

The Effect of Polyquinone and Phenol-Phosphite Stabilizer on the Resistance of Polypropylene to Ionizing Radiation

M.S. Lisanevich^a, E.R. Rakhmatullina^b, Y.N. Khakimullin^c,
R.Y. Galimzyanova^d, R.M. Akhmadullin^e, Y.V. Perukhin^f

420015, Russian Federation, Kazan, 68 Marks St.

^alisanevichm@gmail.com, ^belvina008@gmail.com, ^cgalimzyanovar@gmail.com,
^dhakim123@rambler.ru, ^enmukmeneva@mail.ru

Keywords: disposable medical products, polypropylene, radiation resistance, radiation sterilization, medical clothing and disposable underwear, polyquinones, phenol-phosphite stabilizer

Abstract. For polymeric materials intended for the manufacture of disposable sterile medical devices, resistance to sterilization methods is important. For the manufacture of disposable medical products is widely used polypropylene, destructive during radiation sterilization. It is established that the addition of polyquinone leads to a decrease in the destruction of polypropylene, which is manifested in a decrease in the values of the melt flow index and an increase in the degradation temperature of polypropylene of the irradiated compositions.

Introduction

Production and consumption of disposable medical products is constantly growing. Products from non-woven materials based on polypropylene (surgical gowns, surgical linens, absorbent wipes, etc.) are becoming increasingly important for medicine and hygiene [1-6]. Polypropylene today is one of the most common thermoplastics in the world and is used in various areas of industry due to its low cost and its valuable practical properties. High strength, heat resistance, lack of toxicity make it indispensable in the manufacture of medical products of a wide range. In addition to the above nonwoven materials, medical devices, containers and packaging of medicines are made from polypropylene (PP).

For these products is often used sterilization with ionizing radiation [7, 8]. However, polymers having tertiary or quaternary carbon atoms in their structure, when exposed to ionizing radiation, are mainly destructed by a radical mechanism [9-11]. These polymers are polypropylene. Under the influence of ionizing radiation, polypropylene undergoes deep chemical and structural transformations, leading to a change in physicochemical properties; processes of destruction, crosslinking, destruction of crystal structures occur [12, 13].

During radiation destruction, the mechanical properties deteriorate: elongation decreases and the strength at break, the polymer becomes brittle and cracks. The ability to resist the effects of radiation and maintain the original properties is defined by the term "radiation resistance". In terms of their radiation resistance, substances and materials are significantly different. This is due to the differences in their physicochemical characteristics: the elemental composition, phase state, chemical and electronic state of the molecules, the defectiveness of the structure [14].

The mechanism of interaction of radiation with polypropylene:

1. $RH + \gamma \rightarrow R\cdot + H\cdot$
2. $R\cdot + O_2 \rightarrow RO_2\cdot$
3. $RO_2\cdot + RH \rightarrow ROOH + R\cdot$
4. $ROOH \rightarrow RO\cdot + \cdot OH$
5. $2ROOH \rightarrow RO\cdot + RO_2\cdot + H_2O$
6. $ROOH + RH \rightarrow RO\cdot + R\cdot + H_2O$
7. $RO\cdot + ROOH \rightarrow ROH + RO_2\cdot$
8. $ROOH \rightarrow$ inactive products
9. $RO_2\cdot + RO_2\cdot \rightarrow$ inactive products [15].

In this regard, it is relevant to increase the radiation resistance of polypropylene and its copolymers. Today, the solution of this problem is possible either by using polypropylene copolymers or a mixture of polypropylene and ethylene to obtain composite materials, or by using stabilizing additives [16].

As is known, compounds of the quinoid structure are traps of alkyl radicals. Polyquinone can be attributed to a number of conjugated polymers. Conjugated polymers are compounds with a chain of sp^2 -hybridized carbon skeleton, due to which electrons on the orbitals are delocalized and have a high density. They are also called electroactive polymers [17]. It was interesting to study the effect of polyquinone on the radiation resistance of polypropylene.

Experimental

In the work were used: PP1562R polypropylene produced by PJSC «Nizhnekamskneftekhim»; Polyquinone (PQ), the structure of which is shown in Fig. 1, synthesized at the Department of TSK (KNRTU), Anox BB021 (Addivant™) compound stabilizer.

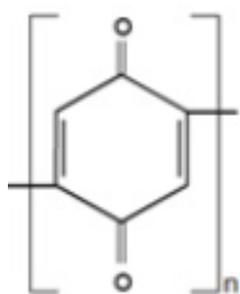


Fig. 1. Structure polyquinone

The compositions were mixed in the Measuring Mixer 350E mixing chamber of the Brabender PlastiCorder® Lab-Station mixing equipment (Germany). The mixing chamber and the stabilizer were sequentially loaded into the mixing chamber. Mixing was performed at a mixing chamber temperature of 190 °C for 3 minutes, the rotation speed of the rotors was 60 rpm. The mixture was then removed from the mixing chamber and leafed on cold rolls.

To obtain samples in the form of ribbons or strands under laboratory conditions, the Extruder Type 19/25 D extrusion prefix of the PlastiCorder® LabStation plastic die was used (auger diameter with single thread cutting - 20 mm, $L / D = 25$). The screw rotation speed is 90 rpm. The temperature in the zones was $T_1 = 170$ °C, $T_2 = 180$ °C, $T_3 =$ ained compositions in the form of ribbons were irradiated with electron radiation in absorbed doses of 37.0 ± 2.5 , 65.5 ± 3.7 , 98.6 ± 5.5 kGy in the radiation installation “Electronic sterilizer” with the electron accelerator UELV-10-10- s-70.

The melt flow rate (MFR) was determined on an IIRT 5m instrument according to GOST 11645-73 at 190 °C.

Thermogravimetric analysis (TGA) of the samples after exposure to electron irradiation with an absorbed dose of 40 kGy was performed on a Perkin Elmer sta 6000 synchronous thermal analyzer (temperature range 30-400 °C, heating rate 10 °C / min), in accordance with ISO 11358-1: 2014.

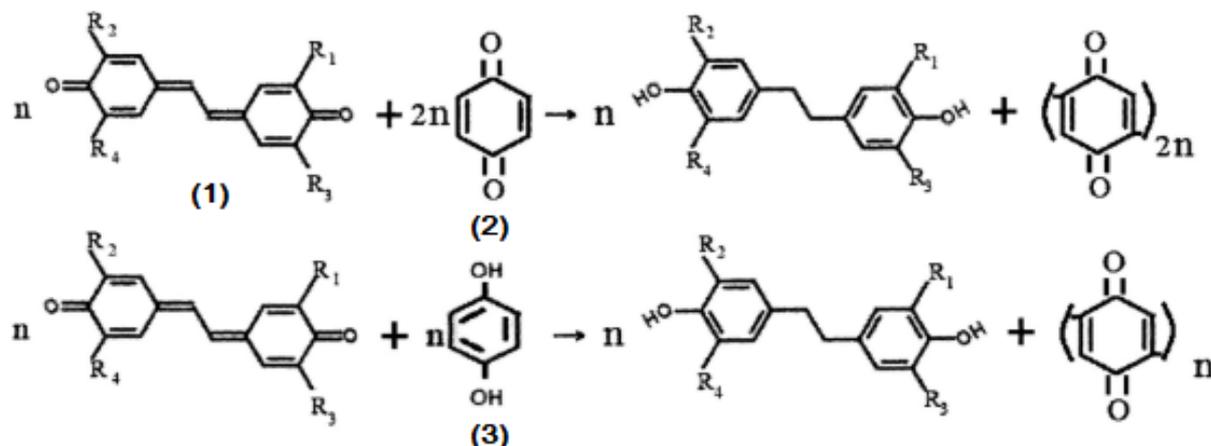
Results and Discussion

Quinones are fully conjugated cyclohexadienones and their annelated (cyclization) analogues. There are two classes of quinones: para-quinones with para - the arrangement of carbonyl groups (1,4-quinones) and ortho-quinones with ortho-arrangement of carbonyl groups (1,2-quinones). Due to the ability to reversibly reduce to diatomic phenols, some para-quinone derivatives are involved in biological oxidation processes as coenzymes of a number of oxidoreductases.

The nucleus of quinones is not aromatic, the contribution of resonant structures of the aromatic type to the properties of quinones is small. The spectroscopic properties are close to those of 1,2-unsaturated ketones, while the properties of 1,4-quinones are closer to the cross-conjugated unsaturated 1,4-diketones, while 1,2-quinones are closer to dydions.

Polyquinone can be obtained by polymerization of hydroquinone, oxidative dehydrogenation of hydroquinone monomers, polycondensation in a solution of aromatic and heteroaromatic compounds and an aromatic tetracarboxylic acid derivative in the presence of anhydrous metal chlorides [18-19].

The polyquinone used in the work was obtained as a result of the oxidative dehydrogenation of the monomers of hydroquinone (3) or benzoquinone (2) in the presence of a mild dehydrating agent - spatially substituted stilbenquinone, general formula (1), to obtain the final product - polyquinone and an equimolar amount of spatially substituted ethylene bisphenol. The reaction proceeds in the presence of water in a neutral medium, or in an acidic medium, or in an alkaline medium with a hydrocarbon proton or aprotic solvent, in which the dehydrating agent and the initial monomer are dissolved. The temperature range of the reaction lies in the range from 100 to 200 ° C, the reaction time is not more than 3 hours. The reaction scheme is presented below.



R_{1-4} is tert-butyl [18].

The effectiveness of polyquinones as antioxidants depends on the nature and number of heterocycles connecting quinone rings in the polymer macromolecule. Polyquinones have a high value of the electron-exchange capacity. From linear polymers to polymers with a ladder structure, the magnitude of the exchange capacity decreases, but the rate of redox processes increases [20-23].

The effect of electron radiation on the melt flow rate of compositions with the addition of polyquinone was studied.

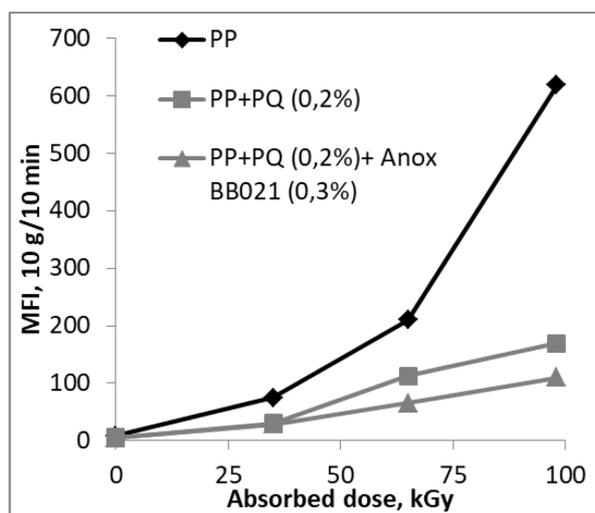


Fig. 2 The dependence of the melt flow index on the absorbed dose of electron radiation for compositions with the addition of polyquinone and polyquinone with Anox BB021

the stabilizer complex consisting of phenol-phosphite antioxidant AnoxBB021 (in the amount of 0.3%) and polyquinone (in the amount of 0.2%). The use of the stabilization complex has led to a further decrease in the melt flow rate by 66% (from 210 to 71 g / 10 min) and by 79% (from 619 to

Due to the destruction of polypropylene, as a result of exposure to ionizing radiation, its molecular weight decreases and, accordingly, the melt viscosity decreases, which leads to an increase in the melt flow rate.

The use of polyquinone in the amount of 0.2% reduces the MFR of polypropylene irradiated with an absorbed dose of 65 kGy (from 210 to 113 g / 10 min) by 54%. Thus, polyquinone can significantly reduce the degradation of polypropylene. An increase in the absorbed dose of electron radiation to 98 kGy naturally leads to an even stronger destruction of polypropylene, which is manifested in an increase in the MFR by a factor of 29 compared with that of the unirradiated. Introduction of HRP allows to reduce the MFR of the irradiated compositions by 73% (from 619 to 169 g/10 min).

It was interesting to study the effect of

130 g / 10 min) with an irradiation dose of 65 and 98 kGy, which indicates the introducing into the polymer a combination of a polyquinone and a mixed phenol-phosphite stabilizer.

Table 1 Thermogravimetric analysis of PP irradiated with electron radiation

Temperature, °C	Absorbed dose, kGy	PP	PP + PQ (0,2%) + Anox BB021 (0,3%)
start of	0	275	325
destruction	35,0±2,5	240	316
intense	0	395	398
destruction	35,0±2,5	340	369

From table 1 it follows that the effect of electron radiation naturally reduces the temperature of the onset and intense destruction of polypropylene. The use of polyquinone and Anox BB021 allows to increase the resistance to thermal destruction of both non-irradiated compositions by 50 °C (initial degradation temperature) and 3 °C (intensive degradation temperature), and compositions irradiated with an absorbed dose of 35.0±2.5 kGy. In the second case, the temperature of the initial degradation increases by 76 °C, and the intensive degradation of 29 °C.

Conclusion

Thus, it was found that the addition of polyquinone leads to a decrease in the destruction of polypropylene, which is manifested in a decrease in the melt flow rate for irradiated compositions. The introduction of polyquinone increases the temperature of the onset and intensive destruction of both irradiated and non-irradiated compositions, which also indicates an increase in the stability of polypropylene. As a result of the data obtained, polyquinone can be recommended to increase the radiation resistance of polypropylene.

References

- [1] Khakimullin Yu.N. et al. Non-woven materials based on polymers used for the production of medical clothes and linen, sterilized by radiation: types of materials, technology of production of radiation: types of materials, production technology // Bulletin of Kazan Technological University. 2011. Vol. 23. P. 97–103.
- [2] Travkina L.S. et al. Influence of ionizing radiation on the properties of nonwoven materials for medical purposes // Bulletin of Kazan Technological University. 2013. Vol. 84. P. 487–492.
- [3] Hosun L. A review of spun bond process // J. Text. Apparel, Technol. Manag. 2010. Vol. 6, No. 3. P. 1–13.
- [4] Acar M., Harper J.F. Textile composites from hydro-entangled non-woven fabrics // Comput. Struct. 2000. Vol. 76, № 1. P. 105–114.
- [5] Czajka R. Development of medical textile market // Fibres Text. East. Eur. 2005. Vol. 13, № 1. P. 13–15.
- [6] Tang S.L.P., Stylios G.K. An overview of smart technologies for clothing design and engineering // Int. J. Cloth. Sci. Technol. 2006. Vol. 18, № 2. P. 108–128.
- [7] Berejka A.J., Cleland M.R. Industrial Radiation Processing With Electron Beams and X-rays. 2011. No. May. 105 p.
- [8] Berejka A. Polymers Status and Prospects. Vienna, 2005. № August. 146 p.
- [9] Kargin V.A. Radiation chemistry of polymers / ed. M.: Science. 1973. 320 p.
- [10] Mamedov S., Garibov A. Radiation physics and chemistry of polymers / ed. Deutschland S.A.P. 2015. 547 p.

-
- [11] Perova M.S. et al. Influence of the Molecular Weight of Oligoisobutylenes on the Properties of Uncured Sealants // *Int. Polym. Sci. Technol.* 2011. Vol. 38, No. 12. P. 9–11.
- [12] Rakhmatullina E.R. et al. Effect of processing conditions on the properties of polypropylene // *Deformation and destruction of materials.* 2017. Vol. 12. P. 35–39.
- [13] Veselovsky R.A., Leshchenko S.S., Karpov V.L. On some features of the radiation chemistry of polypropylene in the field of low doses // *M.: Nauka.* 1966. 268-271 p.
- [14] Gahleitner M. et al. Sterilization effects on polypropylene: technology and polymer type effects // *9th EUROPLACE Conference.* 2003. P. 25.
- [15] Emanuel N.M. Modern ideas about the mechanism of action of oxidation inhibitors. *M. : Neftekh.* 1976. 216 p.
- [16] Lisanevich M.S. et al. The use of phenol and mixed phenol-phosphite antioxidants for anti-radiation protection of polypropylene for medical purposes // *Bulletin of the Technological University.* 2015. Vol. 18, No. 2. P. 181-182.
- [17] Akhmadullin R.M. et al. Polyquinone synthesis by dehydrogenation agent 3,3',5,5'-tetra-tert-butyl-4,4'-diphenoquinone // *Res. J. Pharm. Biol. Chem. Sci.* 2016. Vol. 7, No. 2. P. 577–585.
- [18] Akhmadullin R.M. et al. Getting 4,4'-Bis (2,6-Di-Tert-Butylphenol) And Polyquinone In the Alkaline Oxidizing Dehydrogenation Reaction of Hydroquinone 3,3',5,5'-Tetra-Tert-Butyldifenoquinone // *Bulletin of Kazan Technological University.* 2014. Vol. 17, No. 6. P. 160–163.
- [19] Adams M.D. Models for activated carbon: extraction of aurocyanide by polyxanthenes, polyquinones and graphite // *React. Polym.* 1993. Vol. 21, No. 3. P. 159–170.
- [20] Gurov A.A., Liogon'kii B.I., Berlin A.A. Oxidation-Reduction properties of polyquinones // *Bull. Acad. Sci. USSR Div. Chem. Sci.* 1971. Vol. 20, No. 5. P. 917–923.
- [21] Liogon'kii B.I. et al. Stabilization of polycarbonates with polyquinones // *Polym. Sci. U.S.S.R.* 1968. Vol. 10, № 11. P. 2891–2898.
- [22] Shiraishi K., Yamamoto T. Synthesis and Electrochemical Properties of New Main Chain Type Polyquinones Constituted of Thiophene-Fused Benzoquinone and Transformation of the Polymers to a Dicyanoquinonediimine Type Polymer // *Polym. J.* 2003. Vol. 34, № 10. P. 727–735.
- [23] Muramatsu Y., Yamamoto T. Preparation of New Main-chain Type Polyquinone and Its Properties // *Chemistry Lett.* 1997. № 13. P. 581–582.