UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

TÍTULO: REINFORCEMENT OF RECYCLED PET: A REVIEW

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímico

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Por su apoyo incondicional,
A Dios,
A mis padres Edward Guzmán y María Cajamarca,
A mis hermanos Roser, Ariel y Alejandra

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RESUMEN

En el siguiente trabajo de investigación se hizo una revisión bibliográfica de las estrategias empleadas para mejorar las propiedades del PET reciclado. El tipo de reciclado en el cual se profundizó fue el análisis secundario por la cantidad de información encontrada al respecto. Para llevar a cabo la presente investigación se revisaron los artículos de los últimos cinco años en los que se utilizaron el PET reciclado como matriz polimérica los cuales fueron revisados, analizados y clasificados en cuatro secciones: PET reciclado, mezclas con PET reciclado, extendedores de cadena y nano-partículas de relleno. Los valores obtenidos fueron resumidos en tablas para el análisis de sus tendencias, diferenciando las propiedades mecánicas y térmicas. Para explicar el comportamiento de las mezclas se utilizaron los datos reportados en DSC, TGA, SEM y ensayos mecánicos. Los resultados mostraron dos tendencias principales en las mezclas: la primera enfocada en el endurecimiento de la mezcla usando una fase dispersa con un módulo de Young mayor al de la matriz o utilizar un polímero con una rigidez menor a la matriz pero que debido a mecanismos de endurecimiento incrementa sus propiedades mecánicas; la segunda tendencia se centra en la utilización de polímeros que generan propiedades plastificantes.

Palabras clave: Estrategias para el reciclado del PET, extendedores de cadena, nano-partículas de relleno, mezclas con PET reciclado

ABSTRACT

A bibliographic review was made about strategies used to improve the thermal and mechanical properties of recycled PET in the following work. To carry out this research, articles in which recycled PET was used as a polymeric matrix from the last five years were reviewed, analyzed, and classified into four sections: recycled PET, blendings with recycled PET, chain extenders, and filler nanoparticles. Values obtained were summarized in tables for the analysis of their trends, differentiating mechanical and thermal properties. The data obtained by DSC, TGA, SEM, and Tensile tests were used to explain the behavior of the blends. Results showed two main tendencies in the blends: the first focused on the hardening PET using a dispersed phase with Young's modulus greater than polymeric matrix. The second trend focuses on the use of polymers that generate plasticizing properties in the blend.

Keywords: PET recycling strategies, chain extenders, filler nanoparticles, blends with recycled PET

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LIST OF ABBREVIATIONS

American Society for Testing and Materials   ASTM

Ammonium polyphosphate   APP

Bis hydroxy ethylene terephthalate   BET

Differential Scanning Calorimeter   DSC

Dimethyl terephthalate   DMT

Ethylene glycol   EG

Fourier transform infrared spectroscopy   FTIR

International Organization for Standardization   ISO

Maleic anhydride   PP-g-MA

Melt Flow Index   MFI

Montmorillonite   MMT

Poly(butylene adipate-co-terephthalate)   PBAT

Poly(butylene terephthalate)   PBT

Poly(ethylene 2,6-naphtalate)   PEN

Poly(ethylene terephthalate)   PET

Poly(ethylene)   PE

Polycarbonate   PC

Polypropylene   PP

Recycled poly(ethylene terephthalate)   R-PET

Scanning electron microscope   SEM

Styrene-ethylene-butadyene-styrene copolymer   SEBS

Terephthalic acids   TA

Thermogravimetric analysis   TGA

Virgin poly(ethylene terephthalate)   V-PET

CHAPTER I
INTRODUCTION

1.1. Introduction

The use of synthetic polymers in the food industry allows extending the life cycle of aliments, representing an energetic saving and money saving[1]. However, the fast residues generation becomes an environmental problem due to the accumulation of these in the terrestrial layer [2–4].

Poly(ethylene terephthalate) (PET) is one of the most widely used thermoplastics due to its relatively low production costs, recyclability, mechanical attractiveness, barrier properties, moisture resistance, and low permeability to gases such as oxygen and carbon dioxide [2,5]. That is why this material is industrial and economically attractive; its production has increased exponentially from 13 million tons in the '90s to 16 million in 2013 [6]. The global production of PET in 2018 exceeded 20.1 million tons with an increase of 5.2% annually between 2012 and 2017[6], and average annual growth of 6.9% is expected between 2017-2025[2]. Its production is destined between 83-84% to the packaging of beverages and soft drinks worldwide[6].

PET is a polymer that does not create a high quantity of contaminants during its production or degradation. The increase in plastic waste and its high resistance to biological and atmospheric agents can be considered a polluting material because of its accumulation [7].

The high demand for PET worldwide and its resistance to biological agents have made researchers focus on recycling PET as the primary option for its final use. The recycling of a material is a strategy to: i) reduce the emission of gases during the manufacture, transport, and disposal of solid waste and ii) conserve non-renewable natural sources [2]. The implementation of this strategy is essential because, in addition to those mentioned above, it helps to save energy, lower fuel consumption, reducing landfills, and reduction of greenhouse gases [8]. Recycling one ton of PET saves the emission of 1.5 tons of carbon

dioxide, representing a saving of 70% compared to V-PET in the manufacture of plastic bottles[9].

According to the Guidelines for the recovery and recycling of plastics waste, established by the International Organization for Standardization (ISO) [10] and the Standard Guide for Waste Reduction published by the American Society for Testing and Materials (ASTM), 4-four main processes have been established for the recycling of materials:

- **Primary recycling.** It is about reusing flakes of PET-based materials that were produced during the shaping of the product.

- **Mechanical recycling.** During this process, the main structure of the material is preserved, and many of its potentials can be used in similar applications by replacing the virgin material [11]. Low investment is required for this and the use of affordable equipment and the low adverse environmental impact [5]. This process consists of several stages such as separation, washing, and milling of waste containers.

- **Chemical recycling.** It includes the depolymerization of waste materials to restore (recover) monomers that can be re-polymerized. This route requires a significant capital investment, high energy costs, and needs large scales to be economically viable[5]. This process can be carried out in several types: methanolysis, glycolysis, and hydrolysis.

- **Quaternary recycling.** It leads to getting energy from the incineration of polymer wastes.

Despite the advantages mentioned above regarding recycling, several obstacles arise when carrying out recycling processes, such as the high cost of collection and separation, the presence of colored debris, and oxidative degradation products that cause yellowing compromising mechanical properties of PET. The recycling of PET supposes a deterioration of its physical-mechanical properties due to the reduction of its molar mass, viscosity, and melting point [12].

According to recent studies, the properties of R-PET are modified by the reactive extrusion through chain extenders, copolymers, and some additives. Despite the extensive use of mechanical R-PET, with various applications such as reinforcement in cementitious matrices, coatings, insulating materials, bottles for beverage, its use is limited due to the detrimental effect of the recycling process on its properties. That is why the need to use external (addition of) compounds that allow modifying PET properties so that its use is massified as its similar V-PET [5].

Immiscibility of polymers, such as PET, during the blending, can be improved by adding copolymers, particularly block and graft copolymers, with segments capable of undergoing specific interactions through chemical reactions with the constituents of the blend, or by mixing suitable functionalized polymers promoting improved interactions. These copolymers, which are called compatibilizers, can be added or formed in situ during fusion by fusion through the interfacial chemical reaction of the polymer components [13].

On the other hand, the addition of well-dispersed nanoparticles in a polymer matrix favors polymer reinforcements, changing the mechanical behavior, the barrier properties, the thermal and rheological properties, which depend on the degree of dispersion and amount of the added additive [14].

Among the different processes involved in material recycling, primary recycling would seem to be the best treatment when the waste material to be recycled has been very little contaminated. However, this requirement of high purity, cleanliness, and homogeneity of the material could result in a disadvantage. That is why it seeks to take advantage of mechanical recycling, the second-best from an environmental point of view produces fewer greenhouse gases than its two subsequent processes [15]

1.2. Problem Statement

R-PET properties are less attractive than virgin material; that is why many researchers work on an economically feasible solution to this problem. To date, there is no compilation of these efforts in the recent literature. The present review surge as a response to the necessity of the researchers to have updated results on this matter, and a comparative analysis, that will help to establish a state of the art in the strategies employed to improve the mechanical and thermal properties of R-PET.

In the present review, an analysis of the strategies used to improve the properties of R-PET is developed to analyze its mechanical and thermal properties. Based on the information collected (reviewed), propose the best options to be implemented to carry out the recycling process of PET.

1.3. Objectives

1.3.1. General Objective

- To review the literature published since 2015 about the reinforcements used in R-PET matrices.

1.3.2. Specific objectives

- Identify in the literature how thermal and mechanical properties of reinforcements with R-PET are modified.
- To review the most used strategies in the reinforcement of R-PET.
- Identify in the literature what are the problems associated with polymer blends and analyze their reinforcing effect.

CHAPTER II

THEORETICAL FRAMEWORK

2.1.   Recycling of PET

PET is the third most widely used thermoplastic in the world [16], [17]. This semicrystalline thermoplastic can be found in films, sheets, strapping, packaging, and fibers used for sacking. The recycling of PET is inferior visually, physically, and chemically; that is why recycle companies intend to join efforts to obtain a recycled material as close to V-PET [18]. Once V-PET is used, the recycling process begins and is carried out into 4-main processes that will be developed in detail in the present chapter.

Figure 1 shows the polymerization, formulation, and processing stages to convert crude oil to final products. Once consumed, the plastic is discarded by the consumer and turned into waste taken to first recycling; This recycled material is introduced into the main processing production line. The new waste produced is taken to secondary recycling and introduced into the Formulation and Compounding line. After tertiary recycling, the waste is taken to the Quaternary recycling where this material is converted into energy in the form of heat[19].

Figure 1. The life cycle of plastics[19] (Adapted from R. Clift)

These stages allow optimal use of the plastics for their recovery, which will be discussed in the next section.

2.1.1. Primary recycling

Primary recycling is about the reintroduction of processing waste into the extrusion cycle to produce the same products. These residues can be edges or scrap. This type of recycling is the best recycling method because it uses less energy and fewer resources than the following three recycling processes[15],[20].

These wastes must be carried out for some process: collection and identification, selection and separation of cleanest materials from those with additives, grinding and homogenization of the wastes to be extruded, washing with hot water finally, the material is extruded to be processed once again [15].

2.1.2. Secondary recycling

This process is also known as mechanical recycling. It is about recovering solid plastic waste through mechanical processes to obtain sufficient properties instead of V-PET [15].

To carry out secondary recycling is necessary to follow some steps[18][21]: separation and classification of wastes depending the shape, density, size, and color; washing and drying to eliminate organic compounds, grinding of the material to homogenize it and make easier its mobilization and extrusion, and finally composite and granulation of the flakes of R-PET with other components for posterior extrusion.

This process eventually degrades the polymer partially and, therefore, deteriorates the properties of its V-PET predecessor. In order to improve the properties of the material, it is necessary to use new components that complement the R-PET, forming blends of V-PET with other compounds. Currently, different components are used, such as virgin polymer, fillers, fibers, or compatibilizers[18],[5],[13].

2.1.3. Tertiary recycling

Tertiary recycling or commonly known in the industry as chemical recycling. It consists of a chemical transformation of polymer chains into monomers or smaller molecules that can be used as raw materials to produce new polymers for the same or new applications[15],[5]. This process has several reaction pathways, as presented in *Figure 2*, this

scheme shows four main reactions by which chemical recycling can occur, depending on the reaction medium. [22],[17],[21]

Figure 2. Reaction pathways of chemical recycling (Adapted from Thiounn et al.[22])

2.1.3.1.   Hydrolisis

It is a depolymerization process in which intervenes large water-PET ratios (5:1) at elevated temperatures and/or in the presence of catalysts. The main products obtained in this process are terephthalic acids (TA) and Ethylene glycol (EG)[22]. It can be carried out by acid hydrolysis, alkaline hydrolysis or neutral hydrolysis.

2.1.3.2.   Methanolysis

Methanolysis is based on the treatment of PET with methanol at temperatures between 180 and 280 °C and pressures between 20-40 atm in the presence of a catalyst, zinc acetate is commonly used. This reaction gives as main products dimethyl terephthalate (DMT) and ethylene glycol (EG).[21],[22]

2.1.3.3.   Aminolysis

Aminolysis is a reaction that uses amines for the depolymerization of PET. This process has not been widely studied due to the costs of amine and its toxicity. This reaction yields TA diamides as main products[22],[23].

2.1.3.4.   Glycolysis

Glycolysis is the simplest and oldest method for the depolymerization of PET [21],[22]. This process is carried out in a batch reactor, obtaining as main product bis hydroxy ethylene terephthalate (BET) [17],[24]. Glycol diffuses into the polymer to react with an ester and breaks down PET into smaller fractions [21]. The catalysts that are normally used to increase glycol activity and decrease reaction time are methyl acetate, titanium phosphate, and ferrous oxide. [24] This recycling method is the most used due to the various applications of the products obtained. [21],[17],[24]

2.1.4.   Quaternary Recycling

Quaternary recycling consists of the incineration of plastic for energy recovery through the production of heat. Currently, this type of recycling is widely used due to its ease of using[15]. In the European Union, 39.5% of plastic waste is still recovered through this process[25]. This process is used when mechanical processes fail due to contamination excess[15]

2.2.   New Techniques for Recycling

In recent years, new recycling techniques have been developed to improve the reaction and purity of polyesters in chemical and mechanical processes, respectively.

2.2.1.   DEMETO technique

This patent was developed in 2013 by Gr3n company, and it improves the depolymerization performance of polyesters with additives such as pigments and textiles. The process is known as depolymerization by microwave technology, and it is capable of reducing the time of reaction to 10 minutes[26].

2.2.2. Chemical wash

In mechanical recycling, one more step is added to improve the purity of the recycled material. An additional step could be implemented in industrial processes after conventional washing and before the drying stage. This wash consists of removing the Surface layer of the PET material, with sodium hydroxide, with the proposal of forming a new cleaner surface than the original one. This process allows obtaining PET with fewer contaminants and greater added value.[18]

2.3. Degradation of PET

As it is already known, Mechanical recycling is about eliminating impurities by sorting, grinding, washing, and extruding (at a controlled temperature). One of the drawbacks of mechanical recycling is thermo-mechanical and hydrolytic degradation, which decreases molecular weight. Eventually, its viscosity, melt strength, mechanical properties, and so on limit its usefulness for many applications [3,6,27–30]. This degradation makes mechanical recycling a finite process due to its constant degradation[27].

Figure 3 shows the scission reactions that PET undergoes during extrusion corresponding to thermal and hydrolytic degradation, respectively. In *Figure 3a*, the thermal decomposition of an ester linkage is shown, caused by an increase in temperature during the extrusion process resulting in carboxylic acid end groups and vinyl ester end groups. In *Figure 3b* it is shown the hydrolysis reaction of PET is caused by the presence of water that gives; as a result, carboxylic acid end groups and hydroxyl-ester end groups. Increasing carboxyl groups result in a decrease in molecular weight [27].

Figure 3. Effect of processing on the chain scission reactions of PET ester linkages (Adapted from Asensio et al. [27])

CHAPTER III

RECYCLED PET: GENERAL PROPERTIES, BLENDS, AND ADDITIVES

3.1. Recycled PET properties

Mechanical and thermal properties of PET deteriorate with the recycling process, in contrast with V-PET. It is due to degradation, pollutants, recycling mechanisms, among others. During the recycling process occurs a cleavage of chains, an increase of carboxylic groups, a reduction in molecular weight, and so on a decrease in intrinsic viscosity, resulting in a deterioration of the mechanical and thermal properties of R-PET. Such is the case reported by Lee et al.[31], who studied properties of R-PET, V-PET and blends at different sample compositions. **Figure 4** shows thermogravimetric analysis results where can be compared thermal degradation of R-PET and V-PET in function of the temperature increase. It can be seen that for 2 and 5 wt% V-PET experienced a high resistance to weight loss related to cleavage of chains during recycling process of PET.

Figure 4. Thermal degradation of weight loss of 2 wt% and 5 wt% It c

According to Oromiehie et al., [29] samples of R-PET go down their intrinsic viscosity. *Figure 5* shows the composition of several R-PET/V-PET samples with several compositions and intrinsic viscosity according to the extrusion technique applied. Like it can be seen, all the samples tend to decrease their intrinsic viscosity, and this trend is associated with the amount of R-PET used.

Figure 5. Intrinsic viscosity of several samples with virgin and recycled PET (Recovered from Oromiehie et al.[29])

This trend is because of the thermal exposure as well as shear degradation of R-PET. As a direct result, it produces a plastic material with a reduced melt viscosity, which means molecular weight decreases while the amount of R-PET increases. One of the reasons for this phenomenon is the retained humidity from the specific surface of the wastes. In consequence, traces of humidity promote chain scission with a low intrinsic viscosity [29],[32],[33].

The mechanical properties and the standards employed for testing the samples of neat R-PET, are compiled in Table 1. Even though several samples were tested under the same international standards, considerably different values were obtained depending on the sources of R-PET employed by the authors. Such is the case of Srithep et al. [34], who reported tensile strength of 60 MPa compared to Thumsorn et al. [3], who obtained a tensile strength of 10 ± 5 MPa. This may be due to several factors such as i) the source of obtaining the PET, ii) the post-collection treatment of the PET, iii) the extrusion process that can take place in a single crew, co-rotating or counter-rotating (twin-screw extruder)[32,35].

Table 1. *Mechanical properties of representative R-PET without additives*

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
			Tensile strength	ASTM D-638 at cross-head speed of 20 mm/min	Tensile testing	60 MPa	[34]
			Tensile modulus			2.8 GPa	[34]
			Flexural strength	ASTM D-790 with span length of 48mm and testing speed of 3mm/min	Flexural test	70 MPa	[34]
			Flexural modulus			2.3 GPa	[34]
			Tensile strength	ASTM-D-638-02	Tensile testing	10 ± 5 MPa	[3]
			Elongation			2.5 %	[3]
			Tensile Modulus			1500 ± 50 MPa	[3]
R-PET	None	100/0	Tensile strength	ASTM D 638	Tensile testing	460 ± 94 MPa	[36]
			strain at break			49.2 ± 1.05 MPa	[36]
			Tensile modulus			5451 ± 69 MPa	[36]
			Impact resistance	ASTM D638-10	Tensile testing	8.1 KJ/m^2	[37]
			Toughness			12.8 MJ/m^3	[37]
			Tenside modulus	ISO 527 standard 10kN at 50 mm/min	Tensile testing	3461 ± 81.8 MPa	[38]
			strain at break			1.8 ± 0.1 %	[38]
			Tensile strength			40 ± 3.3 MPa	[38]

Property	Standard	Test	Value	Ref
Tensile strength	ASTM D638-10 crosshead speed of 5 mm/min	Tensile testing	35 ± 3 Mpa	[39]
Tensile modulus	ISO 527-1:2012	Tensile testing	600.3 ± 19.1 MPa	[40]
Tensile strength			56.8 ± 0.8 MPa	[40]
Elongation at break			494.6 ± 9.7 %	[40]
Charpy Impact strength	ISO 179-1:2010	Charpy Impact	2.87 ± 0.42 KJ/m^2	[40]

In all cases, a decrease of intrinsic viscosity is reported, such as the data reported by Oromiehie et al.[29], who dated a decrease of intrinsic viscosity of 23.81%. This decrease is related with molecular weight as shown in the next formula [41]

$$n_{sp,i} = K_m C_i M_i^a$$

Where K_m is the Mark-Houwink-Sakurada coefficient, a is a variable usually in the range between 0.5-1, C_i and M_i are the concentration and the molecular weight, respectively, of i the component. As it can be seen, molecular weight affects directly proportional intrinsic viscosity of a blend. It means if molecular weight decreases, then intrinsic viscosity will as well. This decrease allows the presence of carboxylic acids, and in such a way, a greater cleavage of PET chains can occur. According to Oromiehie et al.[29], this cleavage decreases the molecular weight in a 30.61% contrasting molecular weight of V-PET with R-PET. This fact eventually promoted a decrease in mechanical properties such as Tensile Modulus and Flexural strength, as shown in *Table 1*.

On the other hand, the degree of crystallinity varies depending on several factors like chain entanglements and branching. Such is the case of Kiliç et al.[42], who used R-PET flakes provided by SASA Plyester San. A.Ş., Company of Turkey as matrix for being blended with organoclay nanocomposite fibres in order to analyze morphological, thermal, surface and mechanical properties. They reported a crystallinity value for R-PET of 3.53%. This value is contrary to the exposure by Torres et al.[35] who used post-consumer PET bottles and V-PET resins to study the thermal an mechanical properties of V-PET and R-PET. They reported a loss of crystallinity of 33% (from 46% to 31%) which was related with the structure of V-PET (isotropic character) versus R-PET (Anisotropic character). Han et al.[43] studied and characterized V-PET and R-PET fibers. They reported an increase in crystallinity of 59.84% (from 26.57% to 42.47%) which was related with a bigger intermolecular force because of the presence of dome kinds of polymers with high mechanical properties such PC, PEN, among others. *Table 2* presents thermal values of R-PET with no presence of additives, recovered from different researches at different test conditions.

Table 2. *Thermal properties of representative R-PET without additives*

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
R-PET	None	100/0	Thermal degradation 5%	None	Thermal degradation temperature	399.3 °C	[34]
			Thermal degradation 50%			436.8 °C	[34]
			Descomposition activation energy			262.2 KJ/mol	[34]
			Glass transition temperature	Specimens of 4 to 5 mg were placed in aluminium sample pans and heated from -10°C to 280°C at a 10 °C/min	DSC	81.5 °C	[3]
			Melting point			245.9 °C	[3]
			Melting Enthalpy			41.2 J/g	[3]
			Cristalinity degree			34.3 %	[3]
			Thermal degradation 10%	None	Thermal degradation temperature	409.1 °C	[3]
			Thermal degradation 20%			425.2 °C	[3]
			Thermal degradation 10%			420 °C	[44]
			Thermal degradation 20%			429 °C	[44]
			Glass transition temperature	Heating from 25 °C to 300 °C at a rate of 5 °C/min	DSC	68.43 °C	[37]
			Melting point			256.03 °C	[37]
			cristalization temperature			117.89 °C	[37]
			Melting Enthalpy			47.74 J/g	[37]
			Cristalinity degree			100.47 %	[37]
			Melt flow index	ASTM D1238	MFI	89.3 ±12.3 mm/10min	[38]

Property	Conditions	Technique	Value	Ref
Crystallization temperature	Samples heated from 30 °C to 300 °C at a rate of 10 °C/min under nitrogen atmosphere	DSC	204 °C	[38]
Glass transition temperature			78.9 °C	[38]
Melting point			251 °C	[38]
Melting Enthalpy			36.6 J/g	[38]
Cristalinity degree			30.5 %	[38]
Onset temperature	None	TGA	432 °C	[38]
Thermal degradation 50%			453 °C	[38]
Endset temperature			470 °C	[38]
Glass transition temperature	samples were heated from 25°C to 300°C with a heating rate of 10°C/min	DSC	73 °C	[39]
Melting point			250.7 °C	[39]
Melting Enthalpy			35.2 J/g	[39]
Cristalinity degree			26.1 %	[39]
Glass transition temperature	sample was nearly 5 mg and the thermal cycle for the determination of the crystallinity was a temperature ramp from 20 until 280 °C with 10 °C/min heating rate.	DSC	75.7 °C	[13]
Crystallization temperature			127.7 °C	[13]
Melting point			250.7 °C	[13]
Melting Enthalpy			55.4 J/g	[13]
Glass transition temperature	samples of 6.1 ± 1.2 mg were heated from 30 to 280 °C with a speed of 10 °C /min	DSC	82.0 ±0.7 °C	[40]
Cold crystallization temperature			150.8± 0.4 °C	[40]
Melting point			244.9 ± 0.9 °C	[40]
Crystallinity degree			10.6 ± 0.5 %	[40]
Thermal degradation 5% (air)		TGA	405.4 ± 0.2 °C	[40]

Property	Conditions	Technique	Value	Ref
Residual mass at 700 °C (air)	5-7 mg heated from 30-700 °C. Speed 20 °C /min		1.26 ± 0.04 %	[40]
Glass transition temperature	Samples in a nitrogen atmosphere heated from 20 to 350 °C with a speed of 10 °C /min	DSC	79.94 °C	[42]
Crystallization temperature			212.33 °C	[42]
Melting point			241.21 °C	[42]
Melting Enthalpy			28.11 KJ/kg	[42]
Crystallinity degree			3.53%	[42]
Decomposition temperature	samples heated up to 900 °C under N_2 flow with a speed of 10 °C /min	TGA	375.35 °C	[42]
Thermal degradation 5% (N2)			311.39 °C	[42]
Thermal degradation 50% (N2)			355.34 °C	[42]
Melting point	Analysed under nitrogen atmosphere according to the ASTM D3418. Heated from 0 to 270 °C with a rate of 10 °C /min	DSC	244 °C	[45]
Melting Enthalpy			40 J/g	[45]
Crystallization temperature			165 °C	[45]
Crystallinity degree			29%	[45]
glass transition temperature	Heated from room temperature to 270 °C with a rate of 10 °C /min	DSC	72.9 ± 1.2 °C	[46]
Crystallization temperature			133.5 ± 0.1 °C	[46]
Melting point			253.4 ± 0.4 °C	[46]
Crystallinity degree			11.8 ± 1.8 %	[46]
Thermal degradation 5% (N2)	5 mg heated from 23 to 700 °C at 10 °C /min	TGA	382.3 ± 1.4 °C	[46]
Thermal degradation 5% (air)			370.1 ± 1 °C	[46]
Glass transition temperature		DSC	67 °C	[47]

Crystallization temperature	Heated from room temperature until 300 °C at 10°C /min		208 °C	[47]
Melting point			234 °C	[47]
Melting Enthalpy			38.3 J/g	[47]
Thermal degradation 50% (air)	Samples heated from room temperature until 700 C at 10 °C /min	TGA	428 °C	[47]
Weight loss at 420 °C			14%	[47]
Weight percentage residue at 650 °C			0.41%	[47]

In the research made by Jiang et al. can be noticed thermal differences between virgin and R-PET. They used R-PET obtained from Thailand postconsumer waste bottles, and it was blended with PBAT and Wollastonite. From this investigation was recovered *Figure 6* that shows DSC thermograms of R-PET and V-PET.

Figure 6. DSC thermograms of neat recycled (PET-R) and neat virgin PET(PET-V) (Recovered from Kráčalík et al.[48])

Figure 6 shows the difference in the thermal transitions of V-PET and R-PET; The Tg of the R-PET is 3.7 °C lower than the V-PET; this difference could be originated in the molecular weight reduction due to the recycling process. After Tg, it is possible to observe a cold crystallization process; this is expected behavior for polyesters, especially for PET. This phenomenon occurs when the sample does not have the necessary time to crystallize during cooling; when the sample is heated above its Tg amorphous PET fraction gain enough energy to move and arrange in a well-organized structure. In this transition, R-PET shows a reduction of 3.2 °C; this reflects the higher mobility of the R-PET chains compared to the V-PET ones. The last signal is the melting process; in this case, there is no difference in the melting point; in general, the changes in the melting point occurs when the degradation is advanced, and the reduction in molecular weight is dramatic, this result indicates that the recycling process affects the molecular weight, but not enough to produce changes in the melting temperature.

3.2.   PET blendings

In the last section, the thermal and mechanical properties changes after the recycling of PET were evident. During the use of PET, it is known that it is contaminated with some chemicals that can reduce the load capacity of the recycled products, induce fracture, decrease their molar mass and viscosity, and limit the use of R-PET [49]. That is why the blending of polymers during extrusion has been accepted and studied as a tool to produce new materials with properties similar to V-PET or better [50].

When R-PET is blended with other polymers, two main trends are observed:

- Increase Hardness. This option involves the blending of R-PET with a more rigid material, increase the PET crystallinity, or both.

- Reduce Hardness. This trend focuses on adding a second material with plasticizing properties, originating a new material with less rigidity than R-PET.

Table 3 summarized the mechanical properties reported for the blends of R-PET. It is possible to find these tendencies in this table.

Table 3. Mechanical properties of representative R-PET blended with several polymers

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
R-PET	V-PET	50/50	Tensile strength	ISO 527-2 type 1B	Tensile testing	74±3 MPa	[6]
			Young modulus			1081 MPa	[6]
			Cristalinity degree			28.8 %	[6]
			Deformation at break point			28.3 ±0.1 %	[6]
			Deformation			11.6±0.1 %	[6]
	PBT	75/25	Storage modulus (30 °C)			1900± 10MPa	[51]
			Tensile strength	ASTM D638 M-9	Tensile testing	55±5 MPa	[51]
			Young modulus			2200 MPa	[51]
			strain at break			375 ± 75 %	[51]
			Impact strength	ISO 180 standard	Izod impact	3.75± 0.25 KJ/m^2	[51]
	PC	50/50	Tensile modulus	ASTM D638	Tensile testing	3 GPa	[52]
			Yield strenght			2.3 GPa	[52]
			Impact strength	ASTM D256	Izod impact test	1.9 ± 0.1 KJ/m^2	[52]
			Fracture toughness	ASTM D 5045	Fracture toughness	2.3 ± 0.1 MPa/m^2	[52]

Material	Ratio	Property	Standard	Test method	Value	Ref
SEBS (Styrene-ethylene-butadyene-styrene copolymer)	50/50	Tensile strength	ASTM D638 with strain rate of 5 mm/min	Tensile testing	8.63 MPa	[50]
PBAT	80/20	Tenside modulus	ISO 527 estándar 10kN at 50 mm/min	Tensile testing	2494.1± 74.7 MPa	[38]
		strain at break			2.7 ± 0.1 %	[38]
		Tensile strength			44.2 ± 2 MPa	[38]
PEN (poly(ethylene 2,6-naphthalate)	70/30	Tensile strength	ASTM D638-10 crosshead speed of 5 mm/min	Tensile testing	57.5 ± 3 MPa	[39]
		Elogation at break			300%	[39]
		Izod impact strength	ISO 180 standard	Izod impact test	25 KJ/m^2	[39]
Polypropylene (PP)	50/50	Elastic modulus	ASTM D638 standard	Tensile testing	1697 MPa	[53]
		Yield stresses			31.69 MPa	[53]
		Charpy Impact strength	ISO 179 standard	Charpy Impact	10.54 J/cm^2	[53]
Bio-PET (Obtained from nautural sources)		Tenside modulus	ISO 527-1:2012		820.5 ± 30.2 MPa	[40]
		Tensile strength			57.7 ± 2.8 MPa	[40]
		Elongation at break		Tensile testing	10.8 ±1.4 %	[40]
	45/55	Charpy Impact strength	ISO 179-1:2010	Charpy Impact	1.84 ± 0.38 KJ/m^2	[40]
Fly ash, red mud, silica fume, sand	35/6/25/16/28	Compressive strength	ASTM C39	Compressive testing	109.62 MPa	[54]

Polymers with opposite properties to R-PET are typically used to reduce the R-PET rigidity, with a high strain at break and low tensile modulus. When these polymers are used, a decrease in tensile modulus is experienced as the dispersed phase amount is added. *Figure 7* shows Tensile strength in R-PET/PC and R-PET/PBAT samples. As it can be seen, blendings with PBAT reduce their tensile strength which is attributed to the high flexibility and low tensile modulus of the dispersed phase, which causes a reduction in the stiffness of the blends. However, in R-PET/PC blendings a tensile strength increase can be experienced according the amount of PC that is added to the samples; it is due to an increase in the crystallinity degree of R-PET that reduces the chain mobility of polymers because of the presence of a polymer, in this case PC, with hardness properties[40].

Figure 7. Tensile strength versus second component content, for R-PET/PC and R-PET/PBAT blends (Adapted from Jiang et al. and Negoro et al.[38,52])

Figure 7 shows the main tendencies on tensile strength for the blends based on R-PET. The blends with a more rigid polymer, as PC, tents to increase the tensile strength when the amount of PC increases; that is to say, this material is designed to harden the R-PET. On the other hand, a softer polymer, like PBAT, produces a decrease in tensile strength with the increase of the softer component; in this case, the idea of this blend is to get a material more flexible than PET. Jiang et al.[38] studied the R-PET blended with

poly(butylene adipate-co-terephthalate) (PBAT). ***Figure 8*** shows the SEM images of the blends.

Figure 8. *Representative SEM micrographs (x1500 magnification) of the (a) R- PET, (b) neat PBAT, (d) R-PET/PBAT blend at 80/20 wt%, (g) d) R-PET/PBAT blend at 50/50 wt% (Adapted from Jiang et al.[38])*

These images show a continuous phase; that is to say, the polymers are miscible. Also, it is possible to observe an increase in the deformed zone, indicating an increase in the ductility of the blends when the PBAT is increasing. They found decay in tensile modulus was shown, from 2854 MPa at 10 wt% PBAT down to 981 MPa at 50 wt% PBAT, due to the high flexibility of PBAT, which was confirmed later with DSC analysis. However, the strain at break increased from 1.8% to 5% due to an increase in R-PET crystallinity.

As already mentioned, the polymer blend is used to obtain a new material with higher performance due to the balance between mechanical resistance and thermal properties. The critical factor for correct blendings is the compatibility and interaction between polymer phases[52],[53]. Moreover, when R-PET is being extruded in the extrusion cycle at melting temperatures, the polymer can undergo a degradation process through hydrolysis, oxidation, and transesterification reactions. These reactions lead to the cleavage of the chains into smaller ones with acid and hydroxyl ester end groups generating contamination in the material and drastic losses in ductility[6]. These facts can affect thermal properties, presented in Table 4, and show the result of blending R-PET with other polymers.

Table 4. *Thermal properties of representative R-PET blended with several polymers*

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
			Crystallization temperature	Samples heated from 30 °C to 300 °C at a rate of 10 °C /min under nitrogen atmosphere	DSC	195.8 °C	[38]
			Melting point			245.8 °C	[38]
			Melting Enthalpy			43.6 J/g	[38]
			Crystallinity degree			45.40 %	[38]
			Onset temperature	None	TGA	412 °C	[38]
			Thermal degradation 50%			445 °C	[38]
			Endset temperature			467 °C	[38]
	PEN (poly(ethylene 2,6-naphthalate)	70/30	Glass transition temperature	samples were heated from 25°C to 300°C with a heating rate of 10°C/min	DSC	87.9 °C	[39]
			Melting point			247.5 °C	[39]
			Melting Enthalpy			29.6 J/g	[39]
			Crystallinity degree			7.30%	[39]
	Polypropylene (PP)	95/5	Melting point	Samples were heated from 50 °C to 300 °C with a speed of 10 °C/min. It was kept above 300 °C for 2 minutes to complete the melting	DSC	254 °C	[55]
			Crystallization temperature			207 ± 1 °C	[55]
			Crystallinity degree			25%	[55]
	Bio-PET (Obtained from nautural sources)	45/55	Glass transition temperature	samples of 6.1 +- 1.2 mg were heated from 30 to 280 °C with a speed of 10 °C/min	DSC	82.6 ± 0.9 °C	[40]
			Melting point			237.9 ± 1 °C	[40]
			Crystallization temperature			191.2 ± 0.3 °C	[40]

		Crystallinity degree			37.0 ± 0.7 %	[40]
		Thermal degradation 5% (air)	5-7 mg heated from 30-700 °C. Speed 20 °C/min	TGA	393 ± 0.2 °C	[40]
		Residual mass at 700 °C (air)			2.18 ± 0.05 %	[40]
		Melting point	Less 3mg in Al pan heated from room temp. to 200 °C at 10 °C/min	DSC	133 °C	[56]
PE	50/50	Start degradation temperature	3mg from room temperature to 600 °C under N_2 with a flow rate of 50 ml/min and a rate of 10°C /min	TGA	370 °C	[56]
		End degradation temperature			460 °C	[56]
		Weight loss			83.60%	[56]
		Residue after 500 °C			10.50%	[56]
Fly ash, red mud, silica fume, sand	35/6/25/16/28	Absoption 7 days	Specimens sumerged in 30% HCl solution for several days	Acid resistance	0.105%	[54]
		Absoption 28 days			0.06%	[54]
		Absoption 56 days			0.047 %	[54]
		Weight of specimen before inm.			345.35 g	[54]
		Weight of specimen 7 days			345.17 g	[54]
		Weight of speciment 21 days			344.71 g	[54]
		Weight of speciment 28 days			344.05 g	[54]

The values of the thermal transitions and thermal stability presented in Table 4 are dispersed; there is no clear tendency with the addition of a second phase, the difference in the origin of the R-PET and the nature of the second phase will determine the final properties.

However, the miscibility of a sample could be estimated by determining Tg. When two components are miscible, there is an increasing trend according to the dispersed phase added [57],[53]. This Tg of the new blend can be predicted using Fox equation to obtain an estimated value for Tg that would be confirmed experimentally. If the result of this experimentations are not close with the Fox prediction, or two Tg are observed, then the blend could be considered inmiscible[58].

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Negoro et al.[52], reported two Tgs for the PC/PET blends; these values were similar to the Tg of each neat polymer, indicating that the blends were immiscible; however, they observed a deviation of Tg with the composition, which indicates a possible interaction between phases.

The presence of two phases was proved employing SEM (see *Figure 9*), in all the figures is possible to observe isolated spheres in a continuous matrix; in the case of *Figure9A* and *B* is possible to observe both spherical particles and holes, indicating a lack of interaction between the phases, however in *Figure 9C* and *D* the spheres was incomplete indicating a stronger interaction between the disperse phase (R-PET) and the matrix (PC)

Figure 9. *SEM photograpghs of R-PET/PC blends. (A) R-PET/PC (90/10), (B) R- PET/PC (70/30), (C) R- PET/PC (50/50), (D) R-PET/PC (30/70) (Recovered from Negoro et al.[52])*

As was discussed previously, the blends PET/PBAT are miscible, as was proven with the SEM image (See ***Figure 8***), where a continuous phase can be experimented due to good miscibility between PET and PBAT. ***Table 5,*** shows Tg values for R-PET/PBAT and R-PET/PBAT/Wollastonite samples at different compositions.

Table 5. *Tg values of R-PET/PBAT/Wollastonite samples at different compositios from DSC analysis (Recovered from Jiang et al.)*

Samples (R-PET/PBAT/Wollastonite)	Tg (°C)
100/0/0	80.3
90/10/0	68.1
80/20/0	69.6
70/30/0	70.7
60/40/0	92.1
50/50/0	92.1
72/18/10	70.6
64/16/20	73.1
56/14/30	74.0
48/12/40	74.2

Tg of R-PET was 80.3 °C and the inclusion of 10-30 wt% PBAT in R-PET matrix reduced the Tg of the samples by 9.6 to 12.2 °C compared with pure R-PET. This data suggest that low Tg values is due to PBAT (-31 °C) that increased chain mobility of the blends.

However, Tg increased according PBAT compositions increased in the blendings, owing to the increased chain entanglement that restricted the mobility of R-PET and it proves the high miscibility between the components of the samples.

3.3. Chain Extenders and Compatibilizers

A chain extender is a compound with a low molecular weight that is effective even in small quantities and can react with terminal groups of polyesters, interconnect polymer chains, increase molecular weight, and minimize the adverse effect of contaminants[39][30]. It is important to notice that chain extenders do not prevent degradation but compensate for its effect on the molar mass of the polymer[30]. Chain extenders can be introduced as an alternative method for improving the miscibility of blendings with transesterification reactions[39]. It rejoins polymer chain segments, compensates the molar mass reduction due to degradation [30]. Modifying the miscibility of blends and increasing molecular weight can provide new mechanical properties summarized in *Table 5* This table shows data collected from Tensile, Flexural, Compressive testing, and Charpy Impact of blending with chain extenders.

Table 6. Mechanical properties of representative R-PET blended with several polymers and chain extenders

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
R-PET	Ammonium polyphosphate, Talc	93/2/5	Tensile strength	ASTM D-638 at cross-head speed of 20 mm/min	Tensile testing	51 MPa	[34]
			Tensile modulus			3.4 GPa	[34]
			Flexural strength	ASTM D-790 with span length of 48mm and testing speed of 3mm/min	Flexural test	81 MPa	[34]
			Flexural modulus			3.1 GPa	[34]
	Polycarbonate, Joncryl ADR4370	68/30/2	Tensile strength	ASTM-D-638-02	Tensile testing	55 ± 5 MPa	[3]
			Elongation			45 ± 5 %	[3]
			Tensile Modulus			2100 ± 50 MPa	[3]
	Joncryl ADR 4300, Lotader AX8900	96.5/1/2.5	Impact resistance	ASTM D638-10	Tensile testing	14.6 KJ/m^2	[37]
			Toughness			13.1 MJ/m^3	[37]
	PBAT, Wollastonite	48/12/40	Tenside modulus	ISO 527 estándar 10kN at 50 mm/min	Tensile testing	5576.7 ± 69 Mpa	[38]
			strain at break			1.7±0.1 %	[38]
			Tensile strength			46.6 ± 2.1 MPa	[38]
	Polypropylene (PP), PP-g-MA (Maleic anhydride)		Elastic modulus	ASTM D638 standard	Tensile testing	1753 MPa	[53]
			Yield stresses			31.91 MPa	[53]
		50/48/2	Charpy Impact strength	ISO 179 standard	Charpy Impact	10.98 J/cm^2	[53]

According to **Table 6**, the tensile strength values for these studies were more or less similar; in this case, this value was around 50 MPa. However, the tensile module was affected by the nature of the other components in the blend. The Young´s module is less sensitive to the molecular weight and the interaction between the components; however, the nature of the components highly affects the value. The property that should be more influenced by the interaction between the phases and the molecular weight is the strain at break. However, there is not enough published data to confirm this as a general trend for R-PET blends.

The influence of the chain extenders in the breaking point was demonstrated by Srithep et al.[3] , who used 1% and 2% of chain extender (Joncryl ADR 4370) in R-PET/PC blends with a ratio of 70/30 wt%, respectively. R-PET at the starting point registered a tensile strength value of 10 MPa and, with the addition of 30 wt% PC, it value increased to 17 MPa. These values increased to 39 and 55 MPa for 1% and 2% of chain extender, representing, in contrast with initial blend value, an increase of 229,41% and 323,52%, respectively.

On the other hand, Jiang et al.[38] used Wollastonite as the third component in a blend of R-PET/PBAT to improve the mechanical properties. This improvement was related to the large aspect ratio of Wollastonite which tended to orient in the machine direction during the molding process. For ratios between 0 and 30% by weight, as shown in **Figure 10** by SEM, the Wollastonite dispersed to provide a large contact area that incurred good adhesion of the dispersed phase and the matrix, then the Wollastonite acts as a compatibilizaer in these blends However, for amounts greater than 30% by weight of Wollastonite, the tensile strength decreased due to agglomeration of Wollastonite.

Figure 10. SEM micrographs (x1500 magnification) of the 80/20 wt% R-PET/PBAT blend composites filled with wollastonite at (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 40 wt% (Adapted from Jiang et al.[38])

It is concluded that the rigid particles of Wollastonite restricted the molecular movement of the matrix. However, at higher contents of Wollastonite, the melting flow index increased gradually due to the agglomeration of particles that led to a smaller contact area and facilitated the movement of the polymer chain. Also, Wollastonite induced a carbon residue at high temperature of the compounds, which indicates higher thermal stability of the compounds[59,60] .

Table 7 shows thermal properties of blendings with chain extenders such as Joncryl ADR4370, among others; and the values obtained from different research experiments at different conditions.

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Table 7. *Thermal properties of representative R-PET blended with several polymers and chain extenders*

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
R-PET	2, 4, 6, 8-tetra (2, 3-epoxypropoxy) propane	99/1	Specific viscosity	tetrachloroethane and phenol (the mass ratio was 1:1) at 25 °C using Ubbelodhe viscometer	Dynamic frecuency	0.365	[61]
			Intrinsic viscosity			0.655	[61]
			Viscosity-average molecular weight			18310	[61]
			Glass transition temperature	tests were made at 280 °C at a constant strain amplitude (10% strain) under a nitrogen gas purge	Dynamic mechanical analysis	106 °C	[61]
	Polycarbonate, Joncryl ADR4370	68/30/2	Glass transition temperature	Specimens of 4 to 5 mg were placed in aluminium sample pans and heated from -10°C to 280°C at a 10 degC/min rat	DSC	88.9 °C	[3]
			Melting point			224.1 °C	[3]
			Melting Enthalpy			17.4 J/g	[3]
			Cristalinity degree			21.3 %	[3]
			Thermal degradation 10%	None	Thermal degradation temperature	404.1 °C	[3]
			Thermal degradation 20%			432.9 °C	[3]
	Joncryl ADR 4300, Lotader AX8900	96.5/1/2.5	Glass transition temperature	Heating from 25°C to 300 °C at a rate of 5 °C/min	DSC	68.94 °C	[37]
			Melting point			255.47 °C	[37]
			cristalization temperature			116.33 °C	[37]
			Melting Enthalpy			49.24 J/g	[37]
			Cristalinity degree			100%	[37]

			Melt flow index	ASTM D1238	MFI	87.8 ± 6.3 mm /10min	[38]
PBAT, Wollastonite	48/12/40		Crystallization temperature	Samples heated from 30 ℃ to 300 ℃ at a rate of 10 ℃/min under nitrogen atmosphere	DSC	198.4 ℃	[38]
			Melting point			245.4 ℃	[38]
			Melting Enthalpy			17.3 J/g	[38]
			Cristalinity degree			30%	[38]
			Onset temperature	None	TGA	416 ℃	[38]
			Thermal degradation 50%			480 ℃	[38]
			Endset temperature			473 ℃	[38]

During degradation of PET, some carboxyl groups are generated, which can be confirmed by FTIR spectra[61]. Wang et al.[62], used 2, 4, 6, 8-tetra (2, 3-epoxypropoxy) propane as chain extender and was blended with different amounts of chain extender; 0.1%, 0.5%, 1.0%, and 2.0% by weight and such a way samples were reported as PET-0, PET-1, PET-2, PET-3 and PET-4. This research showed, in *Figure 11,* vibrancies at 1340 and 1410 cm^{-1} for PET-4 which peaks are characteristics for -OH of ending carboxyl groups and, were lower than PET-0. A vibration at 1240 cm^{-1} of PET-0 is observed and is assigned to bending vibration of end -OH groups became stronger and two shoulder peaks at 1 260 and 1 280 cm-1 were observed.

Figure 11. FTIR absorption spectra of unmodified PET-0 and highly modified PET-4 normalized on the peak of C=O stretching vibration (1720 cm^{-1}) (Recovered from Wang et al. [62])

The presence of these end groups can undoubtedly modify the thermal properties of the blends. Such is the case of the research reported by Jian et al. [38], who used various blending compositions of R-PET/PBAT and whose results showed a reduction in Tg between approximately 9.6–12.2 °C. The presence of Wollastonite increases Tg in 3.5 °C compared to the initial blending of 80/20 wt% R-PET/PBAT. This increase is due Wollastonite addition in the blending. However, it is important to note that the addition of a chain extender does not ensure the improvement of the mechanical nor thermal properties of the blends. Such is the case reported by Karsli et al.[37] who used Joncryl and Lotader as components shown in *Table8.*

Table 8. Compounding of components and code names of products (Recovered from Karsli et al.[37])

R-PET/Joncryl/Lotader	R-PET (wt%)	Joncryl (wt%)	Lotader (wt%)
R-PET	100	0	0
R-PET_1J	99	1	0
R-PET_1J_2.5L	96.5	1	2.5
R-PET_1J_5L	94	1	5

They reported that the presence of Joncryl and Lotader either separately or together does not contribute to the increase in the glass transition temperature or in the other properties, but on the contrary, it decreased the crystallinity of R-PET as shown in **Table 9.**

Table 9. DSC analysis results of samples reported by Karsli et al.37 (Recovered from Karsli et al.[37])

Sample code	T_g (°C)	T_c (°C)	T_m(°C)	ΔH(J/g)	Xc (%)
R-PET	68.94	116.33	255.47	49.24	100
R-PET_1J	68.43	117.76	256.03	45.78	93.91
R-PET_1J_2.5L	68.43	117.89	253.41	47.74	100.47
R-PET_1J_5L	68.94	113.87	254.50	41.61	89.90

This result is based on the chain entanglement of R-PET and it is due to the high degree of branching which may resulted from high amount of Lotader impact modifier.

3.4. Filler Nano-particles

The introduction of organic and inorganic nanofillers in polymeric matrices provides the opportunity to improve the mechanical and thermal properties of the polymer matrix. These nanoparticles are characterized by having a large aspect ratio (between 100 to 1500) and a large surface area (between 750 and 800 m^2/ g)[42]. Nanofillers provide the polymeric matrix with mechanical resistance, optical clarity, electrical, thermal, chemical, and UV resistance, gas barrier properties, and dimensional stability[42,47] like the table presented below. **Table 10** can be shown how filler nanoparticles can change thermal properties depending on the additive is being blended.

Table 10. Thermal properties of representative R-PET blended with several filler nanoparticles

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
PET	Cloisite 10A	95/5	Glass transition temperature			78.41 °C	42
			Crystallization temperature	Samples in a nitrogen atmosphere heated from 20 to 350 °C with a speed of 10 °C/min	DSC	206.61 °C	42
			Melting point			245.29 °C	42
			Melting Enthalpy			8.19 kJ/kg	42
			Crystallinity degree			0.94%	42
			Decomposition temperature			436.12 °C	42
			Thermal degradation 5% (N_2)	samples heated up to 900 °C under N_2) flow with a speed of 10 °C/min	TGA	402.06 °C	42
			Thermal degradation 50% (N_2))			447.10 °C	42
	Cloisite 15A	95/5	Glass transition temperature	Samples in a nitrogen atmosphere heated from 20 °C to 350 °C with a speed of 10 °C/min	DSC	82.70 °C	42
			Crystallization temperature			208.66 °C	42
			Melting point			242.62 °C	42
			Melting Enthalpy			4.24 kJ/kg	42
			Crystallinity degree			2.51%	42
			Decomposition temperature		TGA	398.12 °C	42

		Thermal degradation 5% (N_2)	samples heated up to 900 °C under N_2 flow with a speed of 10 °C/min		423.17 °C [42]
		Thermal degradation 50% (N_2)			(not reached) [42]
Cloisite 15A	93/7	Glass transition temperature	Heated from room temperature until 300 °C at 10°C/min	DSC	74 °C [47]
		Crystallization temperature			203 °C [47]
		Melting point			238 °C [47]
		Melting Enthalpy			39.1 J/g [47]
		Thermal degradation 50% (air)	Samples heated from room temperature until 700 °C at 10 °C/min	TGA	432°C [47]
		Weight loss at 420 °C			16.10% [47]
		Weight percentage residue at 650 °C			4.10% [47]
Cloisite 20A	95/5	Glass transition temperature	Samples in a nitrogen atmosphere heated from 20 °C to 350 °C with a speed of 10 °C/min	DSC	76.28 °C [42]
		Crystallization temperature			209 °C [42]
		Melting point			245.41 °C [42]
		Melting Enthalpy			1.95 kJ/kg [42]
		Crystallinity degree			0.44% [42]
		Decomposition temperature	samples heated up to 900 °C under N_2 flow with a speed of 10 °C/min	TGA	388.59 °C [42]
		Thermal degradation 5% (N_2)			408.89 °C [42]
		Thermal degradation 50% (N_2)			635.51 °C [42]
Cloisite 30B	95/5	Glass transition temperature	Samples in a nitrogen atmosphere heated from 20 to	DSC	77.09 °C [42]
		Crystallization temperature			207.63 °C [42]

		Property	Conditions	Technique	Value	Ref
		Melting point	350 °C with a speed of 10 °C/min		246.19 °C	[42]
		Melting Enthalpy			1.59 kJ/kg	[42]
		Crystallinity degree			1.57%	[42]
		Decomposition temperature	samples heated up to 900 °C under N_2 flow with a speed of 10 °C/min	TGA	388.46 °C	[42]
		Thermal degradation 5% (N_2)			395.34 °C	[42]
		Thermal degradation 50% (N_2)			444.24 °C	[42]
		glass transition temperature	Heated from room temperature to 270 °C with a rate of 10 °C/min	DSC	73.8 ± 0.1 °C	[46]
		Crystallization temperature			119.1 ± 0.5 °C	[46]
Graphite	90/10	Melting point			253.5 ± 1.7 °C	[46]
		Crystallinity degree			15.8 ± 2 %	[46]
		Thermal degradation 5% (N_2)	5 mg heated from 23 to 700 °C at 10 °C/min	TGA	386.7 ± 3 °C	[46]
		Thermal degradation 5% (air)			372.7 ± 2.6 °C	[46]

These compounds enhance the mechanical interlocking and bridging effects within the components to interrupt crack propagation, taking into account the amount of nanofillers added. [42]. Despite all the benefits that these compounds present, preferably clays, layered silicates must be taken into account due to their hydrophilic nature. As a result, these nanofillers are less compatible with the PET matrix, generating weak chemical interactions between the clay and the polymer[47].

These nanofillers increased the maximum achievable stretch ratio, leading to a higher molecular orientation and chain extension, subsequently increasing the tensile modulus and tensile strength. On the other hand, thermal stability is also improved since nanocomposites hinder the diffusion of volatiles particles and help carbon formation after thermal decomposition. This slowdown is due to the labyrinth effect of the silicate layers. In the research developed by Kiliç et al.[42] different nanocalys types (Cloisite 10A, Cloisite 15A, Cloisite 20A, Cloisite 30B) were added in R-PET matrices, and their properties were analyzed. From the DSC analysis, as shown in *Figure 12,* the addition of nanoclays decreased the Tg between 1-3 °C for the samples with Cloisite 10A, Cloisite 20A, Cloisite 30B. However, it was observed an increase of 2 °C in the sample with Cloisite 15A. On the other hand, the melting temperature increased in a range of 1-5 °C while the cold crystallization temperature decreased 1-5 °C[42].

Figure 12. *DSC curves of R-PET and clay based R-PET nanocomposite samples (Recovered from Kiliç et al.[42])*

TGA thermogram analysis was also performed and summarized in ***Table 11***. Results showed that the loss of mass increased in the nanocomposites containing organoclay except for the compounds with Cloisite 10A and 20A. Also, it was found that the decomposition temperature is higher in the blend with Cloisite 10A in contrast with Cloisite 30B, a phenomenon associated with greater water retention in Cloisite 30B. Therefore, as the dispersion of the organic clay layers increases, the thermal properties of the samples change and the decomposition temperatures decrease and the mass loss increases[42].

Table 11. *Thermogravimetric decomposition characteristics of R-PET and clay based R-PET nanocomposite samples (Recovered from Kiliç et al.[42])*

Sample	$T_{d\,onset}$ (°C)	Remaining (wt%)	5% Mass loss (°C)	50% Mass loss (°C)
rPET1 [a]	375.35	39.97	311.39	355.34
rPET1 [b]	478.46			
rPET1 + 10A[a]	436.12	24.4	402.06	447.10
rPET1 + 10A[b]	466.55			
rPET1 + 15A	398.12	70.6	423.17	
rPET1 + 20A	388.59	49.2	408.89	635.51
rPET1 + 30B[a]	388.46	1.6	395.34	444.24
rPET1 + 30B[b]	409.53			

a First degradation

b Secondary degradation

On the other hand, and like it was discussed and the beginning of the present section. Filler nano-particles modify mechanical properties. This variation is presented in *Table 12,* where can be seen changes in mechanical properties according to the amount and type of filler nanoparticle is being blended.

Table 12. *Mechanical properties of representative R-PET blended with several filler nanoparticles*

Matrix	Additive	Composition matrix/additive	Property	ISO/ASTM	Test method	Value (unit)	Reference
R-PET	Cloisite 25 A	99/1 %wt	Tensile Modulus	ASTM D638	Tensile testing	2800 MPa	[63]
			Yield Strength			30 MPa	[63]
			Strain at yield			5%	[63]
		99/3 %wt	Tensile Modulus			3000 MPa	[63]
			Yield Strength			20 MPa	[63]
			Strain at yield			3%	[63]
		99/5 %wt	Tensile Modulus			3600 MPa	[63]
			Yield Strength			40 MPa	[63]
			Strain at yield			1%	[63]
	Montmorillonite (MMT)	99/1 %wt	Young´s Modulus	ASTM D638	Tensile testing	2.5 ± 0.4 GPa	[64]
			Yield Strength			21.8 ± 7.5 MPa	[64]
		99/3 %wt	Young's Modulus			2.4 ± GPa	[64]
			Yield Strength			35.4 ± 13.1 MPa	[64]
		99/5 %wt	Young's Modulus			2.5 ± 0.6 GPa	[64]
			Yield Strength			42.0 ± 10.8 MPa	[64]
	Cloisite 10 A	95/5 %wt	Tenacity	ISO 2062 standard	Tensile testing	2.34 cN/dtex	[42]
						3.52 CV%	[42]
			Breaking elongation			42.92%	[42]
						12.43 CV %	[42]
	Cloisite 15 A	95/5 %wt	Tenacity			2.43 cN/dtex	[42]

					3.94 CV %	[42]
		Breaking elongation			42.54%	[42]
					16.06 CV %	[42]
Cloisite 20 A	95/5 %wt	Tenacity			2.28 cN/dtex	[42]
					7.55 CV %	[42]
		Breaking elongation	ISO 2062 standard	Tensile testing	47.58%	[42]
					16.79 CV %	[42]
Cloisite 30 A	95/5 %wt	Tenacity			1.98 cN/dtex	[42]
					9.89 CV %	[42]
		Breaking elongation			40.07%	[42]
					21.68 CV %	[42]

As shown in *Table 12*, several publications are studying the characterization and synthesis of R-PET/filler nanoparticles. As expected, the general values differ from one to another. This difference can be due to several causes: differences in the properties of the material, type of organic clay, the clay modification process, the molecular weight of the polymer, production temperature, among others[42,47] However, in most cases, filler nanoparticles did not improve mechanical properties in contrast with V-PET. It could be due to reduced polymer orientation and the increased variation in fiber cross-section from large agglomerates of nanoclays, as the research made by Kiliç et al.[42]. They studied blends of R-PET with different nanoclays (10A, 15A, 20A, 30B), and they determined that organoclay layers act as a stress collector in nanocomposite fibers, and a deterioration in mechanical properties are observed due to weak interfacing between the clay and R-PET matrix.

The use of nanoparticles as a reinforcement is reported by Yang et al.[64], who studied blends of R-PET with Montmorillonite (MMT), with compositions from 0% to 5% obtained by a co-rotating twin-screw extruder. They reported an increase in stiffness and tensile strength with the incorporation of MMT (see *Figure 13).* This increase is related to the good dispersion that led to an effective interaction of the clay and the polyester.

Figure 13. Mechanical properties of R-PET/MMT (Recovered from Yang et al.[64])

Finally, in the present review, several strategies and additives were presented focused on improving the mechanical and thermal properties of R-PET. One of the strategies that

showed the best results was the combination of polymers and chain extenders or compatibilizers, like the research reported by Jiang et al., who mixed PBAT in the R-PET matrix incorporating small amounts of Wollastonite that functioned as a compatibilizer. This blend allowed to increase the tensile strength, tensile strain, degree of crystallinity, and thermal stability, achieving a hardening of the material, high resistance to melt dripping, and increased the char residue of the composites during combustion.

On the other hand, if the main objective of researchers is to promote plasticizing properties in R-PET, adding only PBAT in high amounts plasticizes the material because it has lower mechanical properties than R-PET.

It is important to note that due to lack of information in this regard, future research would be oriented to investigate for the adequate filler nanoparticles under correct operating conditions and suitable composition for the increase of mechanical and thermal properties and its possible compatibility in R-PET blendings.

Chapter IV

Conclusions and perspectives

From the reviewed articles it is possible to conclude:

- It is important to notice the amounts of additive added in the R-PET matrix, small amounts may not have a considerable effect on the polymer, but excessive amounts could decrease the properties of R-PET due to poor dispersion of the additive.

- It is necessary to add chain extenders (an increase of molecular weight), compatibilizer agents and/or filler-nanoparticles (an increase of miscibility) to improve the mechanical and thermal properties of R-PET with other polymers.

- Two main strategies are observed when obtaining reinforcements with R-PET. The first is aimed at hardening the material using a dispersed phase with a Young's modulus greater than that of the matrix or, due to the dispersed phase, despite having a stiffness less than or equal to that of the matrix, adheres to the matrix, thus generating a hardening mechanism that can result in an increase in the degree of crystallinity of the mixture due to nucleating effects, such is the case presented by PC contents. The second trend focuses on the addition of a polymer in such a way that it generates plasticizing properties, with less rigidity than recycled PET, like the case with PBAT contents.

- The optimal balance of mechanical properties is achieved using blendings with three main components, including a compatibilizer or a chain extender.

- Future research should focus on the study of clay nanocomposites, as the case presented with MMT, because of insufficient information in this regard and the high interest of industries for plastics reusing.

CHAPTER V
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