The Gamma Radiation Tolerance of Polypropylene: Measurement and Enhancement

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Although many tests are currently being used to evaluate the high-energy radiation tolerance of

tolerance without the use of complicated parts or procedures. The use of this test for the validation of several approaches to enhancing polypropylene radiation tolerance is also discussed.

INTRODUCTION

Polypropylene is entering a golden period of applications in medical devices and device and drug packaging. The wide variety of homopolymers, random copolymers, and impact copolymers commercially available at very economical prices is rapidly stimulating the use of polypropylene in medical fields. Especially important to the new popularity of these plastics are their clarity and their ability to withstand all major methods of sterilization. Free of haze and the sensitivity to high-energy radiation that plagued polypropylene in the past, the new formulations are in high demand for uses previously reserved for glass or other, more costly, plastics. Considering the range of capabilities represented by the many polypropylenes now offered to the medical industry, it is absolutely necessary for the medical product designer to understand the factors affecting the radiation tolerance of the resins as well as the methods used to determine tolerance levels. Such knowledge is especially critical given the trend toward high-energy sterilization of medical devices and away from sterilization by ethylene oxide.[1]

Conventionally stabilized polypropylenes are not suitable for sterilization by high-energy radiation because of the severe embrittlement and discoloration that occur immediately in the plastic after sterilization and worsen with aging. Whereas the embrittlement of the plastic after irradiation is an inherent property of the polymer, the discoloration is caused by reaction products of the phenolic antioxidants normally included in standard polypropylenes.[1]

discolor slightly after irradiation.

The modern resins that are most successful in withstanding irradiation exhibit reduced crystallinity and narrow molecular-weight distribution, are formulated with hindered amine light stabilizers (HALS), and contain no discoloring phenolic antioxidants. Ethylene-containing random copolymers are useful substrates for building radiation-tolerant formulations, as are homopolymers with low isotacticity and homopolymers to which hydrocarbon oils or greases have been added. The HALS are, by themselves, noncoloring in polypropylene, but they interact with phenolic antioxidants to produce extremely deep yellow colors after irradiation. Therefore, when HALS are used in a polypropylene formulation, the phenolic antioxidants must be scrupulously avoided.[1-6]

Over the years, numerous methods have been developed to investigate and evaluate the effects of ionizing radiation--such as that from gamma and electron-beam sources--on polypropylene. The types of tests can be categorized broadly as spectroscopic, macroscopic, and end-use-specific. The spectroscopic type, which includes analytical and compositional analyses, involves such methods as electron spin resonance spectroscopy, infrared spectroscopy, and chemiluminescence.[79] Although these methods have given great insight into the physics and chemistry occurring during and after irradiation, the experimentation can be costly, extensive, and complicated. Also, because of the complex nature of polymeric systems, the results can be equivocal. Even though correlations of spectroscopic results with specific physical properties have been made in certain cases, they are seldom used in place of direct physical property measurements.[10,11]

Although the end-use-specific methods--tests such as syringe-flange bending, luer-tip breaking, syringe-barrel crushing, and tube centrifugation[13]--are generally the best indicators of actual field performance, they also have some drawbacks, especially for the resin producer. One of the biggest disadvantages is the expense of acquiring and operating specialized equipment for both parts fabrication and testing. The resin supplier is obliged to set up a separate test method for each end use and according to each customer's protocol, necessitating extensive testing with a broad spectrum of equipment.

The flex-to-failure method described here and in a previous publication[14] is an offshoot of the general bending concepts related by Apostolou,[15] the specific syringe-flange bending method of Williams, et al.,[16] and the notched, three-point flexural method of Narisawa and Ishikawa[17] for investigating crazing in semicrystalline thermoplastics. The test proposed here is an approach to screening resin tolerance to high-energy radiation--especially gamma and electron-beam radiation--as it specifically relates to performance concepts and characteristics sought in the medical field. The method, which involves an extension of flexural stress-strain testing, allows for the convenience and universality of ASTM testing without the use of complicated parts or procedures. In this test, sections from an ASTM tensile test bar ("dog bone") used for the determination of flexural modulus are flexed to failure, either brittle or ductile, whichever occurs first. The test's peak load, deflection, and energy-consumed-to-failure values have been used by Exxon Chemical Co. in the past as gauges of radiation tolerance. As researchers gained experience in this testing, it was determined that the deflection at peak flexural load was the test's most valuable measure of polypropylene embrittlement after irradiation. The method is sensitive to radiation-induced polymer changes and provides a quick, reliable, and relevant screening test, representative of actual medical device failure modes.

This paper presents the results of a number of related experiments demonstrating the power of the flex-to-failure test as part of a total screening regimen in the evaluation of some modern methods of stabilizing polypropylenes to high-energy radiation.

EXPERIMENTAL

In all four experiments, polypropylene formulations were compounded and pelletized, then molded into ASTM test parts in a family mold. Only Gardner disks (88.9 mm diam x 3.18 mm thickness) and tensile bars (165 mm length x 12.7 width x 3.18 mm thickness) were required for the tests performed in this work. Parts from each resin were irradiated by a Co^{60} gamma source at approximately 10 kGy/hr to each of the indicated total dosages (see Figures 112). The parts were then aged at 60°C for 21 days and the testing carried out as soon as possible after the aging period. The tests performed were the determination of Gardner impact strength (ASTM D 3029-84), tensile elongation at break (ASTM D 638-87b), and flex-to-failure (ASTM D 790-86 extended past peak load), all at 23°C. The latter procedure simply extended to higher strain the determination of flexural modulus, and comprised the entire flex-to-failure test. The deflection at maximum stress corresponding to either brittle or ductile failure was observed and recorded as the deflection at peak flexural load.

Experiment 1: Effect of Ethylene Content on the Radiation Response of Random Copolymers. Samples 14 were identically formulated, 25 dg/min melt-flow rate (MFR) polypropylenes, polymerized with 0, 1.5, 2.2, and 2.8% ethylene comonomer, respectively. The formulations contained both hindered amine light stabilizer and nucleating clarifier as well as other standard ingredients used in Exxon's commercial medical device formulations.

Experiment 2: Effect of Mobilizing Oil on the Radiation Response of Propylene Homopolymer. Samples 5 and 6 were identical 25 dg/min MFR propylene homopolymers containing the standard additive package, except that an additional 3% of a paraffin oil was compounded into Sample 6.

Experiment 3: Comparison of the Protective Effect on Irradiated Polypropylenes of Two Different Hindered Amine Light- Stabilizer Packages. Samples 7 and 8 were two 1.5% ethylene random copolymers with 25 dg/min MFR. Sample 7 was stabilized with a high level of Tinuvin 622 (Ciba Geigy Corp., Hawthorne, NY) while Sample 8 was stabilized with a similar amount of Tinuvin 770. Both resins were nucleated and clarified.

Experiment 4: Effect of Reformulation on a Successful Radiation- Tolerant Random Copolymer. Sample 9 was Exxon's commercial, medical device resin PP 9074MED. Sample 10 was the same polymer, stabilized in exactly the same way, but nucleated with Millad 3988 instead of Millad 3940 (Milliken Chemical Div., Spartanburg, SC) and containing other small additive modifications

The Flex-to-Failure Test Profile. In the flex-to-failure test, four different stress-strain profiles have been observed. Figure 13 shows the characteristic ductile failure mode. As the sample is flexed in the three-point bending configuration, the stress increases with deflection until ductile failure occurs, corresponding to the peak load of the profile. As expected, most nonirradiated polypropylenes will exhibit this type of profile. Lower peak loads are generally associated with more flexible samples.

From past studies conducted by the author, it is known that four different failure modes can be observed in the flex-to-failure test. In order of increasing brittleness, the sample may exhibit ductile failure only (Figure 13), ductile failure followed by brittle failure (Figure 14), stepwise brittle fracture without ductile failure (Figure 15), or simple brittle fracture without ductile failure (Figure 16). The stepwise brittle failure is rare, since it occurs only at a very specific balance of ductility and brittleness and may represent a sample that is not uniform throughout its cross section at the point of application of the stress. The more ductile the polypropylene sample, the greater is the deflection until failure, up to a limit of about 11.0 mm. The numerical results recorded here correspond to all of the qualitative failure modes except the stepwise brittle fracture.

The Effects of Formulation Differences on the Radiation Resistance of Polypropylenes. While the experiments described here in no way constitute an exhaustive study of the factors affecting the behavior of polypropylene exposed to high-energy radiation, they do provide some illustration of the primary influences on the radiation resistance of this thermoplastic.

Figures 1 through 3 clearly show the increase in ductility imparted to polypropylene by random ethylene comonomer, an effect that increases monotonically with comonomer content. This increase in ductility is evident in nonirradiated material as well as in the irradiated samples through the improvements in the tensile elongation and impact strength of the materials. The evidence of these changes in nonirradiated samples is valuable to an understanding of the effect of ethylene comonomer on the basic physical properties of resins. However, it complicates comparisons of embrittlement of irradiated materials by giving different starting points for each material. The deflection at peak flexural load is remarkably similar for all four of the ethylene levels studied in Experiment 1. While much less information about the ductility of nonirradiated resin is available from these results, the embrittlement that occurs upon irradiation is much easier to compare for the various examples.

The results for samples 5 and 6 showed a similar enhancement of ductility produced by the addition of 3% of a paraffin oil to a HALS-stabilized propylene homopolymer. All three of the test methods used were complementary in giving an overall picture of the effect of the oil additive. At 3% of the formulation, the oil extended the ductility of the irradiated resin in a manner very much like that of ethylene comonomer at 3% (Sample 4, Figures 13), but had much less effect on the starting properties of the nonirradiated material.

Testing on samples 7 and 8 verified the marginal superiority of Tinuvin 770 as a protectant for irradiated polypropylene compared with a similar concentration of Tinuvin 622. These results from Experiment 3 also showed the value of using all three of the test methods to obtain a comprehensive picture of the behavior of irradiated polypropylene. The Gardner impact strength of the irradiated resin appeared to be most susceptible to damage by irradiation and likewise most sensitive to differences between the two stabilizers, even at dosages below 25 kGy. Tensile elongation at break was less affected, and showed a difference between the stabilizers only above 25 kGy. The deflection at peak flexural load was least affected by the irradiation, and was unchanged for both resins up to 50 kGy. The slight inferiority of the sample stabilized with Tinuvin 622 became evident in the flexural test only at 75 kGy, when the deflection first decreased significantly.

Samples 9 and 10 further emphasized the differences in character among the three tests. For these two nearly identical samples--which differed only in auxiliary additives and not in stabilizers or nucleating agent--very small differences in embrittlement behavior after irradiation were expected. This was in fact observed, especially in the results of the tensile and flexural testing. The flexural testing, particularly, indicated the similarity of the resins, even with 75-kGy irradiation. As always, the Gardner impact strength seemed to be more sensitive than the other tests to very minor differences between materials.

Comparison of the Three Testing Methods. Although the three test methods were all useful in investigating the embrittlement of irradiated polypropylene samples, it is valuable to review their particular strengths and weaknesses as illuminated by this study.

Gardner impact strength was extremely sensitive to very minor differences in resin formulation, with or without irradiation. The minimum level of impact strength representing ductility is, in general,

to detect because this relationship is different for different materials.

The Gardner technique also provides a crude qualitative indication of the embrittlement of each sample. Ductility even in a failed sample is indicated by an otherwise intact specimen with only a smooth hole punched through it by the falling tup. At the other extreme, a brittle sample, upon failure, is shattered by the falling tup. Observations of this type were not recorded in this work, but these kinds of additional insights into the behavior of irradiated resins can be very valuable, especially in light of the difficulty of judging embrittlement based solely on strength results.

The tensile elongation at break gives one a more balanced view of the resistance to embrittlement of irradiated polypropylenes: the numerical response to irradiation seems to more accurately track the general utility of the materials in actual applications. But, as in the Gardner impact test, the effect of sample molecular characteristics and impact modifications on elongation makes it difficult to compare a variety of materials or to establish a single value of elongation that represents the demarcation between ductility and brittleness. And, unlike for a Gardner specimen, it is not so easy to judge the ductility of an elongated sample by the appearance of the test specimen after it is broken.

Deflection at peak flexural load from the flex-to-failure test gives a third perspective on determining ductility. While this measurement seems, at the outset, much less sensitive to irradiation and product stability, it in fact provides a simpler approach to accurately judging resin embrittlement. Basically, nearly all polypropylenes show a deflection of from 9.5 to 10.5 mm when not irradiated. No change in this value is seen at very minor levels of resin degradation after irradiation. Thus, the first decline of this value--even by as little as 0.5 mm--denotes significant degradation and therefore can serve as a useful limiting level of irradiation, storage time after irradiation, or both. The brittle forms of breakage shown in Figures 1416 predominate in samples with lower deflection-at-peak-flexural-load results.

The differences among these three test methods should not be cause for concern. These particular results cannot be unequivocally extrapolated to actual medical devices, in which design, manufacturing, and use factors play so large a role in determining the upper limits of radiation tolerance. The value of these tests is in the consistency of the relative results. The higher-ethylene copolymers, oil-treated homopolymer, and Tinuvin- 770-stabilized homopolymer were shown to be superior in the screening experiments by each of the three test methods. It is this agreement on the

polypropylenes. Numerous factors--including comonomer level, choice of stabilizer, and use of mobilizing oil--can affect the embrittlement behavior of clear polypropylene after irradiation. Measuring the effects of these factors can be done by a variety of simple physical tests. Although the results of the Gardner impact, tensile elongation, and flex-to-failure tests are all complementary, the latter provides the most obvious quantitative and qualitative indicator of resin embrittlement. Differences in the mechanisms of applied stress and sensitivity of these tests make it valuable to use more than one type to obtain a complete understanding of the response of a material to irradiation. If possible, the testing regimen should include a method that mimics the stress experienced in actual use by the device that is to be fabricated from the material. Quite often, this is a bending stress, making the flex-to-failure method an important component of any complete regimen for screening the radiation response of polypropylene.

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