Properties of Polymers after Radiation Cross-linking

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Abstract: - Radiation processing involves the use of natural or manmade sources of high energy radiation on an industrial scale. The principle of radiation processing is the ability of high energy radiation to produce reactive cations, anions and free radicals in materials. The industrial applications of the radiation processing of plastics and composites include polymerization, cross-linking, degradation and grafting. Radiation processing mainly involves the use of either electron beams from electron accelerators or gamma radiation from Cobalt-60 sources. The TPE-E thermoplastic elastomer, PP polypropylene PA6 polyamide 6 and PA6.6 polyamide 6.6 tested showed significant changes of temperature stability and mechanical properties after irradiation. From this point view, new applications could also be seen in areas with service temperatures higher than their former melting point. The comparison of the temperature stability and mechanical properties of irradiated and non irradiated TPE-E, PP, PA6 and PA6.6 are presented in this paper.

Key-Words: - thermoplastic elastomer, polypropylene, polyamide, irradiation, cross-linking, properties

1 Introduction

The cross-linking of rubbers and thermoplastic polymers is a well-proven process for the improvement of thermal properties. The chemical cross-linking or rubber vulcanisation is normally induced by the effect of heating after processing with the presence of a curing agent. The cross-linking process for thermosets is very similar. In thermosets, the polymer molecules are also chemically linked due to heat after processing. Cross-linked rubbers have a wide-meshed molecular network that keeps them soft and their properties change only slightly on a wide temperature scale. On the other hand, thermosets are characterised by a very narrow-meshed network. Due to this fact, they hardly change their high level of stiffness on a wide temperature scale at all. The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) is performed separately, after processing. Generally, ionising radiation includes accelerated electrons, gamma rays and X-rays. [1] These are not only capable of converting monomeric and oligomeric liquids, but also can produce, due to cross-linking, major changes in the properties of solid polymers. The cross-linking level can be adjusted by the irradiation dosage. The absorbed dosage means the value of energy of ionising radiation absorbed by a unit of mass of the processed material. The unit of absorbed dose is 1 Gray (1 Gy= 1J/kg). The main difference between beta and gamma rays is in their different abilities to penetrate the irradiated material. Gamma rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons. Due to electron accelerators, the required dosage can be applied within seconds, whereas several hours are required in the gamma radiation plant (Fig. 1).[1,2]

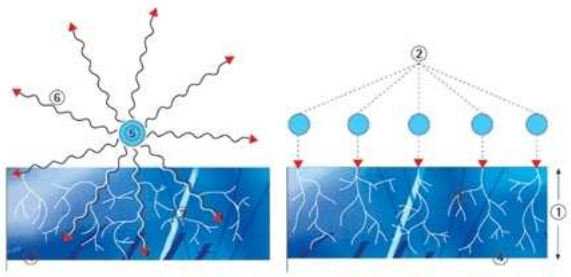

Fig. 1 Design of Gamma Rays (a) and Electron Rays (b), 1 – Penetration depth of an electron, 2 – Primary electron, 3 – Secondary electron, 4 – Irradiated material, 5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [2]

Beta and gamma rays can be used for the irradiation of polyolefines, polyesters, halogen polymers and polyamides from the thermoplastics group, elastomers and thermoplastic elastomers. Some of them need the addition of a cross-linking agent. The dimensional stability, strength, chemical resistance and wear of polymers can be improved by irradiation. [1,6,7,8].

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In this work, Engineering Polyester Thermoplastic Elastomer (TPE-E), polypropylene (PP), Polyamide 6 (PA6) and Polyamide 6.6 (PA6.6) were tested. The main attention was aimed to thermal stability of study materials and the effect of the irradiation dose on thermal and mechanical properties.

In comparison with other construction / engineering materials, mainly metals; polymers including TPEs, PPs PAs have limited levels of both mechanical and thermal properties. These limitations significantly reduce the applicability of polymers. Every improvement of these properties, of course, makes their applicability wider. Irradiation of thermoplastics is an important way to change their thermal properties. From the usage point-of-view, it is mainly the temperature stability which is a very important factor. Plastic parts suitable for radiation cross-linking are extruded products like tubes, pipes and profiles as well as injection-moulded parts.

2 Problem Formulation

The mechanical properties and thermal stability of an irradiated thermoplastic elastomer, PP and PAs after irradiation were tested. An ARBURG Allrounder 420C Advance Injection molding machine was used for sample preparation, with the processing conditional to comply with the TPE-E, PP and PA producer's recommendations.

Polymers Used:

TPE-E, V-PTS-UNIFLEX-E25D/M*M800/20 natur

PP, V-PTS-CREALEN-EP-2300L1 M800 natural

PA6, FRISETTA, Frianyl B63VN

PA6.6, FRASETTA, Frianyl A63 VN

2.1 Testing equipment

2.1.1 Gel Content

Determining the degree of cross-linking by gel measurements – (gel content), according to the standard EN ISO 579.

2.1.2 Tensile Test

The TPE-E tensile strength test was carried out on a T 2000 Alpha Technologies testing machine, under a constant speed of elongation of 500 mm/min. The PP and PA tensile strength test was carried out on a ZWICK 1456 testing machine, under a constant speed of elongation of 50 mm/min. The testing samples used were in the shape of a shovel, and their dimensions complied with the CSN ISO 37 standards.

2.1.3 TMA Test

Equipment: Perkin – Elmer Thermal Analyser DMA 7e, heat from 50°C to 400°C at 20°C/min, hold for 1 min at 50°C

2.2 Irradiation

Irradiation of the TPE-E polymer tested was performed thanks to the kind help of BGS Germany, in the BGS Wiehl plant using accelerated electrons with a dosage range of 0 to 198kGy.

3 Problem Solution

The mechanical and thermal behaviour of thermoplastic elastomers (TPE-E), polypropylene (PP) and polyamides (PA6, PA6.6) before and after irradiation, were studied. For easy of evaluation of the measured data reasons, and the comparison of the irradiated polymer with a non irradiated one, dimensionless values (-) were used in some cases. The property of the non-irradiated polymer had the dimensionless value of 1, while others were expressed as the ratio of measured property of irradiated polymers to the same property of non-irradiated polymer.

3.1 Gel Content

At each irradiated test specimens the gel content was measured which is presented in the Fig. 2. Here you can see that the gel content is stable from dosis 99 kGy in case of TPE-E and PAs and from dosis 15 kGy in case of PP.

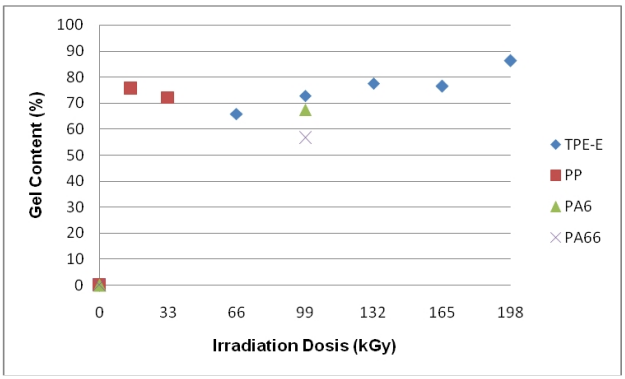

Fig. 2 Comparision of Polymers Gel Content

3.2 Tensile Strength and E-modulus

Irradiation affects the mechanical properties of the polymers studied at the ambient temperature. The TPE-E tensile strength rises 40% after irradiation with a dosage of 66 kGy. The PP tensile strength rises 23% after irradiation with a dosage of 15 kGy. The PA6 tensile strength rises 5% and the PA6.6 tensile strength rises 12% after irradiation with a dosage of 99 kGy. From the point-of-view of its tensile strength a dosage of irradiation of 66 kGy would seem to be optimal for TPE-E, 15kGy for PP and 99kGy for PAs (Fig. 3).

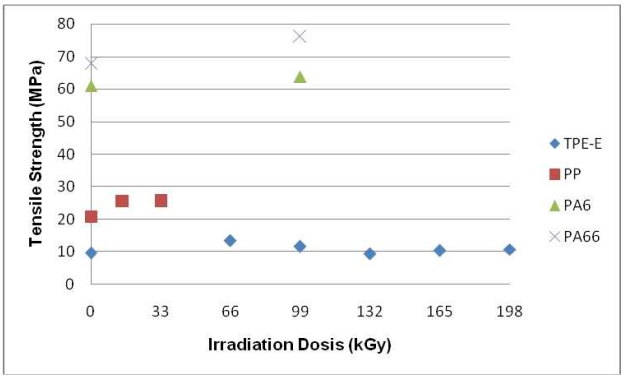

Fig. 3 Comparison of Polymers Tensile Strength

The E-modulus rises more than 25% after irradiation with a dosage of 198 kGy for TPE-E. The E-modulus rises more than 35% after irradiation with a dosage of 15 kGy for PP. The PA6 E-modulus decreases more than 60% after irradiation with a dosage of 99 kGy and 65% for PA6.6 (Fig. 4).

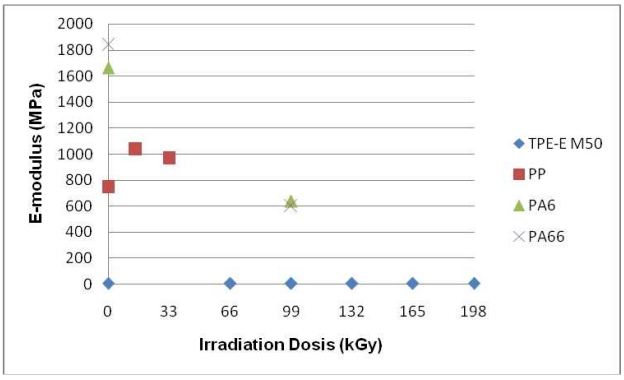

Fig. 4 Comparison of Polymers E-modulus

The TPE-E Modulus of Elasticity rises gradually in line with the dosage of irradiation. The Modulus 100 is higher by 25% and the Modulus 300 is more than 50% higher after irradiation with a dosage of 198kGy (Fig. 5).

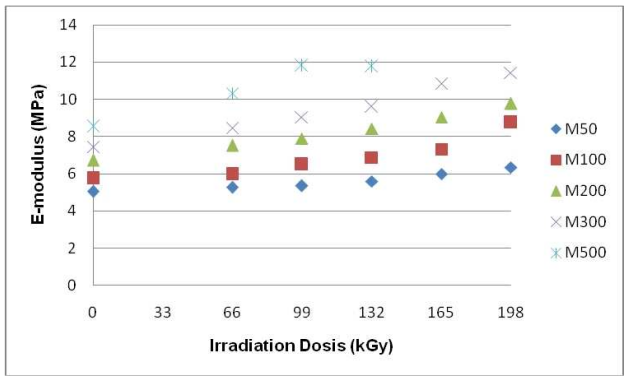

Fig. 5 Comparison of TPE-E E-modulus

3.3 Temperature Stability

The temperature stability of polymers is very low in comparison with other construction materials. Experiments done in this project showed that irradiation cross-linking markedly affected the temperature stability of the TPE-E, PP, PA6 and PA6.6 studied. The higher the irradiation dosage, the better is the temperature stability of these polymers. The TPE-E tested specimen remained without dimensional changes at the temperature of 200°C, after irradiation with a dosage of more than 165 kGy (Fig. 6). The PP tested specimen remained without dimensional changes at the temperature of 200°C, after irradiation with a dosage of 15, 33 kGy (Fig. 7). The same specimen, at temperatures higher than 250°C, creates colour changes due to thermal oxidation - but its dimension/cross-section remains without change. Its better temperature stability makes possible to use this polymer - even at service temperatures higher than its former melting point.

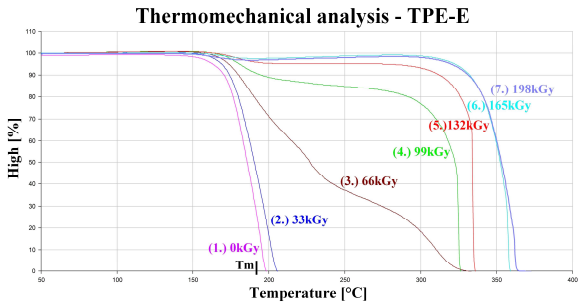

Fig. 6 TPE-E TMA analysis

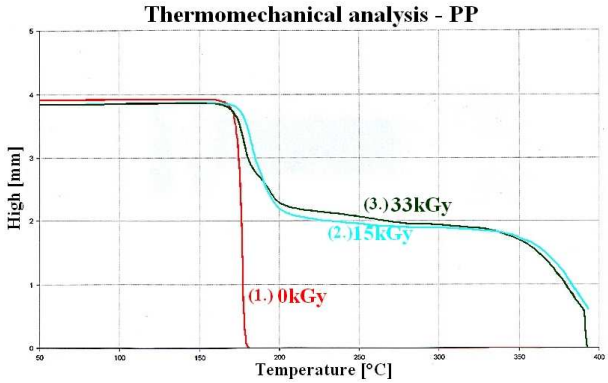

Fig. 7 PP TMA analysis

4 Conclusion

The results of the measurements of TPE-E, PP, PA6 and PA6.6 after irradiation showed significant changes of its mechanical and thermo-mechanical properties. The tensile strength rises for all measured materials, after irradiation with a dosage of kGy. The E – modulus rises gradually in line with the dose of irradiation. The maximum diference (about 50%) between irradiated and non-irradiated TPE-E was measured after irradiation with a dosage of 198 kGy. A very important point is the improvement of the TPE-E, PP, PA's thermal stability, after irradiation. This significantly moves the application possibilities of the TPE-E, PP, PAs we tested to an area with service temperatures much higher than their former melting-point.

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