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The Influence of Gamma Irradiation on Repeated Recycling and Accelerated Acrylonitrile Butadiene Styrene Terpolymer Aging

Sandra Tostar[1*], **Erik Stenvall**[2], **Antal Boldizar**[2] **and Mark R StJ Foreman**[1]

[1]*Department of Industrial Materials Recycling, Chalmers University of Technology, 412 96 Gothenburg, Sweden*

[2]*Department of Material and Manufacturing Technology, Chalmers University of Technology, 412 96 Gothenburg, Sweden*

[*]**Corresponding author:** Sandra Tostar, Department of Industrial Materials Recycling, Chalmers University of Technology, 412 96 Gothenburg, Sweden, Tel: +46 076 12 77; E-mail: sandra.tostar@chalmers.se

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Abstract

Electronic waste also referred to as waste electrical and electronic equipment (WEEE) is the fastest growing waste stream in Europe today. The fast exchange pace of mobile phones, television sets and computers create an important need to develop recycling areas to take care of, reuse and recycle all the materials they contain. One common plastic in WEEE is acrylonitrile butadiene styrene terpolymer (ABS). Repeated recycling of plastic causes it to chemically degrade and one of the unwanted effects is the shortening of the polymer chains. Gamma irradiation is known to be able to crosslink polymers and thus reverse the chain shortening. Therefore, the hypothesis of this study is that gamma irradiation of ABS would have a beneficial effect when recycling plastic. Comparative experiments of gamma irradiation has been done according to two methods: A single gamma irradiation (40 kGy) before the extrusion and aging cycles, and the effect of four 10 kGy doses delivered before each of the re-extrusion steps were completed. The results show that gamma irradiation has an impact on the mechanical and rheological properties of ABS. The yield stress increased with irradiation doses of 0, 10, 50 and 400 kGy. The viscosity also increased in the test samples with irradiation doses of 0, 10, 100 and 200 kGy. In the multi-recycling and accelerated aging test, there was a significant reduction in stiffness for the gamma irradiated samples after the second out of four cycles which cannot be fully explained.

Keywords: Recycling; ABS; Accelerated aging; Degradation; Gamma irradiation

Introduction

Recycling of plastics from electronic waste has become of increased importance since the WEEE directive (Directive 2012/19/EU, Annex V) requires increased recycling levels. This directive will be difficult to comply with if plastics are not included, since plastics can make up to 30 % of electronic products [1-3].

Acrylonitrile butadiene styrene terpolymer (ABS) is one of the main constituents in electronic plastics [1,4-6] since it is highly impact resistant, due to its rubber content, and its moldability [7].

Investigations on multiple recycling and accelerated aging have been reported by several researchers [8-10] but the degradation behavior, to the best knowledge of the authors, has never been compared with gamma irradiated ABS.

It is known that the degradation of plastic is the total amount of weathering it is exposed to during the products' lifetime. Therefore, to be able to simulate repeated recycling of the plastic, service life at room temperature has to be accounted [10]. This can be done by accelerated aging by thermo oxidative degradation.

The aging rate is doubled with every 10°C increase. A service time of one year at room temperature should thus be 72 h at 90°C [7,9,11].

Today's short working life of electronic products, such as mobile phones and computers, was the benchmark for the accelerated aging, simulating one year use of the product.

In this work a comparison between gamma irradiated and unirradiated ABS has been done to compare the degradation behavior of both materials after recycling. If the mechanical properties are enhanced by gamma irradiation, the same material can be recycled numerous times.

Experimental

Material

The ABS used was an electronic equipment grade, named Terluran® GP-35 produced by BASF, which does not contain any flame retardants. It was purchased at ALBIS, Sweden.

Sample preparation and material processing

Three series of sample preparation were performed: unirradiated ABS, ABS irradiated once at the start of the test at 40 kGy, and ABS irradiated at 10 kGy between each recycling cycle, which gives a total dose of 40 kGy.

Depending on the stage of the recycling cycle, the granulate and plastic flakes were irradiated in a Gammacell 220 (Atomic Energy of Canada). The dose rate to water in the irradiation chamber of the unit was on average 14 kGy·h^{-1}.

All recycling cycles had the same setup: drying, extrusion of strips, grinding and aging. Although, the drying step was excluded for cycle 1-4. The extrusions were performed by a Collin extruder 3250- 09-88 (screw length 694 mm, screw diameter 25 mm, and the rotational velocity was kept at 50 rpm for all extrusions). The extruder had five heating zones, three along the cylinder, one at the adapter, and one at the die, with the temperatures 200, 200, 200, 210 and 210°C respectively. The die was of slit type with an opening of 50 to 0.9 mm and gave strips that were 1.0-1.1 mm thick and 32-33 mm wide. Before extrusion, the material was dried at 80°C for 4 h in air using a Heraeus oven type UT 5042. The aging was performed in the same oven at 90°C for 144 h with constant air flow of 72 L·min^{-1}. At halftime, the ABS flakes were taken out and agitated to ensure that the oxygen was evenly distributed around them.

The strips were cut using a granulator of model SG 10 Ni from Dreher. The produced flakes had a size of circa 3.5-4.5 to 32-33 mm. Samples were collected after each extrusion occasion. Test specimens, in the shape of dog bones, were manually punched out from the extruded strips using equipment with the ISO standard: ISO-527-5A. For comparison, test specimens were also produced in an injection moulding machine, model Arburg - Allrounder 221 M 250-55 (maximum clamp force of 250 kN), to compare possible deviations of the test results within each test. The test specimens were conditioned at 25(±2)°C at 50(±5)% relative humidity for a minimum of 24 h before testing. The standard deviation is calculated on five test specimens per irradiation dose and shown in the figures with ± σ.

Gamma irradiation source

The gamma irradiation was performed in a Gammacell 220 (Atomic Energy of Canada, now trading as Norion). The dose rate to water in the irradiation chamber of this unit was 14 kGy·h^{-1} on average. It was a little lower at the edges of the chamber (13 kGy·h-1) and higher at the centre (15 kGy·h^{-1}), and the dose rate was measured with the ferrous-cupric sulphate dosimeter test (19/04/2012). The temperature within the chamber was approximately 50°C.

Rheological tests

Viscosity

The viscosity measurements were performed on a Göttfert rheograph 2002 together with the WinRHEO software. Three repetitions were performed on each capillary length: 10, 20 and 30 mm. The diameter of the capillary was 1 mm and the machine held a temperature of 190°C for all tests. The pressure transmitter is rated at 2000 bar and the shear rate went from 20-1500 s^{-1} in 10 steps. The two first measurements were excluded due to instability. All tests were subjected to both Bagley- and Rabinowitsch corrections.

Mechanical tests

Tensile test

The tensile test was performed on a Zwick 4031 with an Instron load cell (500 N) together with the testXpert® software. The equipment was used with the tensile speed of 2.8 mm·min^{-1}, which is approximately 10% of the length of the dog bone's waist. An additional test was also performed with different tensile speeds, 5.6, 28, 280 and 560 mm·min^{-1}, to investigate if the material became more brittle with increased speed.

Results and Discussion

Effect of the gamma irradiation dose on ABS

Excluding the 10 kGy sample which was not following the pattern, a decrease in stiffness with increasing irradiation dose was observed and illustrated in Figure 1, which is also supported by Figure 2. This is contradictory to the results Perraud et al. found. They saw an increase in stiffness for the hydrogenated nitrile butadiene rubber (HNBR), an elastomer commonly used in the automotive and printing industries, which includes two components of ABS, A- and B-, when it was irradiated with an electron beam [12]. The elongation at break decreased with increasing irradiation dose, which was the same behaviour as we noticed in our test (Figure 3). In addition, the tensile strength decreased in their test whereas it remained similar for our different irradiation doses.

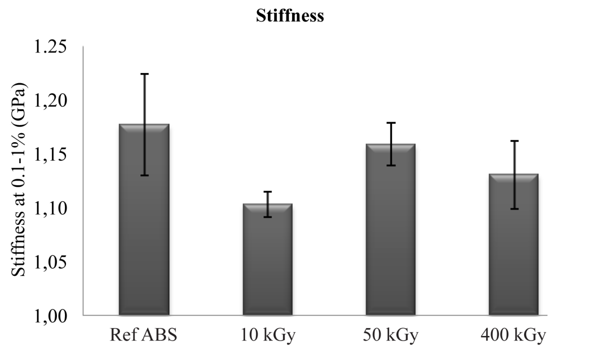

Figure 1: The effect of gamma irradiation (unirradiated, 10, 50 and 400 kGy) on ABS stiffness.

The acrylonitrile content influence how sensitive different plastics are to gamma irradiation. Cardona et al. analysed acrylonitrile/butadiene rubber and saw an increased effect on the rubber with increasing acrylonitrile content when it was irradiated.

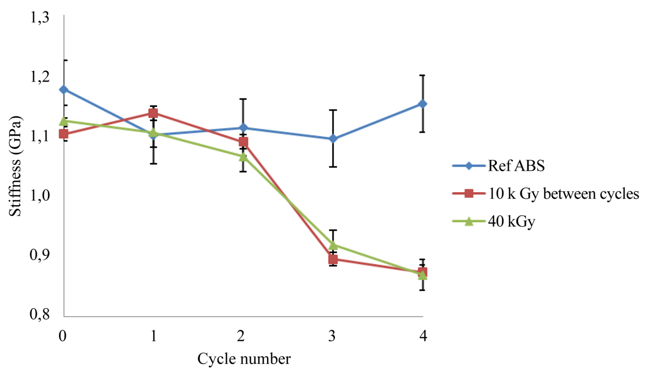

Figure 2: Stiffness comparisons (GPa) between the Reference ABS, 10 kGy between each cycle, and 40 kGy gamma irradiated materials.

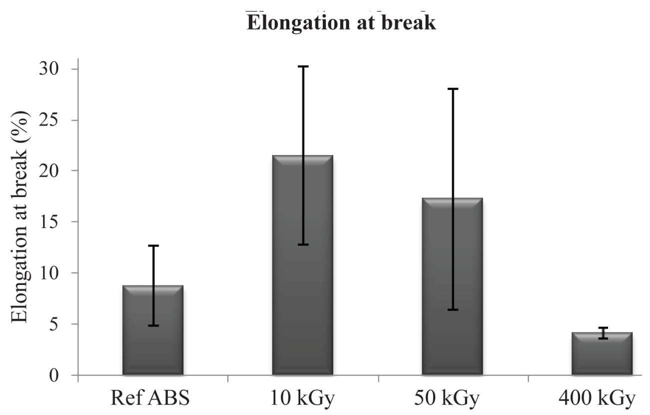

Figure 3: The effect of gamma irradiation (unirradiated, 10, 50 and 400 kGy) on ABS elongation at break.

Secondly, the acrylonitrile part was more sensitive to gamma irradiation than the butadiene part, and thirdly, the reactions observed were the consumption of double bonds and crosslinking, no chains scissoring occurred. This behaviour can explain the increase in viscosity noticed in our comparison of unirradiated and gamma irradiated ABS [13].

A trend towards tougher material with an increasing irradiation dose can be noticed for the yield stress in Figure 4.

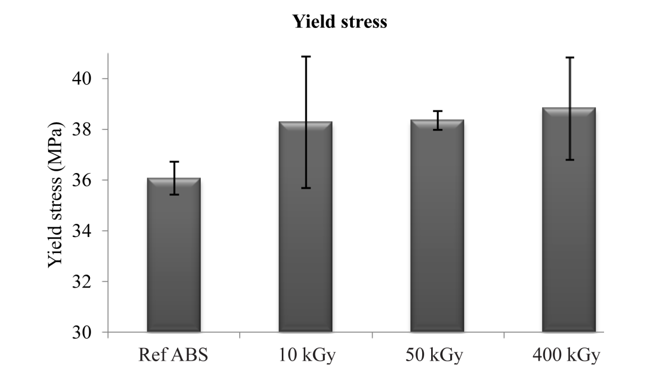

Figure 4: The effect of gamma irradiation (unirradiated, 10, 50 and 400 kGy) on ABS yield stress.

Degradation test of ABS with different gamma irradiation doses and accelerated aging

Elongation at break:

The overall hypothesis was that gamma irradiation would counteract the expected accelerated aging, thus degrading the ABS, and withstand or even increase the mechanical properties. Previous results presented by Boldizar and Möller indicated that the elongation at break increased for each cycle in the extrusion steps up until cycle 6 [9]. Since the deviation of the elongation at break was very high, it was difficult to draw any conclusions about any change during the recycling cycles and aging.

Yield stress:

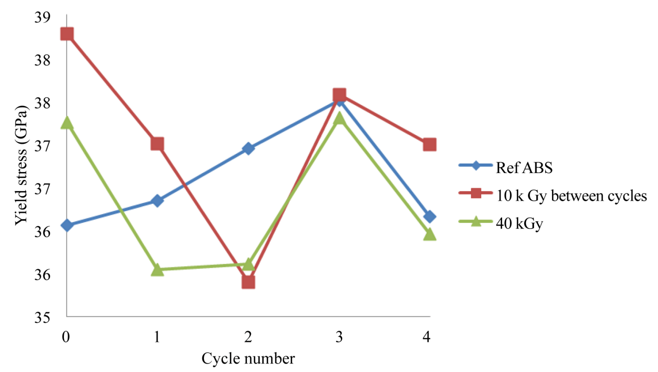

Figure 5: Yield stress comparison (GPa) between the Reference ABS, 10 kGy between each cycle, and 40 kGy gamma irradiated materials.

Stiffness:

The standard deviation is calculated on five test specimens per material and shown in Figures (1,2,5 and 6) with ± σ.

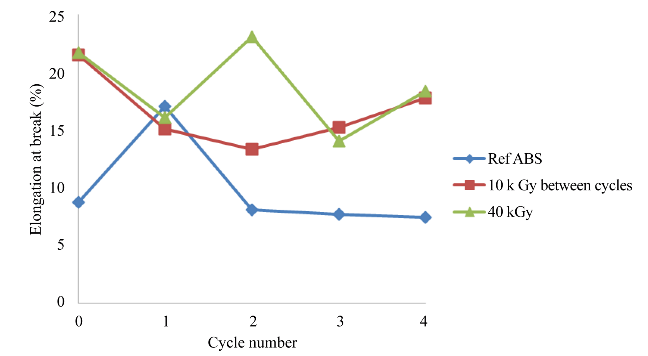

Figure 6: Elongation at break (%) comparison between Reference ABS, 10 kGy between each cycle, and 40 kGy gamma irradiated material.

Ductile to brittle transition test:

A trend to increasing yield stress illustrated in Figure 7 is valid for all tensile speeds except the last, at 560 mm/min, which is a very high tensile speed.

The standard deviation is calculated for five test specimens per tensile speed and shown in Figure 7 with ± σ.

Viscosity comparison of unirradiated and gamma irradiated ABS:

The effect of the gamma irradiation could be observed in the ABS viscosity illustrated in Table 1 and Figure 8, and it increased with increasing irradiation dose. The most likely cause is that the ABS crosslinked, as has been seen in other studies made by Cardona et al and Perraud et al. [12,13].

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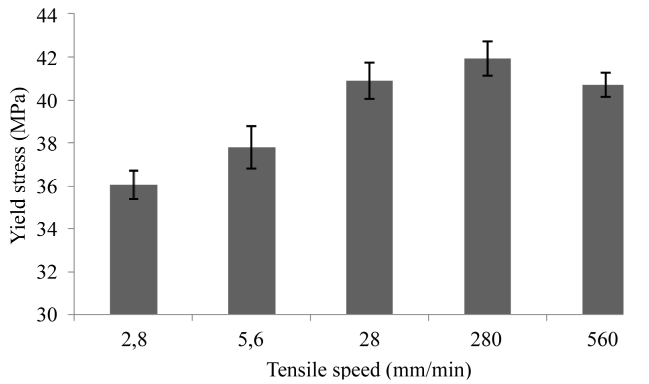

Figure 7: The effect of tensile speed (mm/min) on yield stress (MPa) for ABS.

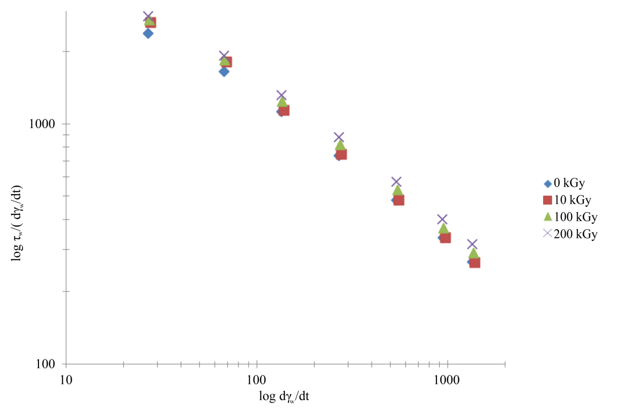

Figure 8: Summary of the viscosities for unirradiated ABS, 10, 100 and 200 kGy gamma irradiated ABS.

	0 kGy	**10 kGy**	**100 kGy**	**200 kGy**
Shear rate (s^{-1})	Viscosity (Pas)	Viscosity (Pas)	Viscosity (Pas)	Viscosity (Pas)
20	2400	2600	2700	2800
50	1600	1800	1800	1900
100	1100	1100	1200	1300
200	740	750	820	880
400	480	480	530	580
700	340	340	370	400
1000	270	270	290	320
1500	200	200	220	240

Table 1: Viscosity data of ABS treated with different gamma-irradiation doses.

Combining the viscosity curves in the same graph shows that the viscosity increased with increasing gamma irradiation dose; this can be observed in Figure 8. 0 and 10 kGy have similar values, especially for higher shear rates, while the 100 kGy lines is between the 10 and 200 kGy lines.

Conclusions

The mechanical properties of multi-recycled, accelerated aged and gamma irradiated ABS test, a difference could be seen in the stiffness results between the different cycles, as well as between the different irradiation doses. The unirradiated ABS sample was stable during all four recycling cycles and did not degrade during the multi-recycling and accelerated aging. Although, the 10 kGy (irradiated between each cycle) sample and the 40 kGy sample, showed a decrease in stiffness after two cycles which cannot yet be explained. Due to the very high standard deviation for the elongation at break, no relevant conclusions could be drawn from the test. For the yield stress test no trend could be distinguished.

The 10 kGy sample irradiated between each cycle, and the 40 kGy sample behaved similarly for all the tested properties and no conclusion could be drawn on whether the material would degrade less for a repeated small dose of gamma irradiation between each recycling cycle than for a higher dose prior to the repeated recycling.

The gamma irradiation had an influence on the mechanical properties of ABS. The ABS seems to crosslink with an increasing irradiation dose, which could be seen as the increase in viscosity and higher yield stress compared to the unirradiated ABS. The high variation in EB results may be explained by the butadiene rubber part of the ABS's structure. It was almost a randomized event if the ABS sample breaks or elongates further. The punching of dog bones from the samples has not caused any major surface damage that can explain the high variation in the EB test results. The comparison with the injection moulded dog bone test specimens supported the theory, since the variation in EB was similar for those test specimens. A trend could be noticed towards higher yield stress with an increasing gamma irradiation dose, and the opposite behaviour was noticed for the stiffness, a decrease in stiffness with higher irradiation dose. However, the 10 kGy sample did not fit the trend line very well, but it may be explained by the high variation within the sample.

No ductile to brittle transition was seen when increasing the tensile speed. The samples showed a plastic deformation (necking) before breakage that did not appear to have any correlation with the tested strain rates. The absence of a brittle to ductile transition with respect to strain rate is possibly due to the multi-component ABS system with the rubber component, which is relatively insensitive to the high strain rates used in this test.

Gamma irradiation also had an influence on the rheological properties; the viscosity increased with increasing irradiation dose.

Acknowledgement

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