

THERMAL PROPERTIES OF IRRADIATED DURAMID WITH 45 % OF GLASS FIBRE BY BETA RAYS

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DURAMID with 45 % of glass fibre (PA 9T) have been successfully modified using beta rays. PA 9T samples were prepared by injection moulding technology and then were irradiated from 33 to 198 kGy in electron accelerator RHODOTRON. The thermal properties (e.g. DSC and TGA) of modified PA 9T samples by beta rays were measured. The tested samples showed significant changes of thermal properties after irradiation. From this point of view, new applications could also be seen in areas where more expensive materials (metals, composites etc.) are used, especially for application in automotive and military industry.

KEYWORDS

thermal properties, DSC, TGA, radiation cross-linking, beta rays, DURAMID and temperature stability

1 INTRODUCTION

The polymers rank among construction materials which find use in industry branches. The advantage of the polymers is a low weight together with excellent mechanical properties, very good chemical resistance and other properties, which assign them for various applications. The disadvantage is mainly low temperature stability which significantly reduces usage of these polymers.

Plastics are by far the largest group of polymeric materials being processed by electron beam irradiation. Cross-linking of polyolefins, PVC, polyesters, polyurethanes, polyamides, fluoropolymers and fiber-reinforced composites are a common practice. Radiation cross-linking of polyamides requires considerably less overall energy and space, and is faster, more efficient and more environmentally acceptable [Clough 1996]. The disadvantage of electron beam cross-linking is a more or less non-uniform dose distribution. This can happen, particularly in thicker objects, due to intrinsic dose-depth profiles of electron beams [Clegg 1991]. Another problem can be a non-uniformity of rotation of cylindrical objects as they traverse a scanned electron beam. However, the mechanical properties often depend on the mean cross-link density [Drobny 2010].

Radiation processing of polymers is a well-established and economical commercial method of precisely modifying the polymer properties. The industrial applications of 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 [Makuuchi 2012].

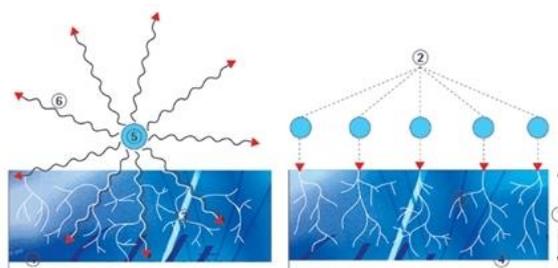


Figure 1. Design of Gamma Rays (left) and Electron Rays (right), 1 – Penetration depth of an electron, 2 – Primary electron, 3 – Secondary electron, 4 – Irradiated material, 5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [Drobny 2010].

During the last few decades irradiation by beta radiation on injected molded polyamides have rapidly increased. Polyamides gradually replace reactoplastics, because many modifications to obtain better properties are available for this material [Gehring 1995]. To obtain even better mechanical properties is possible to reinforce polyamide by glass fiber. Glass fiber reinforced polymer (GFRP) represents conformable design solutions, because of its special production adaptability, structural efficiency and high durability. Its usage is also advantageous due to increasingly low production and erection costs [Landesmann 2015].

Porubská, Janigová, Jomová and Chodák from Slovakia examined the effect of electron beam irradiation on properties of virgin and glass fiber-reinforced polyamide 6. They determined that cross-linking is more beneficial for virgin polyamide, because of the increase in the tensile strength at break and Young's modulus. The properties at yield were not influenced by crosslinking and the thermal resistance was influenced by irradiation only marginally for both glass fiber reinforced polyamide (marginal decrease) and for virgin polyamide (small increase). Their finding is that electron beam irradiation leads to more changes in the properties of virgin polyamide in comparison with glass fiber reinforced polyamide [Porubská 2014].

This study deals with thermal properties of beta radiation cross-linked Duramid with 45 % of glass fiber (PA 9T). Polyamide 9T is a new semi-aromatic high-performance engineering polyamide. This polymer has a long, flexible aliphatic linkage which are consisted of nine methylene groups in a sequence included in the main aromatic polymer chain for lowering the melting point. This polymer has a good balance of manufacturing cost and properties and has good heat stability, low water absorption, considerable resistance to hot water, acid, alkali and organic solvents and high heat moisture resistance. Because of these properties PA 9T is used in electric, electronic and automobile parts. By production its fiber it is now also used for production of fishing nets and other industrial and textile materials [Uddin 2012]. Because this polymer belongs to newer polymers, it is useful to investigate the behavior of this polymer after glass fiber addition and after beta irradiation for investigation of other possibilities how to improve this great material.

This research paper deals with a possibility of using radiation cross-linked PA9T as a suitable material in automotive and military industry, especially from point of view thermal properties.

2 EXPERIMENTAL

Polyamide 9T (V-PTS-DURAMID-9TH2G9*M800/13 natur) was used as the basic polymer. An ARBURG Allrounder 420C Advance Injection molding machine was used for sample preparation, with the processing conditional to comply with the polyamide 9T (PA 9T) producer's recommendations, as can be seen in Tab. 1.

Injection Parameters	Values
Injection Pressure [MPa]	170
Injection velocity [mm.s ⁻¹]	50
Holding Pressure [MPa]	150
Cooling Time [s]	25
Mould Temperature [°C]	140
Melt Temperature [°C]	325

Table 1.: Setting of injection molding machine parameters

Irradiation of tested PA 9T was performed with the kind help of BGS Germany, in the BGS Wiehl plant using accelerated electrons with a dosage range of 0 to 198 kGy. In Table 2, the required and real irradiation dose which PA 9T received during irradiation process is displayed. After that the degree of cross-linking by gel measurements (gel content) was determined, according to the standard EN ISO 579.

Required Irradiation Dose	Real irradiation Dose [kGy]	Gel Content [%]
0	0.0	0.0
33	35.4	46.1
66	69.9	60.4
99	105.8	66.1
132	139.2	74.0
165	173.1	75.4
198	207.2	77.5

Table 2. PA 9T values after irradiation by beta rays

PA 9T thermal properties before and after radiation cross-linking have been tested. The differential scanning calorimetry and thermogravimetric were performed. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1DSC according to standard ISO 11357. Nitrogen was used as a purge gas (flow rate 100 ml/min). Samples between 5 and 10 mg were placed in aluminum pans and heated from 80 °C to 330 °C with a heating rate of 10 °C/min. After first heating, cooling was carried out to 80 °C, cooling rate 10 °C. Crystallization temperature from peaks was determined from DSC thermograms. From second heating diagrams, melting temperature was determined. Thermogravimetric analyses (TGA) were performed on a Setaram Setsys Evolution 1200 according to standard ISO 11358. Helium was used as a purge gas (flow rate 30 ml/min). PA 9T samples between 15 and 25 mg were placed in oxide aluminum pans and heated from 25 to 600 °C at a heating rate of 10 °C/min. The degradation temperature and weight loss at 600 °C were calculated.

3 RESULTS AND DISCUSSION

The first method DSC for determination of thermal properties was used. Melting and crystallization temperature were determined from heating and cooling thermograms. The second TGA was used for evaluation of degradation temperature and weight loss.

3.1 Differential scanning calorimetry (DSC)

In the table 3 and 4, the results from DSC analyses are shown. In the first and second heating melt temperature was evaluated and in cooling crystallization temperature was evaluated.

Irradiation dose (kGy)	m (mg)	Heating			
		1. heating		2. heating	
		1.peak (°C)	2.peak (°C)	1.peak (°C)	2.peak (°C)
0	8.6	279.54	297.48	284.23	293.78
33	7.3	276.62	288.40	279.28	
66	9.4	278.99	290.36	279.80	
99	5.3	271.54	282.40	273.00	
132	6.0	272.62	282.45	274.18	
165	5.3	271.60	286.45	270.88	
198	7.1	270.85	280.99	271.52	

Table 3. Differential scanning calorimetry results - heating

Irradiation dose (kGy)	m (mg)	Cooling	
		1.peak (°C)	2.peak (°C)
0	8.6	271.02	
33	7.3	260.99	268.00
66	9.4	259.43	
99	5.3	249.94	
132	6.0	251.84	
165	5.3	245.88	
198	7.1	251.63	

Table 4. Differential scanning calorimetry results - cooling

In Fig. 2 the first heating is visible. This measurement was done for deleting the thermal material history created during previous processing. It is possible to watch this phenomenon in the form of two peaks, which each curve owns. Furthermore, it is evident that the higher irradiation, the smaller peaks are.

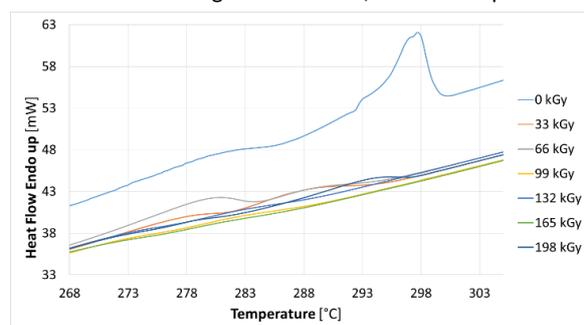


Figure 2. First heating

The second phase of the differential scanning calorimetry - cooling can be seen in Fig. 3, there is visible the crystallization of polyamide 9T. The crystallization temperature is decreasing with the increase of irradiation dose.

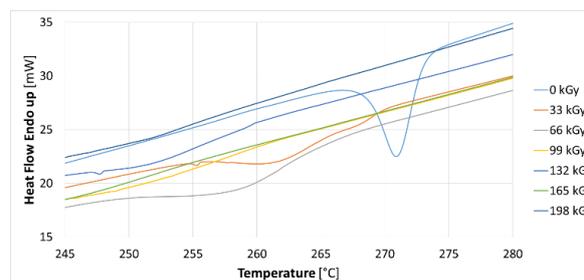


Figure 3. Cooling

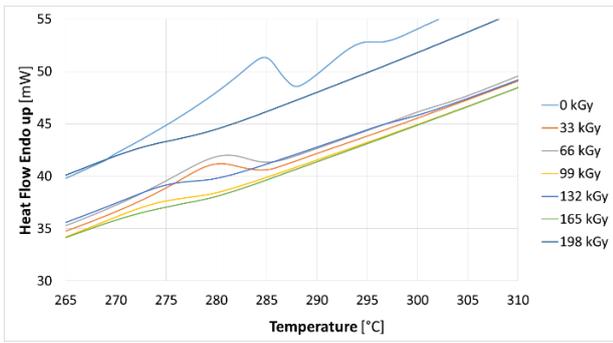


Figure 4. Second heating

From Fig. 5 it is clear that the higher irradiation dose, the lower crystallization temperature and melting temperature of non-cross-linked parts of material are. It is caused by lowering of crystalline phase and creation of thinner lamellae during irradiation.

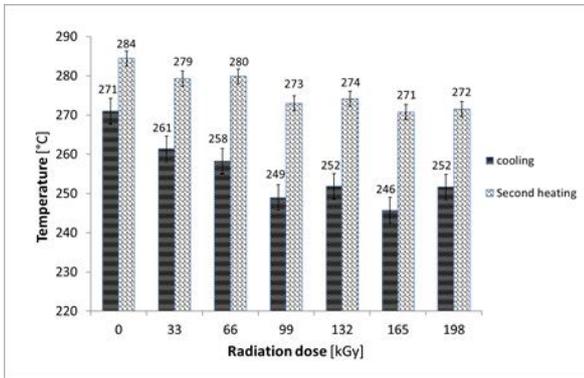


Figure 5. The influence of irradiation on T_m and T_c

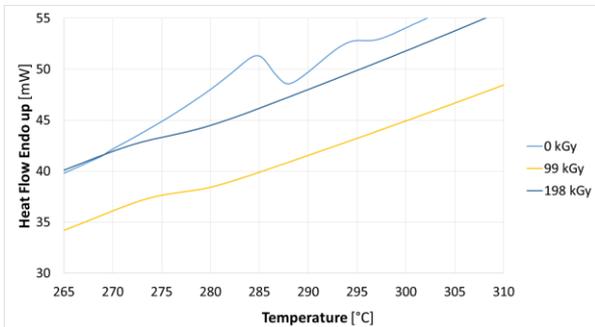


Figure 6. Comparison of second heating at doses 0, 99 and 198 kGy

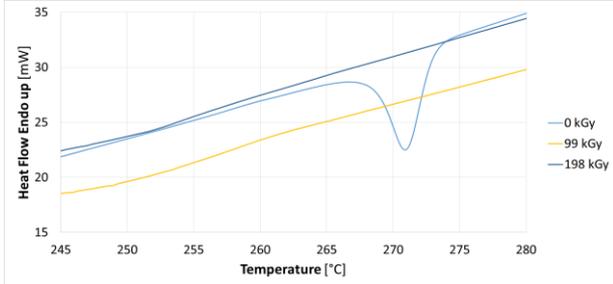


Figure 7. Comparison of cooling at doses 0, 99 and 198 kGy

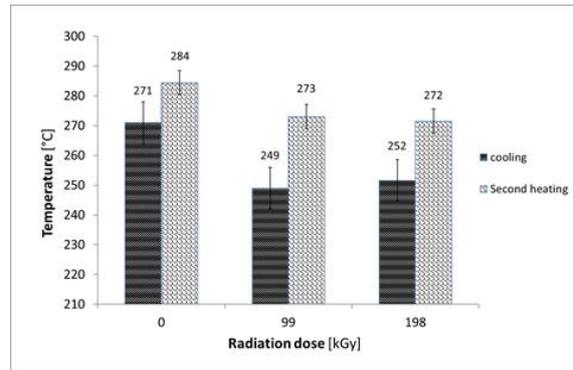


Figure 8. Comparison of T_m and T_c at doses 0, 99 and 198 kGy

3.2 Thermogravimetric analysis (TGA)

In the table 5 and 6, the results from TGA are displayed. Degradation temperature and weight loss were evaluated.

Irradiation dose (kGy)	m (mg)	T_1 (°C)	T_i (°C)	T_2 (°C)
0	21.94	291.12	329.35	340.80
		461.01	485.65	496.99
33	19.32	458.44	484.69	496.99
66	15.16	457.43	482.79	496.66
99	19.01	457.11	484.66	497.45
132	18.80	456.70	489.29	497.22
165	26.35	457.65	484.32	497.92
198	20.01	458.22	484.33	496.99

Table 5. Thermogravimetric analysis – degradation temperature

T_1 – the initial temperature

T_i – the temperature of the fastest weight loss

T_2 – the final temperature

Irradiation dose (kGy)	m (mg)	Weight loss (%)	
		-3.1	-
0	21.94	-51.3	54.4
33	19.32		-55.8
66	15.16		-55.7
99	19.01		-55.1
132	18.80		-55.7
165	26.35		-55.8
198	20.01		-55.3

Table 6. Thermogravimetric analysis – weight loss

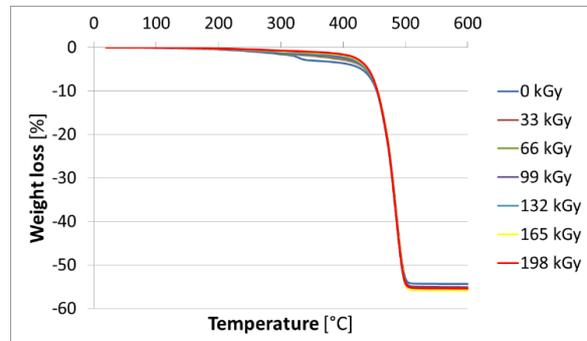


Figure 9. Thermogravimetric analysis

In Fig. 9 it is visible that the non-irradiated polyamide 9T degrades in two degrees. The non-irradiated polyamide 9T is non-crosslinked and in the first degree the crosslinking agent

degrades. First degradation starts at $T_1=291.12$ °C and finishes at $T_2=340.80$ °C. The fastest weight loss is at $T_i=329.35$ °C. In the first degree of degradation the weight loss is -3.1 %. The second degree of degradation occurs at $T_1=461.01$ °C and finishes at $T_2=496.99$ °C. The fastest weight loss is at $T_i=485.65$ °C and weight loss is -51.3 %. Irradiated samples of polyamide 9T degrade in one-degree mechanism. The reason is the consumption of cross-linking agent during irradiation.

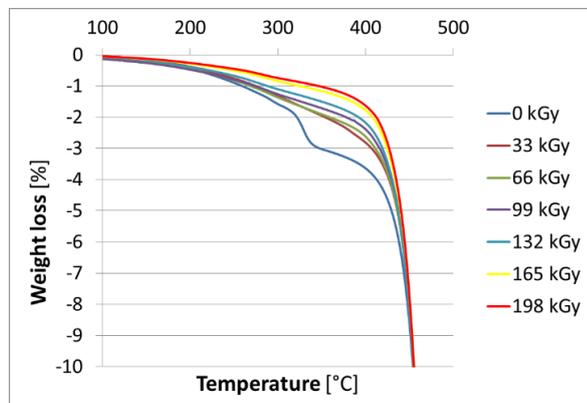


Figure 10. Thermogravimetric analysis

In Fig. 10 it is possible to see the dependence of weight loss in % on the temperature. The biggest differences are in the area from 250 °C to 400 °C where the irradiated material has lower weight loss in comparison with the non-irradiated one. The higher dose of radiation, the higher weight loss is. This difference will be at the same level around 450 °C.

From measured values it is clear that total weight loss of material is the same at all measured samples. It is possible to see it in Tab. 6 where the average of weight loss is 55.4 ± 0.5 %. From which it follows that the rest of 45 % consists of glass fibres, which are in the polymer matrix. It is also clear that above 400 °C occurs to small “evaporation” of material. After test just glass fibres will stay from the sample.

4 CONCLUSIONS

Experiments done in this project showed that irradiation cross-linking markedly affected the thermal properties of the PA 9T studied. The higher the irradiation dosage, the better the thermal behavior of studied polymer is. As can be seen from the tests results, the radiation cross-linking improves the PA 9T temperature stability, because the material after irradiation is not meltable. From DSC result is possible to see that crystallinity and crystallization temperature decrease which points to semi-cross-linked structure. Cross-linking reaction takes place in the amorphous phase and the edge of the crystal phase, because of crystals are smaller and temperature of crystallization is decreasing. PA 9T is a high temperature resistant polymer which is filled 45 % of glass fibers. Melting temperature 285 °C which was found from the second heating (DSC) after deleting the history of the material decreased by 12 °C for non-irradiated PA 9T. With increasing dose of irradiation, the range between the first and second heating is minimal.

TGA showed, weight loss beginning at 100 °C for every tested samples. Difference was recorded at 300 °C when irradiated samples have smaller weight loss; however, after the test all variation of PA 9T had similar weight loss (rest of 45 % glass fibers).

These tests confirm that PA 9T is suitable material for special usage in automotive, military and other industry where the temperature can be permanently higher than ambient temperature. Next research will be focused on thermo-mechanical behavior and mechanical properties tested at higher temperature.

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