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EFFECT OF CHAIN EXTENDER ON POST-CONSUMER POLYETHYLENE TEREPHTALATE (PET): A COMPARISON WITH VIRGIN PET[1]

EFEITO DO EXTENSOR DE CADEIA SOBRE O POLIETILENO TEREFTALATO PÓS CONSUMO (PET): UMA COMPARAÇÃO COM O PET VIRGEM

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ABSTRACT

This study aimed to investigate the impact of a chain extender on the thermal properties of recycled polyethylene terephthalate (PET) compared to virgin PET. FTIR analysis revealed no changes in the chemical structure of PET after the addition of the extender. DSC analysis results showed that post-consumer PET with the extender exhibited a glass transition temperature (Tg) similar to that of virgin PET, indicating possible crosslinking. All PET materials displayed cold crystallization behavior, with differences observed between virgin and recycled PET. It is concluded that the chain extender modified the thermal properties of recycled PET, suggesting that it may influence the quality of recycled materials.

Keywords: Chain modification; Thermal behavior; Crosslinking.

RESUMO

Este estudo teve como objetivo investigar o impacto do extensor de cadeia nas propriedades térmicas do polietileno tereftalato (PET) reciclado em comparação com o PET virgem. A análise por FTIR não revelou alterações na estrutura química do PET após a adição do extensor. Os resultados da análise por DSC mostraram que o PET pós-consumo com o extensor apresentou uma temperatura de transição vítrea (Tg) semelhante à do PET virgem, indicando uma possível reticulação. Todos os materiais de PET exibiram

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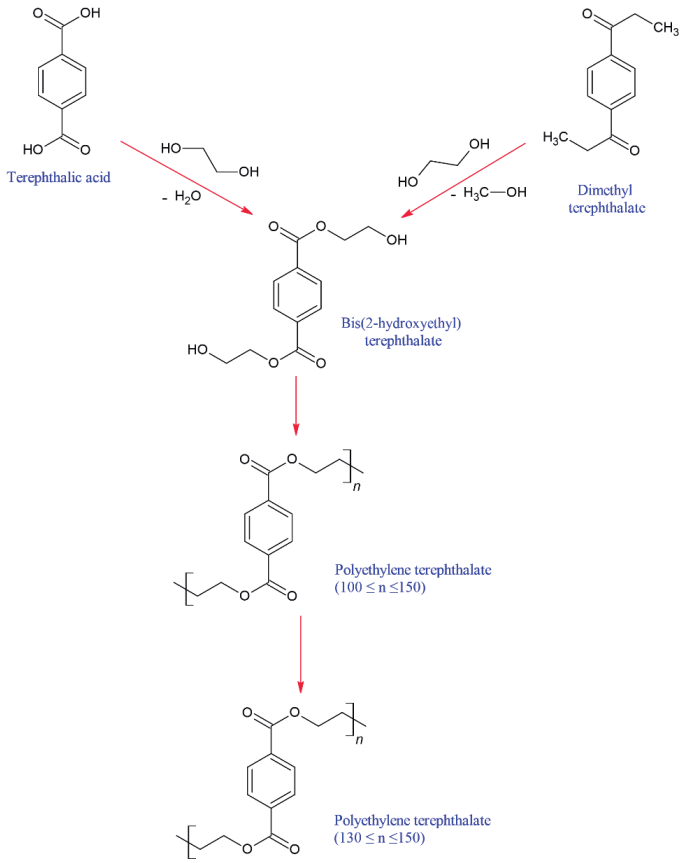
comportamento de cristalização a frio, com diferenças observadas entre o PET virgem e o reciclado. Conclui-se que o extensor de cadeia modificou as propriedades térmicas do PET reciclado, sugerindo que ele pode influenciar a qualidade dos materiais reciclados.

Palavras-chave: *Modificação de cadeia; Comportamento térmico; Reticulação.*

1 INTRODUCTION

PET is classified as thermoplastic polyester, a transparent plastic, extremely light, with high mechanical (impact), physical (impermeability) and chemical (odor and gas) resistance, mainly used for packaging carbonated drinks (Silva, 2010). Commonly, PET is obtained from the reaction of terephthalic acid with ethylene glycol or from dimethyl terephthalate, which react to form bis(2-hydroxyethyl) terephthalate. Under the action of a catalyst, polycondensation occurs to create oligomeric chains between 100 and 150 repetitions. These chains are melted and re-esterified to form polymeric chains with between 130 and 150 repetitions and with a molar mass exceeding 30.000 repetitions (Glaser; Sahle-Demessie; Richardson, 2022). A simplified scheme of this reaction is available in Figure 1.

Figure 1 - PET synthesis.



Source: Adapted from (Glaser; Sahle-Demessie; Richardson, 2022).

Because they have a large volume in relation to their weight, these materials occupy extensive space in landfills after their disposal, which generates, in addition to visual pollution, due to

inadequate disposal on the streets, serious flooding problems due to clogging of storm sewers and a reduction in useful life of landfills (Rodrigues *et al.*, 2020).

In order to minimize the environmental impact due to incorrect disposal of PET, an alternative would be to recycle this polymer. Among the existing types of recycling (mechanical, energy and chemical). In the case of mechanical recycling, which is the most used in Brazil, post-consumer recycled PET could be used for the production of non-woven fabric, carpets, ropes, broom bristles. However, the mechanical recycling of PET causes progressive degradation of this polymer during its reprocessing, which leads to a considerable decrease in its mechanical, thermal and rheological properties. In this case, the decrease in molar mass, due to chain scission, is the main cause of these effects (Benyathiar *et al.*, 2022; Coelho; Castro; Gobbo, 2011; Glaser; Sahle-Demessie; Richardson, 2022).

To minimize the reduction in molar mass during PET reprocessing, a widely used procedure for this is the use of chain extenders. These materials are chemical agents that react with the ends of the chains, resulting in an increase in the molar mass of the polymer, thus minimizing the process of polymer chain breaks due to degradation that occurs during reprocessing. Extenders are normally incorporated by reactive extrusion. During the reactive extrusion process, heating and shear generate the necessary conditions for the reaction and incorporation of the extender into the polymer. Furthermore, chain extenders have the advantage of low system cost, greater flexibility and faster extension reaction without the need for additional investment. Therefore, reactive extrusion is a very attractive technique because it is cheap and easy to implement in a mechanical recycling system, using an extruder (Awaja; Pavel, 2005).

In this way, this work aims to clarify the influence of chain extenders on the thermal properties of PET during processing. The incorporation of this additive modifies the polymer's viscosity and may help mitigate the effects of degradation caused by hydrolysis, potentially bringing the properties of degraded PET closer to those of virgin PET.

2 MATERIALS AND METHODS

2.1 MATERIALS

Table 1 presents the materials used in this work, such as virgin PET, recycled PET, and the chain extender. All materials were supplied by the company Colormaster.

Table 1 - Materials used.

Name	Acronym	Density	Supplier
Polyethylene terephthalate	PET	1.03	Colormaster
Recycled polyethylene terephthalate	Rec PET	0.63	Colormaster
Chain extender	Ext	0.57	Colormaster

Source: Author's construction.

Table 2 below illustrates the proportions of virgin PET, recycled PET and the Chain extender used in this work. The proportions of the chain extender were adapted from other studies in the literature, ranging from 0.5% to 1.5% by weight (Duarte *et al.*, 2016; Vozniak *et al.*, 2024).

Table 2 - PET and chain extender proportions.

Material	Percentage (% w/w)	Mass (g)	Extender (g)
Virgin PET	0.0	5.000	0.0
Recycled PET	0.0	5.000	0.0
Recycled PET + Extender	0.3	4.985	15.0
Recycled PET + Extender	1.0	4.950	50.0

Source: Author's construction.

2.2 SAMPLE PREPARATION

First, 5 kg of virgin PET and 5 kg of recycled PET were dried separately for 4 hours at a temperature of 120 ºC. This procedure was necessary due to the high hygroscopicity of PET. After 4 hours, 200 g of virgin PET was weighed to be injected into the Battenfeld brand injector. After the injector was cleaned, 200 g of recycled PET was weighed to be injected at a temperature of 270 ºC.

Next, 5.985 kg of recycled PET was weighed, and 15 g of the extender was added. The mixture was dried at 120 ºC for 4 hours and then extruded in a Rullis-Davis single-screw extruder with a heating zone of 190 ºC to 260 ºC. After extrusion, the mixture was dried again for 4 hours at 120 ºC and injected at a temperature of 270 ºC.

Finally, 5.950 kg of recycled PET was weighed, and 50 g of the extender was added. The mixture was dried at 120 ºC for 4 hours and extruded with a heating zone of 190 ºC to 250 ºC. After extrusion, the mixture was dried again for 4 hours at 120 ºC and then injected at a temperature of 270 ºC. There was no need to heat the chain extender; it was injected at a temperature of 180 ºC. All formulations were prepared only once, corresponding to a single sample for each experimental condition.

2.3 SAMPLE CHARACTERIZATION METHODS

2.3.1 Fourier Transform Infrared Spectroscopy - FTIR

FTIR analyzes were carried out on a Perkin Elmer equipment, model Spectrum 65, with ATR module, wavenumber between 4000 and 400 cm^{-1}, 32 scans, and resolution of 4 cm^{-1}.

2.3.2 Differential Scanning Calorimetry (DSC)

DSC analyzes were carried out on a DSC 25 model equipment, from the TA Instruments brand. Approximately 9.26 mg of each sample were used, which were analyzed in a temperature range between 40 and 300 °C, with a heating rate of 30 °C/min. After reaching 300 °C, the sample was cooled to 30 °C, with a 5-minute isotherm, with a heating rate of 30 °C/min. After this time, the sample was heated to 320 ºC with a heating rate of 10 ºC/min. All properties were obtained from the heating curve. To calculate the crystallinity index (CIDSC), Equation 1 was used, according to the literature (Canevarolo, 2019). Standardized values of ΔH0 were obtained from the same reference.

$$CI_{DSC} = \frac{\Delta H}{\Delta H_{100\%}} \times 100\% \text{ (Eq. 1)}$$

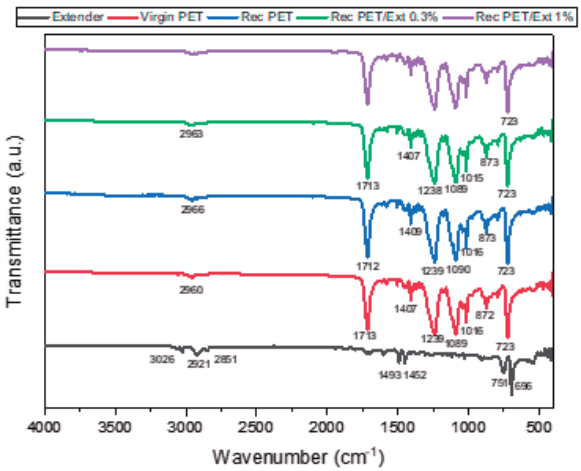
Where: ΔH = melting enthalpy of sample and ΔH100% = melting enthalpy of an ideal crystal of PET.

3 RESULTS AND DISCUSSION

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY - FTIR

Figure 2 shows the FTIR absorption bands of the chain extender, virgin PET, recycled PET, as well as the addition of the chain extender to recycled PET in proportions ranging from 0.3 to 1%.

Figure 2 - FTIR spectra of chain extender, virgin PET, recycled PET and recyled PET with chain extender.



Source: Author's construction.

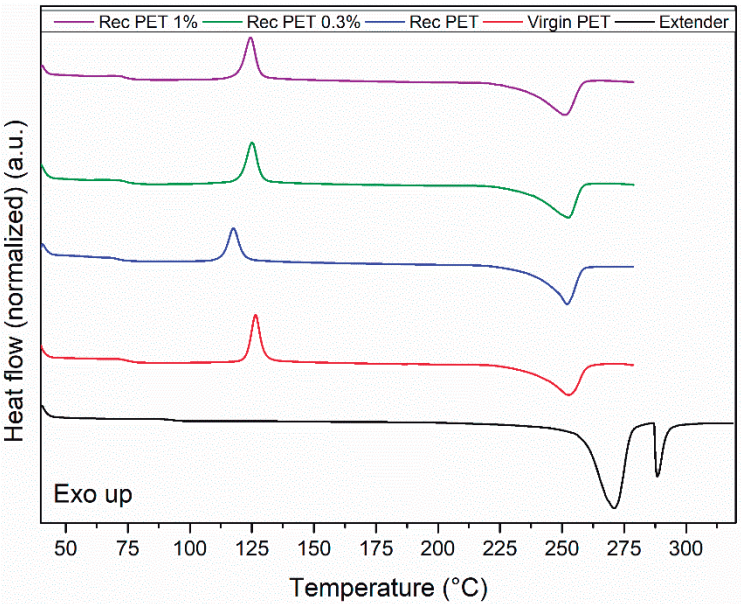
According to the literature, virgin PET presents a characteristic band at 872 cm^{-1} related to the para-disubstituted benzene stretching bending of benzene ring and at 723 cm^{-1} attributed to CH_2

bends-rocking. The band at 1240 cm^{-1} is related to the C-C(O)-C stretch of esters. It is possible to notice bands around 1407 cm^{-1} and 1500 cm^{-1} referring to the CH groups and C=C strecthing vibration of the aromatic ring, respectively (Lubna *et al.*, 2018). The band at 1713 cm^{-1} is attributed to the stretching of the bond of the carbonyl group (C=O), which is found predominantly in the ester segments of the chain PET polymer, or aromatic groups for degraded samples (Alves *et al.*, 2023; Mendiburu-Valor *et al.*, 2022). At 2960 cm^{-1} there is a band related to the extended single bond (C-H) (Bimestre; Saron, 2012). For both recycled PET and PET with the chain extender, no variations were observed in the characteristic bands of the PET segments after the addition of the chain extender, regardless of the content used (Zhang *et al.*, 2010). According to the literature, this is due to a possible chemical reaction between the epoxy groups of the extender with the terminal groups of PET, carboxylic and hydroxyl groups after chain extension (Ghanbari *et al.*, 2013).

3.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Figure 3 illustrates the DSC curves of all samples.

Figure 3 - DSC heating curves of all samples.



Source: Author's construction.

According to the data in Table 3, it is possible to observe that all PET materials presented similar values of Tg, irrespective to the concentration of extender used. Since each formulation was prepared only once, the data refer to a single sample for each experimental condition (Bartolotta *et al.*, 2003). When comparing Tg values of samples with extender and recycled PET, it's observed a small increase after the reactive extrusion process (Makkam; Harnnarongchai, 2014). In this case, the Tg of recycled PET with a chain extender was similar to that of virgin PET, suggesting a possible

cross-linking effect. This may indicate a reduction in chain mobility, which could partially counteract the decrease in molar mass caused by the recycling process. However, the observed changes in Tg alone do not fully confirm the extent of this effect (Awaja; Pavel, 2005).

Despite this, the presence of the chain extender appears to have influenced the thermal behavior of the recycled PET, as all PET samples exhibited cold crystallization in the range of 113-123 °C, a commonly observed phenomenon. Additionally, virgin PET presented a double exothermic peak during cooling, associated with the formation of crystals with different levels of perfection (data not shown) (Nofar; Oğuz, 2019).

Table 3 - Relationship between samples and Tg failures by DSC.

Sample	Extender quantity (%)	Tc (°C)	Tonset (°C)	ΔHc (J/g)
PET	0.0	215.4	218.6	50.3
Recycled PET	0.0	212.6	217.0	48.4
Extender	100.0	230.4	230.6	15.5
PET + Extender	0.3	212.2	218.7	48.0
PET + Extender	1.0	210.6	215.7	51.5

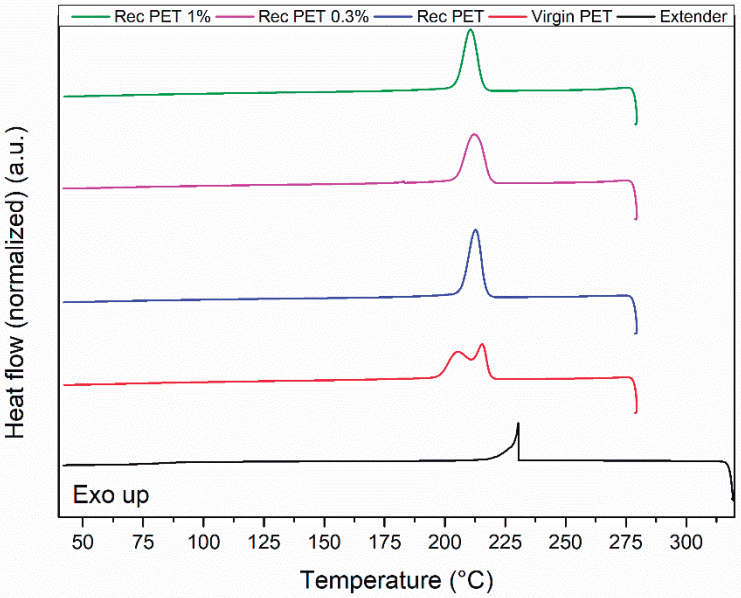
Source: Author's construction.

Regarding the melting temperature (Tm) values, it wasn't observed significative changes when adding the extender, observing a maximum variation of around 1 °C. The starting point of melting crystals, called Tonset, also presented a small variation, respective of the addition of chain extender, which may produce less stable and organized crystals that melts under lower temperatures (Nofar; Oğuz, 2019; Ou; Ho; Lin, 2003), and was discussed in terms of crystallization kinetics. These authors observed that the presence of montmorillonite acted as a nucleator to PET chains, accelerating and increasing the crystallization during cooling. In this work, this effect was less pronounced due to the lower quantity of extender used (0.3 to 1%) but is also observed. In addition, (Liu; Xu, 2013) discussed differences in enthalpy and temperature of melting of PET with extenders regarding the molecular weight.

Authors commented that during the reactive extrusion, different molecular weights may be obtained by different reactions, influencing crystallinity properties obtained. In general, less molecular weight formed by the chain extender may produce higher crystallinity materials (Liu; Xu, 2013). Also (Ou; Ho; Lin, 2003) stated that low contents of extender may facilitate crystallization, opposite of high contents.

Figure 4 contains DSC cooling curves of all samples.

Figure 4 - DSC cooling curves of all samples.



Source: Prepared by author.

Virgin PET presented a double exothermic peak during cooling related to the formation of crystals with different perfections (Nofar; Oğuz, 2019). Remaining samples presented a single exothermic peak, related to the crystallization during cooling, in the region of 210-215 °C. Slightly larger and shorter peaks are observed for samples with the addition of extender, indicating more heterogeneity between crystals and maybe that it is occurring more slowly than the others (Nofar; Oğuz, 2019), but not conclusive, as long as time are not being considered here.

Different to the observed in PET/montmorillonite, the chain extender as it is possible to notice at table 4 decreased all the cooling features of the samples, when compared to the virgin PET (Ou; Ho; Lin, 2003).

Table 4 - Thermal properties of the samples obtained during cooling.

Sample	Extender Quantity (%)	Tc (°C)	Tonset (°C)	ΔHc (J/g)
PET	0.0	215.4	218.6	50.3
Recycled PET	0.0	212.6	217.0	48.4
Extender	100.0	230.4	230.6	15.5
PET + Extender	0.3	212.2	218.7	48.0
PET + Extender	1.0	210.6	215.7	51.5

Source: Author's construction.

It may be related to the formation of less perfect crystals, as discussed earlier, demanding lower temperatures to its total formation. Similar observations were made by (Liu; Xu, 2013; Nofar; Oğuz, 2019).

4 CONCLUSION

In summary, the FTIR analysis demonstrated that the addition of the chain extender did not induce any discernible changes in the chemical structure of the PET samples, irrespective of the extender concentration. Conversely, the DSC findings revealed that the Tg of the post-consumer PET with the chain extender exhibited a comparable value to that of virgin PET, suggesting effective cross-linking. Furthermore, all PET samples displayed cold crystallization behavior within the temperature range of 113-123 °C, with virgin PET exhibiting a distinctive double exothermic peak during cooling. These results indicate that chain extenders influence the thermal properties of recycled PET and suggest their potential role in modifying the performance of recycled polymers. However, further studies are needed to evaluate their full impact, particularly on mechanical and rheological properties.

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REFERENCES

ALVES, L. R. *et al.* Synthesis and characterization of polyurethane and samarium(III) oxide and holmium(III) oxide compositess. **Polímeros**, v. 33, p. e20230039, 2023.

AWAJA, F.; PAVEL, D. Recycling of PET. **European Polymer Journal**, v. 41, n. 7, p. 1453-1477, 1 jul. 2005.

BARTOLOTTA, A. *et al.* DSC and DMTA study of annealed cold-drawn PET: a three phase model interpretation. **Polymer**, In Honour of Ian Ward's 75th Birthday. v. 44, n. 19, p. 5771-5777, 1 set. 2003.

BENYATHIAR, P. *et al.* Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: A Review. **Polymers**, v. 14, n. 12, p. 2366, jan. 2022.

BIMESTRE, B. H.; SARON, C. Chain extension of poly (ethylene terephthalate) by reactive extrusion with secondary stabilizer. **Materials Research**, v. 15, p. 467-472, jun. 2012.

CANEVAROLO, S. **Polymer Science: A Textbook for Engineers and Technologists**. [s.l: s.n.].

COELHO, T. M.; CASTRO, R.; GOBBO, J. A. PET containers in Brazil: Opportunities and challenges of a logistics model for post-consumer waste recycling. **Resources, Conservation and Recycling**, v. 55, n. 3, p. 291-299, 1 jan. 2011.

DUARTE, I. S. *et al.* Chain extension of virgin and recycled poly(ethylene terephthalate): Effect of processing conditions and reprocessing. **Polymer Degradation and Stability**, v. 124, p. 26-34, 1 fev. 2016.

GHANBARI, A. *et al.* A novel approach to control thermal degradation of PET/organoclay nanocomposites and improve clay exfoliation. **Polymer**, v. 54, n. 4, p. 1361-1369, 18 fev. 2013.

GLASER, J.; SAHLE-DEMESSIE, E.; RICHARDSON, T. Are Reliable and Emerging Technologies Available for Plastic Recycling in a Circular Economy? Em: [s.l: s.n.].

LIU, B.; XU, Q. Effects of Bifunctional Chain Extender on the Crystallinity and Thermal Stability of PET. **Journal of Materials Science and Chemical Engineering**, v. 1, n. 6, p. 9-15, 6 nov. 2013.

LUBNA, M. M. *et al.* Modification of Thermo-Mechanical Properties of Recycled PET by Vinyl Acetate (VAc) Monomer Grafting Using Gamma Irradiation. **Journal of Polymers and the Environment**, v. 26, n. 1, p. 83-90, 1 jan. 2018.

MAKKAM, S.; HARNNARONGCHAI, W. Rheological and Mechanical Properties of Recycled PET Modified by Reactive Extrusion. **Energy Procedia**, 11th Eco-Energy and Materials Science and Engineering (11th EMSES). v. 56, p. 547-553, 1 jan. 2014.

MENDIBURU-VALOR, E. *et al.* Valorization of urban and marine PET waste by optimized chemical recycling. **Resources, Conservation and Recycling**, v. 184, p. 106413, 1 set. 2022.

NOFAR, M.; OĞUZ, H. Development of PBT/Recycled-PET Blends and the Influence of Using Chain Extender. **Journal of Polymers and the Environment**, v. 27, n. 7, p. 1404-1417, 1 jul. 2019.

OU, C. F.; HO, M. T.; LIN, J. R. The Nucleating Effect of Montmorillonite on Crystallization of PET/Montmorillonite Nanocomposite. **Journal of Polymer Research**, v. 10, n. 2, p. 127-132, 1 jun. 2003.

RODRIGUES, N. DE P. *et al.* Incorporação de PET pós-consumo em misturas de PEAD virgem compatibilizadas / Incorporation of post-consumer PET into virgin PEAD compatible blends. **Brazilian Applied Science Review**, v. 4, n. 3, p. 1748-1764, 4 jun. 2020.

SILVA, G. A. DA. A descoberta do plástico e uma imersão no pet (politereftalato de etileno). **Jornal Eletrônico Faculdades Integradas Vianna Júnior**, v. 2, n. 2, p. 18-18, 2010.

VOZNIAK, A. *et al.* PET mechanical recycling. A new principle for chain extender introduction. **Sustainable Materials and Technologies**, v. 40, p. e00886, 1 jul. 2024.

ZHANG, Y. *et al.* Chain extension of poly(ethylene terephthalate) with bisphenol-A dicyanate. **Journal of Applied Polymer Science**, v. 117, n. 4, p. 2003-2008, 2010.