**UNIVERSITY OF LJUBLJANA**

Faculty of Mechanical Engineering

# Effect of recycling and additives on physical properties of Polypropylene (PP)

A Master's thesis of the second-cycle master's study programme in
MECHANICAL ENGINEERING – a research and development programme

**Carlos Alamar Tarazona**

Ljubljana, July 2020

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Adviser: dr. assist. prof. Lidija Slemenik Perše

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Candidate
**Carlos ALAMAR TARAZONA**

MAGISTRSKI ŠTUDIJSKI PROGRAM II. STOPNJE: **MAG II/866 E**

NASLOV TEME: **Vpliv recikliranja in aditivov na fizikalne lastnosti polipropilena (PP)**

Polipropilen (PP) je drugi najpogosteje uporabljen polimerni material (po polietilenu), pokriva namreč 19% svetovnega povpraševanja in se v večini uporablja pri pakiranju. Zaradi krajše življenjske dobe, predvsem pri uporabi kot embalaža, nastaja ogromno PP odpada. Recikliranje je zato eden najpogostejših načinov ponovne uporabe PP. Vendar z večkratnim recikliranjem polimerni materiali degradirajo, kar vodi do sprememb v molekularni in morfološki strukturi. Te spremembe posledično povzročijo izrazito spremembo v fizikalnih lastnostih (termične, mehanske, reološke, itd.), ki so pomembne za proizvodni proces in kvaliteto končnega izdelka.
V sklopu magistrske naloge bodo (na osnovi pregleda literature) opredeljeni temeljni mehanizmi degradacije in aditivnega pomlajevanja PP tekom recikliranja. Te spremembe bodo povezane z makroskopskim odzivom materiala, ki ga običajno opazujemo preko njegovih fizikalnih lastnosti, s poudarkom na termičnih, mehanskih in reoloških lastnosti. Rezultati naloge bodo tako nadgradili temeljna znanja o recikliranju in pomlajevanju PP, ki jih lahko uporabimo tudi kot alternativni način za manipulacijo molekularne strukture ter s tem krojenje novih materialov s ciljanimi lastnostmi.

Magistrsko delo je treba oddati v jezikovno in terminološko pravilnem angleškem jeziku. Rok za oddajo tega dela je šest mesecev od dneva prevzema.

MASTER THESIS – MASTER'S DEGREE STUDY No. **MAG II/866 E**

TITLE: **Effect of recycling and additives on physical properties of polypropylene (PP)**

Polypropylene (PP) is second-most widely produced commodity plastic (after polyethylene) covering 19% of world demand, usually used for packaging. Considering the problem of its short lifetime, a lot of PP lands as a plastic waste. Recycling is thus one of the simplest and easiest ways to reuse PP. However, multiple recycles lead to the degradation, which results in changes of materials' molecular structure and consequently profound changes in physical properties (thermal, mechanical, rheological, etc.), which is important for production process and quality of the final product.
The proposed Master thesis will investigate (through literature research) the underlying mechanisms of PP degradation and additive rejuvenation during recycling. The observed changes will be correlatted with materials' macroscopic response, which is usually observed through its physical properties, focusing on thermal, mechanical, and rheological properties. Therefore, the results presents the fundamental knowledge on recycling and rejuvenating additives of PP, however it can be also used as an alternative way to manipulate molecular structure to tailor materials with targeted end properties.

The submitted master thesis must be written in standard English. The master thesis must be submitted six months after it was accepted.

Mentor
doc. dr. Lidija Slemenik Perše

I hereby confirm the receipt of the master thesis

Date: 24/08/2020
Student Signature: Carlos Al CAT

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Ljubljana

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# Declaration

1. I, the undersigned Carlos Alamar Tarazona, born 3 November in Valencia 1998, a student at the Faculty of Mechanical Engineering at the University of Ljubljana, hereby declare that this master's thesis titled *Effect of recycling and additives on physical properties of Polypropylene (PP)* is my own original work created under the supervision of my advisor dr. assist. prof. Lidija Slemenik Perše.

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Ljubljana, July 2020 Signature of the author:__________________

# Abstract (in English)

UDC 123.45:678.91:234.56(789.1)

Serial No.: MAG II/866 E

## Effect of recycling and rejuvenating agents on physical properties of Polypropylene (PP)

Carlos Alamar Tarazona

Keywords:
physical properties
polypropylene
recycling
additives
molecular weight
polymer

Plastic waste grows every year, therefore the recyclability of plastics has been studied vastly to get the higher performance of the used polymers. In this thesis, the effects of recycling and rejuvenating agents are explained in a polymer commonly know as polypropylene (PP). First, a wide theoretical overview where the physical properties (thermal, mechanical and rheological) are explained and their dependence with the structure and molecular weight and methods of recycling are presented. Later, the effects of the recycling process and how physical properties decrease with the molecular weight reduction and extruding cycles are explained. Also, the study of the addition of the additives is explained in this thesis and how physical properties are increased, depending on the different types of fillers or concentrations. This thesis is supported by several studies that enable the understanding of the behavior of recycled PP; moreover, the results of different experiments are shown.

# Povzetek (in Sloven)

UDC 123.45:678.91:234.56(789.1)
Serial No.: MAG II/866 E

## Vpliv recikliranja in pomlajevalnih dodatkov na fizikalne lastnosti polipropilena

Ključne besede: fizikalne lastnosti
polipropilen
recycling
aditivi
molekulska masa
polimeri

Količina plastičnih odpadkov vsako leto močno narašča, zato je mnogo razisakv usmerjenih v recikliranje z namenom dobiti višjo učinkovitost recikliranih plastičnih odpadkov. V predstavljeni nalogi so razloženi vplivi recikliranja in pomlajevalnih dodatkov recikliranemu polipropilenu. Najprej so obširno predstavljene teoretične osnove z razlago fizikalnih lastnosti (termične, mehanske in reološke) in vpliv na strukturo in molekulsko maso. Predstavljene so tudi metode recikliranja. V drugem delu so predstavljeni procesi ekstrudiranja, vplivi procesa recikliranja in sprememba fizikalnih lastnosti z molekulsko maso. V nalogi so predstavljene tudi raziskave vpeljave pomlajevalnih dodatkov in vpliv vrste in koncentracije dodatkov na fizikalne lastnosti. Magistrska naloga je podkrepljena z vrsto raziskav iz literature, ki omogočajo razumeti obnašanje recikliranega polipropilena. Predstavljeni so tudi rezultati različnih eksperimentov.

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# List of tables

# List of symbols used

| Symbol | Unit | Meaning |
|---|---|---|
| $A$ | $m^2$ | surface area |
| $D$ | $Pa^{-1}$ | creep compliance |
| $E$ | Pa | Young's modulus |
| $E$ | Pa | relaxation modulus |
| $F$ | N | force |
| $\Delta G$ | J | Gibb's free energy |
| $G'$ | Pa | storage modulus |
| $G''$ | Pa | loss modulus |
| $H$ | J | enthalphy |
| $K$ | $W\ K^{-1}m^{-1}$ | thermal conductivity |
| $Mw$ | $G\ mol^{-1}$ | molecular weight |
| $S$ | J | entropy |
| $T$ | K | temperature |
| $P$ | Pa, bar | pressure |
| $V$ | $m^3$ | volume |
| $X$ | | degree of crystallization |
| | | |
| $\alpha$ | $W\ K^{-1}m^{-1}$ | thermal expansion |
| $\varepsilon$ | | strain |
| $\varepsilon$ | | elongation |
| $\eta$ | Pa s | dynamic viscosity |
| $\sigma$ | Pa | stress |
| $\varphi$ | Rd | phase shift |
| $\tau$ | Pa | shear stress |
| $\gamma$ | | shear strain |
| $\omega$ | Hz | frequency |
| $\rho$ | $Kg\ m^{-3}$ | density |
| $\bar{y}$ | $s^{-1}$ | shear rate |

| Index | |
|---|---|
| 0 | initial |
| c | crystallization |
| e | equilibrium |
| g | glassy state |
| i | index |
| m | molten state |

# List of acronyms used

| Acronym | Meaning |
|---|---|
| BAL | Boehmite Aluminia |
| C | Graphite |
| $CaCO_3$ | Calcium carbonate, nanopowder |
| CB | Carbon black |
| CNT | Carbon nanotubes |
| $CO_2$ | Cabon dioxide |
| DMA | Dynamic Mechanical Analysis |
| DSC | Differential Scanning Calorimetry |
| GN | Graphene |
| GPC | Gel Permeation Chromatography |
| HALS | Hindered Amine Light Stabilizers |
| HDPE | High Density Polyethylene |
| MFI | Melt Flow Index |
| *Mw* | Molecular weight |
| PET | Polyethylene terephthalate |
| PI | Polydispersity |
| PP | Polypropylene |
| PS | Polystyrene |
| PVC | Polyvinyl chloride |
| $SiO_2$ | Oxidum of silica |
| SGWPF | Stone Groun Wood Pulp Fillers |
| SS | Shrimp shells |
| UV | Ultraviolete |
| UTS | Ultima Tensile Stress |
| ZnO | Zinc oxide, nanopowder |

# 1. Introduction

## 1.1 Background

In today's world, the consume of polymers is increasing every year, with a bigger production than 300 million tonnes of plastic since 2018. This yearly increase has negative consequences as the increase of plastic waste produces an environmental impact that has led to several studies of the recyclability of the polymers, only being recycled less than 15% of plastics in the world. The main problem with recyclability is the different structures that the polymer present, not allowing thermosets to be recycled, and the continued loss of physical properties e.g. molecular structure, viscosity, degree of crystallinity or Young's modulus. This is due to the extrusion process, which starts the degradation of the polymer by several factors as oxidation or chain scission. The loss of physical properties negatively affects the final performance of recycled polymers only being useful with the introduction of additives that improve the properties to the virgin polymers levels.

In this thesis, Polypropylene was chosen to research the effects of recycling and rejuvenating agents on physical properties. Polypropylene belongs to the polyolefin group and is one of the most used polymers in the world. This is because the ease of PP to be produced due to the high meltig point, lower density or higher toughness compared to the rest of the polymers or the several uses it can have. It is stimated than more than 50 tonnes of polypropylene are produced yearly in the world and the levels increase yearly.

## 1.2 Objectives

In this masther thesis, the effect of recycling and the addition of additives on the internal structure of polymers is going to be studied. This effect characterises the final performance of the polymer and the properties of final polymer product. The starting hypothese is that recycling reduces molecular weight and chain length and consequently physical properties. The main objective is to explain by the experience of several studies with different additives the different influences they have on the performance of PP.

In the following chapters the following topics will be discussed:

- In chapter 2, i.e. Theoretical background, the general information about polymers, effect of molecular and morphological structures on physical properties. Later, the recycling in polymers is discussed, how the polymers are

degraded and what are the mechanisms of the rejuvenating agents during recycling.
- In chapter 3, i.e. Literature research, the effect of recycling on physical properties is discussed.
- In chapter 4, i.e. Conclusions, Summay of literature research as well as future work is presented.

# 2 Theoretical background

The use of polymers as engineering materials has increased significantly during past decades, their increased usage in construction and automatization is the result of better engineering, economic and environmental advantages compared to other currently utilized materials such as metals. However, the polymer industry in the past was restricted by the lack of information about them, and it was not until the twentieth century, when Hermann Staudinger discovered the real structure of polymers, suggesting a large chain of little molecules called monomers, linked with covalent bonds, which allowed the study and progress in this field.

Nowadays, we can distinguish different structures of macromolecules, such as linear structures and non-linear structures, Figure 2.1. The latter can be further divided in cyclic polymers or ring polymers, branched polymers, and cross-linked polymers presenting three dimensional structures where macromolecules are connected with primary, i.e. covalent, bonds. The point where macromolecules connect are called junction points and the number of junction points per volume represents the degree of crosslinking.

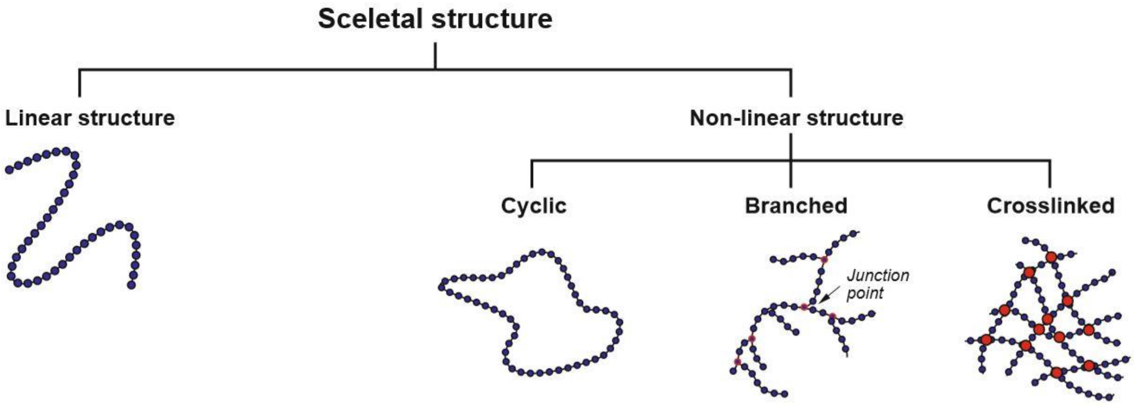

Figure 2.1: Classification of polymers, based on the structure of macromolecules [1].

There are a lot of different classification of polymers depending on the mode of formation, crystallinity, tacticity, etc., but the most common classification for polymers is related to their thermal response. Based on this, three different types of polymers can be observed, each of them exhibiting their physical response, which can be classified as thermosets, elastomers and thermoplasts as show in Figure 2.2.

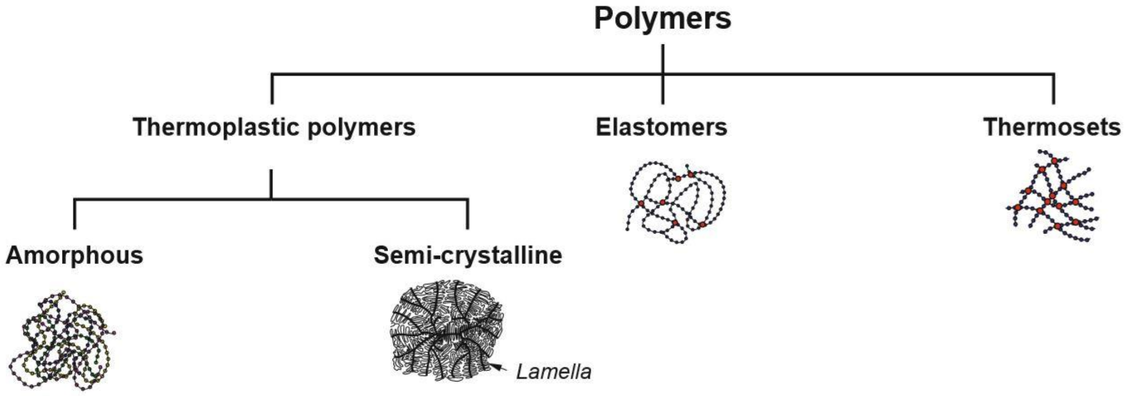

Figure 2.2: Classification of polymers based on thermal response [1].

Thermoplastics are linear or branched polymers which become viscoelastic liquid under sufficient exposure to heat. In this state, they can be molded into any shape using different processing techniques, therefore they present the bigger portion of polymer production in the world. Within thermoplastics, two different types can be observed, i.e. semi-crystalline and amorphous. Semi-crystalline polymers consist of highly entangled macromolecules linked with secondary or van der Waals bonds, which have tendency to form a quasi-crystalline structure with crystalline and amorphous regions. Their molecules align in regions called lamellas, which compose larger spheroidal structures named spherulites. The other type of thermoplastics are amorphous polymers, where molecules are also linked together with secondary or van der Waals bonds, but compared to semi-crystalline polymers, amorphous thermosets are not able to crystallize, as their structure remain chaotic under solidification. Due to the absence of crystalline regions, amorphous polymers exhibit a transparent look. On the other hand, elastomers are cross-linked polymers, meaning that the macromolecules are linked together with primary or covalent bonds, however, the degree of crosslinking in elastomers is low. They achieve high extensions and rapidly recover to their original shape when the load is removed. This is known as entropy driven process. The last group of polymers, known as thermosets, are polymers with high degree of cross-linking. They are known to be rigid materials because the motion of chains is restricted by high degree of cross-linking [2].

Among above-mentioned polymeric materials, the main advantage of the thermoplastic polymers is structural oriented, since weak intermolecular forces, i.e. Van der Waals forces or bonds, allow these materials to be re-shaped and remolded by the application of heat. Therefore, the majority of thermoplastic materials can be recycled with various commonly established techniques (chemical recycling, mechanical recycling, etc.) and reused in further applications. However, recycling and reusing a polymer can deteriorate molecular structure, producing irreversible changes and reducing the life-time of the polymer. Therefore, various rejuvenating agents are applied in the recycling process, in order to mitigate the structural and subsequently physical changes.

In this chapter, we outline the most important physical properties of polymers, recycling in general, and the commonly used rejuvenating agents, which provide the theoretical basis for the literature research, where the effect of recycling and rejuvenating agents on the physical properties will be studied.

## 2.1 Physical properties of polymers

Within this chapter we address the most common physical properties of polymers utilized during processing and later on during their utilization, coupled with various environmental effects (mainly related to temperature), which could profoundly alter the behavior of polymer products. Therefore, thermal, rheological and mechanical properties will be thoroughly discussed in continuation.

### 2.1.1 Thermal properties

Among several thermal properties of polymers, such as thermal expansion, conductivity, etc., phase transition temperatures and their underlying aspects of molecular reconfiguration are the most fundamental in order to understand macroscopic behavior of the polymers. In general, temperature presents an average kinetic energy or the random walk of constituents (Brownian motion). For polymers, such motion of macromolecules induced by the temperature is hindered because of their chain structure. In this respect, the temperature induces the molecular motion or vibration allowing molecules to reconfigure in available space, also called as backbone mobility or segmental mobility of the molecules.

When the temperature increases, the mobility of macromolecules does as well, occupying more space, which is vividly shown through volume, Figure 2.3. Thus, from volume observations three distinct regions of polymer behavior can be observed, namely glassy region, rubbery region and melt. The three regions are distinguish by so called phase transition temperatures, that present the fundamental aspects of molecular reconfiguration, and their effect on polymer's macroscopic behavior. The first transition is common for all polymers and is called the glass-transition, usually characterized with glass transition temperature $T_\mathrm{g}$, Figure 2.3a. Below this temperature, the Brownian motion of polymer main chain ceases and the side chain movement is severely hindered. Within this region, denoted as glassy region, molecular configuration of polymers is more or less "frozen", resulting in negligible change in volume and elastic behavior of the polymer. With increasing temperature, above $T_\mathrm{g}$, segmental mobility profoundly increases, representing global movement of the molecules, which can be observed with increase in volume. Within this region, denoted as rubbery region, molecular movement is not hindered, resulting in viscoelastic response of material. From the Figure 2.3b, another region can be observed, which is common only for semi-crystalline polymers, distinguished from the others with melting temperature $T_\mathrm{m}$. Within this region, the Brownian motion of macromolecules overcomes the van der Waals bonds holding lamellas and spherulites together, which results in abrupt change in volume. Above $T_\mathrm{m}$ where the polymer is in molten state, it exhibits viscous behaviour, and therefore can be considered as a fluid. Besides phase transition temperatures, thermal expansion coefficient $\alpha$, given as $\alpha = (1/V)\,\partial V/\partial T$ can be also determined through volume, which as other physical properties, changes through phase transitions.

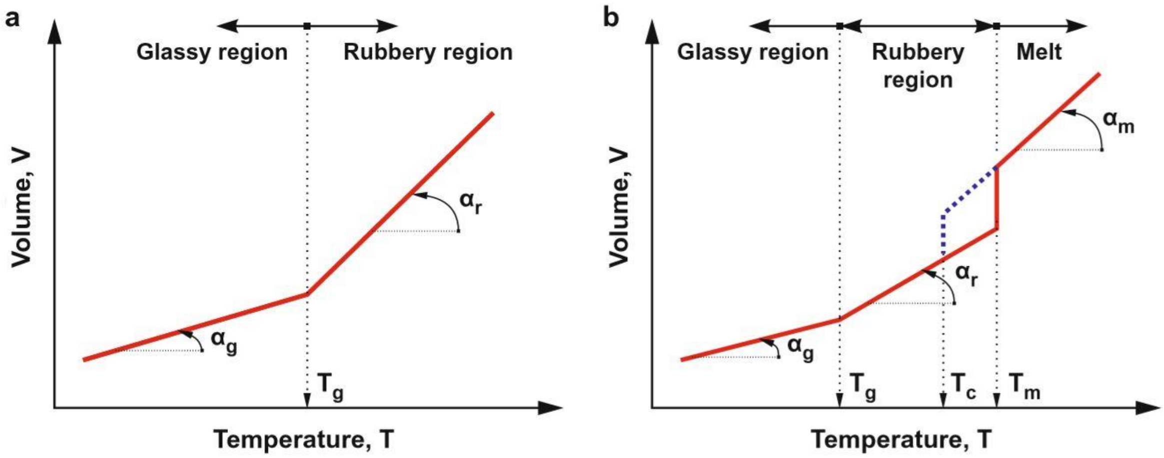

Figure 2.3: Effect of temperature on volume for amorphous, elastomers and thermosets polymer (a) and semi crystalline polymer (b) [3].

Next to the volume observation of phase transition temperatures, other more commonly used techniques can be applied for the determination of thermal properties of polymers. One of such is differential scanning calorimetry (DSC). This technique works on the principle of heat exchange between the sample and the environment, while transitions related to endo- and exothermic reactions takes place, i.e. for semi-crystalline polymers, the melting is classified as endothermic and for the determination of thermal properties the crystallization is classified as exothermic reaction. To measure the heat exchange between the sample and the environment, two heating chambers are used, where one is empty and serves as a reference, i.e. measures the temperature of the environment without the sample, while the other one includes the sample, i.e. measures the temperature of the environment with the sample, determining the corresponding exo- or endothermic reactions and indicating the phase transition temperature. Usually $dT = 0$ principle between the chambers is applied, meaning that the heat flow is regulated in order to obtain equal temperature between the reference and sample chambers, thus heat flow should vary during exo- or endothermic reactions or so-called phase transitions. As a result, the thermograms (heat flow vs. temperature) can be obtained indicating phase transition temperatures of polymers, which is schematically presented in Figure 2.4.

The heat capacity is defined as the energy required to increase or decrease the temperature by one unit. When a polymer is subjected to a temperature above its glass transition temperature $T_\mathrm{g}$, the polymer shows a higher heat capacity because of the entrance into the rubber state. Thus, the thermogram will represent an increase of the heat flow as an indication of the $T_\mathrm{g}$ , according to criterions of normalizing, $T_\mathrm{g}$ is set in the middle of the rise of the heat capacity.

For semi-crystalline polymers, during the increasing of the temperature, the internal structure of the polymer becomes more and more ordered. The more the chains are ordered the more heat is emitted by the polymer. This is called an exothermic transition. The exothermic transition is reflected by a reduction of the heat flow in the thermogram, the sample emits heat to the surroundings, so the sample heater needs less heating rate. This is known as the crystallization point $T_c$. The minimum point of the decrease in the heat flow is $T_c$ and the area under the curve is known as the latent heat of crystallization, important value to know the degree of crystallization or calculate the required energy of the process.

The last temperature is melting temperature $T_m$. When the temperature of the polymer is close to $T_m$, the intermolecular attractions or Van der Waals forces and chains become from ordered state to disordered nature again. An additional heat is therefore required to break the bonds, so the sample heater will have to provide more heat. The peak in the rise is known as $T_m$ and the area under the curve is the latent heat of melting, also used to calculate the crystallization degree of a material [4].

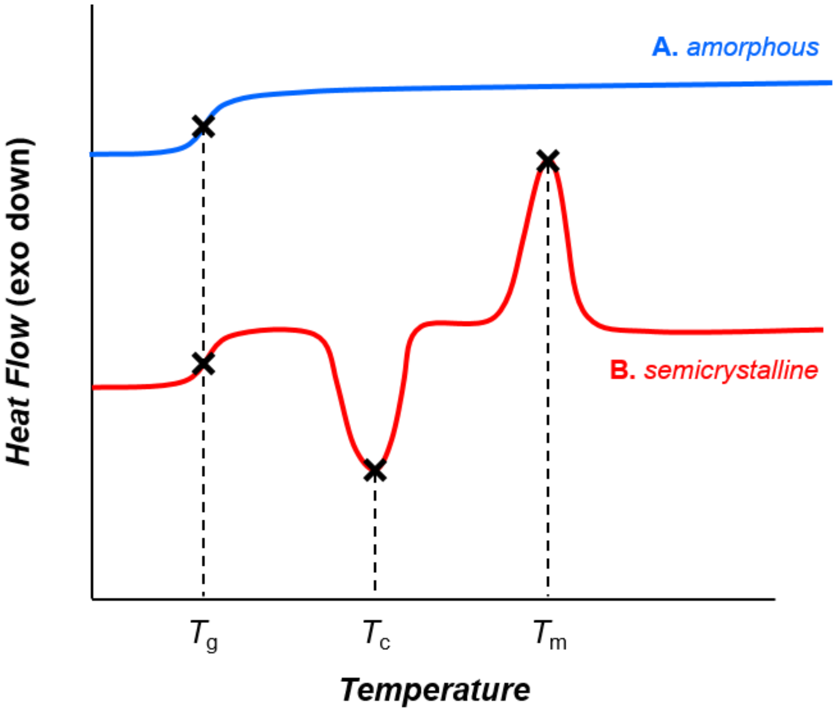

Figure 2.4: Classical DSC thermogram for example of A.) amorphous and B.) semi-crystalline polymers [5].

We can determine the degree of crystallization with the following equation:

$$X\% = \frac{\Delta H_i}{\Delta H_o} \text{x}100 \qquad (1)$$

Where X is the degree of crystallization, $\Delta H_i$ the melting heat enthalpy of the polymer and $\Delta H_o$ is the specific heat of completely melting material, with a constant value of 205 J/g for polypropylene.

### 2.1.1.1 Viscoelasticity of polymers

Unlike elastic materials, such as metals, ceramics, etc., polymers exhibit both solid or elastic-like (recoverable) as well as fluid or viscous-like (non-recoverable) behavior, mainly because of their unbounded morphological structure.

The tensile stress ($\sigma$) measurements consist of applying a load in the form of stress onto a small area and studying the results. For polymers it is characteristic that with the stress induced over time, the area is decreased and the material starts to elongate. This is usually carried out with an ultimate tensile stress (UTS) machine, that uses the intensive property of the polymer as elongation and stress, which means that it does not depend on the size of the tested polymer. The stress can be defined by the following equation:

$$\sigma = \frac{F}{A} \tag{2}$$

This directly affects Young's modulus, which is a measure of how much stress or strain a material is able bear under tensile or compressive load. The Young's modulus is defined by the equation:

$$E = \frac{\sigma}{\varepsilon} \tag{3}$$

Where $E$ is Young's modulus, $\sigma$ is the stress in the material and $\varepsilon$ is the elongation of the polymer.

Polymers undergo time-dependent mechanical changes (strain or stress) under the application of an external load (stress or strain), as they are commonly referred as viscoelastic or time-dependent materials. The difference between elastic and viscoelastic materials may be observed in Figure 2.5. It can be seen, taht under the application of external stress, the polymer exhibits instantaneous elastic strain and progress in a viscous manner, which is then recovered in the same way when the load is removed.

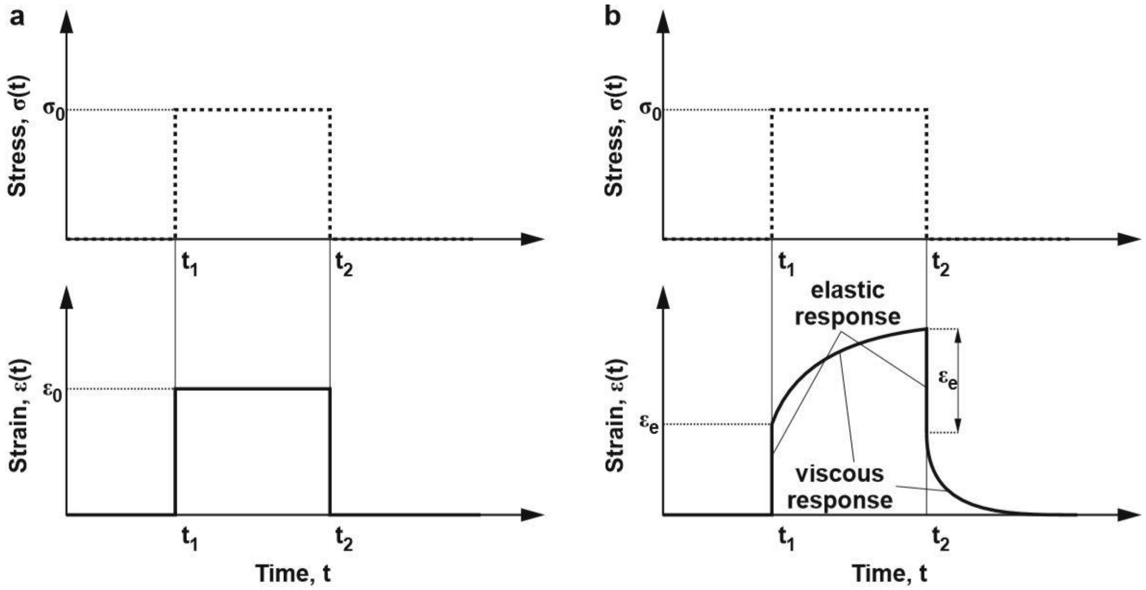

Figure 2.5: Different responses of a) elastic and b) viscoelastic materials to external loads [1].

To understand the relationship between the cause (stress or strain) and the response (strain or stress) of viscoelastic materials, linear theory of viscoelasticity may be applied, which is given either in integral or differential formulation. The main equations to describe the linear theory of viscoelasticity are the same as for linear theory of elasticity, except that the generalized Hook's law of elasticity is replaced by a constitutive description that is sensitive to the materials (past) history of loading with convolution integral, written as:

$$r(t) = \int_{-\infty}^{\infty} Q(t-u)\frac{\mathrm{d}c(u)}{\mathrm{d}u}\,\mathrm{d}u, \tag{2}$$

where $r(t)$ represent the response (either stress or strain), $c(t)$ cause (either strain or stress) and $Q(t)$ represents the mechanical property (moduli or compliances) also refered as a material function. However, due to the nature of the polymers, we can now differ between two processes within polymeric materials when subjected to the external load, namely creep and relaxation process, which will be in continuation explained on simple case, using uniaxial step loading format.

### Creep Process

When a material is subjected to step load in the form of stress, all polymers exhibit increasing deformation with time, which is known as the creep process, shown in Figure 2.6.

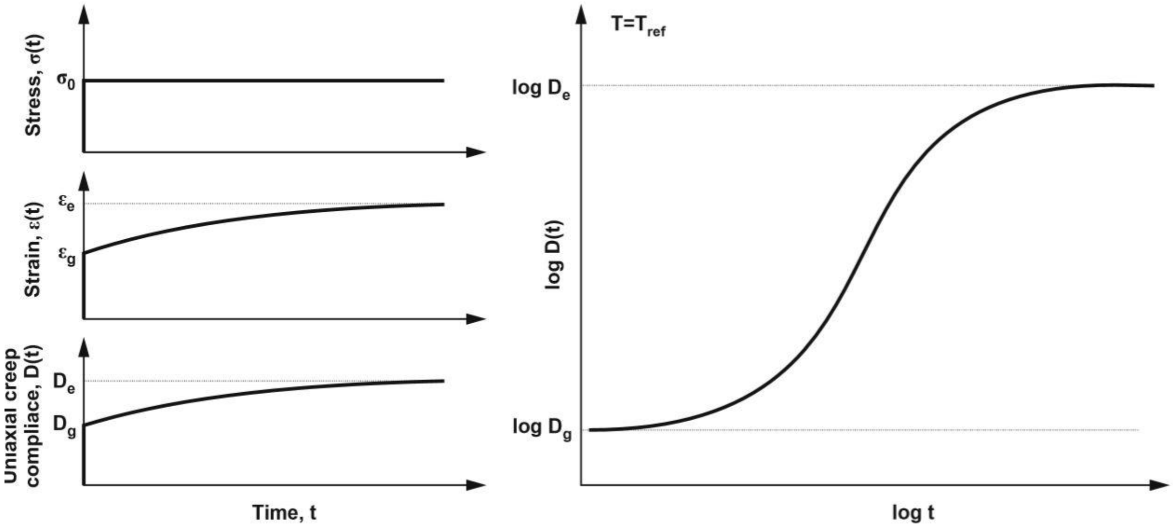

Figure 2.6:Creep process in polymers [1].

Therefore, creep process describes a time-dependent response of viscoelastic material in the form of strain $\varepsilon(t)$ when it is subjected to the constant external load in the form of stress $\sigma_0$. The relation between stress as load and strain as response is described by material property (material function) known as creep compliance $D(t)$, given as:

$$D(t)=\frac{\varepsilon(t)}{\sigma_0}, \tag{3}$$

### Relaxation Process

On the other hand, when polymers are subjected to a step load in the form of deformation, all polymers exhibit decaying stress response, which is known as relaxation process, Figure.2.7.

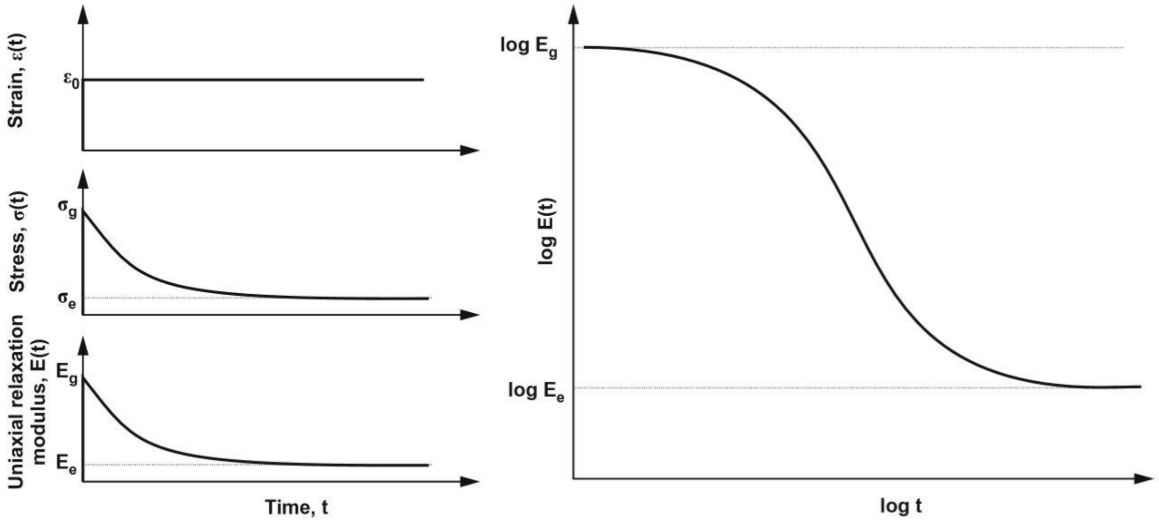

Figure 2.7: Relaxation process in polymers [1].

Therefore, the relaxation process describes a time-dependent response of viscoelastic material in the form of stress $\sigma(t)$ when it is subjected to the constant external load in the form of strain $\varepsilon_0$. The relation between strain as load and decaying stress as response is described by a material property (material function) known as relaxation modulus $E(t)$, given as:

$$E(t)=\frac{\sigma(t)}{\varepsilon_0}, \tag{4}$$

From the energy point of view, during the process of relaxation the material is loaded with diminishing amount of energy. When all the imposed energy is consumed for the molecular rearrangements, the relaxation process ends. On the other hand, during the creep process, the energy used for the rearrangement is continually supplied to the material, therefore creep process evolves until the material failure, which means that although similar mathematical expressions for the mechanical properties are not interrelated $E(t) \neq 1/D(t)$, except in the plateau regions (glassy denoted with index g and equilibrium denoted as e) but rather with expression as:

$$t = \int_{-\infty}^{\infty} E(t)D(t-\ u)\,\mathrm{d}u, \tag{5}$$

We can notice the values 'g' and 'e' as limiting values, this represents glassy response (g) and equilibrium (rubbery) response (e), typical for polymers like elastomers, thermosets and the semi-crystalline polymers, while amorphous polymers do not exhibit equilibrium values, because of their molecular structure, which allows them to creep until the mechanical failure or relax until the process stops, as shown in Figure 2.8.

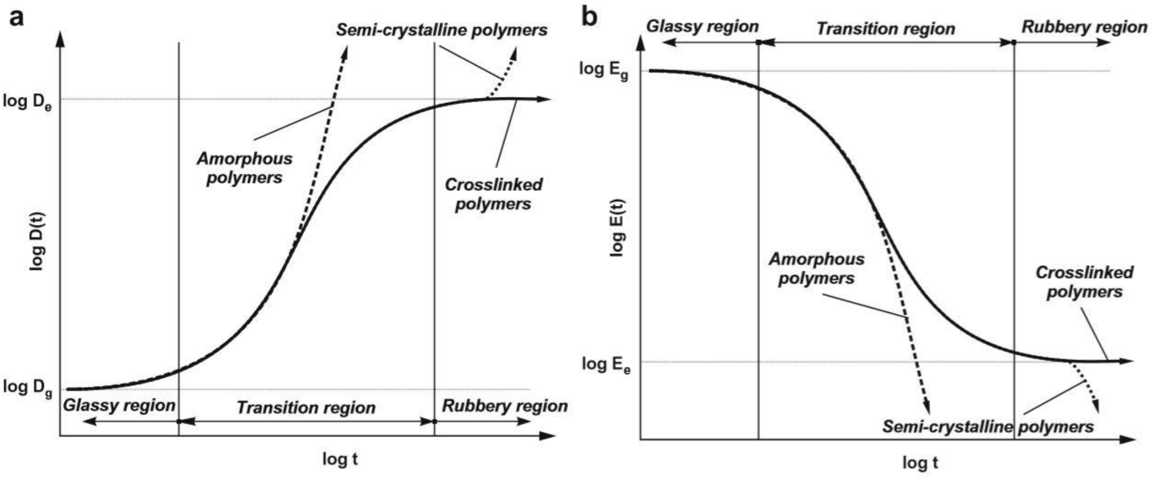

Figure 2.8: Effect of molecular structure on creep (a) and relaxation (b) process [1].

Finally, the viscoelastic behavior of solid polymer can be determined using the 21 material functions presented in the Table 2.1, which were expressed from Eq. (1) using different types and modes of loading. Material functions are useful to choose the correct polymer for specific applications. When some applications are exposed to dynamic excitations, like car tires, one should use the dynamic material functions, but if applications are exposed to static load, like structural elements, one should use time-dependent material functions. All material functions are interrelated; therefore, Laplace transformation can be used to measure two material functions and calculate the remaining ones.

Table 2.1: Viscoelastic functions of polymers

| **Mode of loading/Type of loading** | | | **Uniaxial** | **Shear** | **Bulk (volumetric)** | **Poisson's ratio** |
|---|---|---|---|---|---|---|
| **Static** | **Relaxation** | | $E(t)$ | $G(t)$ | $K(t)$ | $\mathfrak{z}(\omega)$ |
| | **Creep** | | $D(t)$ | $J(t)$ | $B(t)$ | |
| **Dynamic** | **Relaxation** | **In phase** | $E'(\omega)$ | $G'(\omega)$ | $K'(\omega)$ | $\mathfrak{z}'(\omega)$ |
| | | **Out-of-phase** | $E''(\omega)$ | $G''(\omega)$ | $K''(\omega)$ | $\mathfrak{z}''(\omega)$ |
| | **Creep** | **In phase** | $D'(\omega)$ | $J'(\omega)$ | $B'(\omega)$ | |
| | | **Out-of-phase** | $D''(\omega)$ | $J''(\omega)$ | $B''(\omega)$ | |

### 2.1.1.2 Effect of temperature

To understand the effect of temperature on mechanical properties we have to take a look into the free volume concept, explained in the thermal properties. When the temperature rises, the free volume increases, which results in increase of available space for the motion of macromolecules (reconfiguration) that consequently accelerates the creep or relaxation process. This acceleration can be on macroscale observed by horizontal shifting of time-dependent mechanical properties to shorter times, as shown in Figure 2.9.

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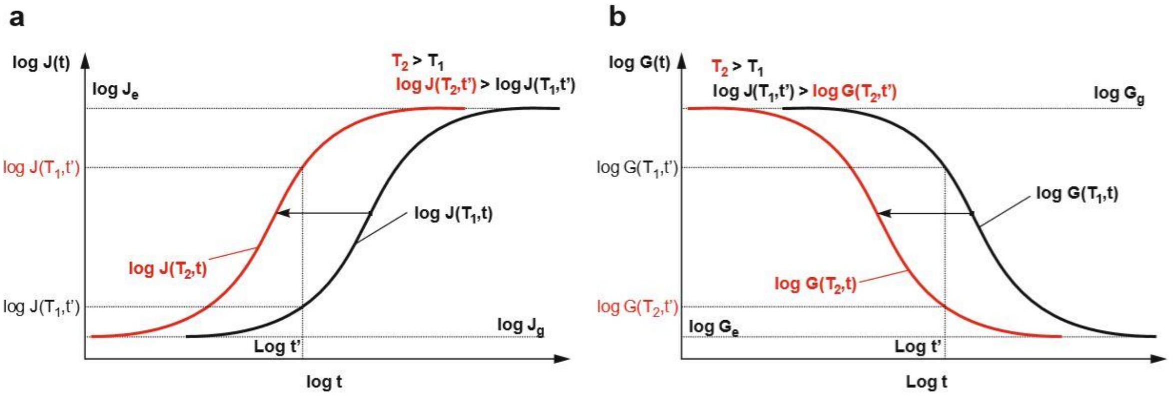

Figure 2.9:Effect of temperature in creep (a) and relaxation (b) process in the case of shear loading [1].

The most common representation of the effect of temperature on mechanical properties is through so-called isochronal curves, which showthe material behavior at different temperature for specific time or frequency, Figure 2.10. However, the procedure for constructing isochronal curves from creep or relaxation process in either time or frequency domain can be found elsewhere [1]. Nevertheless, based on the results three distinct regions can be observed as also shown via volume measurements, i.e. glassy, rubbery and flow (melt) region as well as phase transition temperatures, i.e. glassy transition and melting temperature [6].

Please note that using frequency results (utilizing dynamic mechanical analysis or DMA), three types of glass transition temperature may be determined: i.) onset of the storage modulus $G'$, ii.) the peak in loss modulus $G''$ or the iii.) peak in $\tan\delta$. The first value represents the $T_\mathrm{g}$ as the temperature where the short-range relaxation can occur, reducing the resistance against the load. The second value represents the match or link of the vibrational frequencies of small chains of polymers and results in a peak in the loss storage. The third value is the $\tan\delta$ peak, which represents the $G''/G'$ ratio. It is common, that the $T_\mathrm{g}$ is determined by the peak of $G''$ (small chain movement or transition from local to global movement of molecular chains), meanwhile $T_\mathrm{m}$ is determined as the drop of $G'$.

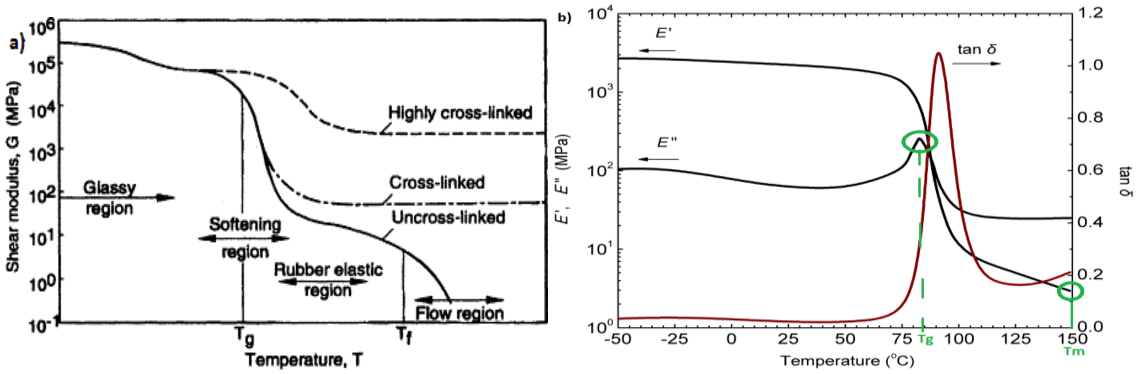

Figure 2.10: Isochronal curves for shear relaxation modulus in a) time and b) frequency domain [2].

### 2.1.2 Rheological behavior

Rheology is the field that studies the flow and deformation of a matter in response to an applied external force. It can be used to establish a direct link between material characteristics (molecular weight, molecular size, structure) and final physical properties of a material.

#### 2.1.2.1 Flow behavior

Flow behavior of polymers may be, beside elongational, described in shear as several layers of fluid (here considered as polymer melt) sliding over each other with upper layer moving faster than the layer below, Figure 2.11.

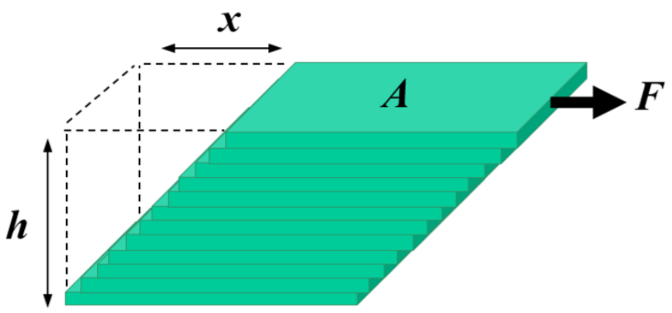

Figure 2.11: Layers of sliding fluid layer one over another [7].

The bottom layer of fluid is considered to be stationary and the top layer has the highest velocity. For shear flow to take place a shear force $F$ must act on the unit area $A$, taking a form of shear stress $\tau$ as:

$$\tau = \frac{F}{A}, \tag{6}$$

In response to the applied force, the upper layer will move for a distance $x$, while the bottom layer remains stationary. Hence, we have the displacement gradient across the sample, known as shear strain $\gamma$, written as:

$$\gamma = \frac{\mathrm{d}x}{\mathrm{d}h}, \tag{7}$$

For a fluid where the constituent components can move relative to one another the shear strain will continue to increase for the time period of applied stress, which creates a velocity gradient known as shear rate or strain rate $\dot{\gamma}$ given as:

$$\dot{\gamma} = \frac{\mathrm{d}\gamma}{\mathrm{dt}}, \tag{8}$$

Based on the Newtonian relation, the coefficient of proportionality between shear stress and shear rate is defined as the shear viscosity $\eta$, which presents quantitative measure of the internal (molecular) fluid friction as:

□=□□, (9)

Depending on the relationship between the viscosity and shear rate we can define different types of flow behavior in polymers as shown in Figure 2.12. In general, one can divide between Newtonian and non-Newtonian flow behavior, based on the response to shear rates. Viscosity of Newtonian fluid does not change with increasing shear rate, while for non-Newtonian fluids the viscosity can increase or decrease with increasing shear. therefore, non-Newtonian behavior can be further divided to shear thickening and shear thinning behavior.

Shear-thickening behavior, also known as dilatant, is characteristic for those polymers where the viscosity increases as the shear speed is increased due to reorganizations in the microstructure of the polymer. This happens because normally particles tend to organize in lubricated layers lowering the viscosity. At higher shear rates the mixture dilates, and there is not enough liquid to fill all the space (higher than before because of the shear rate) and the friction happens, this increases shear stress and consequently rises the viscosity of the polymer [8].

Plastic or yield stress behavior is observed in those polymers that behave as a rigid body at low stresses and as a viscous liquid at high stresses. It can be observed when a load is applied in the polymer, keeping the deformation energy until a point, called plastic point where the polymer starts to show a fluid behavior, being deformed in a Newtonian or non-Newtonian way, to get an example of the real-life material, a jam can be considered as yield stress material.

Shear thinning behavior is characteristic for those polymers, where theviscosity reduces with an increasing shear rate. The majority of polymer melts or non-filled systems behave as shear thinning so this is the most common behaviour for polymer melts. The shear thinning behaviour depends on the molecular weight distribution and the structure of the polymer. When a melted polymer is at equilibrium, the chain mobility is a result of the temperature so the higher temperature the higher chain mobility there will be, and therefore lower viscosity. When a shear rate is applied to the polymer, there is a bigger destruction of the interactions between the polymeric chains, if the shear rate is bigger than the limit, the destruction of interactions produces a loss of the structure and an alignment of the chains, that produces a bigger separation between them, producing finally a loss of viscosity.

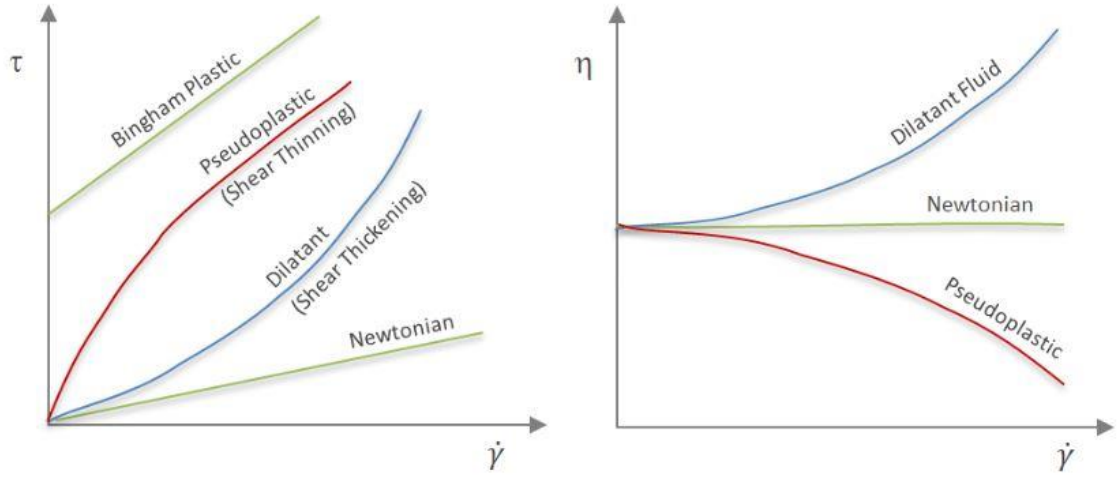

Figure 2.12: Different flow behavior of polymers [8].

### 2.1.2.2 Oscillatory behavior

Oscillatory behavior of polymers, also known as dynamic viscoelastic properties, have been a subject of various studies for a long time. Viscoelastic properties represent the response of the material to dynamic excitation, it determines the storage $G'$ and loss modulus $G''$ over short time scale, useful to understand how the structure changes depending on the operating conditions and gives the information about the phase transition temperatures [9].

Dynamic properties are obtained by applying a sinusoidal load or stress and analyzing the response or strain, depending on how delayed the strain to the stress is. The delay between both signals is called phase angle $\delta$, shown in Figure 2.13. Please note that below presented relationship is valid also for solids as well as for polymer melt.

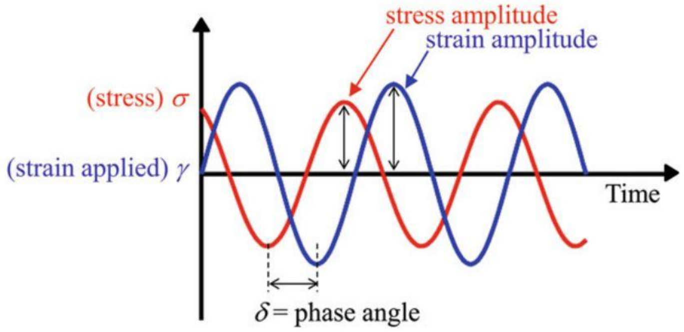

Figure 2.13: Stress-strain response of polymers during oscillation tests [10].

Dynamic excitation of polymers may be given in sinusoidal form as:

$$\gamma(t) = \gamma_0 \sin \omega t \tag{10}$$

Where $\gamma_0$ represents the amplitude of excitation, $\omega$ the frequency of excitation and $t$ time of excitation. Response of the dynamically excited material can be obtained by implementing Eq. (10) in Eq. (2) thus:

$$\tau(t) = \tau_0 \left[G' \sin \omega t + G'' \cos \omega t\,\right], \tag{11}$$

Where $G'$ and $G''$ can be defined as:

$$G' = G^* \sin \delta \tag{12}$$

$$G'' = G^* \cos \delta \tag{13}$$

$$G^* = \frac{\tau_0}{\gamma_0} \tag{14}$$

$$tan(\delta) = \frac{G''}{G'} \tag{15}$$

One can notice that the response is divided in two parts, the real and imaginary response, represented by the G′ and G′′. G′ is associated with energy storage and is called ‘dynamic storage modulus’ and G′′ is associated with the loss of energy as heat, known as ‘dynamic loss modulus’. They represent the stored and lost deformation energy, i.e. G′and G′′, during one loading cycle.

Implementation of Eq. (10) and (11) into Eq. (9) results in the complex viscosity or dynamic viscosity, with real part $\eta'$ or and imaginary $\eta''$ [11]:

$$\eta^* = \sqrt{\eta'^2 + \eta''^2} \tag{16}$$

$$\eta'(\omega) = \frac{G''(\omega)}{\omega} \tag{17}$$

$$\eta''(\omega) = \frac{G'(\omega)}{\omega} \tag{18}$$

Rheological properties are also influenced by the molecular weight and structure of the polymer. The higher molecular weight, the higher entanglements occur between chains, which affects the viscosity as well as viscoelastic properties. By increasing molecular weight, the zero-shear viscosity or the viscosity measured in 'shear' deformation at zero shear rate, known as $\eta_0$, increases because the more entanglements the more resistance the polymer will show. It also affects the viscoelastic properties, as molecular weight affects the loss and storage modulus, by increasing the molecular weight, one increases this modulus, as the number and strength of entanglements affect the elastic response directly. This is shown in Figure 2.14.

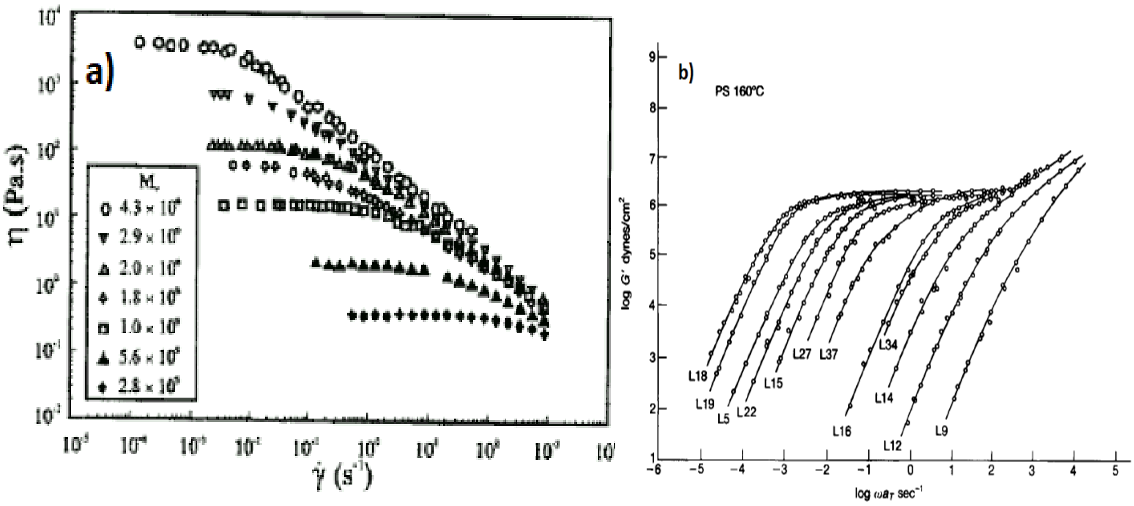

Figure 2.14: Effect of molecular weight in viscosity (a) and viscoelastic properties (b) [12].

Molecular weight distribution of the polymers also affects the viscosity and viscoelastic properties, normally they are distributed in narrow and broad distributions, represented in Figure 2.15, where two different MWD were studied, narrow and broad with frecuency domain, this was done due to the impossibility to measure higher shear rates with rotational instruments [12]. Narrow distributions consist in smaller molecules, so when frequencies or shear rates are applied, a sharp decrease of viscosity can be observed, meanwhile, broad distributions present different behaviour, the loss of viscosity modulus is less pronounced at higher frequencies or shear rates of the broad distribution than the narrow one, so broad MWD show less dependency on shear rate. Also broad MWD modulus is always lower than the narrow MWD modulus.

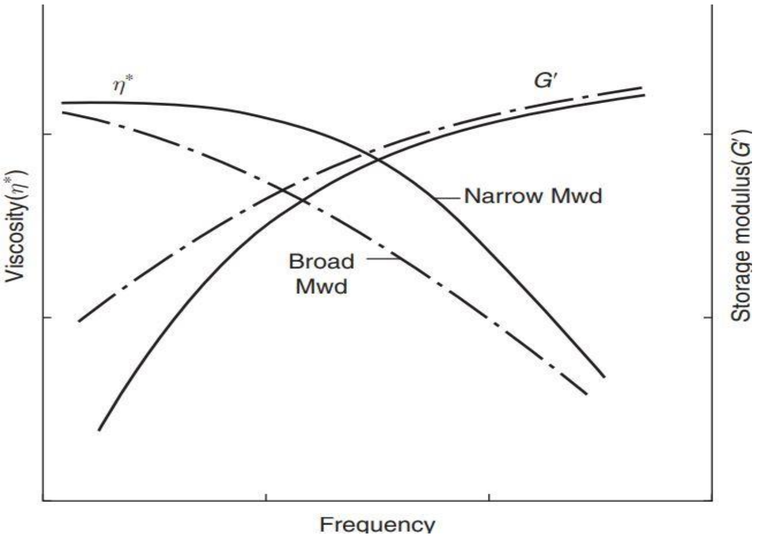

Figure 2.15: Effect of molecular weight distribution on viscosity and viscoelastic properties [12].

## 2.2 Recycling of polymers

Plastic has suppressed traditional materials in many fields because of their inexpensiveness, lightweight or ease to be molded. However, their increasing use over the years has created the need for reusing the plastic waste. Recycling is the transformation of used polymers into new and useful products, this means that post consumed plastics are given new use and properties. Recycling has been a field of study for many scientists due to the benefits it has and the problem of plastic consumption over the years.

The main benefit of recycling is having new products made from previous polymers, which prolongs the lifecycle of plastic products. Moreover, recycling of the plastics is positive also in the economic field, as the recycled polymer can have the same properties as a virgin one and is still cheaper. Another benefit of recycling is reducing the amount of yearly plastic waste, while the environmental impact, that this product generates, is the main issue in the present. Besides, recycling of post consumed polymers reduces the energy used in the process, as the step of material extraction is eliminated, post consumed polymers process save 6000 kWh normally compared to the normal process. On the other hand, the main problem of recycling plastics is that with every cycle of recycling 5-10% of contamination appears in the process, which lowers the final properties, so one can affirm that the recycling of the plastic is not an endless way to get new materials.

We can recycle thermostable and elastomer polymers, but not thermosets. This is because of their structure, explained in Figure 2.2. Thermostable and thermoplastics in general consists of weak Van de Waals bonds, and strong main covalent bonds. When heat is applied to the polymer, with the consequently vibration of the main chain, the wear bonds break sooner than the strong covalent bonds that hold the chain tohether, thus one obtains the polymer melt. Upon cooling, the weak Van de Waals bonds re-sestablish, thus the polymer solides again. On the other hand, thermosets establish a network of covalent bonds, therefore under the application of extreme heat, this network is deteriorated (the covalent bonds that hold the main chain are destroyed) and cannot be re-established, so thermosets can not be remolded or recycled. This phenomenon is also schematicaly presented in Figure 2.16.

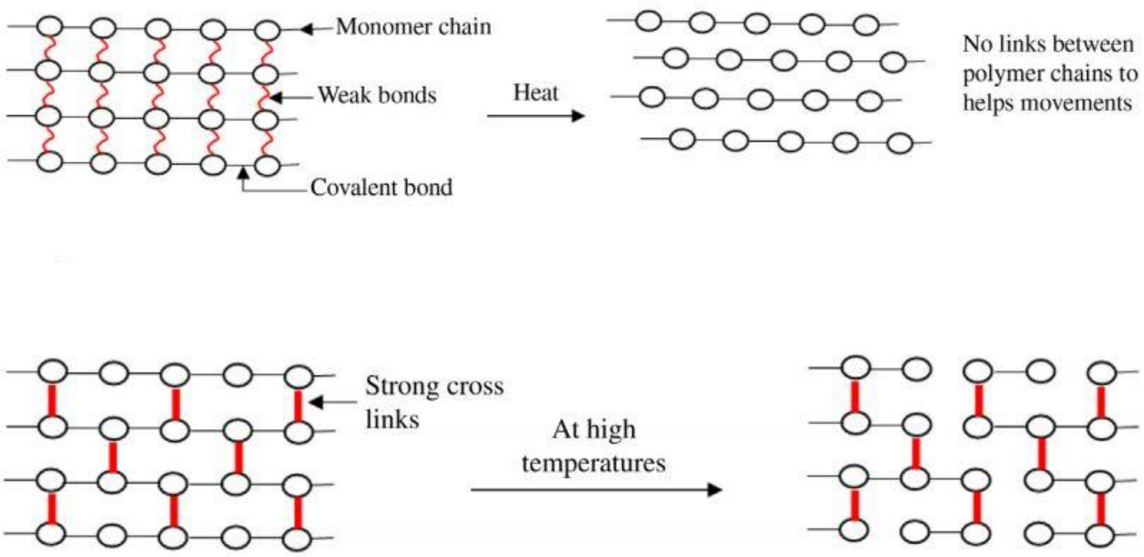

Figure 2.16: Differences between thermoplastics (upper part) and thermosets in recycling [13].

### 2.2.1 Methods of recycling

There are four methods to recycle the plastic: mechanical, chemical, energy recovery and reusing of plastic products. The reusing of polymers is the process of giving a polymer other use without changing its structure.

Chemical recycling is breaking down the polymer chain in order to get the monomer, that can be reused or re-polymerized by forming new chains or melting the monomer into oils or gases to be used in other processes. There are different processes of chemical recycling. The first one is purification, which dissolves the plastic in solvent to remove additives and resulting into a near virgin plastic. Depolymerization is a process where the molecular bonds are broken and the monomers are created by the earlier degradation produced by chain scission, and followed by a conversion, where the molecular bonds of used plastic are recombined, producing hydrocarbons and chemical feedstock.

Another form to recycle polymers is pyrolysis. This is the chemical decomposition in absence of air with generation of oils and gases. It is normally used in high molecular weight substances, that cannot be purified by physical processes like crystallization or distillation and the only way to be recycled is pyrolysis. Pyrolysis is economically not profitable for recycling polymers with poor thermal conductivity because it would require a huge amount of energy.

Energy recovery is a recycling process where the energy is recovered by the incineration of the polymer either generating heat or electicity. This is a good way to use non-useful polymers by transforming them into energy that can be used in water heating for different energy creating systems. Normally, this method is used in those plastics that cannot be recycled by other ways because they can not be economically profitable. The main problem is the contamination that this proces produces, as the emissions generated in the process of burning, like $CO_2$, contribute to the greenhouse effect. As one can see in Figure 2.17 [14], the 36% of plastic in Europe was burned for energy recovery during 2015.

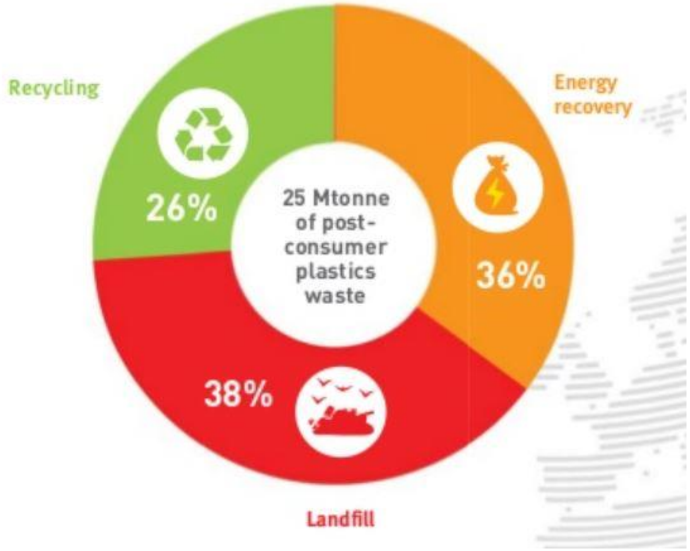

Figure 2.17: Percentage of recycled plastic [14].

Mechanical recycling consists in a process where the polymer is separated by types of polymer and are reprocessed through physical stages of melting and extruding to be transformed to get the final desired properties without changing their chemical structure. This method is the most common method to recycle plastics and it is known that in Europe almost all the polymers are recycled this way. Normally the polymer loses the initial properties due to several degradation mechanisms so additives are used to improve final properties.

The most common groups of recycled polymers are Polypropylene (PP) and High-Density Polyethylene (HDPE) due to their common use. It is calculated that only in Europe there is 114 recycling plants for HDPE and PP, and the amount of recycled PP or HDPE grows significantly every year. These polymers are used in automation, electrical machines or clothing. This is not a coincidence, because HDPE and PP are the easiest polymers to process. However, there are also other groups that are recycled through the same process in the mechanical recycling. Some examples of these polymers are Polystyrene (PS), used in packaging or used in roof constructions due to its excellent thermal isolation, or polyvinyl chloride (PVC), commonly used in pipes construction because of its low weight.

The recycling process involves five steps: collection, sorting, cleaning, reprocessing by melting and extrusion. Collection starts at the pick-up points so the used plastics are picked up. After that thesorting process starts, where every different type of plastic is separated according to the type, so it can be processed. This separation of plastic types is done because of the immiscibility of all of the commonly used polymers that obligate to process them separately e.g. PP, PVC, HDPE or PS, as the polymers are only able to be mixed with themselves and it is impossible to recyclate them together. This happens due to the requirement that Gibbs free energy $\Delta G$ of the blends between different polymers $\Delta G < 0$, where $\Delta G = \Delta H - T * \Delta S$. Normally the entropy $(S)$ of the polymers is small, but the enthalpy $(H)$ is positive and higher than the $T * \Delta S$ product, which leads to positive free energies, making the miscibility of the blends impossible. After being sorted, the plastic is washed to remove all the impurities. The level of the impurities in the plastic will have large influence on the final properties of the recycled polymer.

Once the plastic is cleaned, it goes through the different shredders that turns the plastic into small particles so it can be melted and extruded. The process of cleaning, shredding and separating can be shown in Figure 2.18, taken from a real processing plant [15]. The next processes are usually carried out separately.

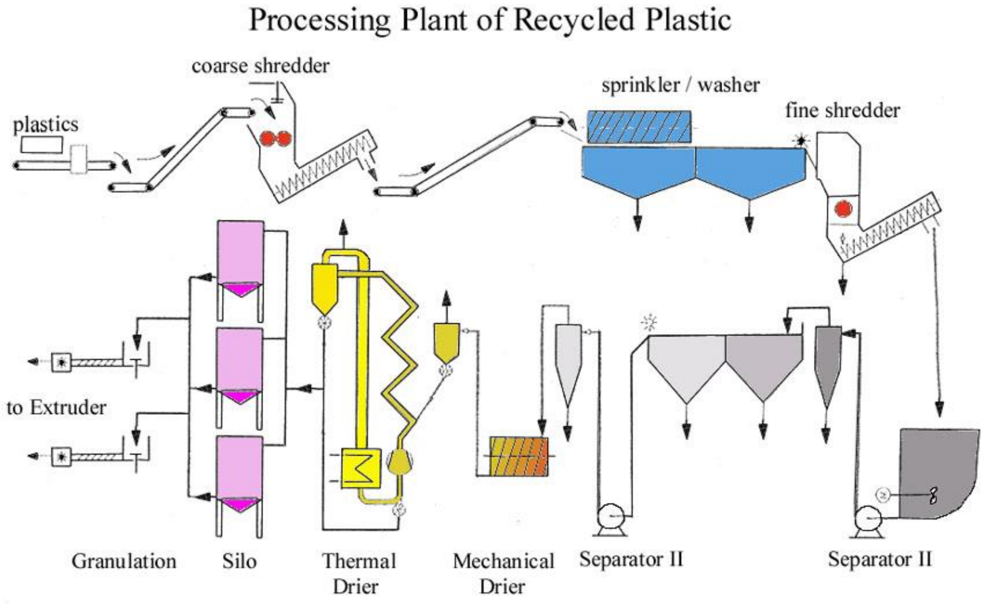

Figure 2.18:Stages of recycling in a processing plant [15].

Once the plastic is already cleaned, separated and shredded, the polymer is melted and extruded. This part consumes the higher ammount of energy, representing 50% of total energy of recycling process.

Melting of plastics occurs in the last part of the recycling process, where thermal decomposition of materials at elevated temperatures in an inert atmosphere transforms the polymer. With increasing of the temperature in reactor, the molecular weight distribution can be varied. The polymer is subjected to the temperatures from temperatures below $T_g$ to temperatures above the melting point, varying in volume and properties.

In the extrusion, the polymer is melted along the side of the extruder barrel and sheared via the screw thread. This is the key stage because several properties deteriorate in this stage, mainly because the molecular weight and structure change significantly with the number of extrusions.

### 2.2.2 Ambiguities and solutions of recycling

Recycled polymers suffer degradation during the recycling process. Usually polymers are susceptible to suffer thermal degradation during the mechanical recycling because of the effect of the oxygen contained in the groups of their structure, resulting in reactions that alter the molecular structure, morphology and later on physical properties. Degradation in polymers can occur by different paths, normally related with the recycling stages, but the most important degradations are produced by the effect of temperature, oxygen and light.

Thermal degradation can limit the processing temperature due to the continued loss of mechanical properties at high temperature. When the polymer starts to degrade due to the temperature, the components of the backbone start to react with each other, changing the polymer structure and properties. There are four main degradation mechanisms: depolymerization, chain scission, elimination and oxidation. Depolymerization consists in the decomposition of the polymer into a monomer, forming free radicals. Random chain scission occurs at any position of the polymer, normally there are two big groups depending on where the chain scission starts. When the chain scission starts in the backbone, the polymer starts degrading and finally it causes the polymer vaporization. On the other hand, when the chain scission starts in the side chains, the process of chain scission produces a high degree of cross-linking, with a final polymer highly crosslinked. In Figure 2.19 general notion of chain scission process is explained.

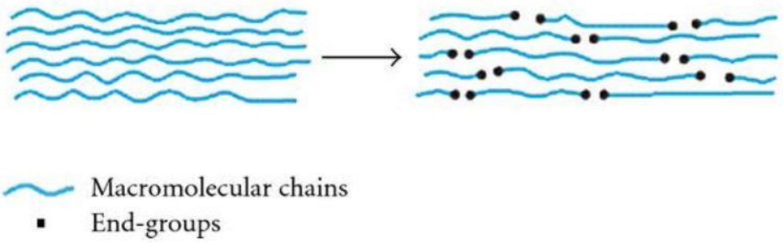

Figure 2.19: Chain scission in polymer [16].

After chain scission, the groups that are attached to the side of the backbone are stripped from the chain, and turned into small groups. Finally, the polymer starts to oxidize by the attack of atmospheric oxygen. The mechanism of thermal degradation is shown in Figure 2.20, and its three main stages (initiation, propagation and termination) with their respectives reactions, it is all started with the heat or light as it is thermal degradation, where the free radical (R*) is created with the hydrogen atom with an umpaired electron (H*). Later, the effect of the Oxygen ($O_2$) creates new free radicals with Oxygen (O*) and peroxides as (OH*). The termination step consists of the creation of inert products that lower the final properties of the polymer.

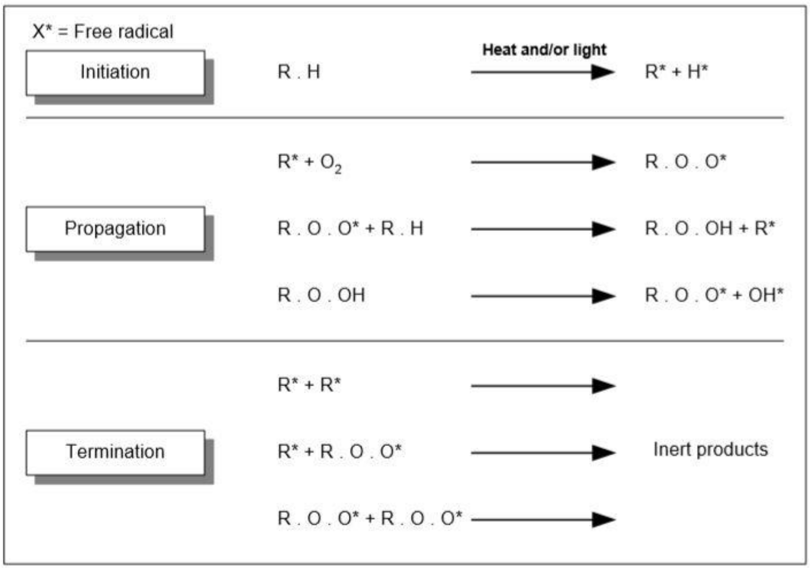

Figure 2.20:Steps of thermal degradation [17].

Oxidative degradation can be produced by thermal degradation, light degradation or high mechanical stresses. When the polymer degrades, the effect of oxygen in the polymer disintegrates the macromolecules, which creates free radicals that will react with the oxygen. The result of these reactions are oxy-peroxy-radicals, that also react with each other creating peroxides, hydroxyl and carbonyl groups or remove the oxygen molecules from the polymer chains. As a result of the oxidation, the mechanical properties are reduced, as the oxidative degradation reduces the molecular weight due to the breaking of the chains and the changes in the structure but also because the high degree of crosslinking as a consequence of the peroxides created, producing embrittlement of the material and softening the polymer surface [18].

Exposure to light have also negatives effects. The visible light radiation or UV breaks down chemical bonds in the polymer, leading to changes in the surface, colour and mechanical properties, always reducing them. The impurities during the process accelerate the degradation in the polymer because they are the main reason of more light being absorbed so more degradation occurs. Moreover, also the amorphous fraction in a polymer is relevant, as the polymer with more crystallinity will oxidize slowly. One may distinguish between photodegradation and photooxidation of a polymer. The second one occurs when the oxygen is involved in the process and produces chain scission, crosslinking and takes place via radical processes as the thermal degradation.

All these changes in the properties and structure of the polymer during the recycling can be diminished by the introduction of additives into the melted polymer. The major challenge in recycling polymers is related to reducing the effects of degradation, specially in virgin polymers due to the oxygenated groups, which are generated and accelerate the degradation. One group of additives are antioxidants. There are two groups: primary and secondary antioxidants. The first group reduces the oxidation of polymers by eliminating the free radicals (i.e. phenols), on the other hand, secondary antioxidants stop the propagation of the degradation by decomposing the oxygenated groups into stable products, we can find examples as phosphites.

The role of stabilizing agents is to prevent the effects of the thermal degradation. The effects of the additive will decrease over the time. In general, we differ two types: thermal and photo stabilizers. When the combination of heat and oxygen causes the thermal oxidation of the polymer and it results in the degradation by the appearance of highly reactive free radicals, additives as hindered phenols help reducing the creation of this groups by acting as peroxide radical decomposers, eliminating the groups. The light, especially in the UV range starts to produce the photooxidation. The effect of photodegradation can be reduced by the addition of UV absorbers, these additives absorb the UV radiation and converts it to harmless infrared radiation or heat energy, an example of this additive is benzophenone. Other type of additive are quenchers. These additives contain chromophore groups, which are special light-absorbing groups that reduces the effect of the light by absorbing the energy and transforming it into other forms less harmful for the polymer. The last group of anti oxidants are HALS or hindered amine light stabilizers, which are small amine groups that remove cyclically the free radicals that initiate the degradation so it never occurs. For example, HALS are normally used with polyolefins or polyethylene [19]. As mentioned before, one of the problems in polymers is the immiscibility between different types of polymers, which can be eliminated by the action of compatibilizers, allowing the blend between two polymers. This is mostly used in recycling blends and adding new polymers to improve the properties. One example is the blend PP/PET which is usually treated with thermoplastic rubbers. With the help of additives, the process of recycling improves the efficiency, as the final properties are not reduced drastically. This leads also to improvements in the economical and applicative field, allowing mixing different polymers and increasing the life cycle of the polymers.

# 3 Literature research

## 3.1 Effect of recycling on physical properties

Recycling and studying of the process and properties of the plastics, especially polypropylene is becoming more important due to its importance in various industries due to its physical properties and variety of uses, such as automotive and household appliances. In this master thesis we are going to focus on the effects of recycling onto the physical properties of the polypropylene.

As it was explained in the previous chapter, the extrusion is the most used technique to process and recycle thermoplastics, since more than half of the reprocessed plastics is being recycled this way. Studying the effect of extrusion on the properties comes from the need to recycle the materials and conserving all of the properties. However, normally we observe decreasing properties during the recycling process.

When a material is extruded, the degradation process starts to accelerate, and the molecular weight loss occurs because the chains start to break and become shorter. This affects first the long chains. A molecular weight loss is observed already after the first extruding cycle and the polypropylene continues to lose molecular weight with the following cycles. After fourth extruding cycle, cross-linking starts to show due to the free radicals formed by the scission of molecular chains. Meanwhile the polydispersity ($PI = \bar{M}_w / \bar{M}_n$) also decreases during the extrusions, mostly because with the continued scission suffered by the molecular chain, homogeneous molecular sizes are produced, but also the imperfections grow with the extrusions, leading to a loss in thermal properties. This results in lower thermal stability with the extrusion cycles, as new free radicals are created, leading to a higher degradation [20].

### 3.1.1 Effect of recycling on thermal properties

The thermal degradation process of the recycled and virgin polypropylene is the same. This is known from the DSC measurements, where the peaks have the same shape and size, and are only shifted, meaning that the degradation suffered by the polymer is only due to the chain scission and there is no different molecular size structure formed. This would lead to different kinetics degradation, so one can affirm that the number of free radicals created after the first extrusion is not big enough to change the kinetic of degradation.

The change in the average molecular weight is illustrated in Figure 3.1 as a result of several extruding processes. In this experiment [20] significant molecular weight decrease was observed after two cycles; after the eighth cycle, a 23% loss was observed. The main reason was the degradation initiated by free radicals, increasing with the number of extrusions.

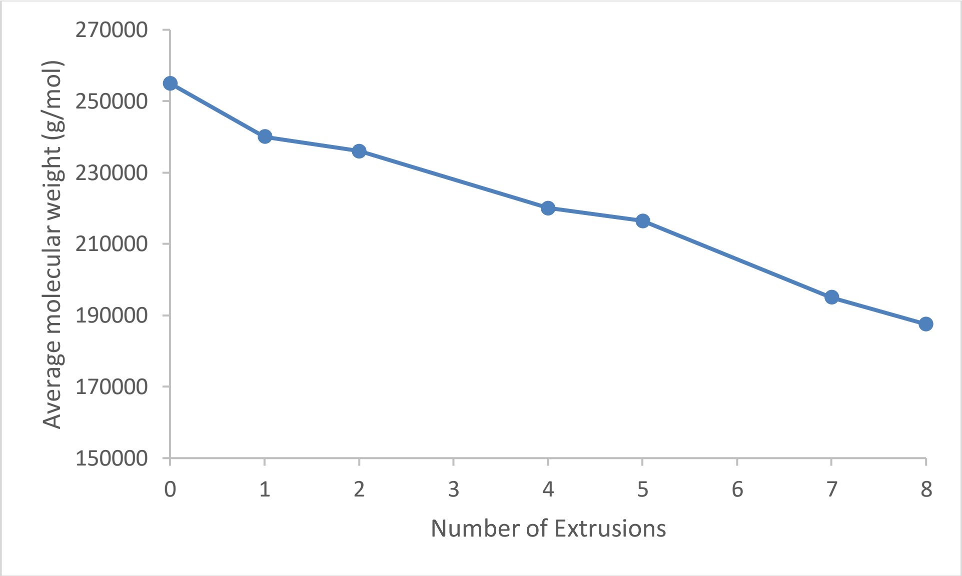

Figure 3.1: Change in the average molecular weight with extrusion cycles [20].

Molecular weight is related with phase transitions temperatures. Glass transition temperature ($T_g$) increases with the increasing of the molecular weight of polymer upon consecutive recycling, but when $M_w$ of the polymer decreases, the $T_g$ also decreases. This is shown in Figure 3.2 [21].

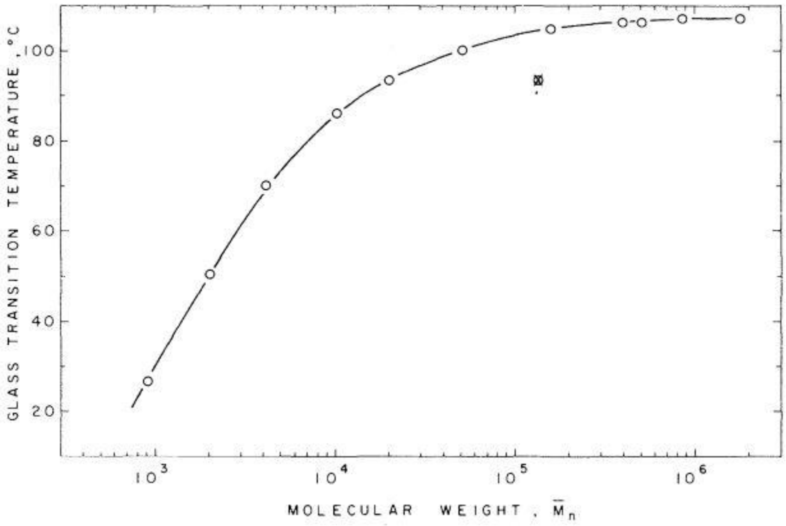

Figure 3.2: Relation between $T_g$ and average molecular weight [21].

As the molecular weight decreases with the processing cycles, the enthalpy of fusion increases, which means that more heat is required to get the polymer into the melted state. The difference in the enthalpy of fusion between the recycled and virgin PP is due higher amount of chains or particles in the polymer, for which the more heat is required to break them. Moreover, the melting temperature ($T_m$) is lower, because of the reduction of molecular weight. Mandelkern [22] tested polyethylene and the results are shown in Figure 3.3. In the study, three different types of polyethylene were tested, each with different molecular weight. In the Figure, the higher molecular weight pallet is represented with black squares, and the lower molecular weight pallet with white circles. The graph shows the different results obtained and it is clearly seen that the enthalpy of fusion increase with the number of extrusions and with the decrease of the molecular weight.

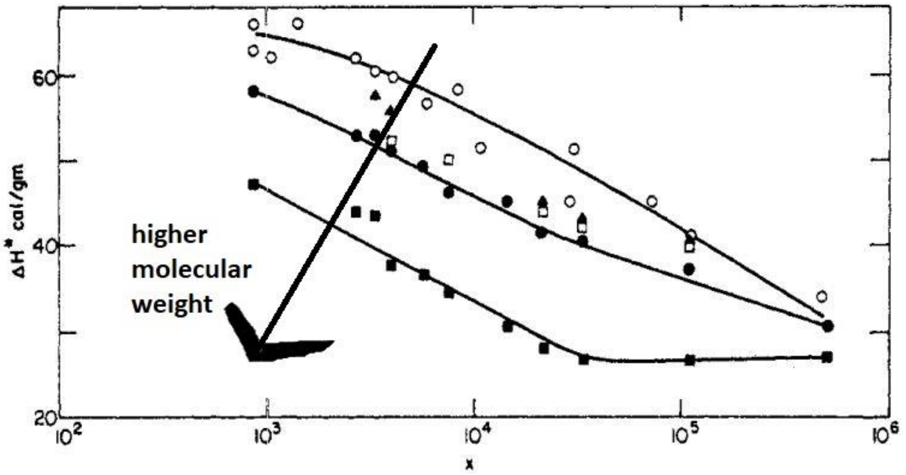

Figure 3.3: Enthalpy of fusion as a function of Molecular Weight for polyethylene [22].

Furthermore, lower molecular weights correspond to lower entanglements, which means that higher mobility of the particles is reflected in higher crystallinity of the polypropylene. This increase can be also explained by the fact that macromolecules with lower molecular weight act as nucleating agents, which leads to the crystallization of semicrystalline polymers by folding and building bigger crystal structures. Also, crystallization temperature increases with the number of extrusions, as a result of the decrease of molecular weight.

To summarize the influence of the recycling on the phase transition temperature Figure 3.4 was recreated, schematically representing the behaviour of the recycled polypropylene during the heating a) and the cooling process b) of a DSC graph.

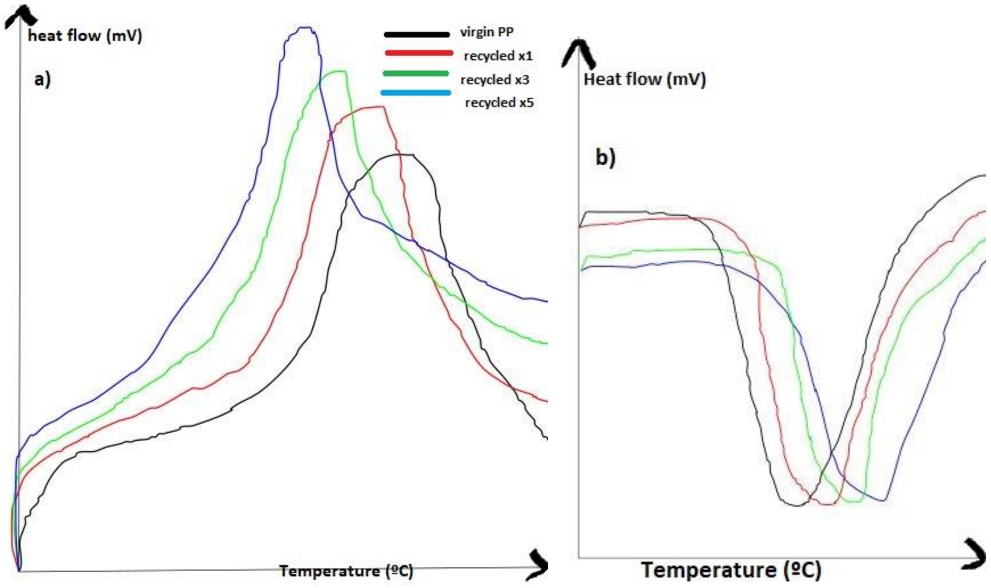

Figure 3.4: Schematic representation on the effect of recycling on phase transition temperatures of PP.

### 3.1.2 Effect of recycling on mechanical properties

As explained before, the process of recycling produces a loss of molecular weight, or rupture of chains into small ones, but there are also other parameters, such as thermomechanical stress, the presence of oxygen, impurities or water in the process that are capable of producing changes in the structure of the recycled polypropylene. This changes start in the backbone chain and are responsible for the increase or decrease of the chain length or the formation of functional groups that modify the mechanical properties of the polypropylene. Thus, the level of degradation and loss of mechanical properties of the polypropylene depends on the extrusion number, the stress the polymer suffers during each process and the crystallinity of the polymer. The main properties to study the impact of recycling on mechanical properties are: tensile stress and Young modulus ($E$) [24].

The elongation ($\mathcal{E}$) is related to the crystallinity and molecular weight of the polymer. The higher the crystallinity of the polypropylene, the less will the polymer elongate. Also, when the molecular weight drops during the extrusions, more but smaller chains are created. This means that there are less completely integrated chains, so the crystals formed are not capable of sustaining the stress carried out and the polymer breaks at lower elongation.

Oblak [24] tested the mechanical properties and processability of polyethylene, and the effect of the extrusions on molecular weight. The results of these experiment are explained in the following pages.

During the process of recycling the elongation starts to decrease since the molecular weight reduction starts, but it is usually in the 4th extrusion cycle, where the elongation drops and decreases drastically as it was studied in the study of Oblak [24] and is presented in Figure 3.6.

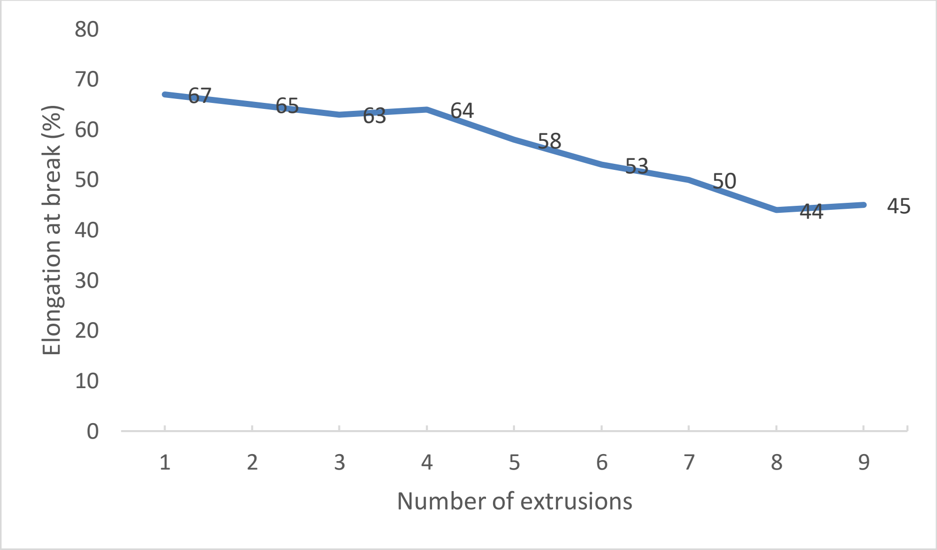

Figure 3.5: Elongation at break depending on extrusion cycles [24].

As explained in theoretical background, with the reduction of the elongation due to the increased number of extrusions, Young's modulus $E$ will increase as it is presented in Figure 3.6[24]. This property is very useful in construction and resistance of materials, being a key property to control during the polymer recycling. It can be controlled by using additives that reduce the elongation loss, which will be explained later on in this thesis.

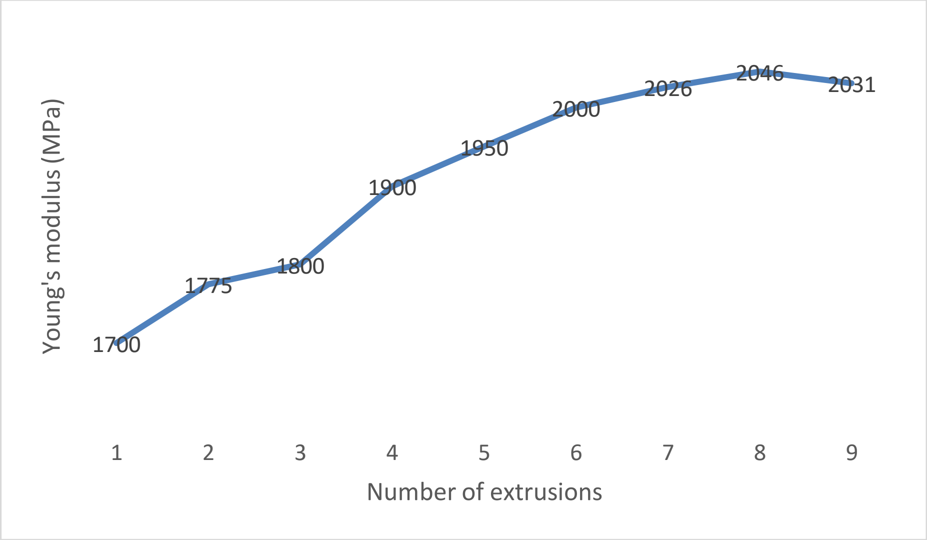

Figure 3.6: Change of Young's modulus with the number of extrusions [24].

Recycling affects also time dependent properties as shear creep compliance measurements in Oblak's study, where one hundred cycles of recycling a polyethylene [24] showed a decrease of the properties after the 30th extrusion cycle. Also, this results suggested that chain branching is the main mechanism of polymer degradation through the first 30 extrusion cycles but afterwards the chain scission and cross-linking appears. This was obtained by a study of the activation energies. The decrease of the activation energy represents the presence of chain scission and higher mobility of the chains, and the increase is related to a crosslinking process, which in the mentioned study appeared in the last 20 cycles.

The increasing shear creep can be related to crystallinity. On the molecular level, the higher crystallinity leads to the higher resistance for polymer rearrangement. Also, the increase of creep compliance with the time is attributed to chain scission and the changes in mobility of molecular chains due to the variation of activation energy.

Figure 3.7 shows the results of Oblak's tests [24] representating the time dependent behaviour of a polyethylene at three years and ten years as a function of number of extrussion cycles. Figure 3.7shows how time dependent mechanical properties, i.e. shear creep compliance, increases after 30 cycles due to chain scission.

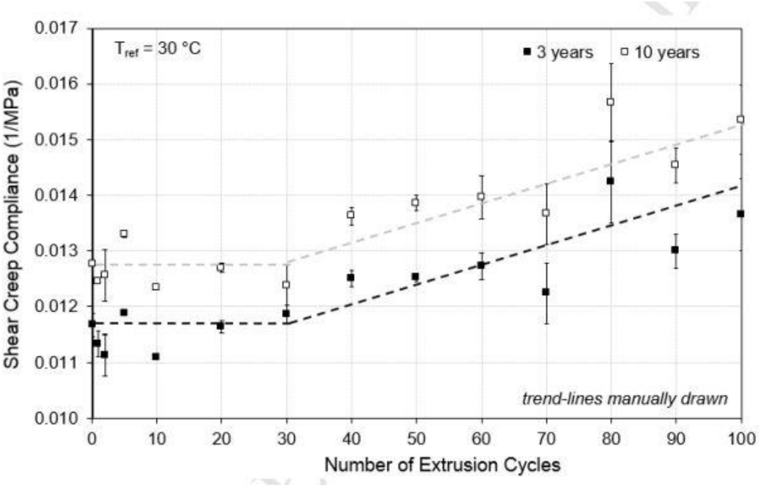

Figure 3.7: Effect of recycling on the time dependent properties of two types of polyethylene [24].

Finally, the hardness is strongly dependent on temperature and time, as fragility or hardness are affected by the extrusion cycles. On the one hand, fragility increases with the processing steps and with low temperatures, being one of the main problems during the life-time of the final product. On the other hand, the hardness increases with the increased number of extrusions [25].

### 3.1.3 Effect of recycling on rheological properties

As mentioned previously, the mechanical recycling affects the molecular weight and molecular weight distribution, which drastically changes also the rheological properties. In this chapter, the rheological behaviour of polymers will be explained, where specific information and detailed data about the chain branching will be given.

Melt flow index (MFI) is dependent of the molecular weight. The MFI is measured using a machine with the melted polymer. A specific weight is applied on the melt to push the melt into a die, after which the melt flow is measured. the MFI increases with the number of extrusions due to the fact that with the further process steps, the entanglements are lower, so the resistance of the melt is lower and consecuently the MFI increases. The absence of the changes in the chemical structure and the increase of the MFI leads to conclusion that chain scission is the dominant degradation mechanism of the recycling process and not the oxidation process. In Figure 3.8 one can observe the increase of the MFI with the number of the extrusions. It is known that lower melt flow rate results in lower mechanical strength.

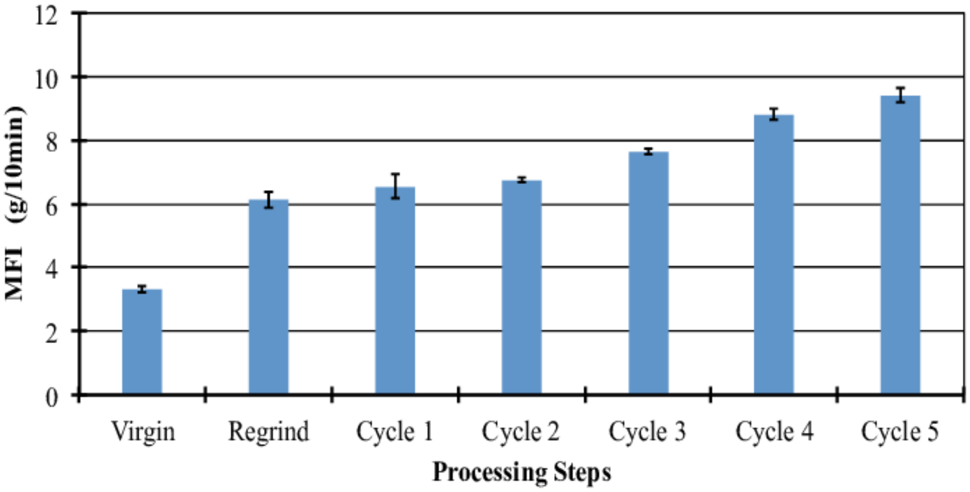

Figure 3.8:Variation of MFI with extrusions [24].

It is well known, that with the number of extrusions the molecular weight or entanglement between chains in the polymer drops drastically. Moreover, chain branching appears also with the recycling proccess. This produces lower packing density of the chains and larger crystallites. Small crystalls are created during the process of cooling or restructuring after the extrusion that give the properties to the final product [26].

The viscosity is the resistance of the polymer to the flow deformation as explained before, and with the drop of the molecular weight, the viscosity is also reduced. As the more entanglements or strenght between the chains exist, the more resistance the material exhibits to flow. However, the viscosity is also affected by the chain branching, as the reduced density of the chains means lower viscosity.

Viscoelastic behaviour of a polymer is usually carried out with a frequency sweep test. From the experiment, which were carried out by Zdiri et al. we can notice the fact that in the low frequency region the change in viscosity is more evident (Figure 3.9 [27]), which happens due to the loss molecular weight, thus the viscosity is lower viscosity. Furthermore, in low frequency regions, big molecules as virgin PP need smaller frequencies to exhibit flow behaviour, this is why the curve of virgin PP doesn’t flatten in the range of low frequencies, which represents flow behaviour. On the other hand, smaller molecules as for the recycled PP present flow behaviour at higher frequencies, due to the chain scission. The result in Figure 3.9 show that at 100 rad/s or higher frequencies, polymers – recycled and virgin - react similar with decresasing of complex viscosity, which is the result of the impossibility for the molecules to adjust or adapt at higher frequencies.

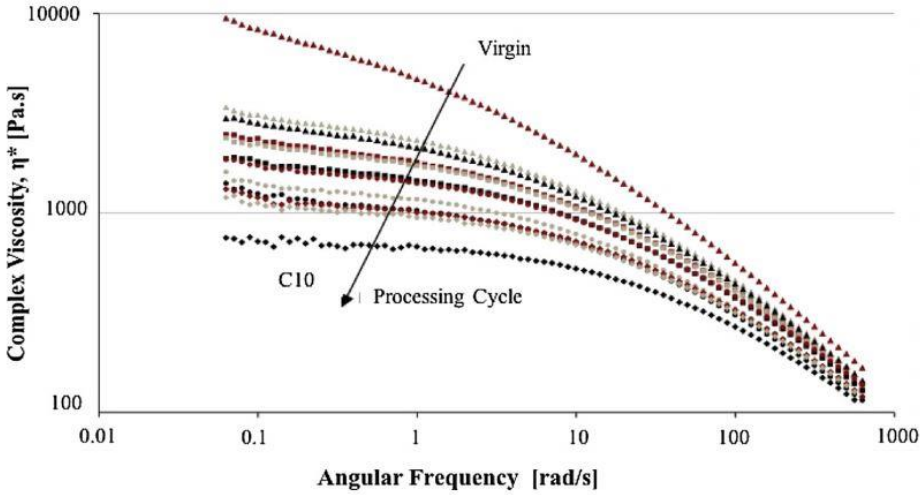

Figure 3.9: Effect of recycling on complex viscosity [27].

Another graph, that is helpful to understand the variation in the viscosity, is so called Cole-Cole plot represented in Figure 3.10. Figure 3.10 presents the study of Hammani [26] with recycled PP and the influence of the recycling process on the real and imaginary viscosity. The results were presented as relationship between the real viscosity ($\eta'$) and imaginary viscosity ($\eta''$). Cole cole plot is also a useful weapon to understand the relaxation time of a polymer. If we compare virgin and recycled PP, we can observe a radius difference between the samples. The smaller radius of the curve in the plot means shorter relaxation time of the polymer. Shorter relaxation times mean that smaller molecules are present in the polymer and the molecular weight distribution is getting narrower, which can be attributed to chain scission.

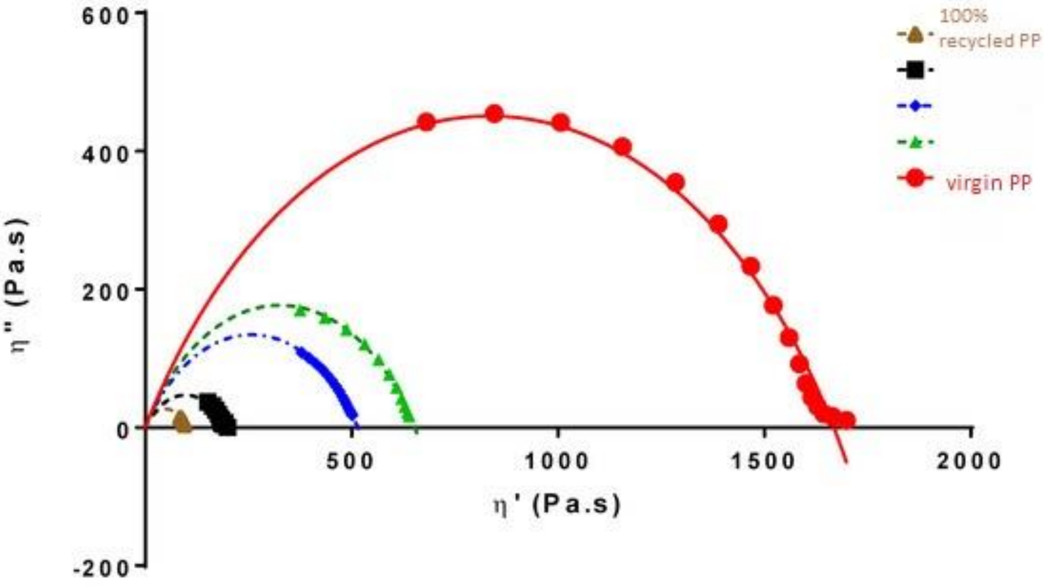

Figure 3.10: Cole-Cole plot for viscosity of recycled PP [26].

Shear modulus is also affected by the extrusions. On the one hand, storage modulus ($G'$) decreases slightly from the virgin polymer to the recycled one, which could be explained by the effect of recycling on to the polymer branching. Also, the terminal behavior changes, as linear polymers have $G'$ proportional to $\omega^2$ and for branched polymers $G'$ is proportional to $\omega^{<2}$

Other experiment useful to this thesis is the one carried by Li [28] of the effect of recycling on the frecuency dependency of storage modulus, loss modulus, cross over point and phase shift for virgine and recycled PP. The experiment consisted in three samples, where P1 represents virgin polypropylene, P2 is a three times recycled and P3 s a five times recycled PP.

The results on storage modulus are presented in Figure 3.11. At lower frequencies the difference between the modulus of virgin and recycled PP is always higher than at high frequencies, which is due to the higher average relaxation time of the recycled polymer chains, since the chains cannot adjust fast enough to compensate the applied load due to the loss of interactions as a consequence of the molecular weight loss.

After three extrusions there is a reduction of chain branching, there is a transition from branched polymers to more linear ones. This is reflected in the change of the slope in the three samples, linear polymers present a sharp increase with lower frequencies.

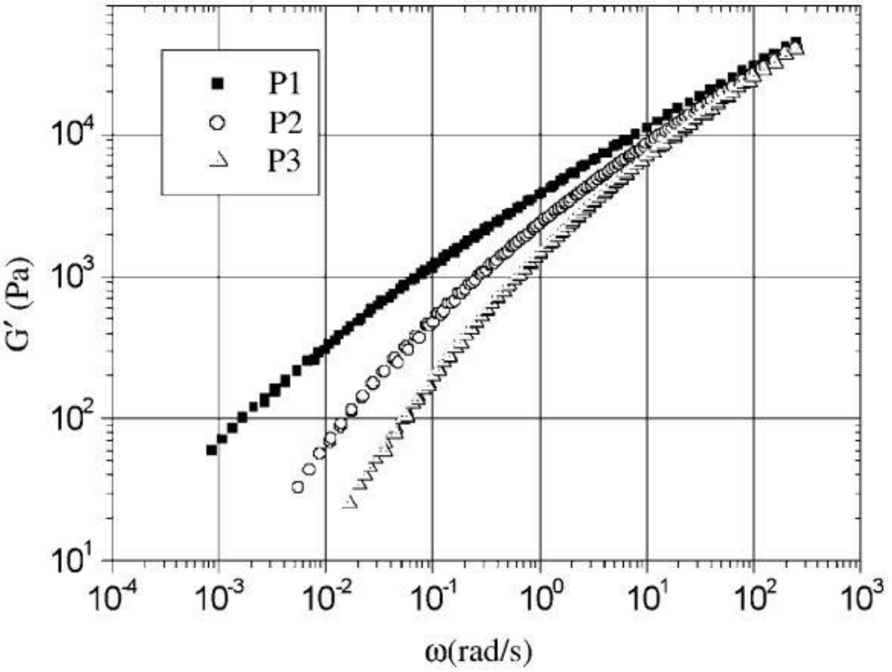

Figure 3.11: Effect of recycling on storage modulus G' for virgin PP (P1), three times recycled PP (P2) and five times recycled PP (P3) [28].

The same trends can be also observed for the loss modulus (G"). The reduction in the entanglements and density as a consequence of the loss of molecular weight produces lower values of the modulus as expected. Moreover, compared to the G' a higher difference in G" was observed at low frequencies. The authors of this study investigated also the slope of the curves. It was explained that when the polymer contains smaller molecules and not branching the slope of the curve is gentle, while the slope of the branched polymers is much more steep due to the effect of strong interactions between the chains.

If we compare the evolution of $G'$ and $G''$ with frequency, we can investigate the point, where the moduli are the same. This point is called cross-over modulus point (G = $G'$= $G''$) and the frequency, at which the moduli are the same, is called cross-over frequency, as it is shown in Figure 3.12. As it can be seen from the figure, with the extrusions, the cross over point is higher (at higher frequencies with higher values of modulus). With the rise of the cross-over point, the relaxation times are smaller for the molecules, which is characteristic for shorter molecules and it reflects chain scission.

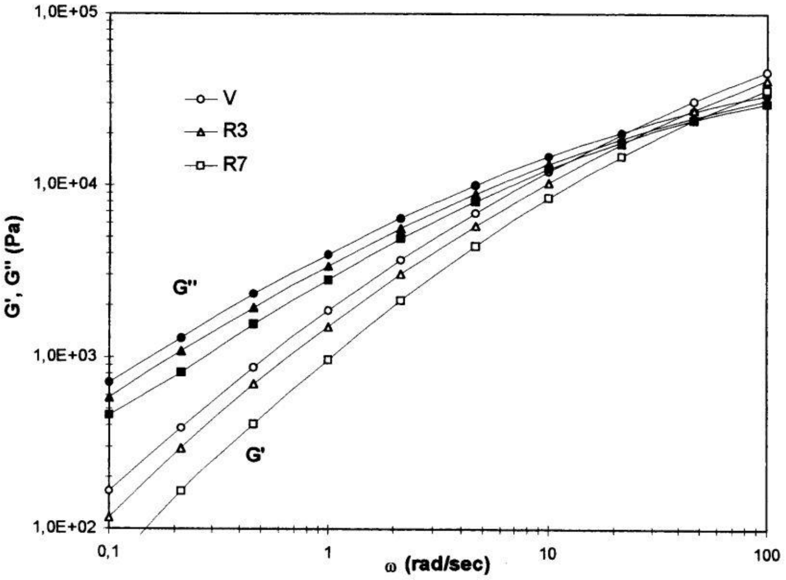

Figure 3.12:Crossover point for virgin polypropylene (V), three times recycled PP (R3) and seven times recycled PP (R7) [28].

It is also important to understand how the phase shift varies during the processing. This relationship between $G'$ and $G''$ can be explained with the cross-over point and the evoluton of $\delta$. One can see that with the number of extrusions $\tan\delta$ decreases as the difference between $G'$ and $G''$ is lower this lower difference between both modulus is explained by the loss of molecular weight. Figure 3.13 shows the behaviour of the PP polymer as the results of the experiment of Li and coworkers [28]. The results showed that the phase shift at low frequencies is higher and reaching the peak at frequency of aproximately 1 Hz. Then at higher frequencies the phase shift decreases because the molecules cannot adjust in time. Phase shift also decreases with the extruding cycles as it is shown with the virgin PP, one time recycled PP, three times recycled PP and five times recycled PP.

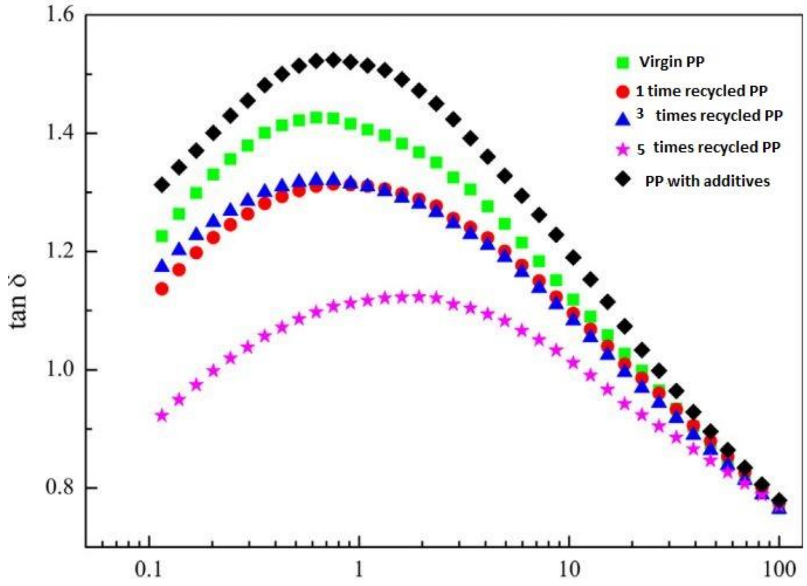

Figure 3.13:Phase shift with the frequency [28].

Based on the literature research on effect of recycling on rheological behavior it is clearly visible that by increasing the number of extrusions of PP the $M_w$ profoundly drops, zero shear viscosity is decreasing, PP does not get crosslinked, which is observedfrom G' and G'', but rather smaller (linear moleculs are obtained). This suggests that during the extrusion chain scisision prevails, which occurs normally in the backbone.

## 3.2 Effect of rejuvenating agents on physical properties of recycled polypropylene

Recycling process reduces physical properties in many ways, while additives help to improve mechanical, thermal or rheological properties. The addition of such substances in order to improve the properties has to be controlled, because every polymer matrix reacts differently on the addition of different proportions, mixtures or fillers. Filler is defined as the additive introduced into the polymer matrix in solid form. Inert or passive fillers are usually used to lower the price, like talc or various minerals, while active fillers are also known as reinforcing for producing improvements in the physical properties, like for example $CaCO_3$.

Some additives are only used to prevent degradation process and help in the prevention of the deterioration of physical properties. These are known as stabilizers. Other specific nanocomposite fillers are used to increase the physical properties. In this chapter, the effect of specific additives on the final physical properties are presented.

The effect of the addition of nanofillers is reflected usually by an increase in the properties due to the high specific area of the nanoparticles. The specific area represents the interactions between the polymer and the filler. Therefore, the higher is the specific area, better are the interactions and material properties are improved. This addition of low concentrations of nanofillers does not represent any increase in density or other properties such as light transmission [29].

There are three major methods of incorporation of nanoparticles into the polymeric matrix. The first one is melt compounding of the nanofillers into the polymer. This is done when the polymer is extruded and the melted fillers are injected into the polymer matrix. The second method is *in situ* polymerization, where the monomer is in a liquid state during the polymerization and the nanofiller is added directly to the liquid monomer. The last method is the solution method, where solvents such as toluene, acetonitrile or chloroform are used to integrate the molecules of the nanoparticles added and the polymer matrix. The most used methods are *in situ* polymerization and melt processing, as the use of a solvent is not environmentally friendly. In this chapter, with the example of different studies, the effect of additives on thermal, mechanical and rheological properties will be explained.

### 3.2.1 Effect of additives on thermal properties

Thermal properties of recycled polypropylene with additives are influenced by the elaboration process, filler content and type of surfactant. Surfactants are compounds that lower the surface tension between two different liquids helping them to mix and interact.

It is known, that the effect of recycling on thermal properties is reflected in a change of phase transition temperatures, as $T_g$ and $T_m$ decrease, $T_c$ increases, and thermal diffusivity is decreased.

The addition of nanofillers into the polymer results in a reduction of the glass transition temperature $T_g$, which can be explained by the effect of the additives into the polymer structure. Once the additive is introduced to the polymer, the spaces between the polymer chains become larger, which results in increasing the free volume. When the free volume is increased, the Brownian motion or segmental mobility increases, which is observed by the decrease of $T_g$.

Moreover, the melting temperatures $T_m$ has been tested as described by Elloumi et al. [30], where incorporation of $CaCO_3$ nanocomposites into recycled polypropylene was presented. The results showed that there were no differences between the virgin PP and the PP- $CaCO_3$ composite. On the other hand, López et al. [31] in their experiment found out that the addition of stone ground wood pulp fillers (SGWPF) decreased $T_m$ in 5 ºC as it can be seen in Figure 3.14. This can be explained by the fact that SGWPF creates oligomers that change the internal structure of the polymer, so the decrease of $T_m$ is more significant.

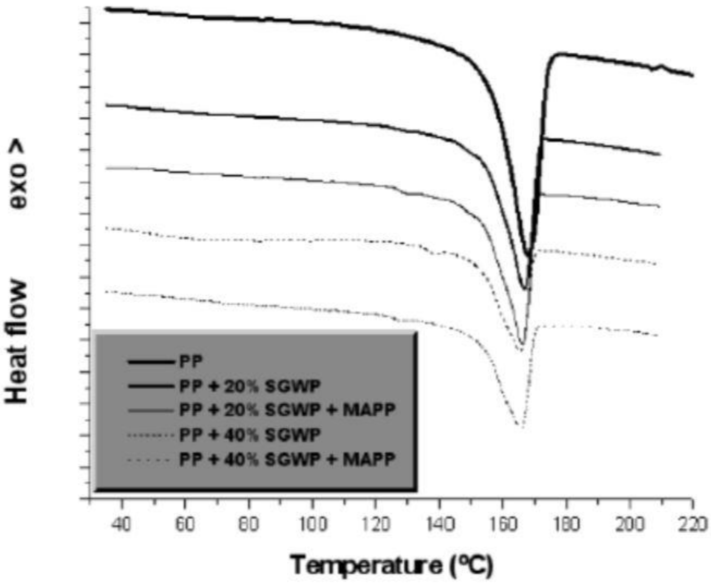

Figure 3.14: Effect of SGWP content on melting temperature of recycled PP 31].

On the other hand, the addition of the aditives increases the crystallization temperature ($T_c$). This can be explained by the role of the additives as nucleating agents, which cause the increase in $T_c$ and crystallinity. In work of Ajorloo et al. [32] the effect of polypropylene/graphite (GnP) nanopallets was studied and the effect of the size as short and long fibers where tested with lenghts of 100$\mu$m and 1500$\mu$m, respectively. Moreover, their dependence on concentration was studied. The results showed that the recycled polypropylene exhibited higher $T_c$ for concentrations higher than 4% as it can be seen in Figure 3.15, where PBH and PBE represent the branched PP and F13E and F13H represent linear PP with different lenghts 100 $\mu m$ (F13H and PBH) and 1500 $\mu m$ (PBE and F13E).

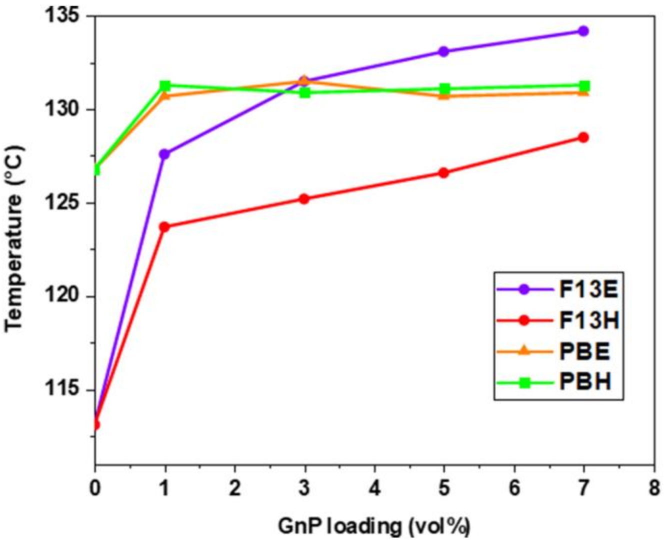

Figure 3.15: Effect of GnP on crystallization temperature for different PP samples [32].

Other authors such as Patnaik et al. [33] tested the composites of recycled polypropylene with the incorporation of different concentration of 500 mesh and 30nm of diameter talc nanofillers with boehmite alumina (BAL). These different concentrations (1%, 2%...) in weight volumetric (%) proved that the higher concentration of nanocomposites had the higher concentration of nuceating agents and the results, that are shown in Figure 3.16, support the previous experiments as $T_c$ increased and $T_m$ decreased with the addition of the aditives.

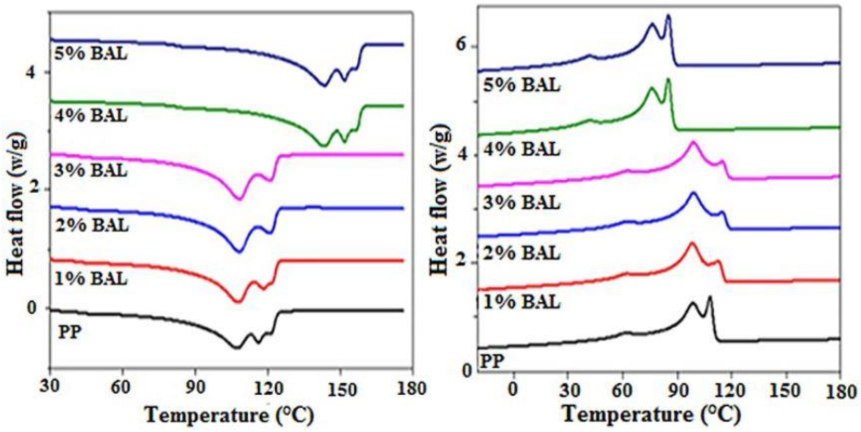

Figure 3.16: Effect of different concentration of talc nanocomposites on $T_c$(left) and $T_m$.(right) [33]

Crystallinity is also affected by the addition of additives. Some experiments revealed that the addition of nanofillers to the polymer increases crystallinity by acting as nucleating agents. The crystallinity at lower concentrations is higher due to the nucleating agent effect of the additive, letting microcrystals to grow in the molecules and also, because the higher specific area of additive increases the crystallization in the nucleating stage. At higher concentrations, the additive decreases the crystallinity due to a rise of the defects in the macromolecular chains which reduces the crystal growth. Figure 3.17 reflects the results of the experiment carried out by Gomes Simanke et al. [34], where polypropylene was tested in addition of two different nucleating agents additives, 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (Millad® 3988 from Milliken) (NA) and sodium benzoate (NB). The first plot corresponds to the PP+NA mix, the content of the additive is represented by an increasing scale of numbers, thus, NA 3 is the sample with the highest content of additive and NA 1 the sample with the lowest concentration. The same criterium is applied in the second plot that shows the PP+NB behaviour. These two substances explain perfectly the influence of additives on crystallinity as the results of the PP + NA and PP + NB mix. As it is presented in Figure 3.17A, the slope or crystallization rate, which is the time to achieve a specific crystallinity degree, increases as the proportion of the additive increase in the PP + NA samples. This leaded to the conclusion that some additives such as sorbitol derivatives (NA) need a minimum concentration to act as a nucleating agent. On the other hand, the crystallization rate decreases with the increase of the NB additive content. The high concentration of NB leads to the agglomeration and the nucleating efficiency of nucleating agent decreases.

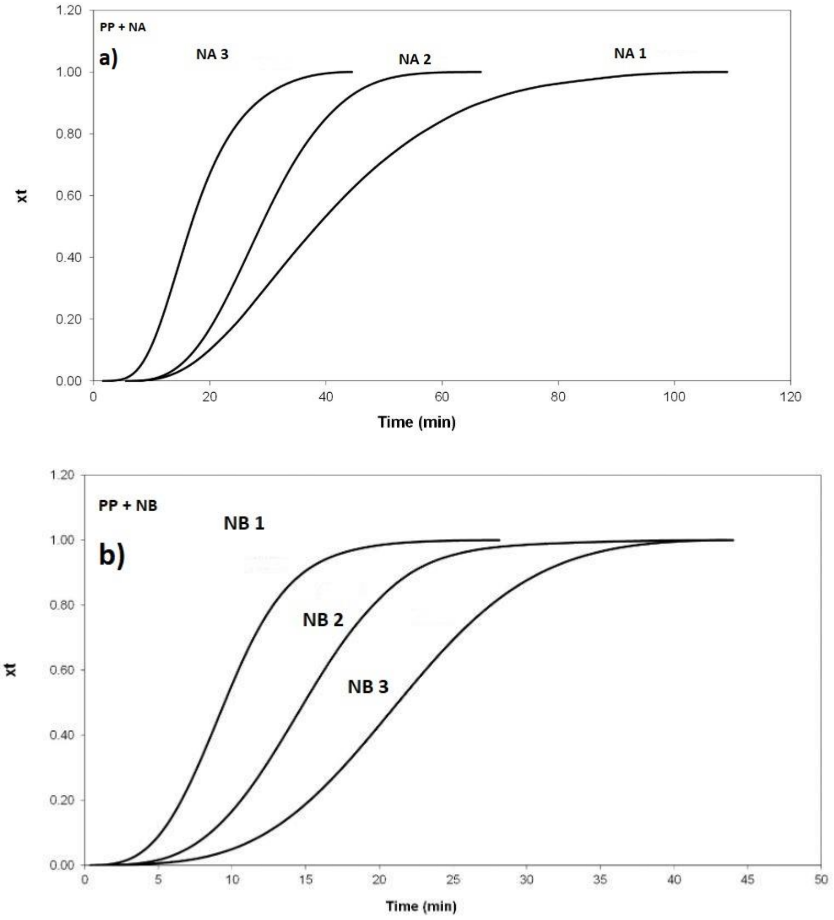

Figure 3.17: Effect of additives on crystallization rate of PP with different additives (A and B) and different concentrations (lowest corresponds 1 and highest 3) [34].

Thermal conductivity also increases with the increasing concentration of nanoparticles and crystallinity level. This is because nanoparticles present high thermal conductivity and when the fillers are in the polymer matrix they transfer the heat. In their study with recycled PP (rPP) and virgin PP (vPP), Hadi and his coworkers [35] studied the influence of $CaCO_3$ on thermal conductivity. The results, shown in Figure 3.18, indicate, that the thermal conductivity is higher with the increased addition of $CaCO_3$.

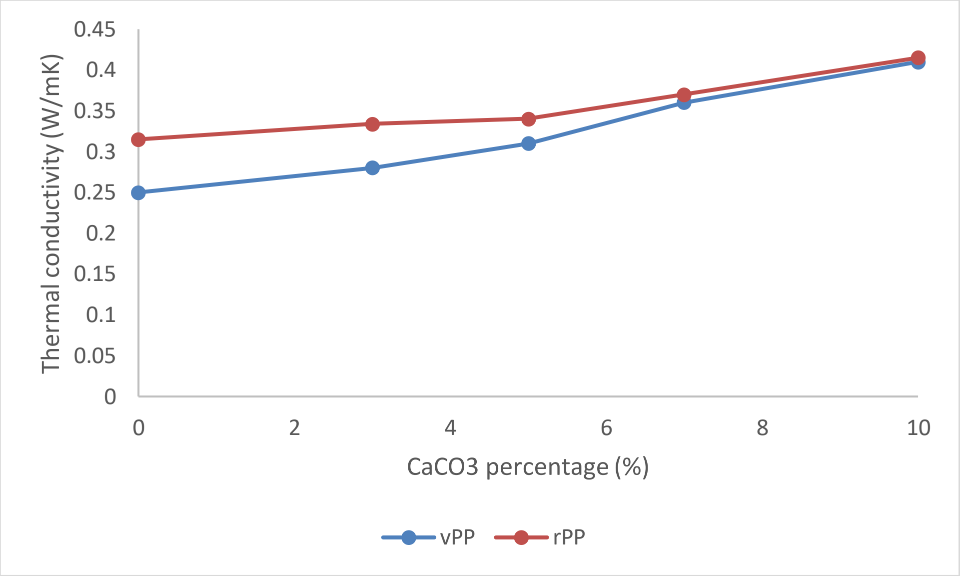

Figure 3.18: Effect of $CaCO_3$ in thermal conductivity of recycled PP (rPP) and virgin PP (vPP) [35].

Thermal additives also help to postpone the onset of thermal degradation, as the additives improve the thermal stability. Patknaik and his coworkers [33] proved that when they tested three different concentration (1%, 3% and 5%) of boehmite alumina (BAL) in recycled polypropylene. The results of the TGA are shown in Figure 3.19, where the addition of BAL retarded the degradation temperature, with a 200 ºC difference between the recycled PP and the recycled PP with 5% of BAL.

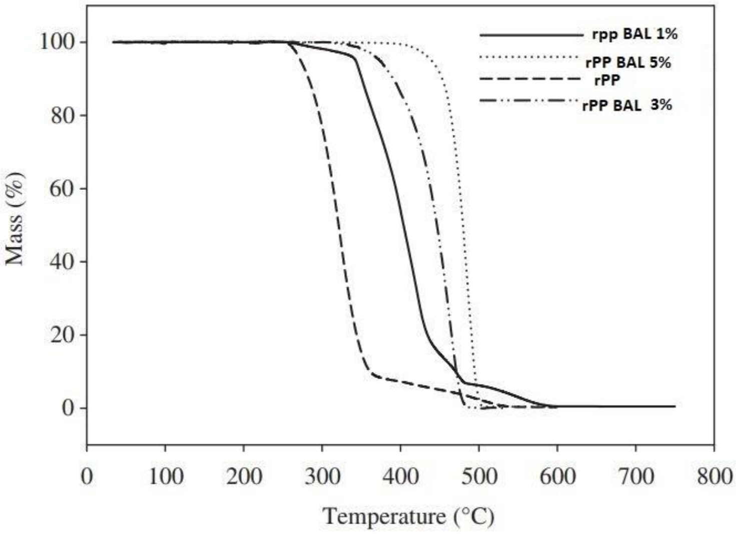

Figure 3.19: Effect of BAL additives on thermal degradation of recycled PP (rPP) [33].

### 3.2.2 Effect of additives on mechanical properties

As explained before, mechanical properties decrease during the process of recycling and additives are needed to improve the final properties. The most commonly used additives are nanofillers, glass or wood fillers, especially the nanofillers, which have been the main focus of several studies. The most frequently used nanoparticles are carbon black (CB), carbon nanotubes (CNT), shrimp shells (SS), graphene (GN) or graphite (C).

Some experiments tested the effects of the addition of graphene [35-37] on tensile strenght and Young's modulus. They showed that the improvement of the mechanical properties was due to the increase of filler content in the polymer, since certain part of external force is also transfered to filler, wich is usually mechanically more resistent than the matrix material. Other reason can be the degree of stiffening, increased with the filler content and producing an increase in $E$. Tensile strength increases with the extrusions as can be seen in Figure 3.20. These results were obtained by Husin et al. [36]. In the experiments polypropylene was tested in different proportions and concentrations of graphene nanocomposites (NC), as there were virgin PP (100v-0r) and recycled PP(0v-100r) and different concentrations of the additive (0, 3 and 5%).

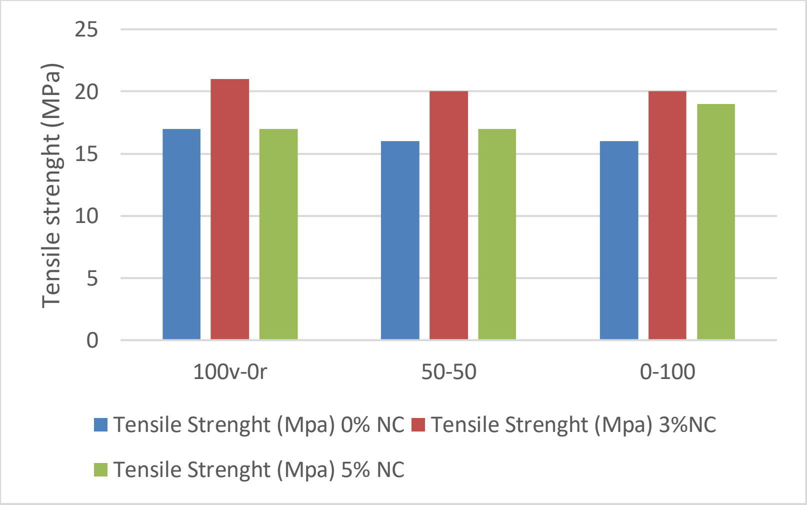

Figure 3.20: Effect of graphite nanocomposites on tensile strength of different concentrations of virgin PP (vPP) and recycled PP (rPP) [36].

Husin and his coworkers tested also the introduction of the nanoparticles as an additive and obtained an increase of the Young's modulus as can be seen in Figure 3.21 where PHR means part per hundred. The results show an increase of Young’s modulus with the addition of Graphene.

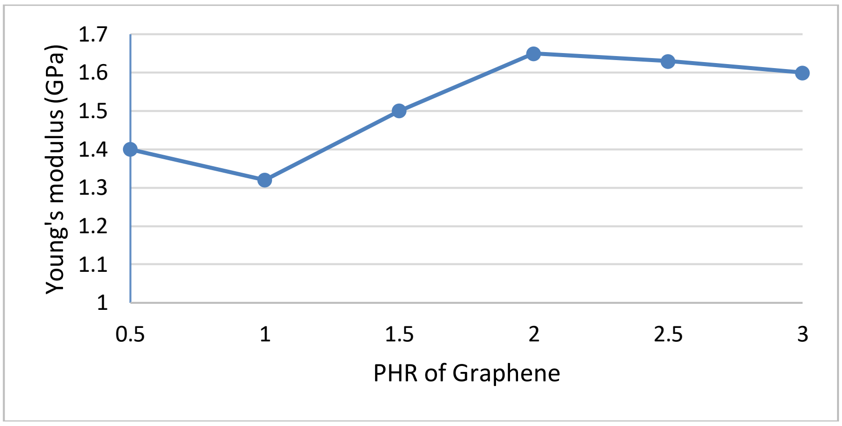

Figure 3.21: Effect of graphene nanocomposites on Young's modulus measured in parts per hundred (PHR) [36].

Other fillers, such as carbon nanotubes (CNT), can also increase mechanical properties as they induce the polymer to crystallize. Besides, CNT fillers could be well dispersed through the PP matrix, thus achieving bigger interactions between PP and CNT, which means that the load transfer from the matrix to the nanotubes is more efficient. On the other hand, the application of long glass fibers and wood fibers improves the mechanical properties to the level of the virgin material. These long glass fibers reinforce the entanglements of the chains, improving the tensile strength, as can be seen in Figure 3.22, where the graph represents the ratio between tensile strength of PP with various concentrations of adiditive and the tensile strenght of virgin PP [38].

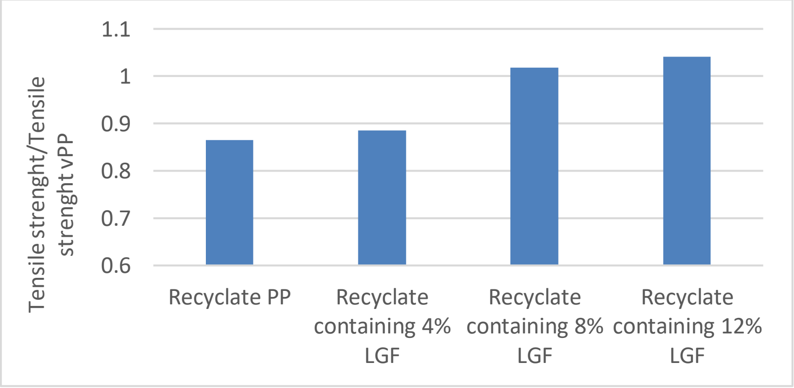

Figure 3.22:Effect of the addition of long glass fibers on tensile strength for the recycled PP [38].

The main problem when adding fillers to the polymer matrix is the proportion to get the best properties, as the experiments show decreasing properties of the polypropylene with the agglomeration of additives. In the experiments with graphene [36], the maximum tensile strength and Young's modulus were not reached at the maximum proportion of nanocomposites in the polymer, 3% and 20 MPa as we see in Figure 3.20 and for 2 PHR and 1.6 GPa of graphene in Figure 3.21. This can be attributed to the good adhesion between the nanoclay particles and the recycled polypropylene matrix, thus the mobility of the polymer chains is restricted at higher concentrations. On the other hand, to get improved properties with long glass fibers one needs to incorporate higher concentrations as can be seen in Figure 3.22.

However, the studies [35-38] revealed that increasing the concentration of nanofiller, the tensile strength and Young's modulus decreases, this is due to non-uniformity of the disperded nanofiller and consequently loss of surface area needed for load transfer between filler and matrix material.

Glass fibers improve tensile strength. This happens because glass fibers adjust in the structure and reinforce the entanglements. Moreover, the addition of virgin PP [39] was studied as a reinforcer with three different polypropylene, recycled PP, virgin PP and recycled PP with glass virgin fibres and the results are shown in Figure 3.23. Virgin PP shows a bigger tensile strength and impact strength than recycled PP, but the results showed that the reinforcement of virgin fibers into recycled polymers increased the impact strength. Moreover, the reduction in elongation with the extrusions and the introduction of additives was observed.

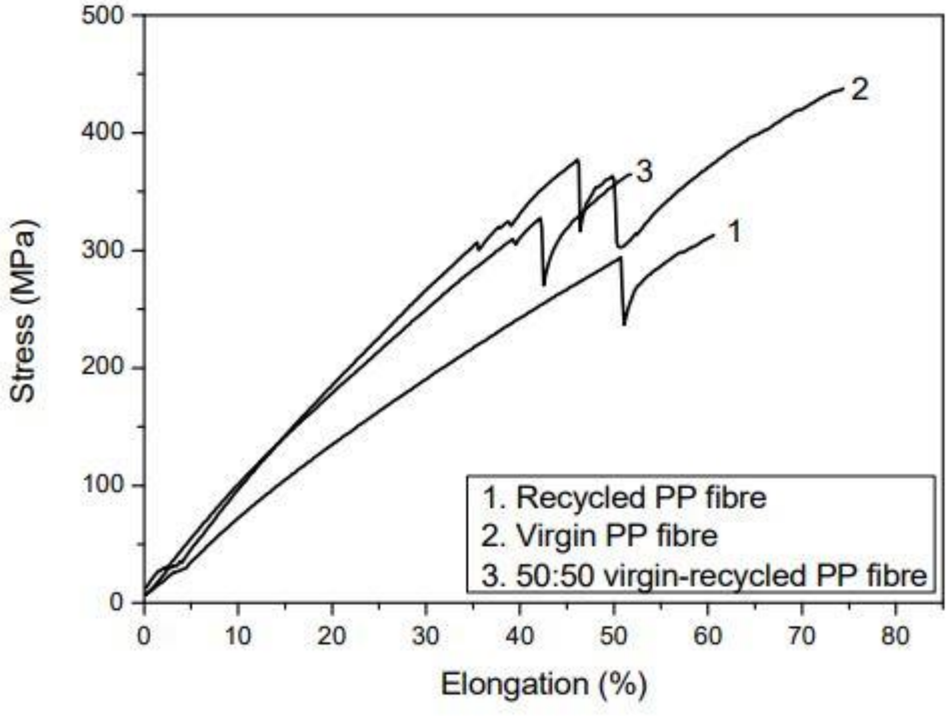

Figure 3.23: Stress-strain curves for different PP compositions [39].

This improvement of properties is a result of the decrease of the impact strenght or toughness. This decrease with the addition of nanoparticles into the matrix happens because of the agglomeration of the nanoparticles stiffening the polymer chains which results in a less impact energy absorbed by the polymer and favoring the crack propagation. To solve the decrease of the impact strenght, impact modifier agents can improve the impact resistance [40-41]. Figure 3.24 shows the results of the study of Husin and coworkers [36], where the impact strenght was with the three concentrations, as already explained before. The impact strenght was reduced with the rise of the percentage of additives. Again, the peak was reached with the proportion of 3% of nanocomposites and not at the maximum percentage, supporting the agglomeration theory [42].

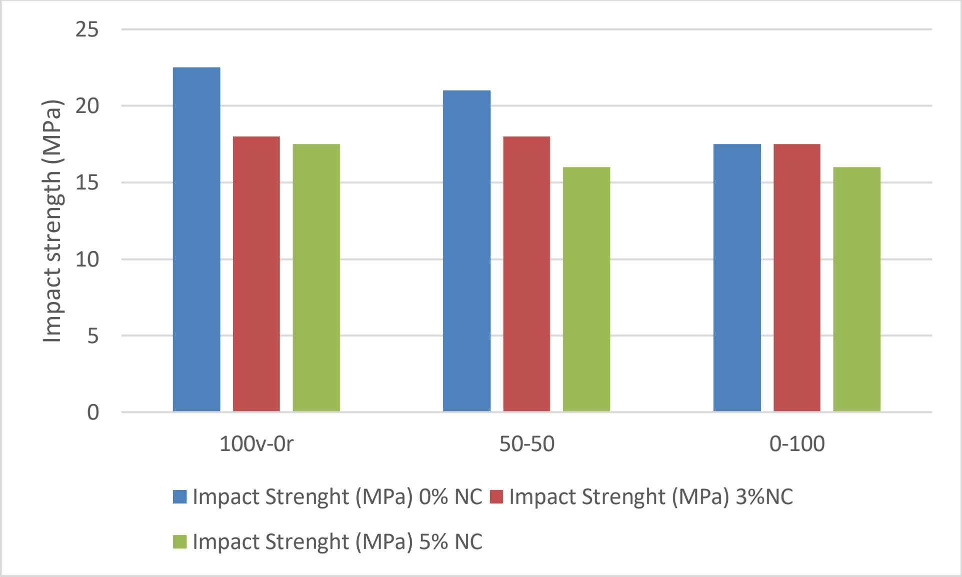

Figure 3.24: Effect of graphene nanocomposites content on impact strength of virgin PP (vPP) and recycled PP (rPP) [36].

Hardness is also affected by additives. This property is related to the crystallinity of the polymer and is very sensible with the introduction of fibers. In low concentrations can fibers act as nucleating agents increasing the content of crystallinity, but at high concentrations the hardness and crystallinity drops due to the formation of amorphous phases, esulting in lower hardness values [42].

### 3.2.3 Effect of additives on rheological properties

Rheological properties are also affected by the influence of the additives., These properties depend on factors as size and type of the additives, as there can be nanocomposites or polymeric additives, interactiosn between additive and polymer or the percentage of additive in the melt. The most fundamental rheological properties to improve during the recycle are viscous and elastic properties.

The torque during processing is a useful parameter for evaluating the recycling process. Torque is a function of the melt in the processing conditions, and gives information about the processability. When the torque is increased, the viscosity increases, decreasing the processability as the polymer exhibits higher resistance to be deformed or restructured. In following research [43] Da Silva et al. experimented with four different matrixes, virgin PP, PP with talc (A) and PP with $CaCO_3$ (B and C) with different proportions.

As can be seen in Figure 3.25, the torque increased with the presence of additives, reaching the highest point in the proportion 85/15. At this concentration the torque of the PP with each additive was higher than the torque of the virgin PP.

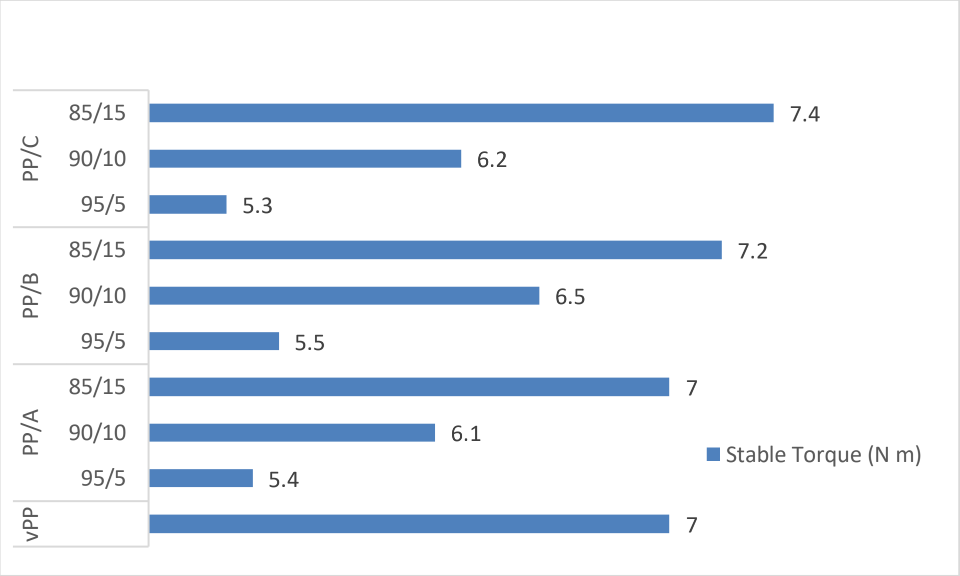

Figure 3.25: Effect of additives on processability of PP with different additives (A, B and C) and proportions [43].

Viscosity is strongly related to the molecular weight of a polymer, which is reduced with the numbers of recycles. The additives, known as viscosity modifiers help to reduce the effect of the extrusions by increasing the viscosity. As one can expect, viscosity increases with increasing molecular chain lenght or molecular weight of the additive, therefore the higher concentration of additives increases the viscosity of the polymer, which leads to a shear thickening behaviour of the polymer at higher shear rates.

Normally, the increase of the viscosity is a result of a decrease in the melt flow index (MFI) of the polymer [45], as the number of particles melted is lower with the higher entanglements in the backbone chain. Different studies [44-45] have tested the effect of additives on the viscosity. Nizar et al. [45] obtained a decrease in the melt flow index and the consequently increase of the viscosity with the introduction of the ZnO nanocomposites. This can be attributed to the interactions of the chains between the matrix and nanoparticles, reducing the chain movements and increasing the viscosity. Figure 3.26 shows the results of above mentioned study [45] with three different PP samples and three different molecular weights as the PP+A sample exhibited the lowest molecular weight sample and PP+C is the sample with the higher molecular weight.

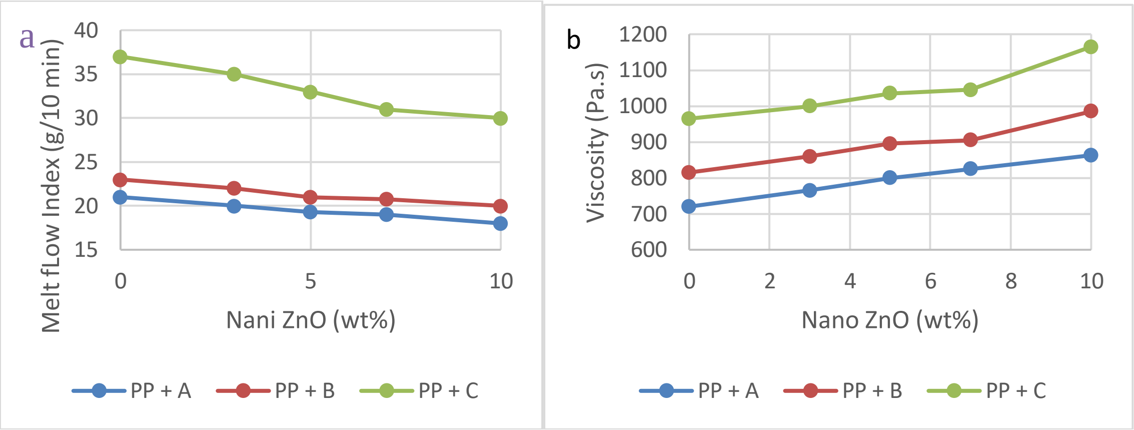

Figure 3.26: Dependence of MFI a) and the viscosity b) on the percentage of ZnO [45].

On the other hand, Hadi and Mohamed [47] in their experiment with recycled polypropylene with $SiO_2$ nanoparticles (NPs) concentrations (0 to 0-0.016 wt%) obtained an increasing MFI and a decrease of the viscosity. This was related to the fact that $SiO_2$ increase the free volume and motion of the macromolecules, which produces a decrease in viscosity and an increase of MFI. Figure 3.27 shows the results of the study of melt flow rate and viscosity with the increasing $SiO_2$ concentration.

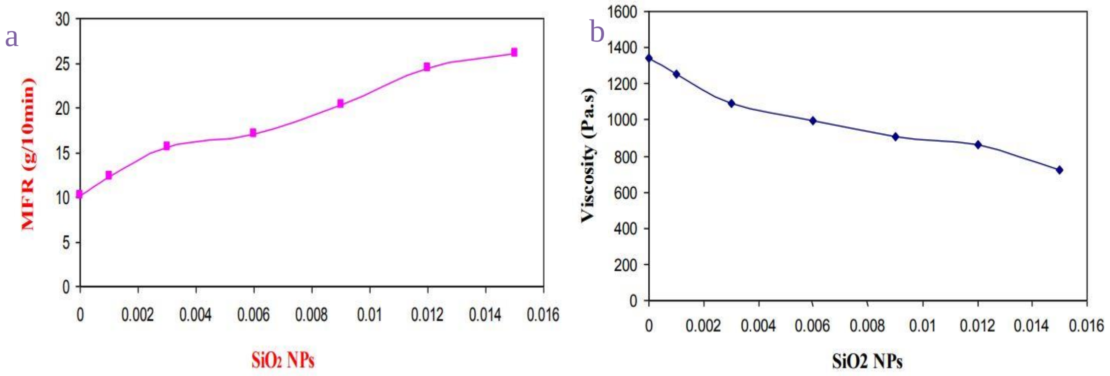

Figure 3.27: Dependence of MFI a) and viscosity b) on the concentration of $SiO_2$ [47].

Some other materials, like oligomers, also reduce the material's viscosity as the increasing percentage of additive increases the spacing of the polymer segments and reduces the interactions between the chains. Figure 3.28 shows the results of the study of Zdiri et al. [27]. They studied the depedence of PP viscosity on the oligomer percentage of nanofillers introduced at three different shear rates. The results showed that the viscosity decreased with increasing percetage of oligomer.

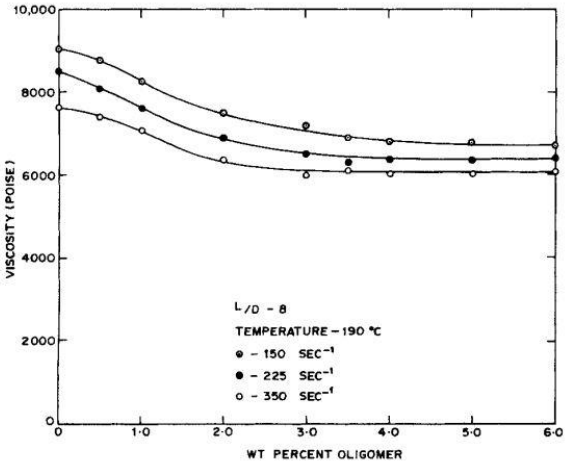

Figure 3.28:Dependence of viscosity of PP on the weight percentage of oligomer [27].

The results of different experiments lead to the conclusions about the importance of different additives in the same polymer. The ZnO increased the viscosity and the $SiO_2$ or oligomers decreased it. This means that different additives are suitable for different processes.

The storage modulus $G'$ increases with the indroduction of nanocomposites. The dispersions of these nanocomposites influence the rheological behaviour as low concentrations have higher storage modules than higher concentrations. In the study, presented by Goel [48] the author obtained an increase in the storage modulus with increasing content of nanocomposites reaching the peak at 3%. This is due to the increased stiffness of the polymer with the addition of nanoparticles. As this concentration is exceeded, the agglomeration of the additive does not allow the chains to interact completely, which reduces $G'$. As can be seen in Figure 3.29, the polymer matrix with the 3% of carbon nanocomposites has higher storage moduluIs than the virgin PP.

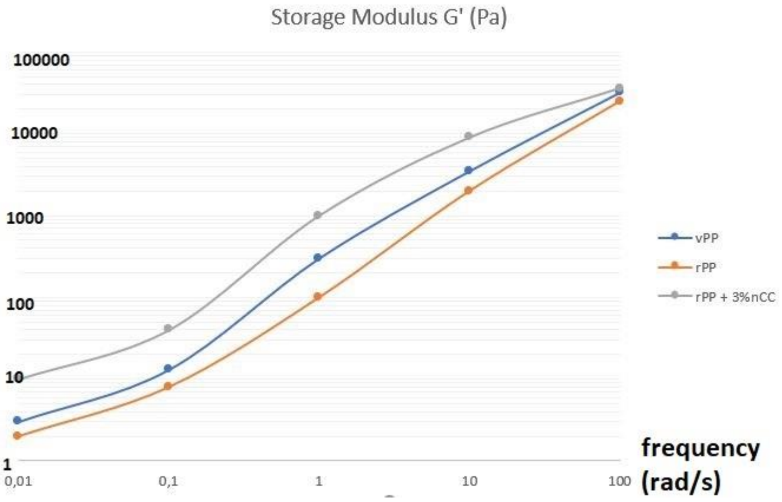

Figure 3.29: Storage modulus (G") over frequency for different PP composites

The last parameter to study is the loss modulus $G''$. This modulus is determined by viscous flow. When the force on a particle reaches a certain value or a limit value, the particle will move from its initial position to a more stable state. This movement from one place to another produces the friction between particles with movement, which dissipates the energy. The energy dissipation is bigger as the movement is increased. The particle cluster (small grups of athoms) becomes larger with the increased concentration of additives. The larg particle cluster result in bigger energy dissipation, which is directly related to the loss modulus of a polymeric chain. This means that the increase of the concentration of additive increases the loss modulus [49].

The experiment held by Xu et al. [50] with three different concentrations of silica and PEG (Polyethylene glycol) fillers in polypropylene (1, 3 and 5%) and the recycled PP (0%) without additives is presented in Figure 3.30. The results showed that the loss modulus increased with increasing concentration of the additive, especially at high shear rates. Moreover, it can be seen that at lower shear rates (< 20 $s^{-1}$) the concentration of the additives has no effect on the loss modulus.

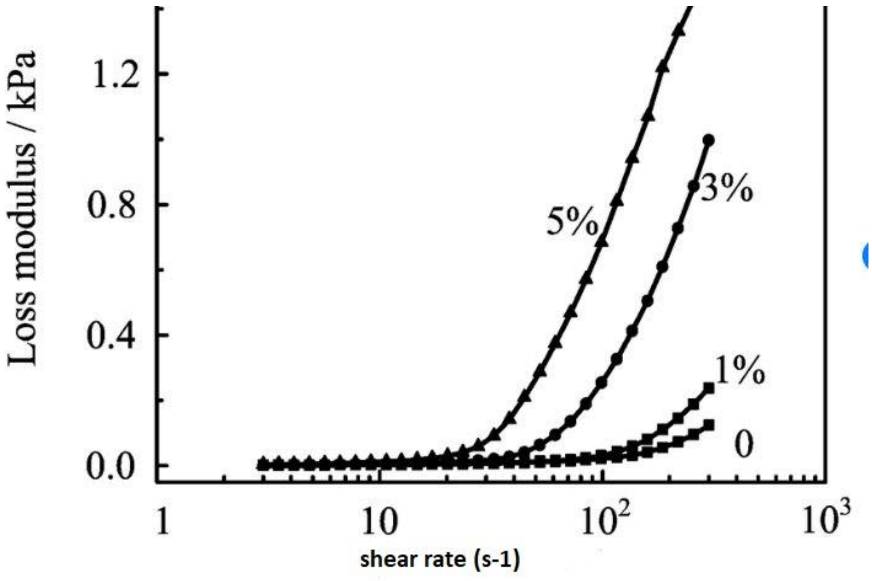

Figure 3.30: Effect of silica and PEG additive on loss modulus of PP [50].

To conclude, the introduction of additives increases the storage and loss modulus. Moreover, the viscosity is strongly related with the MFI. Some experiments noticed an increase of the viscosity (ZnO), while other experiments showed an increase of MFI and a decrease of viscosity ($SiO_2$ and oligomers).

# 4 Conclusions

Because of the increasing usage of the plastic in the world, the recycling has become an essential aspect of reducing plastic waste. Controlling the recycling process enables safe and efficient use of polymers. The conclusion of this Master Thesis can be summarised as:

1) Physical properties of polymers as thermal, mechanical, or rheological properties present a strong dependence on the structure of the polymer as well as the temperature and molecular weight.
2) The recycling process of polymers can be performed in different ways, like mechanical and chemical recycling and energy recovery. The most important method is mechanical recycling, which consists of five stages: collection and cleaning, sorting, shredding, melting and extruding. It was shown that the last part, i.e. extrusion, is the key stage to obtain the desired final properties of the recycled polymer.
3) We explained the effect of recycling on Polypropylene, one of the most widely used plastic because its ease to be used in different applications. It was shown that the molecular weight of Polypropylene decreases due to continued chain scission and degradation of the polymer that increases with the number of extrusions. Consequently, the physical properties deteriorate.
4) To compensate the effects of the recycling process, several additives can be introduced to the melted polymer. The additives prevent the effect of degradation, and can be used as stabilizers, antioxidants or UV light degradation protection pigments. However, there are also other additives as nanocomposites, glass fillers or wood fillers that reinforce the entanglements in the polymer structure and increase the final properties od recycled polymer.
5) We resume in this Literature Research the effects of additives on physical properties with the results of several studies, that indicate that the incorporation of nanocomposites improves physical properties by reducing the degradation, improving the entanglements, or acting as nucleating agents. The improvements depend on the composition and concentration of additives in the polymer matrix as lower concentrations improve the properties and higher concentrations produce a decrease compared to virgin PP.

Recycling process lead to a decrease of the molecular weight of polymers, which leads to a continued loss of physical properties. Additives are added in the polymer matrix to increase and improve various physical properties. Several studies showed that physical properties of polypropylene are increased with the additives but there is a strong dependence of the properties on the concentration of the additives incorporated into the recycled polymer.

### Recommendations for future research

Future research on this field could consist of studying how to improve the performance of additives in the final properties of recycled PP and the maximum number of extrusions that give better properties than the virgin PP. As this Master Thesis was done without an experimental part future researches should focus on this part and get results that support all the theory explained here

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