IJME

Int. J. of Applied Mechanics and Engineering, 2023, vol.28, No.2, pp.113-124
DOI: 10.59441/ijame/168934

RESEARCH ON LOW DENSITY POLYETHYLENE (LDPE), RECYCLED BY ADVANCED THERMAL ANALYSIS (DSC, TG)

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This article presents the issue of recycling and maintaining the processing properties of materials made of plastics. For this purpose, samples from recycled, low-density, polyethylene were tested. The impact of the use of dyes and surface printing on the lifecycles of material and its quality was examined. For this purpose, an analysis was carried out using differential scanning calorimetry and thermos-gravimetry. It was found that the use of dyes may affect the quality of the material and increase the disposal costs of pre-used materials.

Key words: DSC, TG, LDPE, plastics recycling, thermal analysis.

1. Introduction

The rational management of plastic waste is becoming an increasingly popular doctrine of many countries and organisations around the world. Polyethylene is one of the most commonly produced materials, both in Europe and globally and thus requires the improvement and development of ever newer technologies to ensure a closed material cycle. Other scientists have also noted this, for example Jang *et al.* [1] draws attention to the amount of plastic produced, which is set to increase from 300 million tons in 2015 to 1800 million tons by 2050. The situation has also deteriorated due to the SARS-CoV-2 (COVID-19) pandemic, during which the consumption of plastic, disposable, surgical gloves and masks increased. Kalina and Tilley [2] estimate that in 2020 alone, the use of surgical gloves and masks reached the level of 69 million pairs *per* month. According to estimates, around 0.4 billion tons of plastics are produced worldwide annually (Jung *et al.* [3]). Billions of tons of waste are stored in landfills and, due to the low density of plastics, they take up a lot of space. Another threat to flora and fauna are plastics that slowly decompose in soil and water, emitting micro-plastics.

In view of this situation, organisations and communities are adopting a strategy to reduce the production of plastic waste. For example, the European Union has adopted a strategy that aims to ensure that ten million tonnes of recycled plastic are reused in new products by 2025 (Schulte *et al.* [4]). This creates a circular plastic economy that aims to reduce the use of natural resources and minimise greenhouse gas emissions. This means that more and more attention is paid to the recycling of plastics.

Recycling is one of the methods that allows the effects related to the problem of the accumulation of waste, resulting from everyday use of materials, to be reduced. Glass bottles, for example, for milk or water, can be easily recycled. In general, it is enough to wash the bottle and it is suitable for reuse. The situation is completely different in the case of plastic packaging. The division of plastic recycling methods is widely described in the literature, for example, Saikrishnan *et al.* [5]. Saikrishnan presents recycling methods by dividing them into mechanical recycling, in which the basic stages are collecting, segregating, washing and grinding the material into small pieces. Chemical recycling that reduces polymer particles to oligomers and monomers. The whole thing comes down to the production of secondary material (regranulate) from which a new product can be obtained again. Another method is combustion, *i.e.*, the recovery of energy from carbon-

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based plastics. Recycling methods were also presented by Pan *et al.* [6] who point out that various heavy metals and aromatic compounds are often released during incineration. Biological recycling using, for example, bacteria capable of breaking down plastic into simpler compounds such as CO_2, could be an interesting method in the future. Research on this topic was carried out by Yang. Y *et al.* [7], who used whitefly larvae to degrade polystyrene, which was completely broken down and mineralised in the fatty tissue of the insects.

Any recycling method that aims to reuse recycled material for a new product involves problems such as material losses, due to the processing activities and quality losses of the recycled material. As a result of processing, polymers lose their physical and chemical properties (Cullen [8]). The problem with the mass production of recycled products while neglecting the quality of the manufactured product was highlighted by Eriksen *et al.* [9]

In order to check the quality of the material, tests, as widely reported in the literature, have been carried out by Techawinyutham *et al.* [10], who conducted macro- and microscopic tests on LDPE, in addition to the testing of the hardness and strength of materials, as well as DSC and TGA thermal analysis. DSC studies on polyethylene have also been carried out by Aumnate *et al.* [11], where the article highlights the level of crystallinity of the material studied and the value of this parameter.

In order to ensure better quality of recycled materials, attempts are being made to combine multiple materials such as r-PET with polyethylene; a study on this issue has been conducted by Tao and Mai [12]. Another method was proposed by Li *et al.* [13] improving the compatibility of recycled polyethylene with glycidyl methacetate, thus achieving better mechanical properties and shifting the melting point towards high temperatures.

2. Materials and methods

The study used re-granulate, formed from recycled low-density polyethylene (LDPE) from a discarded finished product in the form of rubbish bags, taking into account the colour additives of the printed surface used. Small fragments with a diameter of about $0.3\,mm$ and of average weight were cut $11mg \pm 1mg$ from the re-granulate obtained for the purpose of testing its properties. The samples were stored in a dry room with controlled humidity away from heat and direct sunlight. Before the test, the samples were cleaned of surface contaminants. Examples are shown in Fig.1.

Fig.1. Test samples.

The types of specimens to be tested were divided according to the colour of the dye and the type of surface printing used, dividing the specimens into (a) unprinted (b) surface-printed above $35\ \%$, in order to check whether the dyes used can affect the quality of the material and whether the use of surface printing reduces the quality of the recycling. A list of samples is presented in Tab.1.

Table 1. List of samples for testing.

Colour of the sample	Type of print used
Reference sample	No overprint
Colourless	No overprint
	Imprint $> 35\%$
Black	No overprint
	Imprint $> 35\%$
Red	No overprint
	Imprint $> 35\%$
Yellow	No overprint
	Imprint $> 35\%$
Blue	No overprint
	Imprint $> 35\%$

The properties of polyethylene largely depend on the content of the crystalline and amorphous phases in the material. Research on this subject was carried out by Li *et al.* [14]. Therefore, in order to effectively use recycled materials in industry, it is necessary to assess their quality and determine how they can be re-processed. To this end, tests were carried out using DSC and TG thermal analysis methods to check the melting points of recycled LDPE, the change in mass, during sample combustion in the temperature range from $420°C$ to $550°C$ and the level of crystallinity of the samples.
The Eq.2.1. formula was used to determine the level of crystallinity of polyethylene.

$$X_c = \frac{\Delta H_m}{\Delta H_{lit}}. \tag{2.1}$$

The enthalpy of melting, *i.e.*, the energy that must be applied to material to melt it, is $293\,J/g$ for polyethylene with $100\,\%$ crystallinity, as shown in the literature, *q.v.* Ahmed and Mamat. [15] and Alpati *et al.* [16]. The crystallinity of LDPE was examined in research by Wang *et al.* [17] in which the crystallinity level of low-density polyethylene was obtained at a level of from $18.2\,\%$ to $26.6\,\%$.

2.1. Measurement system

Thermal properties were determined using differential scanning calorimetry and thermogravimetry. The tests were carried out on a Netzsch device (Fig.2.).

Fig.2. STA 449 JUPITER.

2.2. Measurement method

The device was calibrated before testing. The samples were placed in a platinum crucible and then scanned using a developed programme, defined within the temperature range from $40°C$ to $840°C$ with a heating rate $10°C/min$ in a nitrogenous atmosphere $of\ 50\,ml/min$. After reaching the temperature, the $840°C$ experiment was carried out in an oxidising atmosphere with an oxygen flow at a level of $50\,ml/min$.

3. DSC test results

From an analysis of the results obtained, it can be observed that, on a colourless sample, the addition of an imprint does not have a major impact on the melting point, for a sample without $\Delta Hm = 36.04\,J/g$ an imprint $Tm = 115.6°C$ while for a sample with an imprint above $35\,\%$ $Tm = 116.4°C$ and $\Delta Hm = 49.34\,J/g$. The results are also presented in Fig.3 and Tab.2.

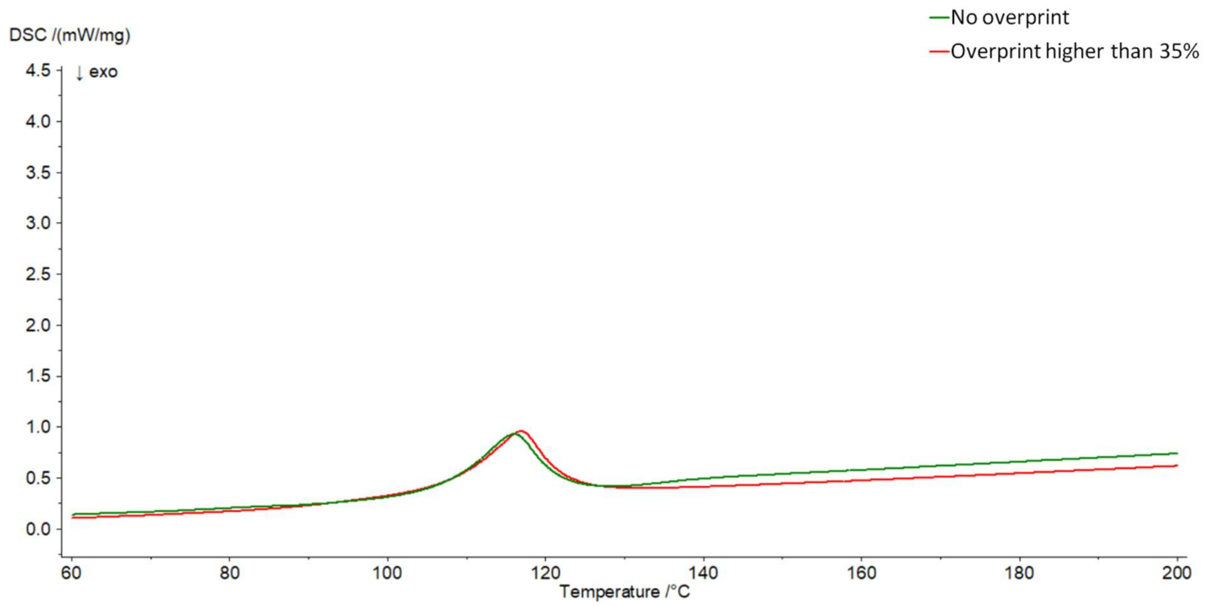

Fig.3. DSC testing of colourless samples within the temperature range $60°C$ to $200°C$.

During the examination of black samples, some differences were visible. The melting point of the samples, with the print above 35 %, was $Tm = 117.2°C$; on the other hand, the enthalpy of the melting of the sample was $\Delta Hm = 38.64\, J / g$. In the case of non-printed samples, the melting point was higher and $Tm = 126.2°C$ interestingly, a decrease in the melting enthalpy was observed, which amounted to $\Delta Hm = 18{,}74\, J / g$. The results are presented in Fig.4, and Tab.2.

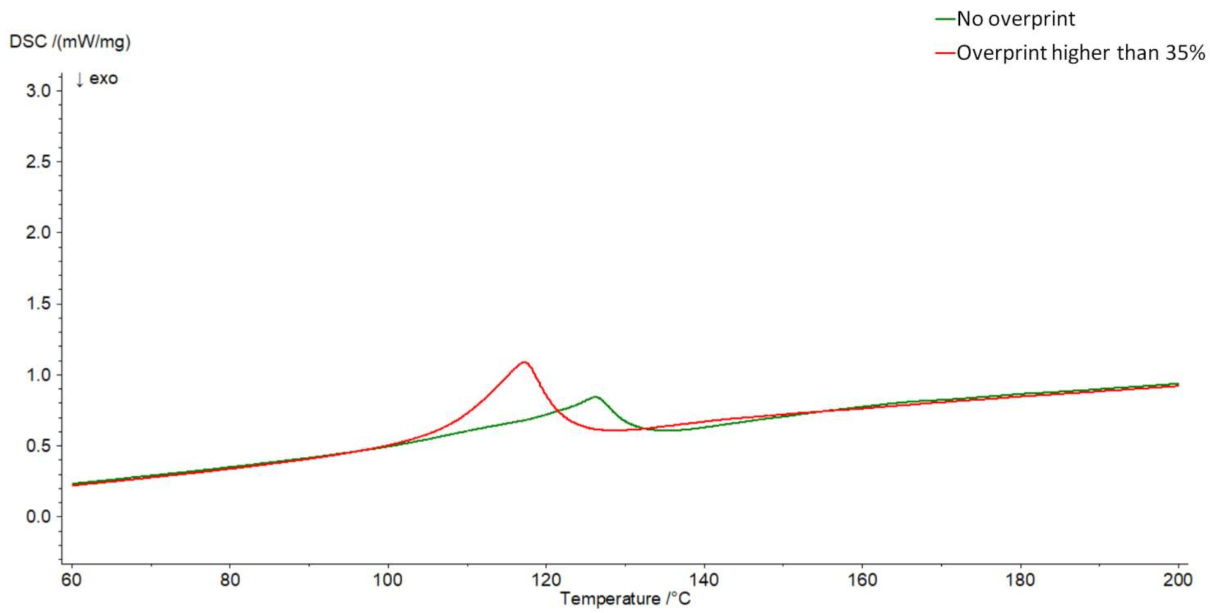

Fig.4. DSC testing of colourless samples within the temperature range $60°C$ to $200°C$.

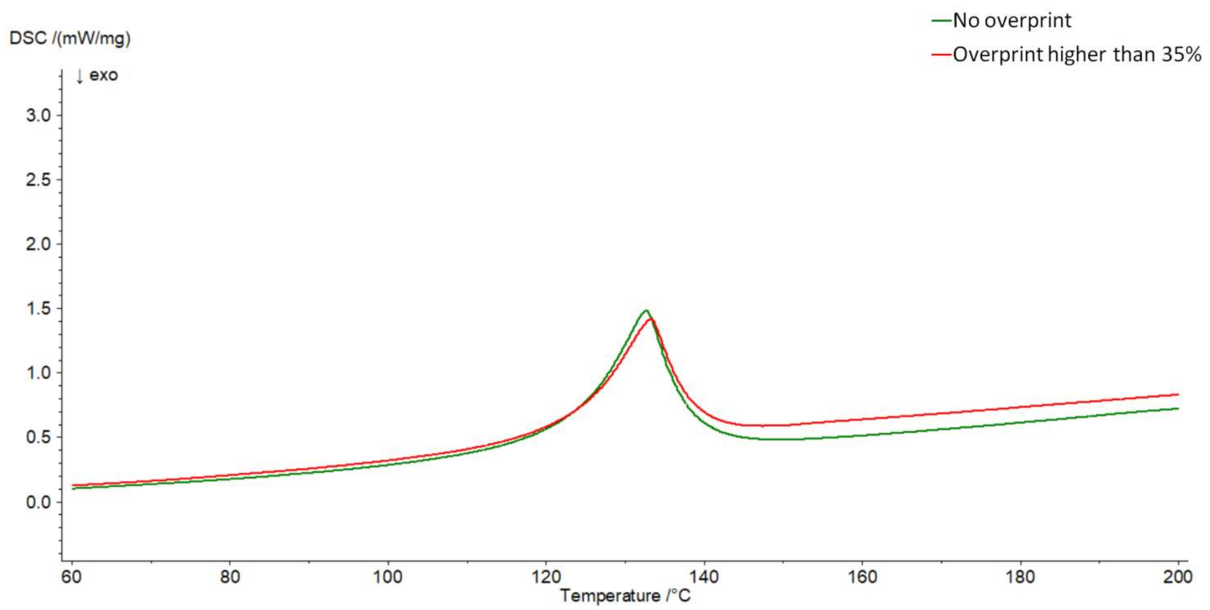

Fig.5. DSC testing of colourless samples within the temperature range $60°C$ to $200°C$.

The melting point for samples with red pigment was $Tm = 132.6\,°C$ for the sample without printing and $Tm = 133.2\,°C$ for the sample with printing. Such melting temperatures also translated into higher results of the melting enthalpy of the samples. For the non-printed sample, the enthalpy was equal to $\Delta Hm = 81.28\,J\,/\,g$ and for the printed sample $\Delta Hm = 66.39\,J\,/\,g$. The results are presented in Fig.5 and Tab.2.

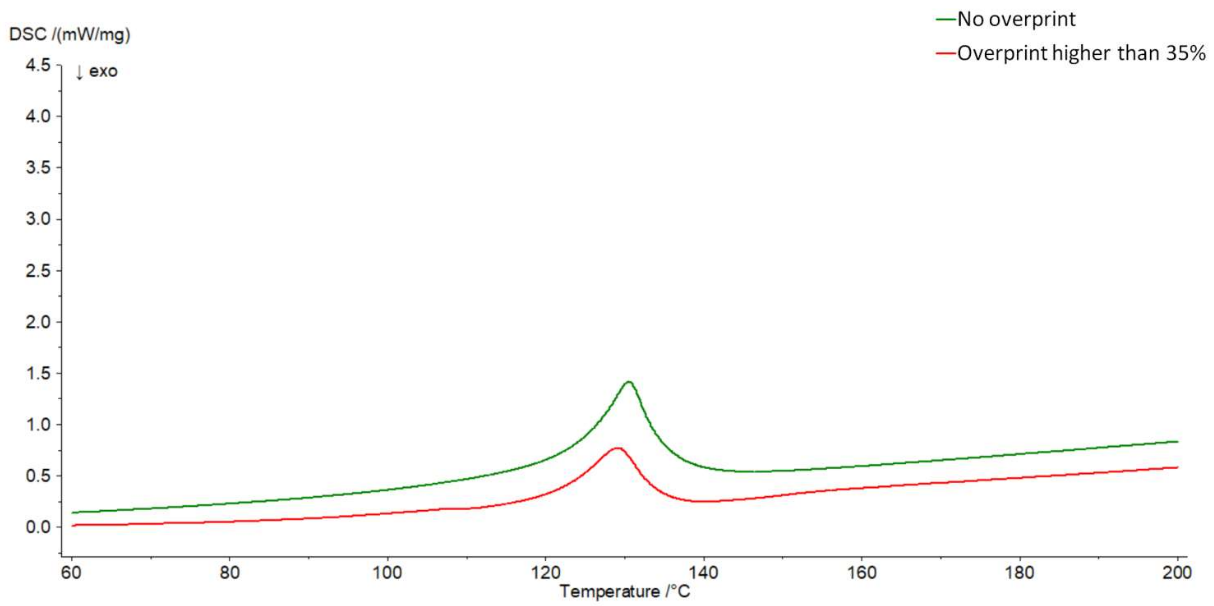

Fig.6. DSC testing of colourless samples within the temperature range $60\,°C$ to $200\,°C$.

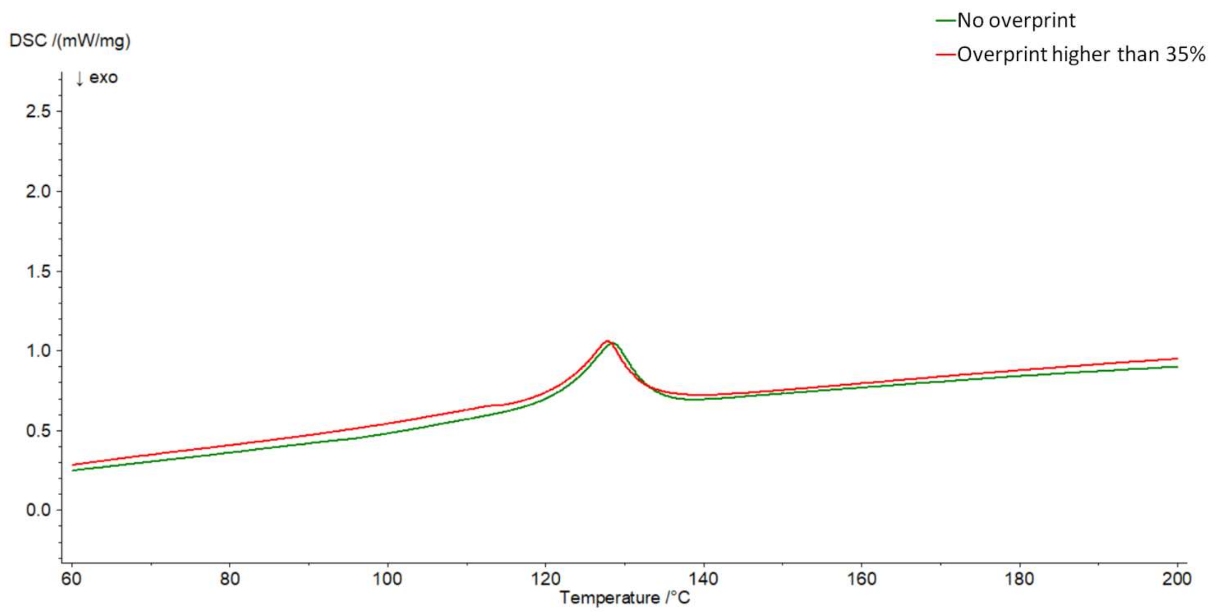

Fig.7. DSC testing of colourless samples within the temperature range $60\,°C$ to $200\,°C$.

The yellow samples have a similar melting point $Tm = 130.5\,°C$ for the non-printed sample and $Tm = 129.0\,°C$ for the printed sample. It should be noted that despite such a small difference in the melting temperature, a significant difference in the melting enthalpy of the tested samples is visible $\Delta Hm = 53.21\, J / g$ for the unprinted sample, as well as $\Delta Hm = 31.6\, J / g$ for the printed sample. The results are presented in Fig.6. The full results are presented in Tab.2.

When examining the samples in blue, no significant difference was noticed between the unprinted samples for which $Tm = 128.4°C$ $\Delta Hm = 19.66\, J / g$ and the samples with surface printing $Tm = 127.8°C$ $\Delta Hm = 18.44\, J / g$. The results are presented in Fig.7, as well as in Tab.2.

The test results for all samples are presented in Tab.2.

Table 2. DSC test results.

Colour	Imprint $[\%]$	$Tm[°C]$	$\Delta Hm[J / g]$	$Xc[\%]$
Reference sample	*0*	*117.1*	*48.60*	*16.59*
Colourless	*0*	*115.6*	*36.04*	*12.30*
	> 35	*116.4*	*49.34*	*16.84*
Black	*0*	*126.2*	*18.74*	*6.40*
	> 35	*117.2*	*38.64*	*13.19*
Red	*0*	*132.6*	*81.28*	*27.74*
	> 35	*133.2*	*66.39*	*22.66*
Yellow	*0*	*130.5*	*53.21*	*18.16*
	> 35	*129.0*	*31.60*	*10.78*
Blue	*0*	*128.4*	*19.66*	*6.71*
	> 35	*127.8*	*18.44*	*6.29*

The results of the research confirm that attention should be paid to the quality of post-recycling materials. The level of the crystal structure of the samples tested is definitely lower than for non-recycled LDPE. Samples with colour additives have a higher melting point than colourless samples. The highest melting point was found in the sample with red pigment and applied print. However, the print used does not appear to affect either the melting point or the enthalpy. An increase in the melting point of most of the samples with the dye is seen in comparison to the reference sample.

3.2. GT test results

The thermogravimetric examination of samples without dye showed that the change in mass for samples without printing, amounted to $96.85\,\%$. The weight change of the samples in which additional printing was applied was $96.73\,\%$. In order to better illustrate the experiment, the results are presented in Fig.8. A full summary of the results can also be found in Tab.3.

The results for samples with black pigment are as follows: unprinted samples burned $81.45\,\%$, while losing weight, while printed samples lost $96.65\,\%$ weight. In order to better illustrate the experiment, the results are presented in Fig.9. A full summary of the results can also be found in Tab.3.

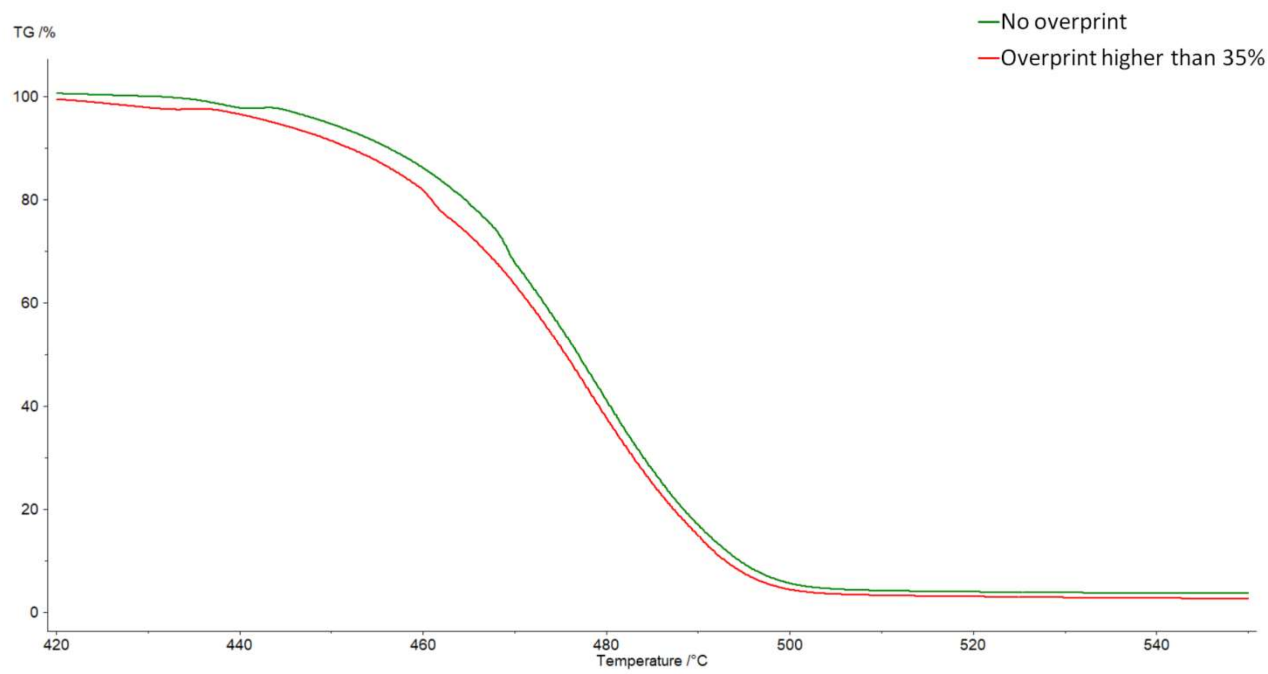

Fig.8. TG testing of colourless samples within the temperature range $420°C$ to $550°C$.

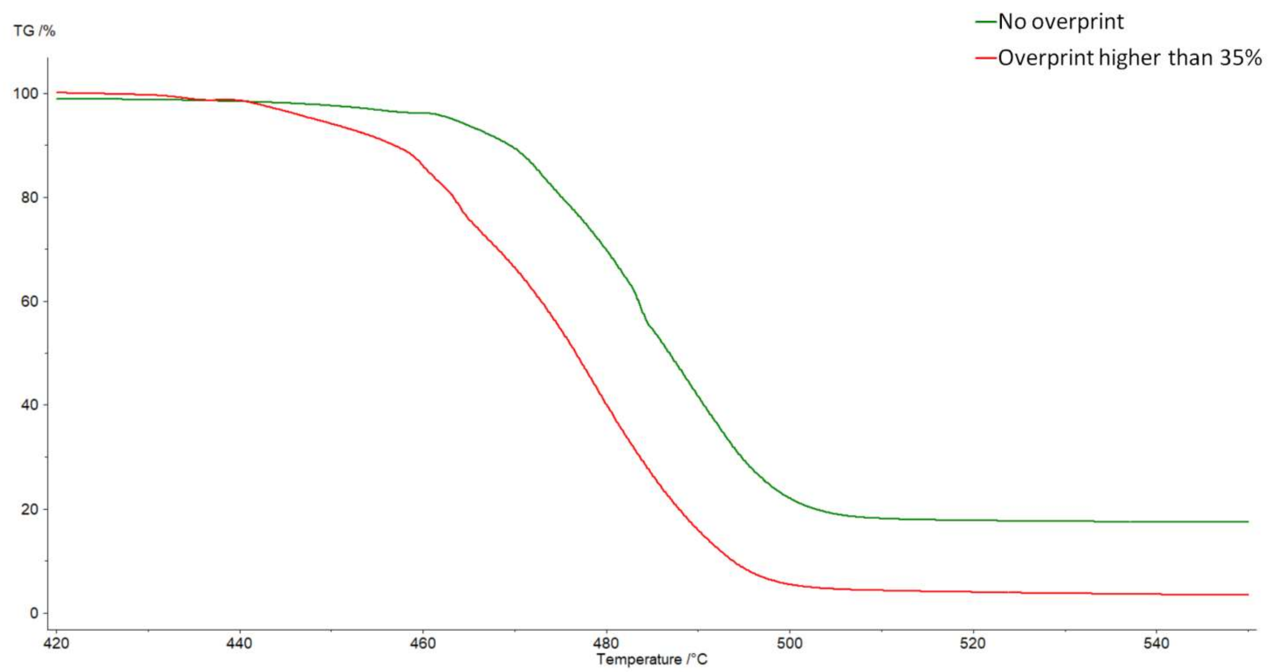

Fig.9. TG testing of black samples within the temperature range $420°C$ to $550°C$.

The samples with the addition of red but without the TG applied, lost $89.07\ \%$ mass during combustion in temperatures ranging from $420°C$ to $550°C$. In the case of printed samples, it was possible to lose $87.38\ \%$ mass in the same temperature range. In order to better illustrate the experiment, the results are presented in Fig.10. A full summary of the results can also be found in Tab.3.

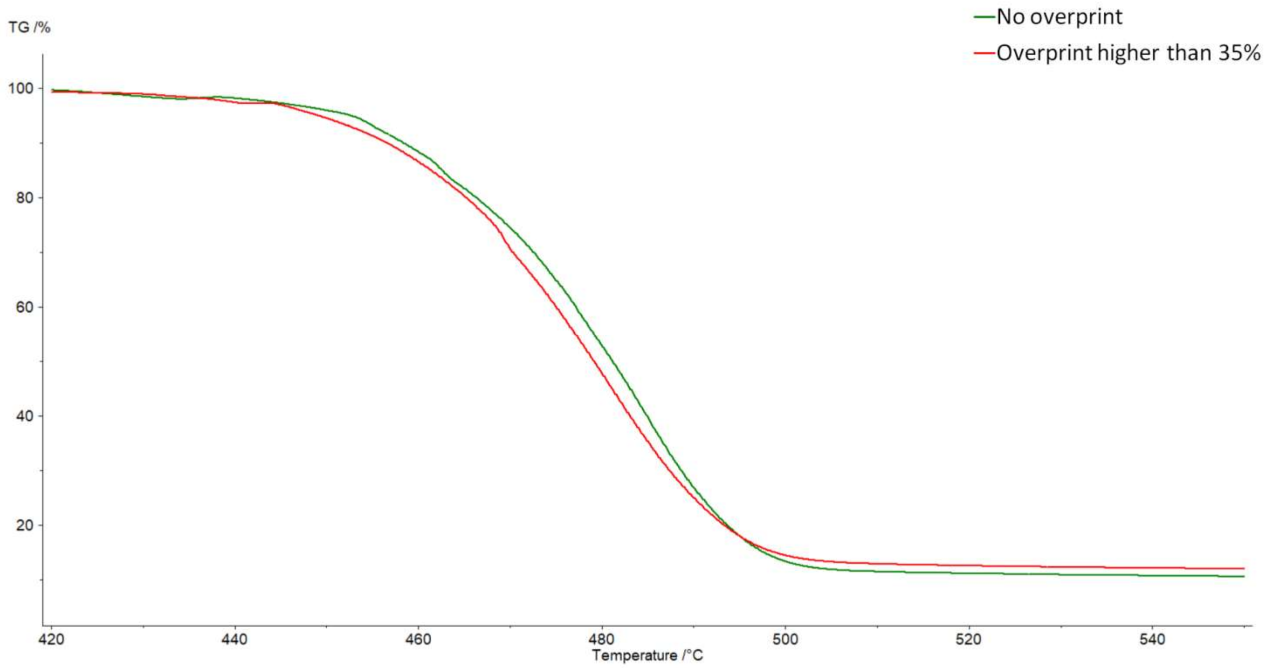

Fig.10. TG testing of red samples within the temperature range $420°C$ to $550°C$.

During the combustion process of the yellow samples, it was possible to lose 92.05 % of the weight of the samples without the applied print and 91.57 % for the samples with the applied print. In order to better illustrate the experiment, the results are presented in Fig.11. A full summary of the results can also be found in Tab.3.

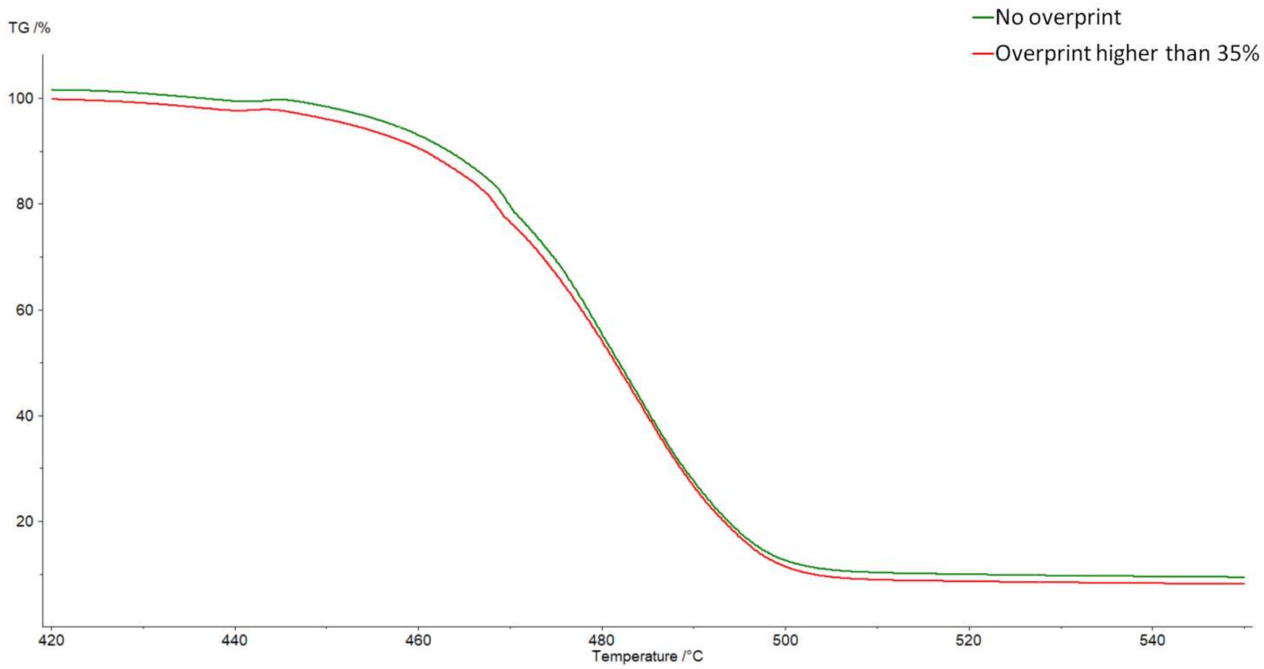

Fig.11. TG testing of yellow samples within the temperature range $420°C$ to $550°C$.

The results of the analysis of the blue samples showed that the samples without the applied print, lost weight by $96.31\,\%$, whereas printed samples burned in the same temperature range in $89.20\,\%$. In order to better illustrate the experiment, the results are presented in Fig.12. A full summary of the results can also be found in Tab.3.

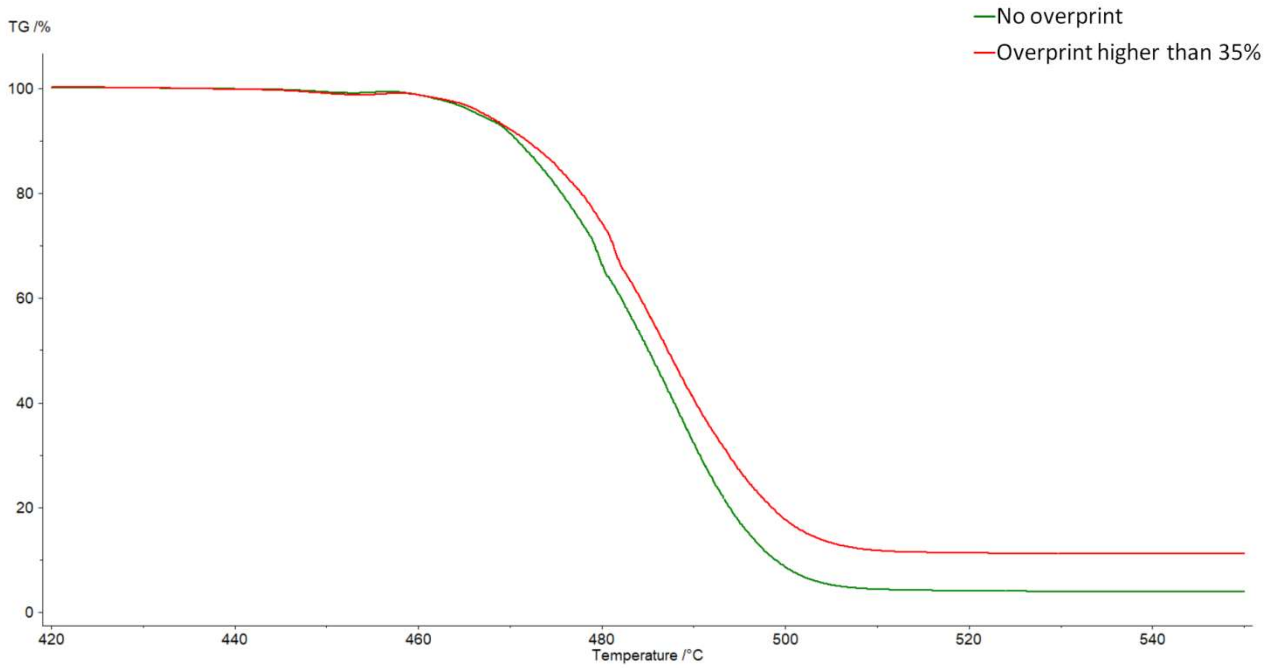

Fig.12. TG testing of red samples within the temperature range $420°C$ to $550°C$.

The exact results of the GT tests are presented in Tab.3.

Table 3. TG test results.

Colour	Imprint	$T_{50}\,[°C]$	Mass change (in temperature $420-550°C$) [%]
Reference sample	0	473.16	$-95,86$
Colourless	0	$476,79$	-96.85
	>35	475.56	-96.73
Black	0	486.70	-81.45
	>35	476.49	-96.65
Red	0	480.97	-89.07
	>35	479.06	-87.38
Yellow	0	481.91	-92.05
	>35	481.53	-91.57
Blue	0	485.00	-96.31
	>35	487.08	-89.20

Samples with colour additives are characterised by a slight increase in combustion temperatures T_{50}. The highest combustion temperature was recorded for the blue sample with the applied print while the lowest recorded was for the colourless sample with the applied print. The difference between these particular samples $11.52°C$ is that it was necessary to provide more energy for the sample to lose $50\ \%$ of its mass. In the temperature range tested ($420°C - 550°C$) of the sample of mass changes, an analogous situation is visible. Samples with dye burned to a lesser extent than samples with no dye. The applied surface printing does not seem to have had a significant impact on the samples tested. Both an increase in the combustion temperature of the samples in relation to the reference sample is visible.

4. Conclusion

In order to ensure the highest quality of the material, which is at the same time recycled, more attention should be paid, not only to the additives used, such as dyes, but also to the surface prints on packaging, because these can reduce the quality of processed materials and reduce their lifecycles.

The analysis showed that the surface print used had no major impact on the thermal analysis of the samples. However, using a different paint and increasing the surface area could have a negative effect on the reprocessing of the material. Research should be expanded to optimise the recycling process.

Studies have also shown that the addition of dyes hinders the combustion process and obliges us to increase energy, in order to use the material, thus increasing utilisation costs.

Conducting additional research on the recycling of plastics should focus not only *vis-à-vis* extending the number of lifecycles of a given material, but also how to optimise and standardise the recycling process so that it can be carried out effectively and safely for people while maintaining product quality.

Nomenclature

- DSC – differential scanning calorimeters
- TG – thermogravimeters
- $LDPE$ – low density polyethylene
- X_c – degree of crystallinity
- ΔH_m – measured melting enthalpy
- ΔH_{lit} – literature value of melting enthalpy
- T_m – melting temperature
- T_{50} – temperature of $50\ \%$ weight loss of the sample

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Received: February 12, 2023
Revised: June 12, 2023