 to 4 illustrates the molecular weight distributions measured by GPC for the as-received and 55 Celsius degree aged sample. The plots depicted in Fig. 1 to 4 include replicates for the sample types, and show a relatively small but reproducible reduction in average molecular weight as a result of ageing. The enlarged proportion of low molecular weight chains in the aged samples is consistent with the generation of degradation products produced by oxidative chain scission. It has been noted that ageing could also result in cross-linking as well as chain scission. The free radical joining of polymer chains will initially produce an increase in molecular weight but if several chains are linked, a network is

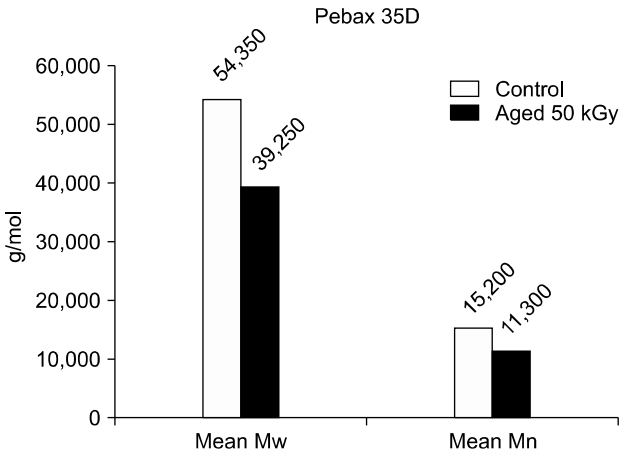

Fig. 1. Molecular weight analysis summary of Pebax 35Dpost e-beam & ageing.

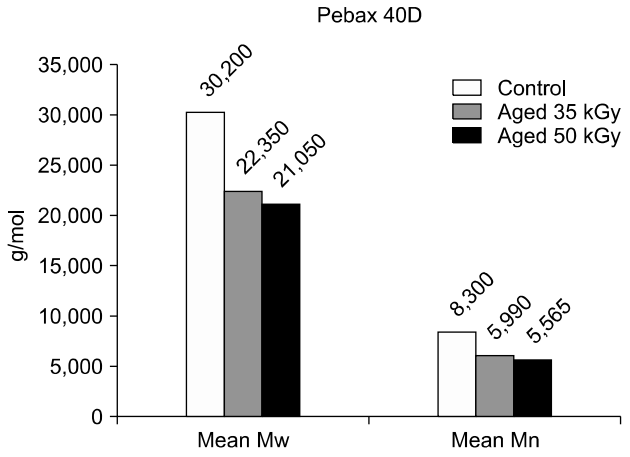

Fig. 2. Molecular weight analysis summary of Pebax40Dpost e-beam & ageing.

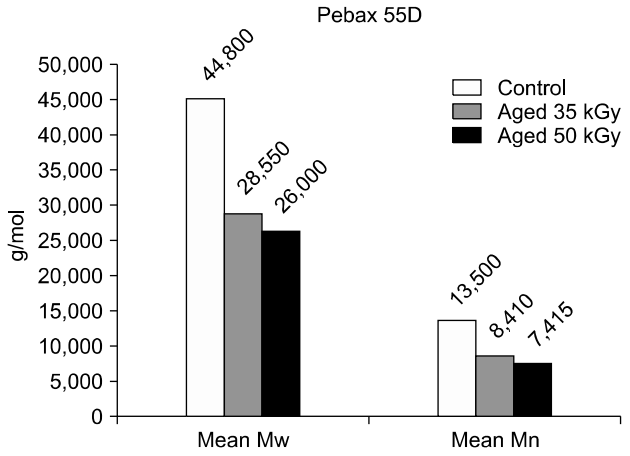

Fig. 3. Molecular weight analysis summary of Pebax55Dpost e-beam & ageing.

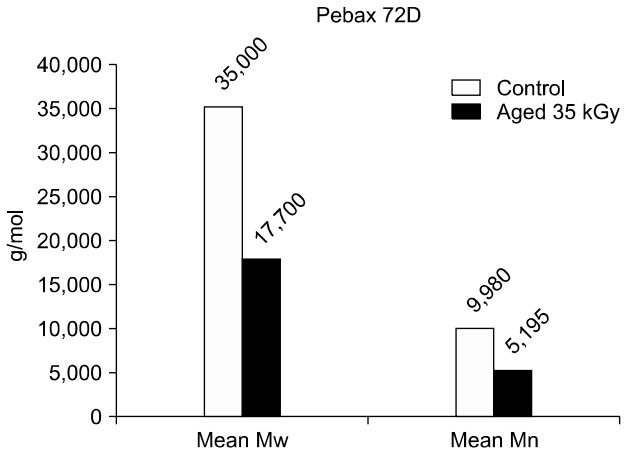

Fig. 4. Molecular weight analysis summary of Pebax 75D post e-beam & ageing.

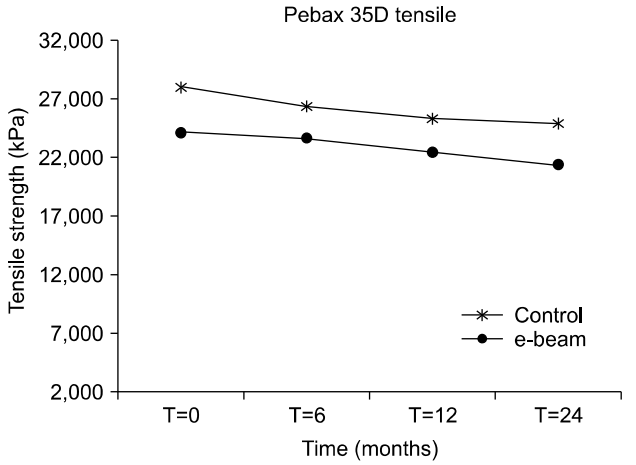

Fig. 5. Tensile strength property summary of Pebax 35D post e-beam & ageing.

established with an effectively infinitemolecular weight. This cross-linked material would be insoluble andislikely to be removed at the filtration step. At time two years, E-beam sterilization showed statistically significant different tensile strengths than respective two-year control materials. When compared against respective controls, E-beam materials have shown decreased tensile strength at all time points, possibly reflecting a trend associated with this material. The actual numerical differences between E-beam groups were in line with differences observed between controls. As seen in Fig. 5, a minimum tensile specification of 2000 psi was available for unsterilized Pebax tubing. Materials from all sterilization groups were above this specification. In Fig. 6, significant elongation differences were observed between two-year E-beam air data and E-beam air data from all other time intervals (time zero, time six, and time twelve months). Again, actual numerical differences were in line with those observed between controls.

Accelerated aging oven tests

Samples were placed in the oven for accelerated aging. Even with considerable scatter in the data, the times to failures for equivalent steriliz ation of the harder grade were observed to be much greater than the softer grade failure times, consistent with

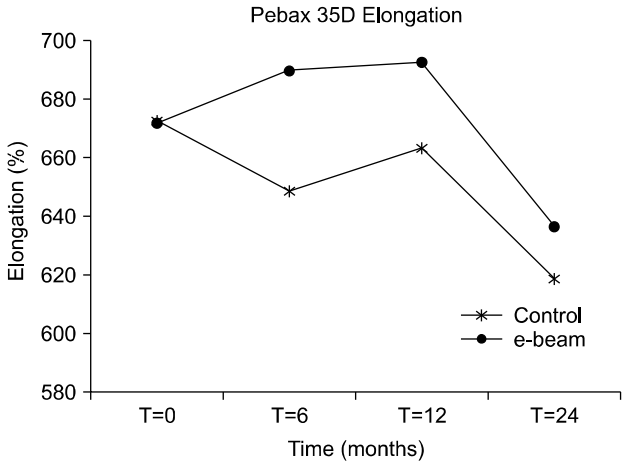

Fig. 6. Elongation property summary of Pebax 35D post e-beam & ageing.

Table 2. Calculated accelerated exposure time for various desired aging time at multiple elevated storage temperature.

		Accelerated Time (Days)			
Desired aging time (Days)		6 month 183	1 year 365	2 year 730	3 year 1095
Accelerated aging temperature (°C)	**60**	14	27	53	79
	55	19	38	75	112
	50	27	53	105	158

the higher polyamide content. The majority of medical polymers perform similarly with equal doses of e-beam or gamma irradiation. Degradation differences in response to radiation type are usually related to the shorter exposure times and higher dose rates provided by electron beam processing. Radiation damage such as chain scission can be increased in stressed polymers compared to unstressed polymers, a relevant factor in the current study. Arrhenius behavior is followed. Assuming a simple, single-rate expression for the degradation and the ten-degree--rule of chemistry, i.e., the rate of reaction roughly doubles for every ten degree increase in temperature, the expression for estimating ambient shelflife can be written as.[7)]

$$T = t \cdot q^{\left(\frac{T_{AA} - T_{RT}}{10}\right)},$$

Where T_{AA} is oven aging temperature, T_{RT} is 22°C, e.g., room temperature, and q is the reaction-rate coefficient, which is estimated as two.

The reaction rate coefficient of two is considered conservative for most medical polymers.[7)] Using the rate expression above, the simulated aging time was determined from theoven tests. It is calculated and tabulated in Table 2.

Conclusion

Accelerated aging tests performed on medical grade PEBA samples indicate the harder grade is more stable as a result of its decreased polyether block content explained by degradation during aging occurs in the polyether backbone. Significant difference in tensile strengths and elongation property after e-beam and ageing indicates a material degradation associated with this material. For medical use in case of radiation sterilization required, it is recommended to avoid Pebax material. If Pebax material must be in use for medical device, recommend to use alternate sterilization method such as Ethylene Oxide sterilization.

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전자 빔 조사후 PEBA (Poly Ether Block Amide)의 구조 및 기계적 특성 변화

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의료기기에 사용되는 고분자제품은 주로 감마선 또는 전자 빔을 이용하여 살균을 하는데, 살균에 의해 재료특성이 변화한다. 카테터에 많이 사용되는 고분자 폴리머인 poly(ether-block-amides) (PEBA)는 살균에 의한 물성변화가 더욱 심하다고 알려져 있다. 따라서 본 연구에서는 살균 후 PEBA의 물성변화를 측정하여 전자선 살균이 미치는 영향에 대해 평가하였다. PEBA에 전자선을 조사하고 노화를 촉진시켜 유효기간 동안의 변화를 확인하였다. 급속노화가 이루어진 환경은 온도가 55도, 습도가 50%인 오븐에서 수행되었다. PEBA의 경도는 polyester 함량에 따라 달라지는데 본 연구에서 사용된PEBA 시료의 경도는 35D (soft)부터 72D (hard)였다. 전자빔 살균에 의한 PEBA의 분자량 변화와 인장강도 변화를 측정 하였다. 측정결과, 노화로 인해 분자량이 현저히 감소함을 확인 하였다. 35D 시료의 경우 분자량이 54350 g/mol에서 39250 g/mol으로 감소하였다. 또한 전자 빔에 의해 살균된 PEBA의 인장 강도 및 신장율도 현저히 감소하였다. 35D PEBA시료의 인장강도 역시 28040 kPa에서 24118 kPa로 14% 이상 감소하였다. 결론적으로 전자선 빔으로 의료용으로 사용되는 PEBA제품을 살균할 경우 물성변화가 심각하게 발생하므로 전자 빔 살균은 문제가 많음을 알 수 있었다.

중심단어: 의료 고분자, 전자 빔X선, PEBA 물성