## Recycling Process of Permanent Magnets by Polymer Binder using Injection Molding Technique

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#### DEDICATION

I dedicate this work to my grandmother, the first women after my mother, who showed me that there is no such thing as male and female jobs. She taught me how to repair engines and bake cakes in the same oven. Even though you are no longer with us, I am still grateful for all your advice and impartiality. For the fact that you always said- you can do whatever you want when I was 4 years old soldering my first circuit boards. Your motivation to work motivated me to finish this dissertation – thank you Grandma.

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#### ZUSAMMENFASSUNG

Seltene Erden-Elemente (REE) werden aufgrund ihrer technologischen Bedeutung und geopolitischen Versorgungskriterien als kritische Metalle eingestuft. Sie werden in einem breiten Spektrum von Anwendungen eingesetzt, einschließlich der Herstellung von Magneten, Batterieelektroden, Katalysatoren und Polierpulver. Viele dieser Anwendungen sind wichtig für die sog. "grünen" Technologien. Dauermagneten sind hinsichtlich der Marktgröße die wichtigste Anwendung insbesondere für Neodym-, Praseodym-, Dysprosium- und Terbium-Magnete, die in NdFeB-Magneten verwendet werden. Die Nachfrage nach Seltenerdelementen für die Herstellung von Magneten nimmt zu und es wird erwartet, dass sich dieser Trend in den kommenden Jahren fortsetzt. Um die mit der Nachfrage verbundenen Risiken zu verringern, wurden Maßnahmen zur Entwicklung von Recyclingtechnologien zur Wiederverwendung von NdFeB aus Magneten ergriffen. Während der industrielle NdFeB-Schrott bereits zurückgewonnen wird, ist das Recycling von Magneten aus Altprodukten noch weitergehend auf Labor- und Pilotprojekte beschränkt. Diese Abhandlung stellt die Ergebnisse der Materialanalyse vor, die die Möglichkeit bestätigen, magnetische Materialien durch die Einarbeitung in eine Polymermatrix zu recyceln und mittels Spritzgussprozess vorzubereiten.

Kern der vorliegenden Dissertation ist die Frage, wie der geschlossene Kreislauf und das Recyclingverfahren von Neodynium Magneten aus Elektroschrott gestattet sein soll. Um diese Frage zu beantworten, sind folgende Aspekte relevant:

- Die Wahl der Technologien/Prozesse, die für das Recycling eingesetzt werden.
- Nachweis der Wiederverwendung von Neodym-Magneten, die aus WEEE (Waste of Electrical and Electronic Equipment) gewonnen sind.
- Herstellung und Analyse von Polymer/Magnet- Compound.
- Einfluss der Magnetpartikel, abhängig von ihrer Anzahl und Größe, auf die Viskosität und Fließverhalten des Materials während des Spritzgussprozess.
- Analyse des Einflusses der Restmagnetisierung auf das Fließverhalten und einer gezielten Anordnung von magnetischen Partikeln im Bauteil.
- Technisch-ökonomische Analyse, die entscheidend dazu beitragen wird, ob und in welchem Ausmaß die Einführung des Prozesses erreichbar ist und damit geschlossene Kreisläufe möglich sind.

Auf der Grundlage einer umfangreichen Analyse wurden die optimalen Prozessparameter und die Spritzgussmöglichkeiten des verwendeten Materials vorgestellt. Die Nachfrage nach NdFeB-Magneten in Motoranwendungen wächst und wird in den nächsten Jahren voraussichtlich noch zunehmen. Vor allem die Nachfrage nach E-Bike und E-Autos gewinnt an Bedeutung. Infolgedessen wird die Nachfrage nach schweren Seltenen Erden steigen, was die Entwicklung von Recyclingsystemen für diese Materialien erforderlich macht.

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#### ABSTRACT

Rare earth elements (REE) are classified as critical metals due to their technological importance and geopolitical supply criteria. They are used in a wide range of applications, including the manufacture of magnets, battery electrodes, catalysts, and polishing powders. Many of these applications are important for so-called "green" technologies. Permanent magnets are the most important application in terms of market size, particularly for neodymium, praseodymium, dysprosium, and terbium magnets used in NdFeB magnets. The demand for rare earth elements for the production of magnets is increasing and this trend is expected to continue in the coming years (Langkau S. 2020; Li J. 2020; Goodenough K.M. et al. 2018). To mitigate the risks associated with that demand, have been taken to develop recycling technologies to reuse NdFeB magnets. While industrial scrap is already being recovered, recycling of magnets from end-of-life products is still further limited to laboratory and pilot projects. The following work presents the results of the material analysis, which confirm the possibility to recycle magnetic materials by using a polymer matrix.

The main goal of this dissertation is the question of how the closed-loop and recycling process of neodymium magnets from electronic waste should be designed. To answer this question, the following aspects are relevant:

- The choice of technologies/processes used for recycling and processing.
- Evidence of reuse of neodymium magnets obtained from WEEE (Waste of Electrical and Electronic Equipment).
- Process flow analysis and final product evaluation (polymer/magnet compound).
- The effect of magnetic particles characteristics (size, distribution, and contribution) on the viscosity and flow behavior of the material during the injection molding process.
- Analysis of residual magnetization on the flow behavior and a targeted arrangement of magnetic particles in the component.
- Technical-economic analysis, which decisively contributes to whether and to what extent the introduction of the process is achievable.

Based on an extensive analysis, the optimal process parameters and the maximum injection possibilities of the material used is discussed along the whole processing line. The demand for NdFeB magnets in motor applications is growing and is expected to increase in the coming years. In particular, the demand for e-bikes and e-vehicles is gaining importance (Kampker A. et al. 2021; Pollák F. 2021; Flores P.J 2021). As a result, the demand for heavy rare earths will increase, necessitating the development of recycling systems for these materials, where this thesis is one basic concept to close the loop.

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#### TABLE OF CONTENTS

ZUSAMMENFASSUNG7
ABSTRACT9
INTRODUCTION AND MOTIVATION 13
The aim of the thesis15
Overview of thesis structure
Technological background20
CHAPTER 123
RESEARCH BACKGROUND OF MAGNETS23
1.1. Basics and terminology23
1.2. Crystallographic structure and phase diagram of NdFeB alloys26
1.3. Parameters of hysteresis curves30
1.4. Demagnetization
1.5. Anisotropy
CHAPTER 2
CHAPTER 2 38   THE STATE OF THE ART 38   2.1. Hard magnetic types. 39   2.2. Manufacturing process of neodymium magnets 41   2.2.1. Powder metallurgy of rare earth permanent magnets 41   2.2.2. Spark plasma sintering 43   2.2.3. Mechanical alloying 45   2.3. Recycling methods of permanent magnets 45   2.4. Summary 48   CHAPTER 3 50
CHAPTER 2

3.2. Viscoelastic material behavior	53
3.3. Thermorheological behavior	54
3.4. Summary	57
CHAPTER 4	59
EXPERIMENTAL AND METHODS	59
4.1. Thermoplastic matrix	59
4.2. Filler material	66
4.3. Influence of particle size and geometry of polymer and filler	69
4.4. Compounding	72
4.5. Injection molding	75
CHAPTER 5	80
TECHNICAL CHALLENGES IN DEVELOPED RECYCLING PROCESS	80
5.1. Extraction	80
5.2. Demagnetization	85
5.3. Pulverization	86
5.4. Summary	88
CHAPTER 6	89
CHARACTERISATION BY ANALYTICAL METHODS	89
6.1. Microscopy analysis of NdFeB powder	
6.2. Scanning microscopy analysis (SEM) of powder	91
6.3. X-ray diffraction patterns (XRD)	
6.3.1. Chemical composition	95
6.4. Packaging density and particle distribution	
6.5. Filling level	
6.6. Thermal characterization – TGA	102
6.7. Flow behavior	106
6.8. Degree of filling - dependent flow behavior - viscosity	108
6.9. Magnetic properties	112

6.10. Influence of magnetic field of NdFeB particles on rheological properties of the composite
6.11. Summary
6.12. Modeling facilities and visualization example126
6.13. Summary
CHAPTER 7 136
ECONOMIC PROCESS EVALUATION 136
7.1. Process Failure Mode Effects Analysis
7.2. VSD – Value Stream Design
7.3. Results of Value Stream Analysis147
7.4. Summary 153
CONCLUSION 154
OUTLOOK 156
BIBLIOGRAPHY157
APPENDICES 176
Appendix A 177
Appendix B183
Appendix C 186
Appendix D188

### LIST OF FIGURES

Figure 0.1	Schematic representation of technology considered in this work
Figure 0.2	. Schematic presentation of the systematic procedure for the characterization of
	processing and material properties22
Figure 1.1.	Magnetic hysteresis loop for permanent magnets
Figure 1.2.	The crystal tetragonal structure of $Nd_2Fe_{14}B$
Figure 1.3.	Quasibinary phase diagram of the NdFeB system with ratio Nd/B=2/1, based on (Filip
	O., Hermann R., Gerbeth G., Priede J. and Biswas 2005)
Figure 1.4.	Quasibinary phase diagram of the NdFeB system with 80 $\%$ Fe, based on (Kaszuwara
	W. 2015)
Figure 1.5.	Torque on rectangular coin in magnetic field
Figure 1.6.	Torque on rectangular coil in a magnetic field
Figure 1.7.	Magnetic anisotropy in ferromagnetic (Chen et al. 2020)
Figure 1.8.	The mutual orientation of the easy-axis, magnetic field vectors H and saturation
	magnetization M <sub>s</sub>
Figure 3.1.	Viscosity curves for different fluid types (Norton et al. 2011)
Figure 3.2	Factors influencing the rheological material behavior (Bek et al. 2020)
Figure 3.3	Influence of molecular weight and molecular mass distribution on viscosity (Nadgorny
	M., Gentekos D. T., Xiao Z., Singleton S. P., Fors B. P., & Connal L. A. 2017)57
Figure 4.1.	Molecular Structure of Polypropylene59
Figure 4.2	Main polypropylene types A) Isotactic; B) Syndiotactic; C) Atactic (Karger-Kocsis,
	1995)60
Figure 4.3	Molecular Structure of Polyamide (Hopff 1954)64
Figure 4.4	. Model of NdFeB particles based on the particle size analysis
Figure 4.5	Diagram of the NdFeB particle fraction as cumulative distribution
Figure 4.6	. Agglomeration of particles with a size of 50 $\mu m$ , microscopic magnification x1000 69
Figure 4.7	Schematic representation of the effect of particle shape on the relative viscosity.
	Adapted from (Rueda M. M. et al. 2017)
Figure 4.8	. PolyLab Rheo-mix 600p kneading elements
Figure 4.9	. Relationship of the percentage of filler to the density and volume composite (Matrix
	PP)74
Figure 4.10	o. Schematic of a fully hydraulic injection molding machine
Figure 4.1	1. Schematic drawing of the injection molding process
Figure 4.12	2. Used injection molding tools (A) Rectangle (35x10x3 mm), (B) Circular disc (Ø25
	mm, d=1 mm, 2 mm)78
Figure 5.1.	Technical challenges during the recycling process with a plastic matrix80
Figure 5.2.	Hard drives with identified screws (marked red by the program) ready to be
	dismantled in an automatic process

Figure 5.3. Requirements for suitable demagnetization processes
Figure 5.4. Schematic drawing of the hydrogen decrepitation process
Figure 5.5. Pulverization with the vibrating disk mill, Siebtechnik
Figure 6.1. The microstructure images of RE-M-B magnetic material recovered from electric
motors (marked ferromagnetic, Nd-rich and B-rich phases)
Figure 6.2. Results of scanning electron microscope of RE-M-B magnetic powder microscopic
magnification (A) x1000, (B) x200
Figure 6.3. Powder X-ray diffraction pattern (IOBS) and Rietveld refinement (ICALC) of
Nd2Fe14B93
Figure 6.4. X-ray powder diffraction of NdFeB after heat treatment by magnetic field defined by
Rietveld method94
Figure 6.5. XRD analysis for different samples- 100/70/30 Vol.% of NdFeB95
Figure 6.6. Characterization of the surface and shape of NdFeB particles SEM magnification (A)
2000x (B) 3000x
Figure 6.7. Microscopic analysis of particle distribution 70 Vol.% NdFeB in polypropylene matrix;
Magnification(A)x100, (B) x20097
Figure 6.8. Microscopic analysis of particle distribution 40 Vol.% NdFeB in polypropylene matrix;
Magnification x10098
Figure 6.9. Characterization of the surface and shape of NdFeB particles SEM magnification (A)
500x (B) 3000x98
Figure 6.10. Microscopic analysis of particle distribution 50Vol.% NdFeB in polyamide matrix;
Magnification x10099
Figure 6.11. Difference between the weight percentages determined thermogravimetrically after
injection molding and the volume fraction of the fillers
Figure 6.12. SEM images of NdFeB magnets 70 vol. $\%$ and polypropylene after compounding,
granules; Magnification (A) x3000, (B) x500101
Figure 6.13. SEM images of NdFeB magnets 40 vol.% and polypropylene after compounding;
Magnification (A) x3000, (B) x1000101
Figure 6.14. Visualization of filling levels with real particle size distribution (D/d=19.3) of NdFeB
particles (~50µm) at a fraction of 30/50/70 Vol.%
Figure 6.15. Thermal stability of PP as a function of the NdFeB filling ratio normalized to the
thermoplastic fraction (TGA: heating rate: 10 °C/min, atmosphere: N2) 104
Figure 6.16. Thermal stability of PP as a function of NdFeB filling level, time derivative of
thermograms to show decomposition behavior based on peak temperature (TGA:
heating rate: 10 °C/min, atmosphere: N2) 105
Figure 6.17. The change of the decomposition temperature with the amount of filler 106

Figure 6.18. Diagram of temperature dependent viscosity shift using PP+ 50 $\%$ NdFeB
(temperature: 180/200/220/240 °C), geometry: plate/plate, diameter: 25 mm,
thickness: 2 mm) 107
Figure 6.19. The effect of hard magnetic particle content on compound viscosity 108
Figure 6.20. Filling degree dependent intersection of storage and loss modulus of PP and PP+50
Vol.% NdFeB (temperature: 200 °C, geometry: plate/plate, diameter 25 mm,
thickness: 2 mm)
Figure 6.21. Verification of the structural change via the intersection $G' = G''$ 110
Figure 6.22. Dependence of friction energy of flowing material at 200 °C on volume of filler 111
Figure 6.23. Percentage dependence of flow energy as a function of the volume number of NdFeB
particles112
Figure 6.24. M(H) dependence of NdFeB/PP composites with different magnetic powder content
at room temperature113
Figure 6.25. Temperature dependence of magnetic moment (emu) for NdFeB+PP, the applied
field for all the samples is 1T114
Figure 6.26. E-bike with built-in recycled magnets115
Figure 6.27. Motor power comparison a) with RE-magnets 70 Vol.% NdFeB and PP, b) 100 Vol.%
NdFeB magnets115
Figure 6.28. Influence of particle content in compound on viscoelasticity and magnetism116
Figure 6.29. Storage and loss modulus as a function of angular frequency118
Figure 6.30. M(H) dependence of NdFeB particle size at room temperature, samples with 50
Vol.% of PP and 50 Vol.% of NdFeB powder118
Figure 6.31. Magnetic field dependences of the viscosity
Figure 6.32. Viscosity vs. shear rate for different particle size, samples with 50 Vol. $\%$ of PP and 50
Vol.% of NdFeB powder 120
Figure 6.33. The dependence of compound density on the amount of filler 123
Figure 6.34. Compound with a) 70 Vol.% of NdFeB and 30 Vol.% Polypropylene b) 40 Vol.% of
NdFeB 124
Figure 6.35. Retsch grinder SM 100 model 125
Figure 6.36. Magnetic components with 70 Vol.% NdFeB and 30 Vol.% Polypropylene 126 $$
Figure 6.37. Computer modeling in quality enhancement 127
Figure 6.38. Geometry of analyzed part- screw in the injection molding machine 128
Figure 6.39. Tetrahedral mesh defined for fluid and solid domains
Figure 6.40. Viscosity Measurements of Polypropylene NdFeB Particle Compound 50 Vol.% 133
Figure 6.41. Visualization of pressure during compound flow 134
Figure 6.42. Velocity profiles of the flowing compound 135
Figure 7.1. Technological approach of recycling of magnets - extrusion process of magnetic
compound (1) Storage of electronic waste WEEE: (2) Dismantling of multi-material

#### LIST OF TABLES

Table 1 Properties of Polypropylene
Table 2 Properties of Polyamide 6
Table 3 Properties of filler NdFeB
Table 4 Particle size analysis of NdFeB
Table 5 Particle size and their rotary diffusivities in the case of Brownian particles (Rueda M.
M. et al. 2017)
Table 6 Material dosage in kneader: polyamide and filler
Table 7 Material dosage in kneader: polypropylene and filler74
Table 8 Parameter change versus Property Effect
Table 9 Used molding parameters
Table 10 Classification of the test samples to the characterization methods
Table 11 Chemical composition of NdFeB
Table 12 Correlation of processes steps
Table 13 Process parameters influence of the injection molding 125
Table 14 Governing equation for the simulation
Table 15 Governing equations used to model the heat and laminar flow
Table 16 Experimental conditions of Polypropylene and NdFeB particles
Table 17 Density, Melt Flow Rate and Thermal Properties of Polypropylene NdFeB Particle
Compound
Table 18 Experimental and Numerical Data
Table 19 The value scale of indicators used in PFMEA analysis of recycling of magnet process
Table 20 The PFMEA analysis of recycling of magnets according to preliminary designed
process (Figure 7.1)
Table 21 The PFMEA analysis of recycling of magnets according to improved process (Figure
7.2.)
Table 22 Eight types of waste
Table 22 Eight types of waste

(Max Mustermann)

#### INTRODUCTION AND MOTIVATION

To date, recycling of rare earths has not been a significant strategy to reduce the supply risks of the Nd-Fe-B supply chain compared to other strategies, such as substitution (Mancheri N. A., Sprecher B., Bailey G., Ge J., & Tukker A 2019). However, with growing NdFeB market, this could change in the near future (Yang Y., Walton A., Sheridan R., Güth K., Gauß, R., Gutfleisch, O., et al. 2016). Although individual life cycle assessment studies have been conducted and found the analyzed techniques to be beneficial over primary production, they have focused process-specific impacts. The overall change to the impact of the production system is a function of both process-specific impacts and the overall magnitude of the recycling activities, and market effects. The demand for NdFeB magnets has grown in recent years and is expected to do so in the future. The magnets are a crucial "ingredient" in many green technologies such as electric bike (e-bike) and electric vehicles (e-vehicles), wind turbines, and many other motor applications. As a consequence, the availability of end-of-life (EOL) magnet scrap is expected to increase in the coming years, and secondary supply is deemed capable of playing a significant role in supply mix (Yang Y., Walton A., Sheridan R., Güth K., Gauß, R., Gutfleisch, O., et al. 2016). Hence, the development of recycling processes is becoming a relevant issue.

The main reason why recycling of rare earth has gained increasing attention in recent years is the perceived risk of supply shortages or price fluctuations for these elements, which have been an issue for industry players outside China, the main producing country of rare earth on the global market. Recycling is seen as a possible strategy to diversify rare earth supply. Other strategies include the development of new mining projects outside China, material development towards a reduced use of the elements which are highest in demand, and material substitution (*Bonfante M.C. and et al. 2021; Guzik K. and et al. 2021; Lewicka E. and et al. 2021)*. Before 2010, prices for these metals began to increase sharply due to the introduction by China of limits on exports of rare earth oxides (REO) and a reduction in supplies from about 65 000 tons to 30 000 tons (*Mancheri N. A., Sprecher B., Bailey G., Ge J., & Tukker A 2019*). The trade restriction was caused by the displacement of industries using rare

earths and was a major reason for China's export barriers. The strategy was aimed at building an advantage in these sectors (Pothen F. and Fink K. 2015). The export barriers are also meant to slow down the depletion of resources, the consumption of which is growing rapidly (Zepf V. 2020). Rare earth primary production is associated with environmental impacts during mining and processing (Dang D. H. et al. 2021). The process is elaborated, with high energy and chemical requirements. The elements occur in low concentrations in the ores. They co-occur as a group and jointly with other combined metals such as iron, thorium, uranium or titanium (Binnemans K. et al. 2017). Rare earth mined from mineral deposits as found in Baotou Obo, China, are open-pit mined. After the extraction and milling of the ore, the rare earth elements are concentrated in a number of physic-chemical processing stages referred to as beneficiation. During dry ore processing, workers may be exposed to dust containing toxic components present in the ores (Li Z. et al. 2020; Wang Y. et al. 2020; Liu L. et al. 2021; Tian S. et al. 2020). In a wet processing step, the rare earthrich fraction is separated from a concentrated iron ore fraction. Slag, i.e. the part of the ore which is left behind after the extraction of the rare-earth concentrate and iron ore, mixed with chemicals and wastewater from the extraction process, are stored in ponds near the processing site. These slags contain radioactive thorium and uranium which can be damaging to the health of the workers and local population if inappropriately managed, e.g. in case of infrastructure failure or severe weather events. Besides the ionizing substances which co-occur with the rare earths in the ores, the tailings contain heavy metals, fluorides, sulphides, arsenic and other substances. The largest slag pond in Baotou Obo lacks sufficient lining, and its contents have been polluting the surrounding ground water reservoirs, with severe health implications for the local population, which has eventually been relocated (Binnemans K. et al. 2017).

After separation of the rare earth concentrate from iron ore, the concentrate needs to be further treated to make the REE accessible. For LREE-rich mineral deposits such as bastnaesite-monazite ores mined in Bayan Obo, the acidic processing route is most common (*Balaram V. 2019*). The concentrate is roasted in sulfuric acid, leached with water, and the rare earths are precipitated with ammonium carbonate. The rare earth carbonates are then treated with HCl, with brings them into a chloride form, suitable for the following solvent extraction step (*Kołodyńska D., Hubicki Z., & Fila D. 2019*). In the solvent extraction process, the individual REE are separated from

each other. Then, the rare earth oxides need to be reduced to metals through an electrolysis process. Especially the last step is associated with high energy consumption (*Huijing Deng and Alissa Kendall 2019*). Furthermore, it is likely to be associated with the emission of perfluorocarbons, which are potent greenhouse gases (*Bo Yao et al. 2019*). Due to the fact that the rare earths co-occur in the ore, it is not possible to produce them individually. However, the market is not balanced for individual elements, which means that some of the elements are produced in oversupply. It has therefore been argued that reducing the demand for the primary production of those elements which are highest in demand would reduce the overall impact of primary rare earth production.

At the time of writing, only a small number of life cycle assessment studies had been conducted to quantify the environmental impacts of NdFeB magnet recycling. However, they agreed with regards to their observations that the impacts for the analyzed secondary productions routes are found to be lower than those of magnet production from primary REEs. In reality, commercial recycling of REEs is still extremely low. Despite the existence of a vast literature dealing with (mostly labscale) research efforts on REE recycling (*Binnemans K., Jones P. T., Blanpain B., Van Gerven T., Yang Y., Walton A., & Buchert M. 2013*), less than 3% of the REES are being recycled in 2020 (*Gaustad et al. 2021*).

#### THE AIM OF THE THESIS

The question to be addressed in this dissertation is to what extent recycling of NdFeB magnet material could reduce the environmental impact of the global REE production for use in NdFeB magnets. The main aim is recycling strategy alloy the complete processing line. The "production system" considered in the thesis compromises the global production of rare earth required for the production of NdFeB magnets. To what extent environmental impacts can be reduced by the recycling of NdFeB magnet material depends on the following aspects:

- respective processing technologies applied in primary REE production
- and recycling (and, when direct recycling is included, the magnet production processes).

In the thesis, the influence of irregularly shaped NdFeB microparticles from recycled magnets on the processing and material properties of hard magnetic compounds is illustrated using polypropylene (PP) and polyamide (PA). For this purpose, the particles used are characterized regarding the maximal achievable packing density. The processing possibilities from unfilled to highly filled compound melts are discussed in detail by means of compounding and injection molding. The imaging accuracies and aspect ratios achieved in injection molding are shown in detail and show the applicability of particle-filled compounds in the production of injectionmolded surface structures for micro injection molding. The influence of the filling degree and geometry of the particles used on the flow properties of the compound melts processed in injection molding will be described. They will demonstrate the effects of filler particles on the properties of thermoplastics in the melt and solids area. The functional properties of the compounds processed in injection molding are displayed and dictated depending on the degree of filling and the geometry of the particles. Finally, the processing and material properties of selected thermoplastic Compounds in the transition from melt to solids are correlated in order to verify the systematic approach used to characterize highly filled thermoplastics. The main facts to be discussed:

- Technical possibilities of producing permanent magnets on polymeric matrix
- Influence of the number of magnetic particles on various material parameters
- Change of magnetic properties depending on the amount of the leaching material
- Economic analysis of the process and its profitability.

By answering all these points will create a logical closed-loop recycling process for permanent magnets.

#### **OVERVIEW OF THESIS STRUCTURE**

This dissertation consists of seven chapters. In the first chapter a review of the literature was made in order to present the most important issues of magnetism. The topics discussed are closely related to the research methods used and form the basis for their understanding. The main focus is on the presentation of the crystallographic structure of neodymium magnets, hysteresis curves. The last two subchapters deal with the demagnetization process and magnetic anisotropy, which are relevant to this topic. Chapter 2 reviews current research. Commercially available magnetic materials based on rare earth elements and methods of their production are presented. A large part of the chapter is devoted to the presentation of available methods of recycling not only magnets but also rare earth elements. Considering the polymer matrix used, reference is made to the theoretical knowledge on the viscosity of polymers, described in detail in Chapter 3. The influence of the presence of molecules on the viscosity of dispersion systems is a very complicated issue. The flow of highly filled material is also described based on modern research and the present knowledge on the subject. Chapter 4 presents a detailed analysis and characterization of selected materials - polypropylene and polyamide. Also analyzed is the filler material - particle size and density - NdFeB magnets. On the basis of the analyses carried out, compounds with different percentage volume of the leaching agent have been prepared. This section describes the technology used to produce the samples compounding with an extruder and extrusion process with an ARBURG machine. The focus is on providing background information on the processes and presenting the parameters used to fabricate NdFeB-based polymer matrix magnets. Due to the complexity of the process, Chapter 5 describes the technical challenges encountered and methods for solving or preventing them. This chapter focuses on the disassembly of magnets and the proposed solution, demagnetization, and pulverization. In the next chapter 6 a detailed analysis of the prepared samples is discussed. It is an extensive chapter that contains a detailed analysis that allows the choice of generation parameters to be configured in such a way as to achieve the best possible results. The chapter starts with a basic microscopic analysis which also serves as quality control. In the next step, the results of scanning microscopic analysis are described in order to determine the shape and size of the extruded powder. The chemical composition of the magnetic powders used is presented in one of the subsections. This is one of the most important factors influencing magnetic properties. The distribution, the density of the particles and the amount in the

polymer matrix significantly change the magnetization and thus the destination of the finished product. Thermal analysis allows for optimal machine setup during compounding and injection molding. Skipping this step is a big mistake. The effect of the amount of filler on the magnetic properties is described in one of the subsections. This work focuses on achieving maximum magnetic properties, so a large part of the chapter concentrates on the analysis of magnetic properties and their dependence on other parameters. The chapter ends with modeling and visualization of the results carried out on the basis of the obtained experimental results. This part allows comparing the theoretical results with the experimental ones and is the culmination of this chapter. The design of a new process cannot do without economic analysis. In Chapter 7, two analyses were performed, the first of which is the Process Failure Mode Effects Analysis. The results indicated weaknesses in the process that can be eliminated at this stage. The second method is Value Stream Analysis of the current state. The results of both methods are used to optimize the recycling process of neodymium magnets. These results can be directly implemented in industry.

The conducted analyses and collected research material are also interesting problems that encourage further research and are presented in the last chapter of this thesis. This dissertation is a complete work on this subject, and it can be considered as a modest but significant contribution to the understanding of the role, as well as the possibility of recycling magnets based on polymer matrix.



#### **TECHNOLOGICAL BACKGROUND**

For a better understanding of the purpose of this work and a logical presentation of the different stages, a description of the technology used is given at the beginning. A systematic description of each stage is included. It is also a presentation of the way of thinking. The Figure 0.1 presents the systematic methodology and implementation of the thesis. The necessary steps to recycle permanent magnets on both laboratory and industrial scale are logically presented. The first step is to determine the exact properties of neodymium magnets used in the process - determination of chemical composition, magnetic properties, crystallographic structure. This process should also be carried out after the magnets are pulverized into powder. Time and method of magnet pulverizing influence the crystallographic structure and magnetic properties. The pulverizing should take place in an argon sheath in order to minimize the oxidation process. The next step is to select a suitable polymer that ensures the achievement of the necessary mechanical properties such as corrosion resistance, temperature resistance, mechanical strength, flexibility, etc. The polymer should be selected based on the specific properties of the end-product. Changes in properties are also possible by adding the additive. The requirements of the injection process for a highly filled compound should also be considered when selecting the polymer. Rheological properties must be analyzed in terms of flowability, degree and temperature of crystallization and density. All necessary parameters have been analyzed and presented in the chapters below.



Figure 0.1 Schematic representation of technology considered in this work

In the next stage the compounding and injection molding processes are analyzed. An important step is the adequate selection of the compounding parameters. This is especially important regarding the Curie temperature of the magnets, which must not be exceeded. For different permanent magnets, this temperature varies, so it is important to know the chemical composition and to choose the right temperature. In order to obtain a high quality of particle distribution in the polymer matrix, the magnetic powder is mixed in steps with the polymer and the mixing speed selected see Chapter 5 for details. Rheological analysis of the produced compound is performed to determine optimum temperatures during the injection molding process. Based on rheological tests, the compound flow behavior is analyzed. Changes in location of magnetic particles in polymer matrix caused by residual magnetization are observed. The influence of this effect on the final properties of the product and possible counteractions to this phenomenon are precisely determined. In the injection molding process, different filling ratios from 30-70Vol.% NdFeB are taken into account and the injection parameters are adjusted logically. Based on hundreds of tests, optimum parameters ensuring the highest product quality are determined. The flow of the material, the degree of mixing and the distribution of the particles

have an influence on the final properties of the obtained magnets based on a polymeric matrix. The temperatures of individual heating elements in the injection molding machine are also presented. The final stage is the qualitative and quantitative analysis of the produced neodymium magnets embedded in polymeric matrix. This is done by means of microscopic analysis, thermal analysis in order to determine the exact properties of the final product. The final step is the recycling of the finished product. The final step is to recycle the finished product by regrinding and injection molding the compound into the designed shape. This cycle has been repeated 5 times without significant changes in the thermal, rheological, and magnetic properties of the compound. In the case of industrial production, it is necessary to pay attention to several steps which are presented in the detailed technological analysis. Based on the research carried out, it is possible to design a production line for recycling of permanent magnets.



Figure 0.2. Schematic presentation of the systematic procedure for the characterization of processing and material properties

Figure 0.2 illustrates in a systematic way. The material characterization represents a complete package of characteristic as a basic for processing. The scientific correlation between the material characterization and the manufacturing process.

(Georg Christoph Lichtenberg, 1770)

#### **CHAPTER 1**

#### **RESEARCH BACKGROUND OF MAGNETS**



#### 1.1. Basics and terminology

Permanent magnets have a vital role in todays' industry as they are used in many applications including generators (off-shore wind turbines) (Nejad A. R et al. 2021), electric motors (hybrid and electric vehicles) (Krings A. & Monissen C. 2020), household electric appliances (washing machine, air conditioners, vacuum cleaners, etc.) (Lixandru A. et al. 2017), computer hard disk drivers (HDDs) (Frost K. et al. 2021a), magnetic resonance imaging (e.g. MRIs and NMRs) (Chakravarty S. & Shapiro E.M. 2021), vehicle components (brakes, ABS systems, etc.) (Nguyen R. et al. 2020) maglevs (e.g. magnetic levitation trains) (Jiang Y. et al. 2021), mobile phones, speakers and acoustic devices (Park K. H. et al. 2020). Meanwhile, with continuously advancing technology, these magnets can find new application areas and have more appearances in industrial and daily life products thereby strengthening their role even further. Creation of a permanent magnet is based on two basic principles. The first one is the selection of an appropriate material that compromises good intrinsic properties such as saturation magnetization (the maximum possible magnetization of a material), Curie temperature (the temperature where a magnetic material loses its magnetic properties) and magneto-crystalline anisotropy (the ability of a magnetic material to take more energy for its magnetization in certain directions than in others) (Bi S. 2014). The so-called Heisenberg interaction is responsible for the parallel orientation of the spins of the valence electrons of neighboring atoms. It is a quantum effect resulting from electrostatic interaction between electrons and Pauli's law. Pauli's law forces the symmetry of the orbital part of the wave function for a given spin orientation. It means that the orbital motion depends on the mutual orientation of spins. The formation of the magnetic hysteresis loop can be explained on the basis of the domain structure. Ferromagnetic materials are divided into small areas called domains, each of which is magnetized in a different direction, as a result of which the resultant magnetic moment is equal to zero. In one domain the electrons align their spins in parallel. When an external magnetic field is applied, the boundaries between domains, called Bloch walls, shift as the domains strive to align their magnetic moments with the direction of the field. Changing the direction of the field causes a change in the orientation of the domains, for which some energy must be expended, and this is what causes the formation of the magnetic hysteresis loop. The domain boundary is a region, usually about 100 atomic diameters wide, in which the direction of magnetization changes gradually by 180°. Depending on the shape of the loop can distinguish between magnetically soft materials with a narrow and high loop, i.e., low coercivity, and hard materials with a wide and low loop, i.e., high coercivity. Soft magnetic materials, which are characterized by low energy necessary for magnetization, are used to produce electrical sheets (transformer and generator sheets) and hard ones as permanent magnets. The second principle is translation of these intrinsic properties into functional extrinsic properties including especially a high remanence (the residual magnetism after an external magnetic field is removed) and coercivity (the resistance against demagnetization) by adjusting the material's microstructure through an appropriate processing route. In order to test the magnetic behavior of a possible permanent magnet candidate, one needs to study its behavior in:

- a magnetic field (H) as a function of magnetization; the unit of magnetic field strength is the ampere per meter, [H]=A/m.
- the magnetic flux density (B) a vector quantity to measure the strength of a magnetic field in a particular direction at a particular point; the unit of magnetic field induction is the tesla,  $[B] = T = V \cdot s/m^2$ . This behavior is characterized by a hysteresis or *B*-*H* loop diagram as illustrated in Figure 1.1.



Figure 1.1. Magnetic hysteresis loop for permanent magnets

When a ferromagnetic material is fully demagnetized or has never been magnetized, it will follow the dashed line indicating that as the applied current (H+) increases the magnetic field in the component (B+) will be stronger. At point A, almost all of the magnetic domains are aligned, and the material is said to reach its magnetic saturation. Further increase in the applied current will negligibly affect the magnetism of the material at this point. When the magnetizing force is completely removed, the curve will move towards point B representing the level of residual magnetism stored in the material (e.g. remanence). Here, to move the curve to point C, a coercive force (i.e. reversed magnetizing force) is necessary to remove all the remanence. As the reversed magnetizing force (H-) is increased further, the same pattern will occur but in the opposite direction (Feynman R.P. et al. 2010). The search for an appropriate magnet material and first general use of magnets can be dated back to the Iron Age when lodestones are discovered. Today, NdFeB, SmCo, AlNiCo and ferrite magnets are the most commonly used magnets (Reimer M., Schenk-Mathes H., Hoffmann M., Elwert T. 2018). There have been several research projects conducted for improving these magnets, but the material compositions and manufacturing methods have not changed at least fundamentally to this date. In terms of value, two-thirds of the produced permanent magnets contain rare earth elements. Within REE-based magnet market, NdFeB magnets have a clear domination over SmCo magnets by means of both value and volume shares. Despite their good coercivity, high corrosion resistance and very high thermal stability. SmCo magnets have been traditionally more expensive (*Herraiz L.E. 2017*).

# **1.2.** Crystallographic structure and phase diagram of NdFeB alloys

The chapter begins with a theoretical introduction to the topic of magnetism. The subjects discussed will be used in the further part of the work to analyze the results. The crystal structure and symmetry of  $Nd_2Fe_{14}B$  phase result from mirror symmetry in two orthogonal planes and contribute to its strong magnetic properties. The structure of  $Nd_2Fe_{14}B$  is tetragonal, neodymium and iron are in parallel alignment within the sublattices. This symmetry produces a magnetization of approximately 1,6T at room temperature (*Berkowitz A.E. and Kneller E. 1969*). Microstructure plays a crucial role in the magnetic properties of  $Nd_2Fe_{14}B$  magnets. The magnetization and demagnetization can be modified by controlling the size, shape, and orientation of the grains. To achieve different microstructures, three different processing techniques are currently employed powdered metallurgical methods:

- sintering,
- melt spinning,
- mechanical alloying (Takagi et al. 2021).

The unit cell of Nd2Fe14B (Figure 1.2.) has the tetragonal symmetry P42/mnm with the lattice constants a = 8.80 Å and c = 12.19 Å. At low temperatures, a monoclinic distortion of the lattice cell is observed (Sagawa et al. 1984b) .The unit cell comprises four formula units and thus 68 atoms. Nd2Fe14B exhibits six. Magnetic properties of Nd2Fe14B<sub>5</sub> crystallographically distinct lattice sites for the iron atoms and two crystallographically distinct lattice sites for the neodymium atoms.



Figure 1.2. The crystal tetragonal structure of  $Nd_2Fe_{14}B$ 

The effect of Nd and B content at constant iron content can be traced by analyzing the quasibinary phase diagram shown in Figure 1.3. At 20 % Fe content there is a content range from about 12 % to about 14 % Nd (from 8 % to 6 % B), where besides the  $\emptyset$  phase there is a phase rich in Nd and  $\eta$  phase. If the Nd content increases at the expense of B, the presence of a non-magnetic phase n can be avoided, but it will be replaced by a phase Nd<sub>2</sub>Fe<sub>17</sub> phase with soft magnetic properties. At the same time the increase of B content above 8 % (reduction of Nd content below 12 %) leads to the disappearance, necessary to obtain high coercivity, of the phase rich in Nd, which is replaced by the soft magnetic phase Fe<sub>2</sub>B. The currently known Nd-Fe-B materials can be divided into two groups differing in phase structure determined to a large extent by chemical composition. The first is made up magnets in which there is "magnetic isolation" between the grains of the Nd<sub>2</sub>Fe<sub>14</sub>B phase due to the presence of paramagnetic phase rich in Nd (Leonowicz M. and Wysłocki J.J. 2018). Between the individual grains there are only magnetostatic interactions. With this microstructure model, e.g., in sinter magnets, the grain size can be in the order of micrometers. The neodymium content in these alloys is greater than the stochiometric content in the  $Nd_2Fe_{14}B$  phase. In the published cross-section of the triple NdFeB phase system is the isothermal cross-section at 1000 C° useful to describe the phase composition of hard magnetic materials. The Nd<sub>2</sub>Fe<sub>14</sub>B phase  $\phi$ , occurring at the Nd content of about 12 % at. and B content of 6 % at. At a lower content of neodymium, separation of ferromagnetic phases occurs Fe and  $Fe_2B$ .



Figure 1.3. Quasibinary phase diagram of the NdFeB system with ratio Nd/B=2/1, based on (Filip O., Hermann R., Gerbeth G., Priede J. and Biswas 2005)

If the neodymium content is higher than the stoichiometric content in the phase  $\phi$  a liquid phase occurs at  $\phi$  from which during cooling, the so-called Nd-rich phase and the phase  $\eta$  are to be seen. The phase  $\eta$  with the composition of Nd<sub>1+6</sub>Fe<sub>14</sub>B is paramagnetic at room temperature T<sub>C</sub> is 14 K. In this structure will be built body centred tetragonal Nd structure and primitive tetragonal structure of Fe and B. The Nd-rich phase has a very large influence on the properties of magnets, especially in the powder metallurgy. It occurs in the form of thin films below 2 nm at the grain boundaries of the phase. The second group of NdFeB materials are alloys with the neodymium content equal to or less than the stoichiometric content of the Nd<sub>2</sub>Fe<sub>14</sub>B phase. In these alloys there may only be a hard-magnetic phase or, in addition to it,

there may be a soft magnetic phase. The release of the soft phase leads to an increase in the remanence of the magnet, decreasing the motion of the domain walls. They are observed during the following processes:

- These phases are released during fusion.
- Treatments increasing coercivity such as grain grinding cause a decrease in remanence as the volume of the ferromagnetic phase is reduced (Opelt et al. 2021).

The magnetic properties of such magnets depend on the magnetic interactions between atoms of individual grains. The condition for obtaining good magnetic properties is the existence of nanocrystalline structure (*Kaszuwara W. 2015*).



Figure 1.4. Quasibinary phase diagram of the NdFeB system with 80% Fe, based on (Kaszuwara W. 2015)

In the 1990s, there is a great interest in nanocrystalline magnets. These are materials in which reducing the grain size to the nanometer scale leads to new or enhanced

properties. In nanocrystalline magnets it is possible to influence properties such as remanence. The phenomenon of increased remanence is caused by exchange interactions between the atoms of neighboring grains. The exchange energy reaching minimal values causes parallel alignment of vectors of magnetic moments of neighboring grains. The direction of vectors of magnetic moments depends also on anisotropy which achieves minimal values when vectors of magnetic moments are oriented parallel to the axis of easy magnetization of grains. The phenomenon of increased remanence is particularly important for so-called nanocomposite magnets. These are nanocrystalline materials in which grains of a soft magnetic phase with a large saturation magnetization exist next to grains of a hard magnetic phase. A beneficial combination of the properties of the magnetically soft and magnetically hard phases is only possible at nanometer grain sizes, when exchange forces are the dominant type of interaction between the atoms of the neighboring grains. With a sufficiently small grain size the share of interfacial boundaries is large enough that the effect of interactions does not influence the measured properties (Hirosawa et al. 2017; Zhu et al. 2018; Coey J.M.D. 2020). In the publications one can find various results concerning the optimal proportion of the magnetically soft phase in a magnet (Mody et al. 2013). The increase of the magnetic soft phase share causes the decrease of coercivity and the increase of remanence and in a certain range of this phase share the magnet energy increases.

#### 1.3. Parameters of hysteresis curves

From the basics of electromagnetism, it has been known that if a small rectangular frame with a surface *A*, through which the current of the induction *i* flows, is placed in a magnetic field with induction *B*, then the moment *T* will affect it according to the equation:

$$T = iABsin\Psi \tag{1}$$



Figure 1.5. Torque on rectangular coin in magnetic field

The fundamental microscopic property of magnetic material is the magnetic dipole moment resulting from the orbital motion of the electron and spin. It can be identified with the flow of current through the frame:

$$\mu_m = iA \tag{2}$$

The moment that torques the frame is determined by:

$$T = \mu_m B sin \Psi \tag{3}$$

The selection of material requires consideration of the energy E which it is capable of storing, On the microscopy scale, this energy is the same as the work done with the rotation of the dipole moment vector to the direction of the external field being deposited.

$$E = \int T d\Psi = \mu_m B \int \sin \Psi d\Psi = -\mu_m B \cos \Psi \tag{4}$$

In the volume of a magnetic material there is a differential distribution of the directions of the magnetic dipole moments. When they are directed in the direction of the external magnetic field, we say that the material has reached magnetic

saturation. We can therefore define the macroscopic material parameter – magnetization M as the dipole moment per unit volume:

$$M = \lim_{\Delta V \to 0} \Sigma \mu m \Delta V \tag{5}$$

In hard magnetic material, the important parameter is the magnetic flux B that can be generated by a a magnet with magnetization M. These quantities are related in the expression for the magnetic field strength H.:

$$\mu_0 H = B - \mu_0 M \tag{6}$$

,where:

$$\mu_0 H = 4\pi \cdot 10^{-7} H/m \tag{7}$$

- magnetic permeability of the vacuum.

The magnetization *M* and the associated polarization J\* (J=( $\mu_m M$ ) represent the magnetic properties of the material, and the magnetic field strength H comes from external sources. *H* and *M* are measured in A/m (1*A* =  $4\pi \cdot 10^{-3} \ Oe$ ) and B and J are measured in teslas (1*T* =  $10^{-4} \ Gs$ ).

The interaction of ferromagnetic material with an external magnetic field is illustrated by the hysteresis Figure 1.1. It is formed by plotting magnetization M, polarization J and induction B as a function of external magnetic field H. The value of the magnetization depends on the direction and value of the previously applied field. The hysteresis loop of an ideal magnet has a shape close to a square. The primary curve starts at the beginning of the coordinate system and determines the change of magnetization of a material which has been thermally demagnetized (by heating to a temperature higher than the Curie temperature). When the applied field is able to saturate the material, then the polarization reaches its maximum value J<sub>s</sub>. Decreasing the magnetic field to zero will cause remanence J<sub>r</sub>. When the direction of the external magnetic field is changed, the polarization will be zero in the coercive field <sub>J</sub>H<sub>c</sub>.
Instead of *J* you can plot *B* as a function of *H*. The hysteresis curve obtained this way will show remanence  $B_r=J_r$  and smaller coercivity  ${}_BH_C$ . The harder the magnetic material, the bigger the  ${}_JH_C-{}_BH_C$  difference.

## 1.4. Demagnetization

In practice, due to the action of the demagnetizing field  $H_d$ , the magnetization displayed by the magnet is smaller than  $J_r$ . Its value is determined by the position of the magnets operating point, which is located in the second quarter of the hysteresis loop on the line B=f(H). We can define the parameters occurring inside and outside a magnet:

$$B_m = \mu_0 (H_m + M) \tag{8}$$

$$B_p = \mu_0 H_p \tag{9}$$



Figure 1.6. Torque on rectangular coil in a magnetic field

Intuitively, we know that the induction inside the magnet will be greater than the outside. The demagnetizing field can be calculated as follows:

$$H_d = N_d \cdot M \tag{10}$$

The value of the demagnetization factor depends on the shape of the magnet and can only be calculated for an ellipsoid. The shape of the magnet and its demagnetizing field determine the position of the operating point. The best use of the magnetic material's potential is obtained by optimizing the magnets shape and its demagnetizing field in such a way that the magnetic energy per unit volume of material is maximized. For an ideal magnet with a square hysteresis loop, which hat a rectilinear relationship B=f(H), the maximum density of magnetic energy  $BH_{max}$  is measured in  $kJ/m^3$ :

$$BH_{max} = \frac{1}{\mu_0} \left| \frac{B_r}{2} \frac{\mu_{0B} H_C}{2} \right|$$
(11)

This is the maximum theoretical value of the energy density that can be obtained for a given material. In practice, actual materials only reach about 60% of the value.

### 1.5. Anisotropy

Many types of magnets are manufactured in such a way as to take advantage of the structural feature of maximizing magnetic properties along a chosen crystallographic direction. The characteristic coupling of the magnetic moment to the crystal lattice is called magnetocrystalline anisotropy (*Azuma D. 2018*).

**Magnetocrystalline anisotropy** – the spins of the ferromagnetic atoms sense the crystal lattice through the interaction between the spin moment and orbital moment of the electron (spin-orbit interaction). For this reason, certain directions in relation to the crystal lattice are highlighted – it is easier for the spins to move in these directions. E.g., for iron, magnetocrystalline anisotropy favors the *{111}* direction.

**Shape anisotropy** – anisotropy related to the desire of magnetic moment to align themselves in such a way as to minimize the demagnetization field and magnetostatic energy. This anisotropy applies to magnetic bodies of any size, the shape is important. Determining the magnetostatic energy of a sample and the optimal configuration of magnetic moments for an arbite body is difficult because the magnetostatic interaction is nonlocal. Shape anisotropy is especially strong in thin films and dominates over magnetocrystalline anisotropy causing the magnetization to align in the plane of the film.

**Magnetoelastic anisotropy** – Magnetoelastic energy and its corresponding magnetoelastic coupling constant take into account the interaction between the magnetization and lattice deformation due to strain (*Kittel 1949*). The magnetoelastic energy is defined zero for an unstrained lattice. Magnetostrictive energy is due to deformation of a sample due to magnetic interactions and can be spontaneous when originated from internal magnetic interaction or forced when created by magnetic interaction between the sample and an externally applied magnetic field. Consequently, magnetic and elastic properties in ferromagnetic materials depend on each other and there is a strong influence of crystalline structure and lattice deformation in the magnetization process and elastic properties (*Paes and Mosca 2013*).

**Surface magnetocrystalline anisotropy** - connected with disruption of crystal symmetry on its surface. This anisotropy is important in ultrathin magnetic layers (<10nm) and causes magnetic moments to be aligned perpendicularly on the surface. The external magnetic field – includes in the ferromagnet and additional uniaxial (in the case of a homogenous field) anisotropy. The final configuration of magnetic moments is the result of the action of all of the above anisotropies, not all of which are significant. The significance of the various anisotropies is illustrated in Figure 1.7.



Figure 1.7. Magnetic anisotropy in ferromagnetic (Chen et al. 2020)

If an external field H is acting on such a system at an angle  $\Theta$ , it will cause a deflection of the magnetization vector  $M_s$  by the angle  $\psi$ . The rotation of the magnetization vector is the result of the anisotropy energy  $E_A(\psi)$  and the magnetic field energy  $E_H$ , resulting the total energy  $E_c$ :

$$E_c = E_A \Psi + E_H \tag{12}$$

, where:

$$E_H = \mu_0 M_S H \tag{13}$$

In the case of the hexagonal structure with axial anisotropy, the anisotropy energy can approximate by:

$$E_A = K_1 \sin^2 \Psi \tag{14}$$

, where:

$$K_1 = \frac{\mu_0 M_s H}{2} \tag{15}$$

It is the first coefficient of anisotropy. One can now return to the first part of the equation which macroscopically corresponds to the action of the external field on the magnetization  $M_s$ :

$$E_H = \mu_0 M_s H \cos(\theta - \Psi) \tag{16}$$

Figure 1.8 shown the orientation of the vectors.



Figure 1.8. The mutual orientation of the easy-axis, magnetic field vectors H and saturation magnetization  $\rm M_s$ 

So the total energy of magnet will be:

$$E = \frac{K_1}{4} \sin^2 \Psi - \mu_0 M_s H \cos(\theta - \Psi)$$
<sup>(17)</sup>

From the relation t follow that in every practical application a magnet should work such a way that the magnetic field is directed along the preferred axis of easy magnetization. This relation also allows one to calculate the maximum external magnetic field which is required for the magnet become magnetized. This field will cause the magnetization to change to the opposite direction. This can be obtained by equating the second derivative of the energy with respect to angle  $\Psi$  to zero. Since the field thus deducted must overcome the magnetocrystalline anisotropy, we call it the  $H_A$  anisotropy field.

$$H_A = \frac{2K_1}{\mu_0 M_s} \tag{18}$$

It should be noted that the  $H_A$  field depends only the magnetocrystalline anisotropy of the material and its magnetization and does not take into account the microstructure of the material, which means that in real magnets the magnetization occurs at much smaller fields.

## **CHAPTER 2**

## THE STATE OF THE ART



Until now, a country's economic development has been measured in terms of production, consumption of iron and steel (Mele M. and Magazzino C. 2020). Nowadays, in the era of dynamic development of information technology, electronics and automation, one of such indicators is the demand for magnetic materials (Kalsoom T. et al. 2020; Loesch C.W. 2020; Tesfaye F. et al. 2021). The unique properties of natural magnetic scales are known more than thousand years ago. The first magnetic device is the compass, invented nearly two and half thousand years ago in China. World production on a commercial scale began only at the end 19<sup>th</sup> century, and the real development of magnetic materials did not begin until 20th century (Skomski R. 2015). Modern magnets are based on intercrystalline phases containing rare earth metals (lanthanides) (Dent P.C. 2012). Lanthanides from intercrystalline phases with many other elements, including boron, aluminum and ferromagnetic transition metals (iron, nickel, cobalt - also known as 3d metals due to their partially filled 3d electron sub-blocks) (Benelli C. and Gatteschi D. 2002). The unique properties of rare earths are due to the incomplete filling of the 4f electron subgroup, which results in both orbital and spin magnetic moments (Kirk and Othmer 2003). The real breakthrough is the discovery in 1984 of the properties of the  $Nd_2Fe_{14}B$  phase. Further research and magnets have led to the improvement of the temperature coefficients and to the finding of more economically advantageous production technique (Gutfleisch et al. 2011; Vedmedenko E. Y. et al. 2020; Coey J.M.D. 2020; Skokov K. P. and Gutfleisch O. 2018). This chapter includes a theoretical introduction, in which the most important groups of magnetically hard materials are discussed. The methods of their production are described as well as their properties and microstructures. At the end of the theoretical introduction NdFeB magnets, which are the basic subject of this work, are described. The method of sintering and parameters important for the pressing process as well as the conditions under which the samples were sintered (atmosphere, time, temperature) are discussed. This review is based on the current knowledge and available scientific resources.

## 2.1. Hard magnetic types

#### Alnico magnets

Alnico is a family of alloys, known under various trade name, containing mainly the three ferromagnetic metals Fe, Co, Ni and smaller addition of Al, Cu and other elements (*Zhou L. et al. 2014*). The main advantages are the high Curie temperature reaching 850°C and a large amount of remanence (*Sun Y. L. et al. 2015*). All alnico alloys are very hard and mechanically brittle, and this is the reason that the basic production method is casting or sintering of powders. The magnetic properties improve only after a three-step heat treatment, which results in a two-phase microstructure. (*Ur Rehman S. et al. 2021*). Alnico has a high maximum operating temperature 550°C and high induction, while the disadvantages are low coercivity and high material costs (nickel and cobalt) (*Rottmann P.F. et al. 2021*).

#### Hard ferrite magnets

The substances called ferrites are chemical compounds with the general formula  $MOFe_{12}O_{18}$ , where MO is usually an oxide of barium or strontium. Ferrite magnets owe their anisotropic properties to their hexagonal structure (Jahn L. and Müller H. *G.* 1969). The magnetization of these materials controls the process of easy nucleation of the reverse domains and the motion of the domain walls. Therefore, in order to ensure high coercivity of the material, it is necessary to conduct the technological process in such a way that there are as few elements in the structure of the material as possible acting as nucleation centers of the reverse domains (de Julian Fernandez C. et al. 2020). Thus, in order to ensure a high coercivity of the material, the technological process should be carried out in such a way that in structure of material there are as few elements acting as nucleation centers of the reverse domains as possible i.e., the powder particles should be small, their surface smooth and the grains must not contain structural defects (Du J. et al. 2019). These materials are well suited for flat magnets, magnetized along the thickness (Perigo E. A. and Faria R. N. 2020). Their relatively small magnetization and high coercivity make these magnets very resistant to their own demagnetizing field (Karaagac O. et al. 2019). Therefore,

they are no alternative to alnico magnets, which are characterized by high remanence and low coercivity. The greatest advantage is also the low price of raw materials *(Luk P. et al. 2020)*.

#### Magnets containing rare earth elements

The history of magnets containing lanthanides began in the spring of 1966, when they obtained for the YCo5 phase an exceptionally large axial magneto crystalline anisotropy - K1= 5.7 MJ/m<sup>3</sup> (Dushyantha N. et al. 2020; Cullity B. D. & Graham C. D. 2008). Of the binary rare-earth metal-transition metal systems, only the phases containing Co or Fe and the light lanthanides Ce, Pr, Nd and Sm, as well as La and Y, exhibit sufficiently high spontaneous magnetization to be used for magnetic materials (Bonfante M. et al. 2021). Another important parameter of magnetic materials, the Curie temperature (Frost K. et al. 2021b), depends less on the metal used, but very strongly on the type of phase it forms with the transition metal. The first hard magnetic materials produced by sintering powders had the chemical composition Nd<sub>15</sub>Fe<sub>77</sub>B<sub>8</sub>. At this content of alloying elements the Fe<sub>14</sub>B phase is 82-85 % (Sabbe M. and Zidi C. 2017). There is also an  $\eta$  phase and a phase rich in Nd. The  $\eta$ -phase has a negative influence on the material properties because it is paramagnetic and a decreasing remanence (Nababan D.C. et al. 2021b). Schneider's research has led to the development of biphasic alloys, thus eliminating a large separation of the n-phase (Schneider C. et al. 2020). This phase can only be formed in the eutectic transition together with the Nd-rich phase (Smith B.J. and Eggert R.G. 2018). Its share is about 0.5%. This improves the magnetic properties of the material (Urban N. et al. 2017).

#### **SmCo magnets**

The interest in Sm(Co, Fe, Cu, Zr) magnets, which had declined significantly after the development of neodymium magnets, unexpectedly resumed after 1995 due to the growing demand for magnets with high temperature applications (*Das D. 1969*). Sm(Co, Fe, Cu, Zr) magnets developed in the 1970's are effective at temperatures up to 300°C ((*Liu J. F. and Walmer M. H. 2005*). The needs of the aerospace and defense industries demanded an increase in operating temperature to 500-600°C (*Liu J. et al. 2006*). The properties of magnets at high temperatures depend strictly on the alloy composition. The compactness of a traditional Sm(Fe)-type magnet is typically

u=0.21-0.31 (*Strnat K.J. and Strnat R. 1991*). An alloy composition that provides good performance at room temperature becomes unsuitable at high temperature (*Zhu G. et al. 2018*). One of the main disadvantages of these magnets is the price, they are much more expensive than neodymium. Samarium-cobalt production is also not preferred in terms of environmental impact, from cradle-to-gate perspective (*Bailey G. et al. 2021*).

## 2.2. Manufacturing process of neodymium magnets

The optimal microstructure of NdFeB magnets should be characterized by a fine grain size. For materials containing more Nd than the stoichiometric content of this element in the Nd<sub>2</sub>Fe<sub>14</sub>B phase, a grain size of a few micrometers is required (*Ding G. et al.* 2018). A homogeneous distribution of the Nd-rich phase is also necessary (*Ding et al.* 2015). These conditions can only be fulfilled if powder processing technologies are used (cast magnets have a number of limitations and are not technically relevant). Each of the methods for manufacturing solid NdFeB magnets involves operations typical of powder metallurgy: obtaining powder, forming and consolidation (*Zepf V.* 2013). These methods differ mainly in the way of powder consolidation and crystallographic texturing (*Andriessen F. and Terpstra M.* 1989). The methods allowing manufacturing of solid magnets are described below.

### 2.2.1. Powder metallurgy of rare earth permanent magnets

The first publications on sintered NdFeB magnets as a typical powder metallurgy process are to be found in the article about new compound composed of Nd, Fe, and a small quantity of B (*Sagawa et al. 1984a*). Over the past 30 years, the production of sintered NdFeB magnets has undergone fundamental changes. The way of realization of particular stages of technological process has changed (*Kaszuwara W. 2015*). New equipment has been developed to reduce such microstructure defects as segregation of chemical composition, oxidation of material, incorrect orientation, and reduction of grain size. These measures have simultaneously improved the properties of the NdeFeB magnets and lowered their price (*Takagi et al. 2021*). Remanence can be improved by optimization of microstructure parameters (*Li J. et al. 2021*). However, only such measures are possible that do not negatively influence coercivity. Theoretically, it would be possible to increase remanence by reducing the proportion

of non-ferromagnetic phases (*Takagi H., et al. 2021*). However, one cannot arbitrarily limit the proportion of Nd-rich phases, because this leads to a deterioration of the magnetic isolation continuity of the grains of the  $Nd_2Fe_{14}B$  phase and a decrease in coercivity (*Pan S. 2013*). The scientific work carried out during the last 30 years, in order to improve the properties of NdeFeB magnets, has boiled down to the modification of technological processes in such a way as to optimize the microstructure element determining the magnetic properties (*Park H.K. et al. 2021*). The aim is primarily:

- increasing the proportion of the Nd2Fe14B phase (*Liu et al. 2019*)
- reducing the oxide content (Mazilkin A. et al. 2021)
- improving the grain orientation of the Nd2Fe14B phase (*Yuan X. and Zhu J.* 2020).

The oxygen compactness in NdFeB magnets is the best indicator of the quality of the technological process. It has decreased significantly with the development of manufacturing methods. At present, one of the more advanced technologies is Zhenghai Oxygen-Free Process (ZHOFP), consisting of the following operations: melting, strip casting, grinding using hydrogen grinding and grinding in jet mills, pressing in a magnetic field perpendicular to the pressing direction (transverse die press), and sintering and continuous heat treatment (Xie H. et al. 2006). The drive to increase coercivity makes it necessary to use low-oxygen technology (LOT). This is the main direction of development of sintered NdFeB magnet technology. A distinction is made between dry and wet processes. In the wet process, liquid substances (e.g. low-oxygen oil) are used to protect the powder and to prevent atmospheric oxygen from reaching the material. In the dry process this is achieved by using inert gaseous atmospheres (Takagi et al. 2021). Further stages of progress in maximizing the remanence of the magnets have been achieved by improving the grain orientation of the Nd2Fe14B phase, which is obtained by modifying the pressing methods (Xin W. et al. 2020). The texture improvement is achieved by cold isostatic pressing (CIP) (Genq Z. W. et al. 2020). Isostatic pressing in flexible moulds (RIP) is also used (Sagawa M. et al. 2000). Even better orientation is obtained by wet pressing, called HILOP technology (Matsuura Y. 2006). Another method is "inclined magnetic pulsing" in which the degree of orientation can be increased by isostatic

pressing in a rubber mold. The applied gradient pulse field enables to achieve remanence at the level of 1.5T (Kuniyoshi F. et al. 2004). The work on improving the structure of the cast NdFeB alloys has gone in the direction of improving the homogeneity and reducing the grains of individual phases by increasing the cooling rate when casting the material. In the beginning, liquid alloys are cast on a flat surface in the form of plates of various thicknesses (Abe T. et al. 2018). The cooling rate of flat castings is too low to avoid the formation of primary Fe precipitates (Yamamoto K. and Murakami R. 2016). The application of strip casting is a breakthrough moment in the process of optimizing the technology of these materials. This method allows to obtain an alloy with a very small size of the Nd2Fe14B phase dendrites, very well directed, homogeneous distribution of the Nd-rich phase, and no primary Fe precipitates (Chen 2020). The strip casting method consists in casting the alloys into a barrel rotating at a speed of 2m/s. Thus, alloys are obtained in the form of thin flakes in which there are columnar grains of the Nd2Fe14B phase with a width of several micrometers separated from each other by thin layers of Nd-rich phase (Slinkin I. V. and Chikova O. A. 2020). Nowadays, by combining the HDDR (the hydrogenation, disproportionation, desorption and recombination) (Poenaru et al. 2020) method with the HD (hydrogen decrepitation) process, a technique has been developed which can produce the ultra-fine powders (Sheridan et al. 2014). It involves the transformation of a coarse-grained cast into a highly fragmented material with high coercivity (Yoo J. G.M et al. 2021). This process takes place in a hydrogen atmosphere at elevated temperatures (Liu et al. 2021). The first step is hydrogenation, which leads to the disintegration of the metallic into powder, similar to the HD method. Further heating in a milled medium causes hydrogen desorption and recombination of the material, thus forming metallic Nd, which reacts with Fe and Fe2B to form a fine-grained (<1µm) Nd2Fe14B structure (Nababan D. C. et al. 2021a). Such material is isotropic and shows high coercivity. The addition of gallium or zirconium to the alloy has the effect of introducing microstructure anisotropy in the HDDR process (Ma B. et al. 2021).

### 2.2.2. Spark plasma sintering

The sintering of powders is achieved by the pulsed flow of direct current through the powder. Cyclically repeated current pulses with a duration of a few to several milliseconds and an intensity of thousands of amperes cause heating of the material

with Joule heat and lead to spark discharges between the particles (Grigoras L., et al. 2021). The contribution of both mechanisms of thermal energy supply to the particle system changes with increasing sinter density and powder particle contact area. Sintering by this method is very efficient, because it is characterized by a high energy input. The intensive mass transport by evaporation and condensation, and the diffusion across the particle surface and along grain boundaries, ensure a high efficiency. Complete compaction of the powder is usually achieved after only a few minutes of sintering, which protects the material from intensive grain growth. In this study, sintering temperatures much lower than conventional sintering temperatures are used, but the best results are obtained after sintering at temperatures above 800°C (Vial et al. 2002). The density of the resulting sinter increased with sintering temperature, while coercivity and remanence, after an initial increase, reached a maximum and then decreased. In both the work (Munir Z. A. et al. 2006) and the magnetic properties of sintered materials obtained by the SPS method did not differ significantly from those of conventionally sintered materials. The authors of the paper (Menushenkov V. P. and Savchenko A.G. 2003) stated that the magnetic properties after sintering by the SPS method can be improved by additional heat treatment - annealing at 1000°C. In the work (Korent K., et al. 2020) it is found that just the additional annealing at 1000°C causes the Nd-rich phase to form thin layers isolating the grains of the NdFeB phase and thus improves the magnetic properties. The second characteristic of the microstructure of SPS sintered magnets is the much smaller grain size of the Nd2Fe14B phase (Ikram A., et al. 2020). It increases with the sintering temperature but is still much smaller than after conventional sintering. In the literature a lot of space has been devoted to corrosion studies of sinters obtained by the SPS method. Their corrosion resistance is not worse than that of conventionally sintered magnets. There are also a number of publications (Tomše et al. 2021; Frost K. et al. 2021b; Hu S. et al. 2020) describing the application of SPS sintering to nanocrystalline NdFeB powders. Spark-plasma sintering of NdFeB materials is an interesting alternative to conventional sintering. The possibility of a wider use of this method will be determined by economic reasons. The competitiveness of the SPS method will depend mainly on the cost of industrial sintering equipment.

### 2.2.3. Mechanical alloying

Very fine structures, similar to those obtained by rapid cooling, are produced by mechanical synthesis of alloys called mechanical alloying. The principle of the mechanical synthesis process is to grind the powdered elements that make up the alloy (*Jurczyk M. et al. 1995*). The purpose of grinding is to further break down the particles and to mix or combine them. During the milling process, the powder particles get caught between the balls of the mill and are repeatedly deformed and bonded. The layer structure characteristic of this process is formed (*Suñol J.J. 2021*). Over time, the microstructure becomes finer, generating a large number of effects, resulting in an unstable initial structure and, depending on the thermodynamic conditions, an alloy with the structure of a solid solution, an intercrystalline phase, or a mixture of components (*Schultz L. et al. 1987*). In the case of NdFeB, iron, neodymium and boron powders are grinded. The milling is carried out under an argon atmosphere. During the milling a structure of Fe and Nd layers with boron particles in between is formed. The powder is then carbonized at 700°C. The annealed powder can be used to produce isotropic plastic-bonded magnets.

## 2.3. Recycling methods of permanent magnets

According to reports (*European Parlament 2015; European Commision 2020; Buchanan S. and United States Department of Energy*) the end-of-life recycling rate of neodymium is less than 1 %. Neodymium magnets that enter the waste stream usually retain the physical and chemical properties of the original magnet, even if the properties on its surface are deteriorated due to corrosion or contamination. In addition, it should be noted that the total content of rare earth elements in waste magnets is approximately 30 %. This is a significantly higher concentration of rare earth elements than in virgin raw materials (*Schulze R. and Buchert M. 2016*). So far, the recycling of magnets is possible in two ways: raw material recycling (*Elwert T. et al. 2016*) and mechanical recycling (*Yang et al. 2017*). The first deals with the recycling of rare earths from different magnets. It is a direct solvent-based recycling of the raw material, although this is not practiced on a larger scale because these processes are not yet profitable enough (*Qiu Y. and Suh S. 2019*). In addition, many by-products such as contaminated hydrochloric acid and critical toxins are produced as a result (*Walton A. et al. 2015*). This has a great negative impact on the environment, which is precisely what a recycling process is designed to prevent. The second recycling route, which will be realized in this thesis, involves mechanical recycling. The first step is the separation of the material types from each other. The magnetic parts are often bonded with other metals such as aluminum, iron alloys, and these are often coated with nickel, chromium and copper. Since the magnets cannot be separated absolutely by type, because they are combined with auxiliary materials and are also often strongly contaminated.

### **Recycling or Recovery via Oxidation**

The oxidation method takes advantage of the difference in oxygen affinity between Fe and the rare earth elements (*Firdaus M. et al. 2016*). The recycling of NdFeB magnets by oxidation can generally be divided into the following steps: oxidation of the magnet or its melting, removal of oxygen by reduction and the step of separating the Nd in the form of an oxide (*Kaya E. et al. 2021*). This method is relatively safe for the environment, as it does not require the use of dangerous and harmful compounds. Oxygen gradually diffuses into the interior of the magnet and reacts with its components, resulting in a parabolic enlargement of the internal oxidation zone over time (*Nakamoto M. et al. 2012*).

#### **Recycling via Chlorination**

The process of recycling NdFeB magnets by chlorination is an alternative to the oxidation-based recycling method, which bypasses the problem of oxides and their high melting point and problematic separation (*Mochizuki Y. et al.* 2020). Chlorination is a relatively low cost and simple process. It also generates less wastewater treatment than oxidation (*Zhang Y. et al.* 2020). However, the big disadvantage is the resulting chlorides, which are difficult to process further (*Nababan D. C. et al.* 2021a).

### Liquid Metal Extraction (LME)

This recycling process is based on the assumption that the dissolution of neodymium in magnesium is high. Nd and Mg together form various types of intermetallic compounds and indicate a negative deviation from Raoult's law (*Xu Y. et al. 2000*). In the first step, extraction of neodymium is carried out using liquid magnesium at 800°C. Iron dissolves in magnesium to a very small extent, which allows to obtain

almost pure liquid Nd-Mg alloy and solid Fe-B alloy. By filtration the obtained alloys are separated. Then magnesium is separated from neodymium in the process of vacuum distillation (*Park H.K. et al. 2021*). The greatest advantage of the method is the high extraction rate of neodymium. The complete process is long, the vacuum distillation lasts 6 hours, and requires a significant energy input (*Guo X et al. 2021*).

#### **Electrolysis Using Molten Salt and Ionic Liquids**

The melted salt electrolysis process allows the recovery of rare earth elements of high purity. The anode in the process is rare earth metal scrap. An example of an electrolyte is a mixture of melted salts such as LiF, CaF<sub>2</sub>, NdF<sub>3</sub>. The process temperature varies between 1140°C and 1400°C (Martinez A. M. et al. 2013). During electrolysis, the rare earth elements contained in the anode are oxidized and transferred to the electrolyte as positive ions. They then meet a biopolar membrane where they are reduced (*Poenaru et al. 2020; Gutfleisch O. et al. 2013*). The rare earth alloy is then oxidized in the anode part and finally reduced at the cathode in the form of a high purity metal. In the case where the anode is a scrap Nd-Fe-B magnet, the process is run at 1.7-12V for 12h (*Konishi H. et al. 2014*).

#### **Recycling via Hydrogenation**

An interesting and at the same time high potential method is the recycling process based on the selective synthesis of neodymium hydride by the reaction of hydrogen gas to neodymium contained in NdFeB permanent magnets (*Zakotnik et al. 2008*). As a result of this method, it is possible to obtain a raw material that can be used to produce new magnets with different dimensions, shape and weight from recycled magnets (*Rhys C. 2018*). The hydrogenation process is originally designed and patented by Hariss as a way to decompose SmCO<sub>5</sub> and Sm<sub>2</sub>(Co,Fe,Cu,Zr)<sub>17</sub> alloys. It was further modified in 1985 to disintegrate the newly developed NdFeB alloy. During the HD process, NdFeB alloys are typically exposed to H<sub>2</sub> at 1 bar pressure at room temperature (*Li Chao et al. 2015*). Hydrogen is absorbed by the Nd-rich boundary phase and then by the main phase Nd<sub>2</sub>Fe<sub>14</sub>B. The hydrogenation process causes a volume expansion of 5 %, which promotes the formation of intercrystalline and cross-border cracks, which in turn cause the material to crumble (*Sheridan et al. 2014*). The volume increase takes place over the entire volume of the material and leads to disintegration and the formation of hydrogenated alloy powder (*Ma Bin et*  al. 2020). The reaction to form NdH2 will occur more spontaneously at lower than at higher temperatures (Fredericci C. et al. 2014). At the same time, the other components of the recycled magnet (Fe and B) will not react with the gaseous hydrogen and form hydrides (Li X. T. et al. 2015). One of the key features of the construction of the vast majority of NdFeB magnets is the nickel coating they are covered with. Its function is to prevent the oxidation process of the magnet's components, and thus the loss of its properties. If, prior to the hydrogenation process, the protective layer had been removed and the magnet had been exposed to the external atmosphere for a sufficiently long time, the oxides formed would have made the synthesis of NdH<sub>2</sub> significantly more difficult, or even impossible, and, consequently, recycling would have been impossible (Jönsson C. et al. 2020). Therefore, in this method it is necessary to leave a protective layer. The purpose of the method based on the synthesis of neodymium hydride is to obtain a powder fraction, which is possible due to the fact that  $NdH_2$  has a higher volume in relation to the other magnet components, as well as to Nd itself (Benke et al. 2019 Benke, 2017). The nickel layer can be separated by sieving the resulting powder with a diameter of 90 µm (Sheridan et al. 2014).

## 2.4. Summary

The economic development of the country has so far been measured by production, consumption of iron and steel. Currently, one of the indicators is the development of technology - information technology, electronics, and automation. For the production of which rare earth materials are necessary. Many types of magnets allow selecting the appropriate material for the planned application. Alloy magnets are characterized by high hardness and low mechanical strength; therefore, the basic way of their production is casting or powder sintering. The next group consists of ferrite magnets. To ensure high coercivity of this material, the technological process must be carried out in such a way that powder particles are small, have a smooth surface and grains must not have structural defects. They are mainly suitable for flat magnetized magnet along the thickness. Their biggest advantage is low price of raw materials. Neodymium magnets are mainly known for their high magnetism. Recently they are used in electric motors of cars and bicycles. However, they have a dark side, being extracted together with radioactive elements. For this reason, there are no safe methods of extracting them. Another group of magnets which are an alternative to

high temperature magnets are magnets based on Samarium. One of the disadvantages of these magnets is their high price in comparison with neodymium magnets. There are many methods of producing rare earth magnets. The powder metallurgy of rare earth magnets is one of the first methods. It has evolved considerably during the last 30 years. The aim is mainly to improve the magnetic properties, which has been achieved by increasing the proportion of the Nd<sub>2</sub>Fe<sub>14</sub>B phase and reducing the oxide content and improving grain orientation. Nowadays one of the most used techniques is the Zhenghai Oxygen-Free Process (ZHOFP) which provides an increase of coercivity. Another alternative is the sintering of powders by the pulsed flow of direct current through the powder - the spark plasma sintering technique. By carrying out additional annealing at 1000°C, the Nd-rich phase forms thin layers that isolate the grains of the NdFeB phase and thus improves the magnetic properties. The recycling of permanent magnets has been a very broad topic in recent times. However, statistics show that even though a lot of technology is already available, only 1 % of neodymium magnets are recycled. First of all, there are two ways: recycling of raw materials, i.e., individual rare earth elements, or recycling of entire magnets. One method of recovering rare earths is through oxidation. This method takes advantage of the difference in oxygen affinity between Fe and the rare earth elements. The Nd is separated by reduction as an oxide. A similar method is chlorination, but this produces chlorides that are difficult to process. The method of liquid metal extraction (LME) was presented. Its main disadvantage is the longtime of powder distillation, which lasts about 6h, and the high energy input. This process involves the dissolution of neodymium in magnesium and obtaining an almost pure liquid Nd-Mg alloy. The electrolysis method using molten salts allows the recovery of rare earth elements of high purity. An interesting method is the recycling technology based on the sleek synthesis of neodymium hydride. The advantage of this method is obtaining raw material that can be used for new magnets of any shape. In the following part of the work, the individual stages of the developed technology based on the combination of magnetic powder with a polymer matrix are presented. The technology developed within this thesis presents a different potential than the technologies available so far. First, the environmental impact is minimal (lower energy demand, less waste) and the whole process is safe for the environment.

# **CHAPTER 3**

# VISCOELASTIC MATERIAL BEHAVIOR



## 3.1. Multiphase system of polymers

A separate class of polymer are multiphase systems such as composites, blends, and dispersion systems with low dispersion concertation. Multiphase systems are materials with more than one phase. These may by mixtures of solids, liquids, and gases. The phase is homogeneous and separated by a phase boundary from the rest of the system. The most common phases are the continuous phase and the dispersed phase. Multiphase polymer systems can be very generally described as dispersion systems with different types and sizes of dispersion and different degrees of dispersion concentration. Thus, one can differentiate between systems of high and low dispersion concentration. The first group includes composites and plastic mixtures, the second group includes suspensions, emulsions, and foams. Composites are dispersion systems of solid particles and mixtures are dispersion systems of liquid drops. The presents of a continuous dispersed phase usually cause a significant change in the velocity, pressure and temperature fields during the flow and has a significant effect on the viscosity of this phase.

The viscosity of dispersion systems is often characterized by the following values: - relative or reduced viscosity:

$$\eta_i = \frac{\eta - \eta_s}{\eta_s} \tag{19}$$

Where:  $\eta_s$  is the viscosity of the solvent/ filling. - specific viscosity

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 \tag{20}$$

- intrinsic viscosity

$$[\eta] = \lim_{\Phi \to 0} \left( \frac{\eta_{sp}}{\Phi} \right) \tag{21}$$

, where: [η] is the intrinsic viscosity, Φ- concentration degree of filling phase.
viscosity ratio of the dispersed phase to the viscosity of the continuous phase

$$\lambda = \frac{\eta_D}{\eta_C} \tag{22}$$

, where:  $\eta_D$  is the viscosity of the dispersal phase,  $\eta_C$  is the viscosity of the continuous phase. The rheology of multiphase systems is very complex, and the degree of complexity usually increases with increasing dispersion concentration. In relation to dispersive solid systems, Einstein's law is of fundamental, which, described the viscosity of a system with a very small concentration of spherical solid particles in a Newtonian fluid:

$$\eta = \eta_C (1 + 2,5\Phi) \tag{23}$$

, where:  $\eta$ -viscosity of disperse system,  $\eta_C$ -viscosity of continuous phase,  $\Phi$ -volume fraction of the dispersed phase in the continuous phase. For more complex systems (e.g. composites), many different solutions are proposed, of which the most common is the power equation of the following form:

$$\eta = \eta_C (1 + \alpha_1 \Phi + \alpha_2 \Phi^2 + \alpha_3 \Phi^3 + \dots)$$
(24)

, where:  $(\alpha_1, \alpha_2, \alpha_3)$  - coefficient of the polynomial.

Regards to dispersion systems of liquid drops (e.g. a mixture of plastics), Taylor's equation, which describes the viscosity of a dispersion with a low concentration of spherical Newtonian liquid drops dispersed in a Newtonian fluid, is fundamental and limited relevance:

$$\eta = \eta_C \left[ 1 + \frac{1 + 2,5\lambda}{1 + \lambda} \Phi \right]$$
(25)

where:  $\lambda$  is the viscosity ratio of the dispersed phase to the viscosity of the continuous phase. This equation for  $\lambda \to \infty$ , i.e. for the dispersion of solid particles, reduced to Einstein's equation, while for  $\lambda \to 0$ , i.e. for the dispersion of a gas, it takes the form:

$$\eta = \eta_m [1 + \Phi] \tag{26}$$

Sometimes the simple rule of logarithmic additive is applied to plastic mixtures, according to which the viscosity of a mixture is determined by the compound:

$$lg\eta = \sum_{i} w_i lg \eta_i \tag{27}$$

, where:  $w_i$ - the weight proportion of the component,  $\eta_i$ - apparent viscosity of the component i.

However, this rule is valid only for thermodynamically miscible materials, i.e., those which do exhibit a multiphase structure. Rheology multiphase polymer systems is so complex that the search for rheological models of general significance. Therefore, the most reasonable approach in solving the flow problems of such compositions is to determine each time the rheological properties of the system under consideration on the basis appropriate rheometric measurements. In Kichrberg's dissertation, the Carreu Fluid Model is developed for such cases of high filler polymer (Kirchberg S. 2009b).

### 3.2. Viscoelastic material behavior

Viscoelasticity is the simultaneous occurrence of viscous and elastic behavior. The viscous property is related to irreversible deformation, the degree - under force continues to increase with time. Viscosity is a measure of the resistance of a material flow. Elastic properties are related to elastic deformations (reversible) that disappear spontaneously as soon as the force is removed. Elasticity is a measure of the ability of a material to return immediately after a deformation. The specific behavior of a real material, i.e., more elastic, or more plastic, depends on time, and more specifically on the relationship of the time of deformation on the material to some characteristic natural time of that material  $t_c$ . In general, it can be said that the faster the strain, the more elastic the material behaves and the slower the strain, the more viscous the material is. This is due to the molecular structure of the material. The time of each material is very different, ranging from  $10^{-13} - 10^{13}$ s. For example, the characteristic time of water is 10<sup>-12</sup>s. With such a short material time, practically any deformation that occurs in practice is relatively very slow and therefore water behaves as a purely viscous liquid. In contrast to water, for example the characteristic time of glass is very long, about 100 years. So, the deformation that occurs in practice is very fast in this case and glass is elastic. Materials with a characteristic time of the same magnitude as the actual deformations, i.e., seconds, minutes, or hours, exhibit viscoelastic properties. To such materials belong, among other polymers, whose characteristic time is 10<sup>-2</sup> - 10<sup>2</sup>s. Thus, as the ancient saying that: "everything flows" (panta rhei) and the only time scale determines whether this flow can be observed. A measure of the viscous behavior of a material is the ratio of the characteristic time of the material to the characteristic time of the process. This is determined by the socalled Deborah number

$$De = \frac{t_c}{t_p} \tag{28}$$

Where  $t_c$  stands for the relaxation time and  $t_p$  for the time of observation, typically taken to be the time scale of the process. A typical polymer, whose characteristic time is equal to 1 s ( $t_c = 1 s$ ), will behave differently in the processing, depending on the time of process. For a very long characteristic time of process ( $t_p \rightarrow \infty$ ), the Deborah

number will tend to  $(De \rightarrow 0)$  and the material will behave as a viscous liquid. On the other hand, for a very short process time  $(t_p \rightarrow 0)$ , the Deborah number will be very large  $(De \rightarrow \infty)$  and the same material will behave as an elastic solid. The characteristic time of many flows in the transformation is 0.1 - 1 s, which means that for  $t_c = 1 \text{ s}$  and De = 1 - 10. Thus, polymer demonstrate both viscous and compressible properties in the transformation processes, and they are viscoelastic.

### 3.3. Thermorheological behavior

The term "rheology" refers to the study of the flow behavior of fluids, in which two fundamental aspects are considered. One is the quantitative relationship between the resulting deformation due to a force applied to the material and the resulting internal reactions. On the other hand, the development of relationships that show how the rheological behavior is influenced by the structure or composition of the material as well as by influences such as pressure and temperature. Fluids have different flow properties, which is why a difference is made between Newtonian and non-Newtonian flow behavior. In the case of the non-Newtonian flow behavior, a further difference is made between dilatant, pseudoplastic or Bingham fluids (Chhabra R.P. 2010). Independent of the fluid type, the flow behavior is expressed for physical characterization by means of the dynamic viscosity  $\eta$  and is used for information regarding processability and behavior under mechanical load (Rueda M. M. et al. 2017). During processing, plastic melt is subject to both shear and elongation deformation, which is why the term "viscosity" is divided into shear and strain viscosity for further specification (Dealy J.M. and Wissbrun K.F. 2012). In most cases, the plastic melt is subject to shear deformation due to drag or pressure flows, which is why the shear viscosity is important for the extrusion and injection moulding process, will be discussed in the following (Dealy J.M. and Wang J. 2013). According to Newton's fluid friction law, the shear viscosity of Newtonian fluids corresponds to a proportionality factor, which is formed by the quotient of the share rate  $\gamma$ (velocity gradient) perpendicular to the flow direction show equation (29) (Winter H.H. 2009).

$$\eta = \tau \dot{\gamma} \tag{29}$$

The relationship between the tensile stress and the shear rate due to macromolecular structure represents the relationship between the plastic viscosity and the shear rate. The melting plastic is subject to structurally viscous or pseudo-plastic flow behavior. This means that an increase in the shear rate results in a decrease in viscosity. The correlation of the viscosity curves of the two materials specified above is shown in Figure 3.1., using a graph that doubles the logarithm of viscosity in relation to the shear rate.



Figure 3.1. Viscosity curves for different fluid types (Norton et al. 2011)

Polymer melt show, in addition to the shear viscous behavior of the complex viscosity  $|\eta^*(\omega)|$ , an intersection between storage and loss modulus with  $(G'(\omega) = G''(\omega))$ . At angular frequencies below the intersection, polymer melts exhibit predominantly viscous behavior  $(G'(\omega) > G''(\omega))$ . Above the intersection point, elastic material behavior is predominant with  $(G'(\omega) < G''(\omega))$ .

In the low shear rate occur mechanical connection between the macromolecules which causes Newtonian flow behavior. Constant viscosity in this rage is called zeroshear viscosity and can be observed especially in macromolecules with long chains (*Malkin A. Y., Polyakova M. Y., Subbotin A. V., Meshkov I. B., Bystrova A. V., Kulichikhin V. G., & Muzafarov A. M. 2019*). When the shear rate of the material is exceeded, the molecular chains in the shear field are arranged and positioned in the direction of the flow (*Chen B. et al. 2020*). This contrasts with Brownian disorienting molecular motion. Consequently, the viscosity gradually decreases with the increasing shear rate (*Ouarhim W., Hassani F. Z., & Bouhfid R 2020*).

During the extrusion process, the plastic is exposed to different share rate loads and it's depending on the type of plastic, it has a specific zero-shear rate as well as a specific structural viscosity rate (*Hassan M. et al. 2020*). In addition to the shear rate, there are other factors influencing the rheological material behavior (*Strano M. et al. 2019*). These can be classified according to the influences listed in Figure 3.2. and result from both the molecular structure of the material and process conditions.



Figure 3.2. Factors influencing the rheological material behavior (Bek et al. 2020)

The relationship between molar mass, molar mass distribution and rheology has been documented for linear and non-crosslinked plastic melts in various studies *(Seiffert S. et al. 2020; Schröder T. 2020)*. Figure 3.3. summarizes the relationship and influences between molar mass and molar mass distribution on rheological

behavior. It is shown that the characteristic viscosity function is determined by the type of intermolecular bonding between the molecular chains, the degree of chain branching and the molecular chain length (*Stadler F.J. and Mahmoudi T. 2011*).



Moll mass distribution

Figure 3.3. Influence of molecular weight and molecular mass distribution on viscosity (Nadgorny M., Gentekos D. T., Xiao Z., Singleton S. P., Fors B. P., & Connal L. A. 2017)

The rheological behavior, represented by the viscosity curve, is determined by both the molecular weight and the width of the molecular weight distribution (*Nadgorny M., Gentekos D. T., Xiao Z., Singleton S. P., Fors B. P., & Connal L. A. 2017*). While the mean molar mass has an influence the transition between the Newtonian and the structure-viscous range (*Burgfeld M. 2019*). A narrow molar mass distribution causes a sharper transition, while a wider distribution causes a more gradual transition and low-molecular components act as "lubricants" (*Münstedt H. and Schwarzl F.R. 2014; Kumar N.G. 1980*).

### 3.4. Summary

The multiphase systems described are materials containing more than one phase. The most common are polymeric systems in which there are different types and sizes of dispersions. Composites are dispersion systems of solid particles. In the present work these are dispersed particles of permanent magnets. They contain rare earth particles. The presence of these particles has a significant effect on the viscosity. The rheology of multiphase polymeric systems based on permanent magnets is so complex that a good approach is to determine the rheological properties for these composites each time. For this purpose, appropriate rheometric tests should be performed. The specific behavior of a more elastic or more plastic material depends on time and, more specifically, on the relationship of the deformation time of the material to the characteristic natural time of that material. The faster the deformation the more elastic the material behaves, and the slower the deformation the more viscous it is. The characteristic time of each material is very different and, in some cases, not visible to the naked eye, such as water. Polymers are characterized by viscoelasticity, i.e., the characteristic time is 10-102s. The viscoelastic deformations have the character of a return deformation, and their disappearance is not immediate but delayed. The problems of rheology of plasticized filled polymers include many theoretical and experimental issues. Most attention has been paid to the search for rheological equations of state for dispersion systems, including systems with liquid boundary and the relation between viscosity and the amount and type of filler. The least amount of information is presented on the relation between geometrical features of the filler grains and rheological properties. Equally little information is found on the influence of residual magnetization on the flow properties of the compound. This thesis constitutes a closed work on this problem, and it can be accepted as a modest but important contribution to the knowledge of the role which geometrical characteristics of the extender and residual magnetization play in the rheology of filled polymers.

Knowing that a magnet attracts iron and explain why it does – is not the same thing.

(F.S. Taylor, 1959)

# **CHAPTER 4**

# **EXPERIMENTAL AND METHODS**



## 4.1. Thermoplastic matrix

**Polypropylene** (**PP**), a synthetic resin built up by the polymerization of propylene. Polypropylene is molded or extruded into many plastic products in which toughness, flexibility, lightweight, and heat resistance are required. It is also spun into fibers for employment in industrial and household textiles. PP is the largest single thermoplastic material (*Elvers B. and Ullmann F. 2017*). Polypropylene is a tough, rigid and semi-crystalline thermoplastic produced from propene monomer. The chemical formula of polypropylene is ( $C_3H_6$ )n (*Tripathi D. 2002*).



Figure 4.1. Molecular Structure of Polypropylene

As the propene monomer is asymmetric, polypropylene can be produced with different stereochemical configurations. Figure 4.2. show the types of PP, isotactic (iPP), syndiotactic (sPP), and atactic (aPP). In iPP all methyl groups are located on the

same side of the backbone, in sPP on alternating sides, and in aPP the methyl groups are arranged randomly along the polymer chain (*Tripathi D. 2002*).



Figure 4.2. Main polypropylene types A) Isotactic; B) Syndiotactic; C) Atactic (Karger-Kocsis, 1995)

Commercial interest lies primarily in isotactic, highly crystalline PP, together with its further modifications through copolymerization. The structure, morphology, and properties of iPP have been studied extensively (*Karger-Kocsis J. 1995*). These days, polypropylene is made from polymerization of propene monomer (an unsaturated organic compound  $C_3H_6$ ) by:

- Ziegler-Natta polymerization or
- Metallocene catalysis polymerization

Homopolymers and Copolymers are the two major types of polypropylene available in the market. Polypropylene Homopolymer is the most widely utilized generalpurpose grade. It contains only propylene monomer in a semi-crystalline solid form. Main applications include packaging, textiles, healthcare, pipes, automotive and electrical applications.

The properties of Polypropylene include:

- Semi-rigid
- Translucent
- Good chemical resistance
- Tough
- Good fatigue resistance
- Integral hinge property
- Good heat resistance.

60

PP does not present stress-cracking problems and offers excellent electrical and chemical resistance at higher temperatures (*Gahleitner M. & Paulik C. 2017*). Properties of various grades of PP are shown in Table 1.

Property	Value
Dimensional Stability	
Coefficient of Linear Thermal Expansion	6 - 17 x 10 <sup>-5</sup> /°C
Shrinkage	1-3%
Water Absorption 24 hours	0.01 - 0.1 %
Electrical Performances	
Arc Resistance	135 - 180 sec
Dielectric Constant	2.3
Dielectric Strength	20 - 28 kV/mm
Dissipation Factor	3 - 5 x 10 <sup>-4</sup>
Volume Resistivity	16 - 18 x 10 <sup>15</sup>
	Ohm.cm
Fire Performances	
Fire Resistance (LOI)	17 - 18%
Flammability UL94	HB
Mechanical Properties	
Elongation at Break	150 - 600 %
Flexibility (Flexural Modulus)	1.2 - 1.6 GPa
Hardness Rockwell M	1-30
Hardness Shore D	70 - 83
Stiffness (Flexural Modulus)	1.2 - 1.6 GPa
Strength at Break (Tensile)	20 - 40 MPa
Strength at Yield (Tensile)	35 - 40 MPa
Toughness (Notched Izod Impact at Room Temperature)	20 - 60 J/m
Toughness at Low Temperature (Notched Izod Impact at Low	27 - 107 J/m
Temperature)	

#### Table 1 Properties of Polypropylene

1.1 - 1	ι.6 GI	Pa
---------	--------	----

75 - 90 % 11 %
85 - 90 %
0.9 - 0.91 g/cm³ -10 °C
Poor Fair
-20 to -10 °C 100 - 120 °C 50 - 60 °C 100 - 130 °C -20 to -10 °C

Injection molding is used for a wide range of packaging material and general-purpose items with limited requirements, as well as for most of the technical uses of PP. Two main groups of factors define the selection of PP grades for injection molding applications: part geometry, especially the flow ratio (i.e., the ratio of longest path to the section thickness), the complexity of the part, and the thermomechanical requirements in the respective application. Standard processing conditions used for PP are:

- Melt temperature T<sub>m</sub>: 200–265 °C
- Injection pressure: 50–150 MPa

Young Modulus

- Injection speed: 100–400 mm/s
- Mold (wall) temperature Tw: 30–60 °C.

As a rule of thumb, lower Tm values are used for higher MFRs (Melt Flow Rates), and lower Tw values for thinner parts. Linear post-molding shrinkage of PP is 1.0–1.5 %, of which 85 % occurs within the first 24h. Injection-molded parts of PP range in wall thickness from 0.3 mm (e.g., for thin-wall dairy cups) to 10 mm (e.g. for pressurized ion-exchanger cartridges in coffee vending machines) *(Elvers B. and Ullmann F. 2017)*. PP is 100 % recyclable. Automobile battery cases, signal lights, battery cables, brooms, brushes, ice scrapers, etc., are few examples which can be made from recycled polypropylene (rPP). The PP recycling process mainly includes melting of waste plastic to 250 °C to get rid of contaminants followed by removal of residual molecules under vacuum and solidification at nearly 140 °C. This recycled PP can be blended with virgin PP at a rate up to 50% *(Tratzi et al. 2021; Jeswani et al. 2021; Tavanaie and Ghahari 2021)*. The use of PP is considered safe because it does not have any remarkable effect from an occupational health and safety point of view, in terms of chemical toxicity *(Bora R. et al. 2020)*.

Polyamide (PA) is a polymer that is made of continuous units in the molecular linkage that are bonded by amine groups. The chemical formula CO-NH indicates the amide group. The amide groups may be formed through the polymerization of amino acids, or the interaction of the carboxyl (CO<sub>2</sub>H) group or through amino-acid derivatives (where the constituent molecules are made of the carboxyl and amino groups). Polyamides are made of peptides and proteins, which are naturally, synthesized polymers comprising of amino acid chains. Polyamides are classified based on the frequency and number of phenyl rings in its structure. When about 85% of the amide groups are bonded to the phenyl rings directly, the polyamide is referred to as an aramid. When the percentage is lower than 85 % the polymer is categorized as nylon (Textile Institute (Manchester, England) 2008). Polyamides are typically made by combining two monomers namely, adipic acid with 1.6-diaminohexane. Once these two monomers have reacted together, they form water as a by-product of each polymer chain linkage. This linking of the two monomers is known as polymerization (Nadler and Srebnik 2008; Ukrainsky and Ramon 2018). This creates a nylon salt which is then heated to evaporate the water. This heating is done inside an autoclave at 230°C and 18bar. After the polymerization process, various additives and pigments are added. These can change the physical properties of the polymer (Marianne 2017). Polyamide 6 (PA 6) is a semi-crystalline polyamide.



Figure 4.3. Molecular Structure of Polyamide (Hopff 1954)

PA6 is produced by the polymerization of hexamethylene diamine with a dibasic acid i.e., sebacic acid this case. Melting point of polyamide PA6 is 223 °C (*Wypych 2016*). Most nylons tend to be semi-crystalline and are generally very tough materials with good thermal and chemical resistance. The different types given a wide range of properties with specific gravity, melting point, and moisture. Nylons tend to absorb moisture from their surroundings. This absorption continues until equilibrium is reached and can have a negative effect on dimensional stability.

Property	Value		
General Properties			
Density	1.11-1.17 g/cm <sup>3</sup>		
Melt Volume Flow Rate	24 cm <sup>3</sup> /10 min		
Mechanical Properties			
Tensile Strength	61 MPa		
Tensile Modulus	3500 MPa		
Tensile Elongation at break	1.9 %		
Flexural Strength	131 MPa		
Flexural Modulus	3300 MPa		

Table 2 Properties of Polyamide 6

Charpy Impact Strength	2.5 kJ/m <sup>2</sup>
Hardness Rockwell M	1-30
Hardness Shore D	70 - 83
Toughness (Notched Izod Impact at Room	20 - 60 J/m
Temperature)	
Toughness at Low Temperature (Notched	27 - 107 J/m
Izod Impact at Low Temperature)	
Young Modulus	1.1 - 1.6 GPa
Thermal Properties	
Melting Temperature	220 °C
Crystallization Temperature	174 °C

Polyamide's material absorbs humidity easily, which has an effect on the course of working, like decreasing viscosity of the melt and appearing bubbles and crazing the surface, etc. Therefore, the drying process must be done before shaping up. Besides PA6 and PA66 plastic is easily oxidized, and color changed as well as decomposition under hot temperature, so it will be better with vacuum drying. The temperature of vacuum drying is 85-95 °C and the lasting time is 4-6 h. Standard processing conditions used for injection molding for PA are:

- Melt temperature T<sub>m</sub>: 260-280 °C
- Injection pressure: 75–125 MPa
- Injection speed: 100–400 mm/s
- Mold (wall) temperature Tw: 80-90 °C.

The mold temperature has a significant influence on the crystallinity level of the material, which in turn greatly influences it's mechanical properties. High mold temperature is also recommended for thin-walled parts with long flow lengths. Increasing mold temperature increases the strength and hardness by increasing crystallinity, but the toughness is decreased.

To recycle the PA waste, the material must be stored in dry conditions or dried appropriately before injection-molding. The properties of the recycled material will change as the material is subject to thermal history. The molded product is crushed in a crushing machine. The recycled material is mixed with virgin material at a predetermined proportion and a uniform mixture is created. The mixture then is provided to injection molding. Recycling frequency is 1-5 times. Aside from reduction in elongation at break product maintains nearly 100 % of its properties.

### 4.2. Filler material

Using a magnet with the right chemical composition ensures high magnetic properties of the product. The size of particles and their shape influence the bonding with polymer matrix. Table 3 shows the specific material characteristics of the used neodymium-iron-bor- microparticles.

Properties	Unit	NdFeB
Chemical composition	[%]	Nd, Pd, Dy, Feges, Femet
Curie-Temperature	[°C]	320
Particle shape	-	irregular
Particle size	[µm]	≤ 150

#### Table 3 Properties of filler NdFeB

In order to determine the influence of the particle size distribution and the average particle diameter d<sub>50</sub> on the compound properties, a total of five fractions of the NdFeB particles are produced and analyzed by using a laser diffraction spectroscopy. Figure 4.4. shows that the irregular shape of the NdFeB particles means that no definite screening boundaries can be found. The sieve fractions show an increased fine fraction, which can be explained by presence of irregular particles. The orientation of the particles during screening determines whether the particle is to be found in a lower screening fraction (largest expansion of the particle perpendicular to the screen), or in a higher screening fraction (largest expansion of the particle parallel to the screen). Based on the particle size distributions in Figure 4.5., the geometrical characteristics of the NdFeB particle fractions listed in the Table 4 are obtained from laser diffraction spectroscopy. In the Table 4 presented Sauter diameter mean diameter of collection of different-size objects by taking into account both volume and surface area is introduced by Sauter (Josef Sauter 1926) while dealing with fuel oil drops. Presently, the Sauter mean diameter concept has been widely used for the determination of average size of gas bubbles, liquid drops,

particles, and sediments. In the literature, the Sauter mean diameter is known as the surface-volume mean diameter (*Pacek et al. 1998*).

Properties	Unit	NdFeB-Fraction				
	[µm]	25	36	50	200	200-250
Average particle diameter	[µm]	24	32	48	215	220
Sauter diameter	[µm]	23	31	47	214	218
Standard deviation	-	0.4	0.3	0.3	0.2	0.2

Table 4 Particle size analysis of NdFeB

Based on the analysis of particle size results and microscopic images, a model of a single particle (Figure 4.4.) is prepared together with the averaged characteristic sizes. Thanks to the microscopic tomography, which shows a digital image of the particles, it is possible to apply appropriate algorithms to separate single particles and measure selected parameters (length, width, radius, etc.).



Figure 4.4. Model of NdFeB particles based on the particle size analysis

The figure shows the structure of a single particle ground permanent magnet composed of neodymium, iron and boron. The geometry of the elementary cell of the intercrystalline phases, provides high magnetic properties. A graph is plotted with the cumulative distribution for the prepared particles represented by the y-axis and the particle size represented by the x-axis, as shown in Figure 4.5. The lines represent the cumulative curve for RE-NdFeB particles whose size is calculated using a laser

diffraction sensor. The results show the variation of the particle size depending on the length of the milling time.



Figure 4.5. Diagram of the NdFeB particle fraction as cumulative distribution

It is important to observe that the magnetic properties of permanent magnets depend on the particle size. In the following part the analysis of individual parameters such as viscosity, coercivity, remanence, thermal properties depending on the degree of magnetic particle size distribution is focused. While observing powder with a size below 50 µm, it is reported that it tended to agglomerate into large clusters, show Figure 4.6. This made it difficult to identify the size of the powder particles. To overcome this problem, the demagnetization process is repeated. The test powder is heated to the Curie temperature for 4 hours. This reduced the residual magnetization, thus facilitating a better indication of the true nature of the powder particle size. The cumulative distribution diagram shows that most of the particle sized are around the average, which means that it follows a Gaussian distribution curve. In addition, the grinding magnets as single particles tend to form agglomerates due to their particle shape. The agglomeration phenomenon consists in the assembly of particles into irregular clusters, which in turn affects magnetic properties. The tendency for particles to agglomerate is particularly strong in the case of small particles because of the large proportion of surface atoms in relation to bulk atoms.


Figure 4.6. Agglomeration of particles with a size of 50  $\mu$ m, microscopic magnification x1000

This tendency can also be prevented by maintaining the pH (significantly different from 8.5), which creates a unipolar charge on the surface of the particles, so that the powder particles repel each other, making the agglomeration process more difficult.

## 4.3. Influence of particle size and geometry of polymer and filler

According to their shape, particles are typically divided into four groups: spheroidal, irregular, plate-shaped, dendritic fine crystalline grains (Gahleitner M. & Paulik C. 2017; Hentschel M.L. & Page N.W. 2003; Garboczi E. J. & Bullard J. W. 2017; Deng X.& Davé R.N. 2013). Each of these allotropes presents different structural configuration, which confer specific characteristics to composite due to its shape (Maroof M.A. et al. 2020). Spherical particles are commonly used as the basic shape for mathematical models (Rodriguez J., Edeskär T., & Knutsson S. 2013). However, this approach is in most of cases a vague approximation. The particle shape is generally described in mathematical models by aspect ratio (Ar) (Gahleitner M. & Paulik C. 2017). The aspect ratio represents the deviation of the filler shape form the ideal spherical shape and can by found in many forms, according to the characteristic parameters of the particle like its volume, surface area, projected area, related to the equivalent sphere (Deng X.& Davé R.N. 2013; Blott S. J. and Pye K. 2007). The aspect ratio is also considered as the largest characteristic length (i.e., the diameter for platelet or length for fibers) divided by the opposite length (thickness or diameter), so  $A_r = d_{max}/d_{min} > 1$ . It has been also defined in terms of the axis of symmetry and flow orientation. Table 5

shows the particle rotary diffusivity as a function of the aspect ratio (p), which is defined as the ratio of the length of the particle along its axis of symmetry to its length perpendicular to this axis; for example, p < 1 for platelets and  $p \gg 1$  for fibres.

Particle shape	Aspect ratio (p)	Rotary diffusivity
	Fibers, rods $p \gg 1$	$D_{ro} = 3k_b T (\ln (p - 0.8)) \pi \eta_s L^3$
	Circular disk-like particle $p < 1$	$D_{ro} = \frac{3k_b T}{4\eta_s d^3}$
	Prolate spheroids $p > 1$	$D_{ro} = \frac{3k_b T(\ln 2p - 0.5)}{\pi \eta_s L^3}$
	Particles nearly spherical shape $p \approx 1$	$D_{ro} = \frac{k_b T}{\pi \eta_s d^3}$

Table 5 Particle size and their rotary diffusivities in the case of Brownian particles (Rueda M. M. et al. 2017)

Experimental data have demonstrated that the maximum packing fraction ( $\varphi_m$ ) decreases as  $A_r$  of the suspended particles increases. The mixture viscosity increases with increasing aspect ratio for a given filler content. Figure 4.7. shows the viscosity as a function of the content level for particles with different  $A_r$ . It can be seen from the figure that, for rod particles of length L and diameter D,  $A_r \gg 1$  and the viscosity drastically increases with the filler content compared to the spherical particle suspension viscosity. Indeed, when  $A_r$  increases, their effective volume fraction also

increases. As a result, the friction between them increases, increasing energy dissipation; thus, higher melt viscosity is obtained.



Figure 4.7. Schematic representation of the effect of particle shape on the relative viscosity. Adapted from (Rueda M. M. et al. 2017)

Particle geometry plays an important role in final composite properties and processing (Wypych G. 2016). Well defined and characterized specific particle length are fundamental in industry. For example, the thickness of plate-like particles such as mica and talc are important in the paper and paint industries. Thinner particles can overlap more easily and produce an opaquer coating. Furthermore, the use of high aspect ratio particles reduce the maximum packing fraction and consequently the percolation threshold (i.e. the critical solid concentration level) where interparticle interactions become important (Feng J. et al. 2016). Therefore, it is possible to improve properties such as magnetization, thermal and electrical conductivity with the same quantity of particles by using irregularly shaped particles (Kitano T. et al. 1981). Another remarkable example of how particles properties interplay is for instance the powder injection molding process, in which the combination effect of particle shape and size is imperative to allow the transformation process to succeed (Kirchberg S. 2009b; Genovese D.B. 2012). These materials consist of very high content of metallic powders compounded with a binder (matrix) to obtain, in most cases, complicated shape products. In this regard, it is important to point out the four stages of this process. First, the filler is mixed with the binder formulation (thermoplastic polymers with additives) are compounded to

obtain a feedstock that is then injected into a mold. The particle size, particle size distribution and particle shape are the key parameters that have a strong influence on every single step of process. For instance, spherical particles present higher packing density and lower mixture viscosity, which is required for injection. However, during debinding they have a lower compact strength than asymmetric particles. Then, a compromise can be found to combine hybrid fillers (spherical and irregular shape particles) in order to archive the benefits of both.

The packing fraction affects the properties of porous materials, the viscosity of the particulate suspensions, and the glass- forming ability of alloys (Brouwers H. J. H. 2006). Furthermore, collections of hard spheres also serve as a model for the structure of sample liquids. There is, therefore, practical as well as fundamental interest in understanding the relationship between the particle shape and particle size distribution on the one hand and packing fraction on the other. The packing fraction of particles depends on their shape and method of packing: regular or irregular (random), where the letter furthermore depends on the densification (Brouwers H. J. H. 2006; Deng X.& Davé R.N. 2013).

#### 4.4. Compounding

In principle, the produced powder can be further processed in various processing steps. Compounding by using a kneader has the advantage that small quantities of material sufficient for research purpose can be reproduced and processed. Scaling up to extrusion processing is also possible. Semi-crystalline polypropylene (PP) and polyamide (PA) are selected as thermoplastic matrix materials due to their different industrial application frequency in different areas. These are mass plastics/engineering materials which are used as standard injection molding types and are often used as a matrix material for compounds. More than one third of components in the automotive sector are produced based on PP. The high modulus of elasticity and the low price of raw materials predestine these PP compounds for use in the automotive industry. For compounding the materials, a kneader from PolyLab Rheo-mix 600p, Thermo Haake GmbH, Karlsruhe, Germany with the parameterization shown in Figure 4.8. is used. The design on the laboratory compounder based on a heated and closed swaging chamber, within which there are two counter-rotating (ration 2:3) kneading blades Figure 4.8. Depending on the

position of the blades relative to each other and because of the uneven geometric structure across the depth of the measuring chamber, the mechanical load acting on the material varies.



Figure 4.8. PolyLab Rheo-mix 600p kneading elements

The basic drive unit of the Thermo Scientific HAAKE PolyLab system includes all elements of a torque rheometer needed to drive the measuring system (precise speed controller) and to monitor the torque (accurate torque sensor) needed to process the test material.

Polymer	Polyamide	Density: 1.10 g/cm <sup>3</sup>		Filling RE-MB	Density: 7.4 g/cm <sup>3</sup>
Degree of filling, Vol.%	30	40	50	60	70
Filling mass, g	74.25	81.77	87.06	90.98	94.01
Polymer mass, g	25.75	18.23	12.94	9.02	5.99
Filling Volume	10	11	11.8	12.3	12.7
Mixing density, g/cm <sup>3</sup>	2.99	3.62	4.25	4.88	5.51
Mixing volume cm <sup>3</sup>	33.44	27.62	23.53	20.49	18.15

#### Table 6 Material dosage in kneader: polyamide and filler

Table 7 Mater	rial dosage i	in kneader:	polypropylene	and filler
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Polymer	Polypropylene	Density: 0.9 g/cm <sup>3</sup>		Filling RE-MB	Density: 7.4 g/cm <sup>3</sup>
Degree of filling, Vol.%	30	40	50	60	70
Filling mass, g	78.13	84.57	89.16	92.50	95.05
Polymer mass, g	21.88	15.43	10.84	7.50	4.95
Filling Volume	10.04	11.04	12.0	12.5	12.8
Mixing density, g/cm <sup>3</sup>	2.85	3.50	4.15	4.80	5.45
Mixing volume cm <sup>3</sup>	35.09	28.57	24.10	20.83	18.35

The relationship of the percentage of filler to the density and volume of the composite is shown graphically below (Figure 4.9.).



Figure 4.9. Relationship of the percentage of filler to the density and volume composite (Matrix PP)

In the figure we can see the relationship between two parameters - mixing density (grey) and mixing volume (blue) which change linearly with the amount of filler. These changes are observed by analyzing 50 samples of each filler volume. The diagram shows a linear change in the compound properties that affect the further

analysis shown in the next chapter. Specific changes and their impact on properties will be discussed.

## 4.5. Injection molding

The presentation of the injection molding machine technology in general, its special features as well as the adapted regulations and control systems are, among other authors, comprehensively presented in the "Plastic Injection Molding" manual *(Lerma Valero 2020)*. The basic understanding of the machine used, which is necessary for this work, are presented on the Figure 4.10.



Figure 4.10. Schematic of a fully hydraulic injection molding machine

The structure of an injection molding machine consists of different assemblies, each of which has its own tasks. The following graphic shows an injection molding machine with the most important functional units. The so-called plasticizing unit (injection unit) is of central importance for the functioning of the injection molding process. The plastic to be processed is melted in this unit. In addition, homogenization, conveying and metering of the plastic takes place here. The injection unit also injects the plastic into the injection mold. The tasks of the injection unit therefore include plasticizing the plastic on the one hand and injecting it into the mold on the other, the process show the Figure 4.11. In order to solidify the plastic part in the mold so that it can be removed (ejected), it is usually necessary to cool the mold. The cooling is accomplished by circulating cool water through cooling channels that

are machined into the mold itself. The water is cooled by a chiller, which can either be a free-standing unit nearby the press or by a part of a temperature controller system that may serve several molds in several injection molding machines. Temperature controllers may take the form of chillers, as described, or in other cases, heating units (for thermosets), heat exchangers, and various types of water and oil temperature controlling devices.



Figure 4.11. Schematic drawing of the injection molding process

The molder's raw material plastic, is usually used in pellet form. Each pellet is about size of three millimeters in diameter. In some cases, plastic is purchased in powder form which is a little coarser than flour. Very few plastics, other than thermostat materials are bought or used in powder form today. Moving the plastic from its storage to the press is the function of the loader. A loader may be a simple as a vacuum powered unit with hoses that pull pellets from gaylord and deposit them in the hopper. This unit is called a hopper loader and sits beside the press with hoses that can access gaylords that are nearby. A loader unit may be a complicated as a pneumatic material handling system that connects a large number of injection molding machines to storage silos and distributes a variety of plastics throughout the plant. Unfortunately, most plastics are hygroscopic. If the moisture is not removed to a certain level, the plastic parts produced will contain cosmetic or structural defect and the injection unit components may suffer corrosive wear. As a result, many plastics are processed through a dryer. There are several types of dryers available today, but all involve the circulation of either hot air or dehumidified hot air through the pellets before they are allowed to enter the injection unit. Some dryers are quite small and fit on top of the press as a part of the hooper assembly and other are large enough to dry the plastic that might feed several machines. This introductory discussion of injection molding elements is designed to acquaint with all the pieces

to the molding puzzle. Each element will be discussed in further detail in a succeeding chapter of the thesis. A knowledge of how the elements fit together should help when the basis of each element is pursued further. The Table shows some of the property values that can be adjusted by a higher or lower change in some of the more common molding parameters. There are just some examples. But notice how some properties are changed in the same way by different parameters. For instance, "less shrinkage" can be attained by either increasing injection pressure or injection mold temperature, and "less degradation" can be achieved by lowering back pressure as well as lowering melt temperature. These examples demonstrate that the basic molding parameters do work closely together, and that changing a parameter in one area may affect a value of some property in another area. By understanding this relationship, it is possible to minimize the number of adjustments required when it is necessary to make a correction due to an unexpected change in some variable of the process.

Parameter		Property Effect
Injection pressure	t	Less shrinkage, higher gloss, less warp, harder to eject
Injection pressure	Ŧ	More shrinkage, less gloss, more wrap, easier to eject
Back pressure	ŧ	Higher density, more degradation, fewer voids
Back pressure	Ŧ	Lower density, less degradation, more voids
Melt temperature	t	Faster flow, more degradation, more brittle, flashing
Melt temperature	ŧ	Slower flow, less degradation, less brittle, less flashing
Mold temperature	t	Longer cycle, higher gloss, less wrap, less shrinkage
Mold temperature	ŧ	Faster cycle, lower gloss, greater warp, higher shrinkage

Note interconnection between parameters indicated that each parameter is both affected by and affects other parameters. A change in one may have a major effect on another. All the settings are dependent on the material type. The used injection molding parameters for the magnetic particle and polymer are shown in Table 9.

#### Table 9 Used molding parameters

Parameters	Unit	PP	РА
Temperature	°C	200	220
Tool temperature	°C	80	100
Injection pressure	bar	1000-1500	1500
Injection rate	m/min	22	22
Pressure	bar	800-1200	800-1200
Holding pressure time	S	5	5

Furthermore, different injection molding tools are used to analytically prove the influence of the particle on the material properties (Figure 4.12.). Figure 4.12. (A) shows cavities tool with both rectangular (30x10x3 mm) and circular (diameter: 25 mm, thickness: 1 mm and 2 mm) sample geometry (B). An injection mold is a tool comprised of a series of parts (support plate, ejector retaining, ejector plate, mold core, mold cavity, support plate, sprue, locating ring, gate, runner, etc.) that allows molten plastic to be formed and cooled in such a way as to create a discrete part shape.



Figure 4.12. Used injection molding tools (A) Rectangle (35x10x3mm), (B) Circular disc (Ø25 mm, d=1 mm, 2mm)

The choice of the machine barrel is mainly based on the melting temperature of material. At the same time, it is also related to the type of injection molding machine, type of product and size. Generally, the melting temperature for PP 200 °C and for PA6 is 220-300 Celsius degrees; as the processing temperature of PP and PA6 is narrow, so the temperature of machine barrel must be controlled strictly, in order to avoid decomposition of melt. The setting of the machine barrel has a large effect on plasticizing and speed of melt. The temperature of the middle section of the machine barrel should be higher than the melting point of 20–40°C and lower than the decomposition of 5-10 °C. The temperature of back-end (loading section) is lower than the middle section of 20-50 °C. Cooling of the charging hole must be effective. If the temperature of the middle section is too low and the screw changes its speed too fast, then jamming phenomenon will appear. If the temperature of the posterior section is too high, then the delivering capacity will be affected. A lower speed of screw will affect production efficiency.

# **CHAPTER 5**

# **TECHNICAL CHALLENGES IN DEVELOPED**

# **RECYCLING PROCESS**



The direct recycling involves the reprocessing of material into new magnets (Kapustka K., Ziegmann G., Deutsche Bundesstiftung Umwelt 2020). Before the magnets can be used as an input material for an indirect recycling process, or a reuse of the magnets, magnets need to be extracted from their devices and demagnetized. These steps Figure 5.1. are also necessary for some direct (magnet material) recycling routes. Other direct recycling routes use hydrogen treatment to extract and demagnetize the magnet material (*Gauß et al.* 2015).



Figure 5.1. Technical challenges during the recycling process with a plastic matrix

## 5.1. Extraction

To feed magnets from EOL-components into a recycling system, the recyclers need to efficiently collect and detect the presence of the magnet material in the appliances. The first step, the separation of the magnets from EOPL-appliances, has been

80

identified as one of the key barriers to NdFeB magnets recycling (*Rodriguez J., Edeskär T., Knutsson, S. 2016*). The magnets come in different shapes and sizes from a large variety of applications which poses a challenge to the automation of the extraction step. However, in this work an algorithm is developed to identify the type of waste and automatically disassemble to extract magnets from the case. The presented program has been optimized, increasing its efficiency from 50% to 98%. It allows the scanner to identify the bolted coupling and remove it using a robotic arm with the necessary tools. This process has been repeatedly performed on hard drives with a 98% success rate, the results are shown in Figure 5.2. For each waste product, a one-time check must be made to adapt the program to the requirements.

#### Program

```
clc;clear all;close All;
filename = 'dysk_1';
%read image from graphics file
img = imread(strcat(filename, '.jpg'));
%Convert RGB image or colormap to grayscale.
img = rgb2gray(img);
%adapthisteq Contrast-limited Adaptive Histogram Equalization (CLAHE)
img = adapthisteq(img);
%Global image threshold using Otsu's method.
level = graythresh(img);
BW = im2bw(img,level);
%Morphological structuring element
se = strel('disk', 3);
```

```
BW = imclose(BW, se);
%BW = imfill(BW, 'holes');
s = regionprops(BW,'centroid','area');
centroids = cat(1, s.Centroid);
area = cat(1,s.Area);
circle=[];
for i=1:1:numel(centroids(:,1))
    if ((area(i)>1500) && (area(i)<5000))
       circle = [circle;centroids(i,:)];
end
end
figure(2)
imshow(BW)
hold on
plot(circle(:,1), circle(:,2),'r*');
hold off
%final picture
saveas(gcf, strcat(filename, '-w.png'))
%save the result points in an array
dlmwrite('results_1.txt',circle,'delimiter','\t','precision',3)
```

The presented program consists of 5 steps which include:

1) Changing real colors to grayscale,

2) Adaptive histogram equalization with contrast limitation (CLAHE) - this method consists in improving contrast of the analyzed image using its histogram.

3) Image binarization - is the process of converting color or monochrome images (in shades of sharpness) to binary image. Performing binarization on an image greatly reduces the amount of information contained in it. This is done by thresholding, where a threshold is set below which image pixels are classified as object pixels, and all other pixels are classified as background (not object) pixels.

4) Morphological structuring element. Morphological operations are one of the most important operations on images, because they allow to perform advanced analysis of shapes of individual objects and distances between them. Basic morphological transformations can be combined, which gives rise to building complex image analysis systems. Processing of binary images is performed using mathematical morphology, theory of analysis and processing of geometric structures based on multiplicity theory, topology, and random functions.

The processed image is defined by the set  $I(x, y) \in \{0,1\}$  of pixels p=(x,y), in which two subsets can be distinguished.

Foreground, pixels taking the value 1;  $U_1 = \{I(p) = 1\}$ 

Background, pixels with value 0,  $U_2 = \{I(p) = 0\}$ 

5) Final image (presented on the Figure 5.2).



Figure 5.2. Hard drives with identified screws (marked red by the program) ready to be dismantled in an automatic process

#### **5.2. Demagnetization**

The demagnetized recovered magnets traditionally used in electric motors and hard disk (sintered material of general formula NdFeB) are prepared using described techniques. Taking into account the multi-phase structure of the magnets and neodymium high affinity to oxygen, the preparation of materials has been conducted in a noble gas atmosphere (Ar). For demagnetization, the magnetic material has been heated in an oven to a temperature above Curie temperature or by exposing them to an external magnetic field. Glues and other organics need to by removed prior demagnetization via heating to avoid the formation of hydrocarbon containing vapors (*Kapustka K., Klimecka-Tatar D., Ziegmann G. 2019*). The different requirements for the demagnetized in muffle oven. Demagnetization is possible by variety of thermal processes. The specific Curie temperature for the examined NdFeB magnets ( $T_{Curie}$ (NdFeB)) is about 350 °C. A variant for reaching the Curie temperature is convection and heat conduction. The magnets or even whole rotos can be heated in oven by convection and heat conduction at 350 °C.



Figure 5.3. Requirements for suitable demagnetization processes

Another method presented by Danish scientists in 2020 is a method using an inductive device (Bahl et al. 2020). Large blocks of NdFeB permanent magnets of dimension 10 cm x 7 cm x 2 cm and with the easy axis along the shortest dimension, are shown to demagnetize when heated on a planar induction heating device. The initial magnetization of the magnets is reduced by a factor of 10 within a period of 30 minutes, in which the surface temperature of the magnet reaches 225 °C. This

method simplifies the demagnetization process of the permanent magnets in wind turbine generators as part of the rapidly increasing demand for improved recycling capabilities of permanent magnets. An alternative to mechanical extraction and demagnetization is hydrogen decrepitation (HD), which achieves both on the step, show in Figure 5.4.



Figure 5.4. Schematic drawing of the hydrogen decrepitation process

The magnets are transferred into a hydrogen atmosphere to achieve the absorption of hydrogen the magnet material. In this process, the magnet decrepitates into a demagnetized, hydrogenated powder. Hydrogen decrepitation generally requires a removal of the coatings of glues prior to the process to expose the magnet material surface to the hydrogen.

#### 5.3. Pulverization

During the pulverization of permanent magnets with vibrating disk mill show on Figure 5.5., special attention must be paid to oxidation reactions. Rare earth elements have the highest affinity to oxygen. However, this applies to the observation of pure substances. The NdFeB alloy, when ground, reaches a temperature that causes the transition of metallic components to oxygen phase. For safety it is used argon gas in this process. The high oxidation potential of REE has a pyrophoric character and is prone to spontaneous flaming when exposed to atmospheric oxygen. The danger of oxidation of the powder increases with decreasing particle size. After griding the powder must be removed from the container and compound directly with polymer, or it must be stored very tightly without access to oxygen. The oxygen content of powder is higher when the content of rare earth is higher. The presence of oxygen between the grains of Nd<sub>2</sub>Fe<sub>14</sub>B reduces the occurrence of increased remanence. The high oxygen content and its negative influence on the phase structure explains the

fact that the materials obtained in the mechanical process have lower properties than those obtained from rapidly solidified metallic tapes. From the point of view of improving process efficiency and magnetic properties, powders with small particles as possible should be used. According to the work (*Kapustka K., Klimecka-Tatar D., Ziegmann G. 2019*), the optimal particle size is between 5-15  $\mu$ m. For powders with smaller particles, the share of oxides increases strongly at the expense of the Nd-rich phase.



Figure 5.5. Pulverization with the vibrating disk mill, Siebtechnik

However, striving to increase coercivity forces to use powders with smaller particles. It is therefore necessary to use low-oxygen technology (LOT). This is the main direction of technology development for sintered NdFeB magnets. A distinction is made between "dry" and "wet" processes (*Bora R. et al. 2020; Bae K. H., Lee S. R., Kim H. J., Lee M. W., & Jang T. S 2015; Wang L. et al. 2007*). In the "wet" process, liquid substances (e.g., low-oxygen oils) are used to protect the powder and to prevent atmospheric oxygen from reaching the material. In the dry process this is achieved by using inert gaseous atmospheres. The reduction of the particle size with a simultaneous reduction of oxidation increases the efficiency of the process.

#### 5.4. Summary

To this day, the process of extracting magnets from electrical devices is carried out manually. It should be mentioned here that this activity provides workplaces for many disabled people who are manually active. The introduction of automation as shown above is possible and its further development for further products can be achieved quickly. Thanks to the development of technology, it is possible to use algorithms that allow the machine to learn and autonomously recognize different electrical components and different shapes and positions of magnets. This process will only be economically profitable if a sufficiently large quantity of material is supplied. We are talking here about millions of tons of magnets. At present, there is no market in Europe that would be interested in such quantities of recycled permanent magnets. In the following part of the thesis this topic will be discussed in more detail.

The process of thermal demagnetization has many consequences. Setting the right temperature and maintaining it in classical ovens is very difficult and requires a large amount of energy. Neodymium magnets have a Curie temperature of 350 °C, which is associated with a huge amount of energy that must be supplied over a period of about 3-8 hours depending on the size of the neodymium magnets.

The process of pulverizing neodymium magnets is very demanding because it forces one to constantly observe the prepared powder. As the particle size of the powder changes, its magnetic properties also change. A good alternative to classical grinding is fragmentation by means of electrohydraulic fragmentation. This process has already been successfully carried out at the Fraunhofer Institute in Alzenau, Germany *(Bokelmann K., Hartfeil T., Kunkel K., Binnewies M. 2017)*.

## **CHAPTER 6**

# CHARACTERISATION BY ANALYTICAL METHODS



This is the most comprehensive chapter in this thesis. It focuses on a detailed analysis of the parameters that affect the properties of the material produced. It aims to present and explain the importance of each analysis as well as their interrelationships. The results presented in this thesis will help to answer the main question of this work: How the recycling process of polymer-based neodymium magnets is to be carried out and what parameters affect it? This chapter begins with Table 10 which shows the test methods used and the shape of the necessary test specimens. The testing machines used are located at the TU Clausthal and the AGH University of Science and Technology Krakau.

Sample	Method	Measuring system
Circular dicc	Phoology	AR 1000-N TA Instruments
Circular disc	Kileology	Rheo 5000 CEAST
Rectangular	TGA	TGA 2950 TA Instruments
Rectangular	DSC	DSC 2920 TA Instruments
Powder	Magnatia Magnumant	Vibrating Sample Magnetometer
	Magneuc Measurement	(VSM)
Circular disc/Powder	VDD	Panalytical Empyrean X-ray
	XRD	diffractometers

Tablado	Cleasification	of the toot	an manal on the	41000	le avec atomination	ma atla a da
Table to	LIASSINCATION	of the test	samples to	ine (	naracienzation	mernous
rabie 10	Ciccomicación	or the test	builpico co	uic c	and deter indution	meanoab

Rectangular	Microscope	VK-9700 Keyence
Cincular/Dourdon	CEM	REM DSM Gemini 982 von ZEISS
Circular/Powder	SEIVI	mit EDX-System von Thermofischer

A unique combination of various techniques provides a large spectrum of results allowing the determination of physical, chemical, and magnetic properties.

## 6.1. Microscopy analysis of NdFeB powder

The typical microstructure of a NdFeB sintered magnets is shown in the optical microscopy image in Figure 6.1. The  $Nd_2Fe_{14}B$  grain boundaries and larger grain at the NdFeB grain junctions. The larger, more rounded Nd-rich grains are usually neodymium oxides. The thin metallic grain boundary layers tend to amorphous when the thickness is below 1 nm and become crystalline at greater thicknesses.



Figure 6.1. The microstructure images of RE-M-B magnetic material recovered from electric motors (marked ferromagnetic, Nd-rich and B-rich phases)

During the tests of microscopic analysis of the magnetic material three phases are observed. As the typical NdFeB-magnets structure consists of the phases: the ferromagnetic phase  $Nd_2Fe_{14}B(\varphi)$  about 85 % of the phase volume, the boron-rich

phase NdFe<sub>4</sub>B<sub>4</sub> ( $\eta$ ) about 3 % and the neodymium-rich phase NdFe about 12 % mass. Neodymium magnets are structured in the multiphase skeletal manner, i.e. phases rich in neodymium fill intergranular areas around grain of Nd<sub>2</sub>Fe<sub>4</sub>B phase.

## 6.2. Scanning microscopy analysis (SEM) of powder

After the grinding process, a ready-to-use powder is present in particle sizes of  $20\mu$ m to  $50\ \mu$ m, which consists of a magnetically isotropic conglomerate of small NdFeB crystals with crystal sizes between 50 and a few hundred nanometers. The microcrystalline structure is responsible for the high magnetic and chemical stability of the material. Samples of the SEM analysis (Figure 6.2.) show a finely ground powder.



Figure 6.2. Results of scanning electron microscope of RE-M-B magnetic powder microscopic magnification (A) x1000, (B) x200

Microstructure plays a crucial role in the magnetic properties of NdFeB magnets. The magnetization and demagnetization can be altered by controlling the size, shape and orientation of the grains. In order to obtain different microstructures, three different processing techniques are currently employed:

- powdered metallurgical,
- methods sintering,
- melt spinning,
- mechanical alloying.

Grain size and grain distribution are important criteria for the intrinsic coercivity of the final magnet. Depending on the type of processing technique different grain sizes are found in the magnet. The microstructure of cast and extruded magnets in rather unknown, but first investigations show that the gain diameters are comparable with the one of sintered magnets.

## 6.3. X-ray diffraction patterns (XRD)

X-ray powder diffraction (XRD) showed an increase in the proportion of the amorphous phase and a simultaneous decrease in the proportion of the hardmagnetic phase. After some time, the proportion of the amorphous phase adjusts, but the proportion of Fe is increased in the amorphous phase. There is also a small amount of the paramagnetic phase in the alloy. The fact that Fe appears only when the content (amount) of the amorphous phase has stabilized is a signal of a two-step reaction. First, an amorphous phase  $\alpha 1$  is formed from the phase Nd2Fe14B, in the second phase another amorphous phase  $\alpha_2$  is formed, and from this phase Fe is formed. After heating, only a strongly broadened peak in the Fe- $\alpha$  position is observed on the diffractogram of the obtained powder. On the Figure 6.3. Powder X-ray diffraction pattern (IOBS) and Rietveld refinement (ICALC) of Nd2Fe14B are presented; they correspond to the observed pattern. The red line shows the difference between observed and calculated data. The black bars show the theoretical Bragg peaks of the NdFeB phase and the secondary  $\alpha$ -Fe phase (bottom). In the lower part of the graph, the diagram for the interpretation of the XRD results is presented, as well as a quantitative description of the observed phases.

Heating of the ground phase mixture of NdFeB alloy leads to crystallization. X-ray diffraction, apart from the Fe- $\alpha$  peak, shows the existence of NdFeO<sub>2</sub> phase peaks. Their width depends on the annealing temperature. Studies of the phase composition of powders annealed at different temperatures indicate that crystallization begins above 400 C°. At this point, the NdFeB phase begins to increase while the amorphous phase decreases. Only at temperatures above 500 C° do these phenomena intensify and the Fe phase content increases. The materials obtained by mechanical milling have smaller particle and a more homogeneous particle size distribution.



Figure 6.3. Powder X-ray diffraction pattern (IOBS) and Rietveld refinement (ICALC) of Nd2Fe14B

Coercivity and remanence of the powders obtained by this method are higher than those of the powder subjected to mechanical synthesis based on the literature (*Gabay et al. 2014; Kaszuwara W. 2015*). In addition, a difference between the annealed sample and the non-annealed samples is evident due to the narrow width of the individual reflections. It follows that the crystallite size has increased significantly. A constant chemical composition of the magnets is important for the process even after the compounding process and injection molding. The temperatures used for compounding can affect the chemical composition of the magnets and therefore their magnetic properties.



Figure 6.4. X-ray powder diffraction of NdFeB after heat treatment by magnetic field defined by Rietveld method

No changes in the chemical composition and crystallographic structure of the magnetic particles are observed during the analysis of individual samples. Therefore, it can be assumed that the magnetic powder is not sensitive to the temperatures used in the production of magnets in polymeric matrix. The results of x-ray diffraction of the mixture NdFeB after compounding and injection molding as shown in Figure 6.5. According the XRD patterns and JCCPDS file as seen at Figure 6.5. show that the mixture does not contain impurities and consisted of the phase Nd and Fe. The XRD peaks of Nd and Fe can be obtained by comparing the experiment peaks with

reference peaks data (JCCPDS) of Nd, Fe and B. Boron phase does not appear, it is because the amount of boron is too small, so the boron phase is not detected by XRD. The refinement and peaks search are done by using software Rietveld and it is found that the peaks around the corner  $(2\Theta)$ :  $42.94^{\circ}$  and  $49.62^{\circ}$  which it is an Nd<sub>2</sub>Fe<sub>14</sub>B phase. These observations make it possible to accurately determine the temperatures used in the process and to have a neutral effect on the magnetic particles.



Figure 6.5. XRD analysis for different samples- 100/70/30Vol.% of NdFeB

Magnetic powder with an average particle size of 50µm is used for the study. These results show that the amount of polymer matrix has no effect on crystallographic changes in neodymium magnets. The peaks for both the magnet sample and the sample containing 70 Vol.% of polymer and 30 Vol.% magnets. Therefore, irrespective of the polymer matrix volume, neodymium magnets keep their crystallographic properties and chemical composition remain the same.

#### 6.3.1. Chemical composition

By analyzing the chemical composition, the detailed analysis of the content of individual elements must be obtained. For chemical analysis atom emission spectroscopy ICP-OES Vista MPX, Varian is used. Table 11 shows the results of the

analysis of the chemical composition of the RE-M-B alloy. They indicate that the tested neodymium magnets, apart from the base alloy component, neodymium (ca. 24 %), the presence of other rare earth elements is identified Dy (ca. 6 %), and Pr as well as Tb. Whereas the Fe substituents in the tested alloys are also Co, Al, Pb, Cu and others. Thus, in the tested material is identified RE = Nd, Dy, Pr, Tb and M = Fe, Co, Al, Pb, Cu. The results are presented in Table 11.

Chemical composition	Content [%]	Chemical composition	Content [ppm]
В	0.88	Al	3301
Со	1.03	Ca	129
Dy	5.37	Cr	116
Feges	62.06	Cu	985
Fe <sub>met</sub>	59.29	Mn	291
Nd	23.56	Pb	1729
Pd	0.81		
Tb	0.12		

Table 11 Chemical composition of NdFeB

The chemical composition of a mixture shown in the table can be defined as the quantitative distribution of the individual substances in the mixture.

#### 6.4. Packaging density and particle distribution

The packing density depends on the shape of the particles. First, it is well known that regular parallelepipeds can be stacked so that they completely fill the space (like bricks in a wall). Thus, regular particles can give packing densities greater than irregular ones. In this part, the effect of particle shape on random packing density is studied. The maximum packing density of particle-filled materials is crucially dependent on the particle size distribution and the particle shape. Particles with high sphericity and high fines content favor the increase of the maximum packing density. The irregularly shaped NdFeB particles are shown in Figure 6.6. These particles are obtained during the pulverizing process.



Figure 6.6. Characterization of the surface and shape of NdFeB particles SEM magnification (A) 2000x (B) 3000x

The NdFeB particles show a slate-like structured surface, the high fine fraction of the particles in Figure 6.7. is due to the flaking of the surface by mutual particle friction.



Figure 6.7. Microscopic analysis of particle distribution 70 Vol.% NdFeB in polypropylene matrix; Magnification (A) x100, (B) x200

Therefore, the sum distribution curve in Figure 6.7 shows an increased initial value due to the large fine fraction. At the beginning of the measurement, a large number of fine particles with size ranging from  $0.18\mu$ m to  $10\mu$ m can be observed, then the curve reaches the maximum at 29  $\mu$ m, indicating that the largest number of particles of this size has been reached in the prepared powder. In the Figure 6.7. and Figure 6.8. the difference in the distribution and the number of magnetic particles in the polymer matrix is already visible at low magnification. Between the microparticles there are very fine particles of nanometer size. It is assumed that from the magnetic

point of view they are insignificant because such a high fragmentation has damaged the structure of sintered *magnets (Namkung S. et al. 2009)*, which results in the impossibility of re-magnetization.



Figure 6.8. Microscopic analysis of particle distribution 40 Vol.% NdFeB in polypropylene matrix; Magnification x100

Figure 6.9. shows the results of microscopic analysis for a mixture of polyamide 6 with magnetic particles. Figure A shows agglomeration of the magnetic particles and poor distribution of the molecules in the polyamide matrix.



Figure 6.9. Characterization of the surface and shape of NdFeB particles SEM magnification (A) 500x (B) 3000x

In the observed samples the same magnetic powders are used as for polypropylene. The agglomeration of molecules may be due to the molecular structure of polyamide and its higher density, which makes it difficult for the molecules to distribute themselves in the matrix. Figure B shows that some of the magnetic molecules are not attached to the polymer matrix at all. It can also be seen that the polymeric mass is very compact and brittle. Preliminary microscopic analysis indicates that polyamide is not a suitable polymer for the high-fill injection molding process. The distribution of the magnetic particles observed under a light microscope in the polyamide matrix is shown in Figure 6.10. These particles, as indicated earlier, are not regularly distributed (Figure 6.9.).



Figure 6.10. Microscopic analysis of particle distribution 50 Vol.% NdFeB in polyamide matrix; Magnification x100

On many samples a blank spot is observed which indicates the absence of particles resulting in decreased magnetic properties. The regular distribution of the particles in the polymer is the most important factor for obtaining the optimal magnetic values and ensuring the proper functioning of the devices in which they will be used. The thermoplastic/particle bonding depends not only on the particle shape but also on the thermoplastic properties. The low viscosity PP has a higher flowability than PA, resulting in improved imaging and embedding properties. The particles in the PP matrix are very homogeneously distributed.

## 6.5. Filling level

The filling levels obtained are checked by thermogravimetry (TGA), as shown below. Thermogravimetric investigations are based on the thermal decomposition behavior of materials or their components. The thermoplastics used show significantly lower decomposition temperatures than the filler particles, as a result of which the comparison shown as an example for PP/NdFeB compounds in Figure 6.11. shows the mass fraction of the filler particles due to the complete decomposition of the thermoplastics. Thermoplastics show both thermal and thermo-oxidative

decomposition effects. To prevent thermo-oxidative decomposition effects, the measurements are carried out under an inert gas atmosphere.



Figure 6.11. Difference between the weight percentages determined thermogravimetrically after injection molding and the volume fraction of the fillers

The comparison between the theoretically calculated and the injection molded fill levels shows only minor deviations, so that the predetermined filling levels could be set with sufficient accuracy. In addition to the degree of filling, the homogeneous distribution of the particles in the compound is of high importance for the characteristic material properties. The distribution of the filler particles present in the polymer matrix is verified using scanning electron microscopy (SEM) and is shown for PP/NdFeB compounds at different filler grades in Figure 6.12. and Figure 6.13. Figure 6.12. and Figure 6.13. shows the NdFeB particles partially embedded in the PP matrix. Due to the irregular particle shape and the different filler grades, the picture differs with 70 Vol.% and 40 Vol.% filler. The highly fissured surface indicates that imperfections, such as air inclusions and agglomerates, cannot be excluded in the material. On the other hand, due to the irregular particle shape of the NdFeB particles, a high mechanical interlocking with the thermoplastic matrix can be assumed. Based on the information collected from the quantitative microscopic analysis and particle size analysis, a simulation of the degree of filling of 1 cm<sup>2</sup> of the

sample is prepared. The simulation is carried out on samples with 30/50/70Vol.% magnetic particles.



Figure 6.12. SEM images of NdFeB magnets 70Vol.% and polypropylene after compounding, granules; Magnification (A) x3000, (B) x500



Figure 6.13. SEM images of NdFeB magnets 40Vol.% and polypropylene after compounding; Magnification (A) x3000, (B) x1000

Computer image analysis consists of converting images to digital system and then its detailed processing and analysis. By using an appropriate operation of image processing, it is possible to obtain information, which normally are not distinguished by human visual system. Microscopic analysis consists of 3 stages:

1. Preliminary image processing. It aims to eliminate the irrelevant or interfering elements from the image, as well as to highlight the interesting features of the analyzed image. This processing leads to certain changes in the image, and its result is also an image.

2. Making measurements of the desired features of the analyzed image. The measurements allow to obtain quantitative values describing certain features of the analyzed image.

3. Interpretation of the obtained quantitative results and visualization in COMSOL Multiphysics® program.



Figure 6.14. Visualization of filling levels with real particle size distribution (D/d=19.3) of NdFeB particles ( $\sim$ 50 µm) at a fraction of 30/50/70 Vol.%

The results in Figure 6.14. show a decreasing distance between the particles as the filler increases. On the basis of particle size analysis and quantitative microscopic analysis a simulation of the distribution and filling of the polymer with magnetic particles is presented. The results of the presented model and experimental results are compared. It is concluded that the model can be considered as a visualization of the present state. However, for a more accurate depiction of the particle distribution in the real state, more parameters affecting compounding and injection molding should be taken into account. More information on this subject is given in the following chapters.

## 6.6. Thermal characterization – TGA

Thermogravimetric analysis is a special method of thermal analysis. The general terms are defined in DIN 51005 and DIN 51006. In thermal analysis, the physical and chemical properties are investigated under the influence of a change in temperature. The thermogravimetric method, or TGA for short, provides information on both thermal and thermal oxidative reactions, present in Figure 6.15. The thermal degradation of thermoplastics is due to the temperature sensitive mobility of the molecular chains, which can be influences by the fillers. Reactions accompanied by a

change in mass are, for example dehydration, oxidation, decomposition, or phase change. The results of the TGA analysis depend on many factors. Measurement results are influenced not only by the measuring instrument and method of measurement, but also by the preparation conditions, the sample size, the measuring cell, and the heating rate, the type and speed of the gas in the chamber. Therefore, many samples and repeated analysis are necessary to obtain reliable results. The gas flowing through the sample is required to prevent a back reaction of the volatile component. In the case of the test samples, the temperature is set to a gradual rise of 10  $^{\circ}$ C/min. Nitrogen is used as an inert gas in the sample chamber. Each sample is then heated to 550  $^{\circ}$ C.



- A- Initial poin intersection of the extrapolation line for the initial mass with the tangent in maximum gradient
- B- End point intersection of the extrapolation line for the final mass after the reaction
- C- Mid point intersection of the t curve with the parallel to the abscissa axis through the midpoint between A and B
- $T_{A^-}$  initial point temperature/time  $T_{B^-}$  end point temperature/time  $T_{C^-}$  mid point temperature/time  $m_s$ - initial mass  $m_c$ - final mass



Figure 6.16. shows the influence of the number of particles (Vol.% NdFeB) on the temperature changes occurring in the matrix, a key issue for compound production.

The black circle shows an important temperature peak for the selected compounds. A blue circle marks the point at which total matrix decomposition is complete. These relationships are explained by reducing the thermal mobility of molecular chains and the resulting decrease in the rate of decomposition.



Figure 6.16. Thermal stability of PP as a function of the NdFeB filling ratio normalized to the thermoplastic fraction (TGA: heating rate: 10 °C/min, atmosphere: N2)

Interesting for this process is the study of the influence of hard magnet microparticles on the polymer decomposition temperature. Polypropylene is used as a reference and the mass of polymer degradation is related to the initial mass of thermoplastics using the formula:

$$m_{T,norm} = \frac{(m_C - m_F)}{(m_C - m_F)_0} \cdot 100\%$$
(30)

where,  $(m_c - m_F)_0$  is the polymer output mass;  $m_c$  – is the compound output mass minus the filler mass  $m_F$ . The normalized thermogram to the thermoplastic mass fraction  $m_{T,norm}$  in Figure 6.17. shows the plot of the thermogravimetrically determined decay curves for PP. The effect of NdFeB particles on the degradation behavior of PP is presented. As already reported in the literature (*Kirchberg S.* 2009a), microparticles show a similar effect on the thermal stability of 104
thermoplastics. The decomposition temperature range and the temperature at the point of inflection of the curves are shown by the differentiation of the normalized thermoplastic fraction versus temperature  $(dm_{T,norm}/dT)$ .



Figure 6.17. Thermal stability of PP as a function of NdFeB filling level, time derivative of thermograms to show decomposition behavior based on peak temperature (TGA: heating rate: 10  $^{\circ}$ C/min, atmosphere: N2)

The diagram shows that the decomposition temperature depends on the volume amount of the filler. The decomposition temperature increases linearly as the volume of the filler increases, show in Figure 6.18. The processes occurring in the composite are also observed during the above presented XRD analysis (5.3 X-ray diffraction patterns (XRD) studies). In Figure 6.18. we can see how the degradation temperature of the polymer is significantly increased under the influence of the amount of filler. Degradation of plastics is a change in the molecular structure of the material, consisting mainly of a decrease in molecular weight, a decrease in the number of side-group bonds and a remodeling of the morphological structure. Thermal properties are important for the potential use. It is found that both the mixing and the content of magnetic molecules have a great influence on thermal stability of polymers. Various polymers will react differently, but the results presented for polypropylene are unambiguous. The thermographic curves show a decrease in sample weight as a function of the amount of magnetic filler.



Figure 6.18. The change of the decomposition temperature with the amount of filler

The thermographic analysis also provides information about the stages of decomposition, the loss of mass of the material at each stage, the polymerization reactions, and the productivity. The observed changes in the samples indicate a change in decomposition temperature with increasing amount of filler. The onset of thermal degradation dictates the maximum temperature at which the polymer can be used. At high temperatures the components of the long chain polymer backbone can fracture (chain scission) and react with each other (cross-linking) changing the properties of the polymer. These reactions cause changes in the molecular weight and can affect the properties of the polymer, resulting in reduced ductility and increased brittleness, chalking, burning, color change, crazing and overall reduction of desired physical properties.

#### 6.7. Flow behavior

The flow properties of polymer melts show time- and temperature - dependent characteristics. For thermorheologically simple materials, the effects of time and temperature can be superimposed without disturbance. Since the angular frequency is a time-dependent quantity, the time-temperature shift principle can also be used to describe frequency- and temperature-dependent relationships. As shown in Figure 6.19. for polypropylene and compound with 30/40/50/60/70 Vol.% of NdFeB, the

viscosity of thermoplastic melts generally decreases with increasing temperature. When the temperature is increased, the molecular motions increase, resulting in a larger fraction of free volume due to the melting of the ordered crystalline regions than in amorphous thermoplastics. In the case of filled polymers, if the thermal expansion of the fillers is negligible, the change in free volume can be related to the polymer fraction.



Figure 6.19. Diagram of temperature dependent viscosity shift using PP + 50 % NdFeB (temperature: 180/200/220/240 °C), geometry: plate/plate, diameter: 25mm, thickness: 2mm)

Figure 6.20. shows the results of the analysis of material viscosity for contents of magnetic particles. The presented results show a linear increase of compound viscosity with increasing magnetic particle content. The observed phenomenon may result from two variables – an increased amount of filler and the residual magnetization moving the magnetic particles. A material such as NdFeB in which the grain size has been reduced can lead to new enhanced properties. Both cases will be discussed in the next chapter.



Figure 6.20. The effect of hard magnetic particle content on compound viscosity

Figure 6.20. illustrates the correlation between complex viscosity and degree of filling with variation criteria. Complex viscosity is a quantity expressing the magnitude of internal friction in a fluid, as measured by the force per unit area resisting uniform flow.

## 6.8. Degree of filling - dependent flow behavior - viscosity

Using the characteristic values determined dynamically by oscillatory rheometer, both the viscous (loss modulus G''( $\omega$ )) and the elastic (storage modulus G' ( $\omega$ )) components in the viscoelastic material behavior of thermoplastics as a function of angular frequency are to be defined, show in Figure 6.21. The loss factor tan  $\delta$ =G''/G' describes the ratio of the module to each other. The loss modulus G''( $\omega$ ) represents the viscous melt behavior, while the storage modulus reflects the elastic component. Polymer melts exhibit an angular frequency dependent intercept (crossover) for  $\omega$ (G'( $\omega$ )=G''( $\omega$ ). At angular frequencies below the crossover point, the viscous material behavior described by G''( $\omega$ ) dominates. Above the intersection point, the elastic component predominates. The structural behavior of the PP and PP/NdFeB melts is characterized using the intersection of storage and loss modulus  $\omega$ (G'( $\omega$ )=G''( $\omega$ ). Figure 6.21. shows a clear shift of (G'( $\omega$ )=G''( $\omega$ ) to higher angular frequencies and modulus values at high filler content compared to the unfilled melt. Accordingly, the predominantly viscous behavior of the filled thermoplastic melt is

shifted to higher angular frequencies ( $\omega$ ) with increasing filler content. The increase of the modulus values corresponds to a solidification. The reasons for the results shown may be mechanical, physical, or chemical. In the literature, analogous phenomena can be found for particle-filled elastomers, which are referred to as the Payne effect and are attributed to the formation of a particle network.



# Figure 6.21. Filling degree dependent intersection of storage and loss modulus of PP and PP+50Vol.% NdFeB (temperature: 200 °C, geometry: plate/plate, diameter 25mm, thickness: 2mm)

The macromolecules distributed randomly (amorphously) in the thermoplastic melt exhibit interlocks and agglomerations. The degrees of freedom of movement in this tangle of molecules are restricted by mutual interaction of the molecular chains. This influences the viscous and elastic components in the structural behavior. At low angular frequencies, the macromolecules have sufficient time to relax, allowing the viscous properties to predominate. With further increase of the angular frequency, the relaxation time of the molecular chains is higher than the angular frequency dependent stress time. As a result, the molecular chains react more elastically to the load, so that the elastic component increases and exceeds the viscous component. The thermoplastic melt now exhibits increased elastic behavior. If rigid particles are introduced, they cause a disruption of the thermoplastic structural bond. As a result, the degree of entanglement of the molecular chains decreases, causing them to exhibit a relaxation time that is shifted in the direction of a higher angular frequency. The introduced particles thus act as "interference points" in the amorphous structure of the thermoplastic melt. The molecular chains show increased elastic behavior only at higher angular frequencies, so that the elastic component  $(G'(\omega)=G''(\omega))$  with increasing filling degree predominates only at higher angular frequencies. To conclude on the causes of the structural changes of the material during the study, the change of the intersection points of both moduli for the analyzed PP+0/30/50/70 Vol.% NdFeB samples is considered. This allows, as already mentioned, to interpret the molecular changes of the material. Figure 6.22. shows a plot of the intersection of individual measurements for the compound. As the value of magnetic molecular mass increases, as well as the molar mass distribution changes, compared to the reference material.



Figure 6.22. Verification of the structural change via the intersection G' = G''

Due to the lack of cross-links the strain energy contribution increases as determined by the analysis at 200 °C. The loss modulus shows from the beginning for all the samples higher values than the storage modulus. The loss modulus represents the dissipated strain energy lost due to internal friction processes (*Mezger T. 2016*). The value of G<sup>''</sup> is considered as a measure of the amount of energy absorbed in the specimen material during the shearing process and subsequently lost in the specimen. As can be seen in Figure 6.23., there is a linear relationship between the amount of filler and the increase in strain energy due to internal friction processes.



Figure 6.23. Dependence of friction energy of flowing material at 200°C on volume of filler

Figure 6.23. shows the relationship between loss modulus and angular frequency. It can be assumed that linear increase of friction is caused by increase of movement of particles caused by residual magnetization. The attraction of single magnet particles at 200 °C proves the possibility of movement of magnetic particles in a liquid polymer. These observations provide great opportunities to use this type of compound for targeted applications. Thanks to this, it is possible, even using very small magnetic forces, to control intentionally the direction of particles, as well as to create magnetic force only in necessary parts of elements. This way of producing the elements will allow to maximize the properties while minimizing the amount of material. Figure 6.24. shows the above results in percentage form. The highest increase of the loss modulus is observed for the samples containing 70 Vol.% of NdFeB and 30 Vol.% of PP and linearly decreases with lower content of particles.



Figure 6.24. Percentage dependence of flow energy as a function of the volume number of NdFeB particles

This relationship is consistent with the thermal analysis performed and indicates a strong influence of the magnetic particle content and their residual magnetization. This topic will be analyzed in detail in the following chapters.

#### 6.9. Magnetic properties

The hysteresis curves of the alloy (Pb, Nd,Dy)<sub>2</sub>Fe<sub>14</sub>B - 85.1 wt% are measured in a 1T - permanent magnetic field shown in Figure 6.25. The results are typical of hard magnetic materials (with a HC coercive field greater than 15Oe) that reach saturation in relatively strong magnetic fields. In contrast to these magnetization curves, the M(H) (magnetization/field) dependence of the NdFeB alloy with the highest content of magnetic powder 70 Vol.% NdFeB is typical for hard magnetic powder in line with the raw material. This means that a large percentage of the magnetic powder in the composite has magnetic properties that are only 15 % smaller than those of the raw material. The signal is divided by the mass of the sample expressed in grams; hence the unit is emu/g (emu - magnetic moment/g – mass of sample). The hard-magnetic properties of NdFeB composites are associated with their high magnetic anisotropy, to which the magnetocrystalline anisotropy is their main contributor. The process of magnetization of these materials takes place mainly by the movement of the domain walls and is realized in relatively strong magnetic fields.



Figure 6.25. M(H) dependence of NdFeB/PP composites with different magnetic powder content at room temperature

Based on the conducted studies, it is found that the phase structures of magnets are composed of the hard-magnetic phase  $\phi$ , traces of the paramagnetic phase  $\eta$  and the neodymium-rich paramagnetic phase. This phase plays a very important role in shaping the magnetic properties, its equilibrium and the thin layer distributed along the grain boundaries of the  $\phi$  prevents magnetic interaction, which reduces the coercive force between the grains of the hard-magnetic phase. With the increase of magnetic powder content in composites, the expected increase in saturation magnetization values is observed (Figure 6.26.). In the tested materials, the MS saturation magnetization (determined from the magnetic hysteresis for the magnetic field H=1T) increases linearly with increasing concentration of NdFeB (Vol.%). Ferromagnetism is a collective phenomenon which consists in the spontaneous organization M, defined as the magnetic moment of the unit (emu= Gauss in the CGS system or A/m in SI units). The tendency for spins to be ordered in parallel has been described by Weiss as the effect of a molecular field proportional to

magnetization M. But in fact, this phenomenon is related to the quantum nature of the exchange interaction. As the temperature increases, as seen in Figure 6.26., the magnetization M decreases due to thermal fluctuations of the crystal lattice. Above temperature  $T_c$ , called the Curie temperature, the magnetization disappears.



Figure 6.26. Temperature dependence of magnetic moment (emu) for NdFeB+PP, the applied field for all the samples is 1T, a) 100 % NdFeB, b) 70 Vol.% NdFeB and 30 Vol.% PP, c) 50 Vol.% NdFeB, d) 30 Vol.% NdFeB

To demonstrate the capabilities of magnets that are injection mold from recycled material an electric moto from an electric bicycle is converted, show Figure 6.27. The neodymium magnets were removed and replaced with recycled magnets. Motor power is measured using simple but effective method. Motor power in watts is measured with wattmeter and voltage is measured with a multimeter.



Figure 6.27. E-bike with built-in recycled magnets

The collected data is presented as a graph for the motor with and without recycled magnets, shows Figure 6.28. The results of the first measurements are as expected. The magnetic properties of the composite material confirmed by the earlier analysis has been made.



Figure 6.28. Motor power comparison a) with RE-magnets 70 Vol.% NdFeB and PP, b) 100 Vol.% NdFeB magnets

The presented results confirm the theoretical calculations. The power output of a motor with recycled magnets is 25 % lower than a new motor. The use of 70Vol.% NdFeB particles in the magnet changes the total motor power significantly. At this point, we can also discuss changing the shape of the magnets placed in the motor and replace the bar structure with one continuous disk. In this way, the loss of electrical energy caused by micro-breaks will be eliminated. At this point, it should also be mentioned that the use of magnets produced by injection molding with a particle

concentration of more than 70 Vol.% is currently not technologically feasible. This is mainly due to the very small amount of polymer with reduced flow characteristics and the high pressure and temperature during compound preparation. Other solutions will be presented in the last part of this work as a basis for further experiments. An alternative that is being considered in further research is 3D printing. The attempts made so far have not been satisfactory, and the choice of a suitable polymer matrix is most important in this case. This topic will be further discussed in the outlook. So far, the results achieved in the injection process are very satisfactory and the process itself provides for further optimization to achieve even better results.

# **6.10. Influence of magnetic field of NdFeB particles on rheological properties of the composite**

The number of particles dependence of the storage modulus and loss is shown in Figure 6.29. Three sets of measurements are made, where the volume fraction of magnetic particles is: 30, 50 and 70 Vol.%. All samples showed residual magnetizations ranging from 20 emu/g to 5 emu/g.



Figure 6.29. Influence of particle content in compound on viscoelasticity and magnetism

Firstly, it can be observed that both G' and G'' varied for individual samples. The observed magnetic response is evident and depends on the particle distribution and field orientation. It should be noted that the relaxation time is fast and is due to the residual magnetization. It should be noted that magnetized samples where a magnetic field has been applied exhibit a different behavior, instead they are characterized by rather high relaxation times (in the order of 150 s). The long relaxation processes seem to be caused by some restructuring of the magnetic filler under the influence of the external stress and the internal magnetic field. Indeed, magnetic particles have their own magnetization, magnetic moments interact with each other, but particles cannot move freely in the polymer matrix. As the material flows, the interaction of the magnetic particles leads to local deformations of the polymer network. If the magnetic filler content is large, the distances between the magnetic particles are small and their interactions are very strong and cannot be overcome by elastic forces. However, the applied periodic shearing force disrupts the internal structure of the filler and makes it easier for the magnetic particles to change their initial positions and orientations. However, because the particles have their own magnetization, their ordering changes the total field, which leads to further ordering of the particles, and so on. A sample of 70 Vol.% of NdFeB shows the largest modulus increase, due to the highest magnetic phase content and the highest magnetization. However, the minimum of the conservation and loss moduli is observed for the sample with a small amount of strongly coercive NdFeB particles (30 Vol.%). The influence of the filler particle size on viscoelastic behavior is now analyzed. Figure 6.30. shows the relationship between the storage and loss modulus for the used samples: 25,50, 100  $\mu$  m. Reducing the size of the filler particles doubles increase the maximum modulus value (Figure 6.30.). However, at the same time the behavior of the sample resembles a magnetically soft material, show Figure 6.31. For the particles size  $25\mu$ m the minimum is at 0.50 kOe, while for  $100\mu$ m particles size it moves up to about 1.5 kOe.



Figure 6.30. Storage and loss modulus as a function of angular frequency

This factor can also be explained by the rotation of particles in the polymer matrix under the influence of a magnetic field.



Figure 6.31. M(H) dependence of NdFeB particle size at room temperature, samples with 50Vol.% of PP and 50Vol.% of NdFeB powder

Rotation of smaller particles is easier and therefore re-magnetization of the sample takes place in smaller field. Due to larger magnetic moments, stronger interaction, and stronger coupling with polymer, for the material based on larger particles there is a larger field range in which the modulus of the material can decrease with the field, and this decrease is more pronounced. The dependence of viscoelastic properties on the magnetizing field is related to the appearance of oriented magnetic moments and their interaction in the polymer matrix. Directionally magnetized

magnetic particles start to interact and tend to form chain structures in the polymer matrix in order to minimize the magnetic field energy, shows Figure 6.32.

The higher the magnetic field, the higher the magnetization of particles and the stronger their interaction and formation of structures. Similar results are observed in the work (*Kramarenko E. et al. 2015; Kirchberg S. 2009a*). Composite samples with hard magnetic particles of different sizes and concentrations have been analyzed for viscoelastic behavior



Figure 6.32. Magnetic field dependences of the viscosity

It has been shown that the residual magnetization causes new fascinating properties, namely:

- nonlinear viscoelastic behavior even at small deformations, the shear rates deformations show Figure 6.33.
- modulus growth.

These properties are typical for permanents magnets but for composites they are realized without any external field due to the presence of the residual magnetization and thus of the magnetic particle interactions. These properties become more pronounced as the applied magnetic field increases. Rheological measurements are performed using a Rheo 5000 CEAST and a 1 T magnet is applied to each sample during the measurement.

The magnetorheological response increases with increasing magnetic field and for magnetized samples it is still dependent on the orientation of the field.



Figure 6.33. Viscosity vs. shear rate for different particle size, samples with 50Vol.% of PP and 50Vol.% of NdFeB powder

The compound viscosity decreases with shear rate at low shear rates, i.e., below 5000 s-1, as shown in Figure 6.33. The size of the NdFeB molecules has a significant effect on the compound viscosity also without external magnetic flux. As expected, the viscosity increased with decreasing particle size. The observations show that smaller molecules, which also have residual magnetization, can move more easily in the polymer. Moreover, the attraction between the molecules leads to their rearrangement in lines forming chain structures. Consequently, the spacing between the molecules decreased, which caused the formation of stable chain structures and indirectly increased the viscosity of the compound.

## 6.11. Summary

This part of the work summarizes all parameters important for the recycling process of magnetic materials based on rare earth elements. The presented procedure allows adjusting the parameters in order to achieve the desired result. The production of a high filled compound is a very complex process, the individual steps have an influence on the subsequent steps and results. The choice of temperature, filler and matrix chemistry will affect the various processes. Table 12 shows the relationships of the processes. The influence of each of these processes is described, as well as the appropriate settings to maximize product quality and the importance of each parameter in the overall process and in each of its individual stages.

Influence parameter	Property	Chemical composition	Pulverization	Packaging density	Dorticle dictribution		Filling level	Thermal stability	Flow behaviour	Viscosity	Remanence	Compounding	Injection molding	Recycling
Method														
Chemical composition			x							x			Τ	
Pulverization		х		х	х	х		x	x	x	x	x	x	x
Packaging density					х	х	x	x	x	x	x	x	x	x
Particle distribution						х				x	x	x	x	
Filling level				х	Х	х	X	X	X	X	X	X	X	X
Thermal stability						х		X	X		X	X	X	
Flow behaviour			х	х		х			x		x	x	x	
Viscosity		х	х	Х	х	х	x	x		x	x	x	x	
Remanence		х	х	х	х	х					x	x		x
Compounding		Х	Х	Х	Х	х	X	X	X	X		x	X	
Injection molding		Х	х	х	х	х	X	X	X	X	X			x
Recycling		х	х	х	х	x	x	x	x	x	x	x	x	

As show in Table 12 during the analysis of the chemical composition of magnets used, it is important that the value of rare earth components is at least 25 % of the total alloy composition. These magnets are very strong magnets with high magnetization, so that a high remanence will be achieved in the manufactured product. Another factor is the pulverization process. Magnetic powders must not be grinded too fine, i.e., below 5µm, because the crystallographic structure of individual particles will be changed and thus the remanence of such a powder will be lower. The analyzed optimal value is 5-15  $\mu$ m. Too big magnetic particles are not suitable for the injection process because of the small nozzle diameter. The choice of the right polymer matrix influences the flow characteristics of the whole injection process and the properties of the final product. The above test results show that polypropylene is perfectly suited to produce permanent magnets in polymer matrix. All the properties such as melting point, flow in the nozzle and distribution of magnetic particles as well as the number of particles up to 70 Vol.% are acceptable and the appearance of the final product is very good. The tests carried out with polyamide did not give satisfactory results due to the high density of the polymer and limited binding of the magnetic powder to the matrix. A homogeneous distribution of the magnetic particles is not achieved, and it is not possible to fill the compound in an injection molding machine with 30 Vol.% of NdFeB. The degree of filling with magnetic particles depends on the properties specified for the end-product. The higher the degree of filling of about 70 Vol% the more brittle the product becomes due to the small amount of polymer bonding. In the case of polypropylene, the molded structures produced are solid and did not break without the application of an external force. A regular distribution of the particles can be achieved by a continuous addition of powder in the die. For this a Differential-Weigh feeder (FlexWall 33, Brabender Technologie, Duisburg, Deutschland) and the side feeding of the filler, (Soder T20, K-Tron GmbH, Lengerich, Deutschland) with adjustable powder feeding speed are used. In the polypropylene matrix, the particles are regularly distributed independent of the volume amount of filler. In the case of polyamide, an even distribution of the particles is not achieved. The shape of the particles should be irregular, so that the bond with the matrix is higher and more resistant. The temperature in the kneader for polypropylene is 250-270 °C and for polyamide 220-250 °C. The rotor speed is started at 20rpm and then increased to 60 rpm because the rotor did not take all the product. As shown in Figure 6.35., the molten mixture has a high viscosity and had to be pushed several times to get it into

the rotor. The high thermal conductivity of the neodymium powder of 8.5 W/(m-K), which also influences the crystallization and decomposition temperature of the polymer, has been observed to increase with increasing filler content. In addition to the above mixing temperatures - the decomposition temperature increases with increasing filler content, speed and torque are the decisive process parameters, as described above Table 12. Although it is generally required that the kneader is loaded almost to the limit with respect to these parameters, the very high filling ratio of the thermoplastic material, amounting to almost 70 % of the volume, proved to be a processing limit. Since the mixing is done at the limit of the range, irregular pressure spikes and torque increases are unavoidable. It is likely that there are always short-term disturbances in the solids content during mixing of the ingredients in kneader, which can be resolved by the matrix.



Figure 6.34. The dependence of compound density on the amount of filler

The observed machine behavior at 30 % and 70 % volume shows which tensions occur at these parameters. While the power and pressure at 30 Vol.% are low, these values show an increase at high fill levels. The strong fluctuations observed at high fill levels have resulted in the operation of the overload protection devices, as is to be expected. Consequently, all process parameters are set to a very low level. It is not feasible to pre-set the injection machine for such a mixture at 90 % of the driving power. Such a power can be used for a very low filled compound and with increasing

of the filler the speed of the drive decreases. A powdered thermoplastic mass with a density of about 5.45 g/cm<sup>3</sup> is produced from the materials and processes described so far. The compound contains about 70 Vol.% NdFeB, the dependence of compound density on the amount filler shows Figure 6.34. Due to the milling process, a strongly heterogeneous grain shape is observed. The compounding process is influenced by many factors, the chemical composition of the magnets, the degree of fragmentation of the magnetic particles, the degree of filling with magnetic particles (Figure 6.35.), the demagnetization of the particles in order to achieve an even distribution of the particles, the multing temperature of the polymer as well as the Curie temperature which must not be exceeded due to the possible loss of magnetic properties. This stage is very important to achieve good performance of the final product.



Figure 6.35. Compound with a) 70 Vol.% of NdFeB and 30 Vol.% Polypropylene b) 40 Vol.% of NdFeB

After the compounding to form granules, the prepared compound is ground. The grinder crushes the compound by cutting it through shear deformation. Its use will ensure high surface quality and high accuracy in shape and dimension when forming the specimens. This is an important step for good sample preparation, homogeneity, and subsequent injection. The samples are analyzed optically to determine shape, size and quality using an optical microscope. The mill starts at a speed of 1,500 min<sup>-1</sup>, this is a constant speed for this model. The mill has cutting bars that increase the number of cutting operations per rotation, Figure 6.36.

These cutting bars enable a faster grinding process, they are an important part of the process. The rotor used is a parallel section rotor. It is suitable for plastics, soft and fibrous materials. The feed hopper is standard, and the collector is a 5 L container preceded by a filter. This machine is a standard industrial and laboratory equipment.



Figure 6.36. Retsch grinder SM 100 model

The next important step is injection molding, during which the temperatures of the individual parts are precisely selected. The optimization of these temperatures and pressures during injection molding ensures an accurate filling of the mold and an even distribution of the magnetic particles in the product. The Table 13 shows the most important parameters of the injection molding process based on observations and analyses of the process.

Process Parameters	Influence on the processing of NdFeB-PP
Melting temperature	Fort hick-walled components 200 °C, to minimize the remaining tendency to form vacuoles; for thin-walled components 240 °C
Mold temperature	For the polymer matrix PP consistently 20 $^{\rm o}{\rm C}$

Table 13 Process parameters influence of the injection molding

	For thick-walled components up to 2 cm <sup>3</sup> /s, here, a			
	reduced surface quality due to low velocity is accepted			
Injection speed	in order to exclude the formation of vacuoles as far as			
	possible. For thin-walled components velocity of 25			
	cm³/s are possible			
	For thick-walled components at low injection speeds			
Maximal injection processo	and low melt temperatures up to 1500bar. For thick-			
Maxima injection pressure	walled components at 240 °C melt temperature up to			
	800bar.			
	For thick-walled components between 10 and 12 mm:			
Pressure time	6 s to 8 s. For thick-walled components with a wall			
	thickness of up to 1mm: 0.5 s are chosen.			

Simulation of the actual flow of melt in the mold is not possible. Simulation of the complex interplay of increased thermal and temperature conductivity has been undertaken without success. Simulation of the actual flow of the melt in the injection mold along with capturing the complex relationships between increased thermal conductivity and thermal diffusivity of the plastics, which in reality have low thermal conductivity, increased viscosity of the mixture depending on the cutting speed due to sliding of the melt wall. Figure 6.37. shows the components produced in different shapes. All parameters required to achieve such an effect are presented in this work.



Figure 6.37. Magnetic components with 70 Vol.% NdFeB and 30 Vol.% polypropylene

# 6.12. Modeling facilities and visualization example

The behavior of the process in the mixing extruder under given boundary conditions is determined primarily by the selection and arrangement of the screw elements on its shaft. These must be specified in the design. So far, this has often been done on the basis of experience or by trial and error, combined with experimental studies. Furthermore, numerous computational models for theoretical process behavior can be found in the literature. However, these publications either cover only partial aspects of the process behavior or are mathematically difficult to understand or require numerical solution of the indicated problems (*Tosello and Costa 2019; Guerrier et al. 2017; Szabó et al. 2021*). The models used are not suitable for high filler compound or for magnetic compound. This is the reason why mathematical models are so rarely accepted in industry. Figure 6.38. shows the relevant parameters are called design variables. Only the conversion of these models into easy visualizations can guarantee the acceptance and access to tools.



Figure 6.38. Computer modeling in quality enhancement

The process behavior of a single screw extruder is influenced by the material characteristics of the compound to be processed and the geometry of the screw (Figure 6.39.) (i.e., the configuration of the screw elements and the process parameters), which can be varied as machine settings. These values are thus also the input data for a simulation calculation. The modular design of co-rotating twin screw extruders is taken into consideration during the program development. By means of the definition of screw and barrel elements, any extruder can be projected as a data base for a subsequent determination of a barrel and screw configuration. The description of the material behavior is divided into rheological characteristics, thermodynamic quantities, and densities. The rheology of the melt is described by the Carreau law, which describes the behavior over a large range of shearing rates. The thermodynamic quantities and the densities are divided for the description of the material behavior in solid and melt phase. The generic term process parameter includes the machine settings parameters and the material stages, which will be further described later. The following parameters are to be entered as machine

setting parameters for a simulation calculation: screw speed, barrel temperatures, and the expected pressure requirements or the definition of a die geometry.



Figure 6.39. Geometry of analyzed part- screw in the injection molding machine

This work focuses on the analysis of the behavior of the high-filled compound during the injection molding process. The analysis is performed for the material in the single screw in injection molding machine, since it behaves the most differently due to the temperature applied. In the present case, a three-dimensional conjugate heat transfer model has been developed for non-Newtonian materials processed in the extrusion die. A homogenous PP and magnetic particles with a uniform temperature T=465 Kelvin. The temperature of the die wall is kept a constant value, Tw= 465 Kelvin and the volumetric flow rate of compound melt is fixed at  $Q = 4 \times 10^{-6} m^3/s$ .

According to the computational theory of fluid dynamics, governing equations for solving melt flow problems can be derived from the equation of solid, the equation of motion, and the equation of energy, based on conservation of mass, pedal, and energy, respectively (*Wilkes and Bike 1999*). Considering the flow characteristics of the polymer melt with magnetic particles in the die channel, the following assumptions are made when dealing with extrusion:

1. Non-semi-pressurized steady laminar flow. The variation of the physical variables of the system over time can be ignored when dealing with a steady state extrusion process.

2. Inertia and gravitational forces are not taken into account. The Reynolds number of the polymer melt is low, so the influence of inertial and gravitational forces is negligible. The governing equation of the model can be written in the form below:

Table 14 Governing equation for the simulation

	Governing equations	
Continuity equation	$\nabla u = 0$	(31)
Motion equation	$ abla \sigma = 0$	(32)
Energy equation	$\rho C_p u \nabla T = -\nabla q + Q$	(33)

If  $\nabla$  is the Hamilton differential operator, *u* is the velocity vector, *T* is the temperature,  $C_p$  is the heat capacity, and *Q* is the total source term.

Since the polymer melts are non-Newtonian fluids, the Carreau-Yasadu model is selected to describe dependence of the viscosity on the shear rate and temperature. The model is presented:

$$\eta = a_T \cdot \eta_0(T_R) [1 + (a_T) \cdot \lambda(T_R) \gamma^{\alpha}]^{(\eta - 4)/\alpha}$$
(34)

, where  $a_T$  is a shift factor and  $n_0$ ,  $\lambda$ ,  $\alpha$  and n are model's fitting parameters.

Cauchy stress tensor, which is expressed as:

$$\sigma = pI + S \tag{35}$$

, where p is the hydrostatic pressure, S is the extra stress tensor, and I is the Kronecker delta, respectively.

The CFD code of COMSOL, using Carreau-Yasuda viscosity model, is used to solve the governing equations. For this model, the effect of the viscous dissipation, that is the

shear heating effect, which is responsible for the fluid temperature increase, is taken into account. This is quite important in polymer extrusion processes and their design. When modelling it is important to select a mesh that minimizes the errors in the quantities of interest. However, it is not easy to minimize the error in a desired quantity by manually specifying a mesh. In many applications, the algorithm must resolve the solution in great detail only on small portions of the domain (such as boundary layers, small geometrical details). In such cases, an adaptive mesh generation should be considered which identifies the regions that require a high resolution and produces and appropriate mesh.

The number of finite elements used in the numerical solution is 57.000 tetrahedral elements, show Figure 6.40. For tetrahedral elements, COMSOL Multiphysics a parameter characterizing the mesh quality according to the following equation:

$$q = \frac{72\sqrt{3}V}{(h_1^2 + h_2^2 + h_3^2 + h_4^2 + h_5^2 + h_6^2)^{\frac{3}{2}}}$$
(36)

, where V is the volume and  $h_{1,h_2,h_3,h_4,h_5,h_6}$  the edge lengths of the tetrahedron. For a regular tetrahedron q is equal to 1. If q > 0.1 the mesh quality should not affect the quality of the solution.



Figure 6.40. Tetrahedral mesh defined for fluid and solid domains

130

The ability to accurately predict the pressure drop is extremely important for optimizing the material manufacturing process. The figures show the pressure distribution across the area for the Carreau-Yasadu and Power Law models. It can be seen that the pressure decreases continuously towards the die outlet. The pressure developed in the matrix is 10 Pa and 10.5 Pa respectively. The required inlet pressure for the Power Law Fluid model is higher because this fluid model exaggerates the melt viscosity at low shear rates.

In this case, axial laminar flow along the central axis of cylindrical cross section is considered, known as the Poiseuille flow and a cylindrical bore section. The fluid motion is along the z-axis at a distance, which is equal to the pipe length. All calculations in the following analysis are carried our based on the assumption that the fluid flow is completely developed starting from the pipe entry.

Parameter	Equation	
Equation of		
motion	$0 = -\frac{\partial P}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz})$	(37)
	$-\frac{\partial P}{\partial z} = \frac{\Delta P}{L}$	(38)
	$\tau_{rz} = \frac{\Delta P  r}{L  2} + C_1$	(39)
The power law model	$\tau_{rz} = n_0 \left  \frac{\partial v_z}{\partial r} \right ,$ boundary condition: $\left\{ r = 0, \frac{\partial v_z}{\partial r} = 0 \right\}, \left\{ r = R, V_Z = 0 \right\}$	(40)
Pressure drops	$\Delta P_{cylind.} = 2n_0 L \left[ \frac{3n+1}{n} \frac{Q_R^{-(3n+1)}}{\pi} \right]^n$ , for an infinitesimal s dz of the pipe as shown, the pressure drop is:	section
	$dP = 2n_0 R^{-(3n+1)} \left[ \frac{Q}{\pi} \left( \frac{1}{n} + 3 \right) \right] dz$	(41)

Table 15 Governing equations used to model the heat and laminar flow

The material used in the simulation experiments is a polypropylene with magnetic NdFeB particles (50 Vol.%/50 Vol.%). Because the material properties greatly affect the analysis of the entire-processing operation, the use of reliable models is essential. However, in many polymer process, the elastic memory effects are not very important, since the melts are subjected to large steady rates of deformation for a relatively long period of time. Because this work is concentrated on a qualitative analysis of the flow regimes, the inelastic model is selected. Polymer melts are non-Newtonian fluids. The viscosity shear rate dependence on non-Newtonian liquids is typically represented by one of the several viscosity models, referred to as viscosity. Various models exist for describing the dependence of viscosity on shear rate and temperature. A great deal of flexibility is provided by the Carreau-Yasuda model and the power law. The assumed values for the simulation and the test material are shown in Table 17 and Table 18.

Parameters	Unit	50 Vol.% PP and NdFeB
Temperature	°C	220
Screw speed	rpm	35
Pressure	bar	850
Mass rate	g/s	2.4

Table 16 Experimental conditions of Polypropylene and NdFeB particles

Table 17 Density, Melt Flow Rate and Thermal Properties of Polypropylene NdFeB Particle Compound

Parameters	Unit	50 Vol.% PP and NdFeB
Melt Flow Rate	g/10 min	1.6
Density	g/cm <sup>3</sup>	4.15
Heat transfer coefficient	k (W/m*K)	7.0
Thermal Conductivity	W/m-K	8.00
Specific heat capacity	J/g-°C	0.440

The graph in Figure 6.41 shows the flow results for a sample containing 50 Vol.% NdFeB, the rest is polymer matrix. The results agree with the theoretical calculations. Minor variations in the displacements are possible due to weaknesses in the practical measurements. However, it is concluded that the adopted model and the way of thinking applied to the simulation reflect the real state, and therefore this simulation can be used to plan further experiments with permanent magnetic materials.



Figure 6.41. Viscosity Measurements of Polypropylene NdFeB Particle Compound 50Vol.%

For the first time, a simulation showing the behavior of the magnetic particles and the polymer matrix during mixing in the injection process has been carried out. This is the basis for further, more complex calculations and a deeper understanding of the changes occurring in the composite material.

#### 6.13. Summary

A summary of the analytical, experimental, and numerical results presented in this part, including the pressure drop and temperature rise in the matrix, is shown in Table 18. The pressure drop, calculated by the analytical model (Figure 6.42. and Figure 6.43.) is about 5 % lower than the actual (experimental) results. This can be explained by the fact that the analytical model simplifies the calculation of the pressure drop for complex geometries. Comparison of the experimental data with simulations of non-isothermal or non-Newtonian flow in the matrix shows an overall

pressure drop and good agreement with the constant wall temperature because the effect of viscous energy dispersion is small, resulting in a small increase in cupaverage temperature, with almost no effect on wall temperature. The Table 18 show the experimental and numerical data.



Figure 6.42. Visualization of pressure during compound flow

The pressure data obtained by numerical Carreau-Yasuda and power law models show a good agreement with the experimental results, while the increase in the temperature of the molten compound, which is about 10 % higher than the experimental value. This can be explained by the temperature variation in the assumed material.

			Power Law	Power Law	Carreau-	Carreau-
			(Numerical)	(Numerical)	Yasadu	Yasadu
			Constant	No Heat	(Numeric	(Numercial)
Donomotoro	I Ini+	Experimental	Wall	Flux	al)	No Heat Flux
Parameters	UIIIt		Temperature		Constant	
					Wall	
					Temperat	
					ure	
Pressure	MPa	85	89	89	88	88
Temperature	°C	220	200	240	200	210

Deviation	0/2		5	5	4	4
Pressure	90	-				
Deviation	0/-		10	0	10	
Temperature	90	-	10	0	10	4

In the simulation a mixture of PP material and NdFeB magnet particles is used, as it is known the thermal properties of the magnet particles are higher than those of the polymer and they can change depending on the volume, etc.



Figure 6.43. Velocity profiles of the flowing compound

The simulation and visualization of the results allowed for a more detailed understanding of the complex processes occurring during the coupling of the matrix with magnetic particles. On the basis of the visualization, it is possible to notice a particular influence of particular parameters on the whole process and its result. A small change in temperature, pressure or speed has a huge influence on the quality of the final product. Therefore, special attention should be paid to adjust the injection parameters to the amount of filler and the shape of the final product.

# **CHAPTER 7**

# ECONOMIC PROCESS EVALUATION



Based on material analysis, a process of recycling of neodymium magnets on a production scale is illustrated. This part of the work analyses the potential of recycling and the possible profits resulting from its use on a large scale. In addition, the economic situation with China and possible bottlenecks in the supply of rare earths to Europe should be considered. Recycling and upcycling is one of the solutions that can ensure Europe's permanent access to raw materials, regardless of the current global situation. This work aims to prove the necessity and basis of recycling based on a simple process that can be implemented in industry. Due to a detailed analysis of materials, processes, and optimization of parameters in the processing of polymer-bonded neodymium magnets, a detailed production guideline with improvements is presented. This part of the work is to verify the validity of the analysis carried out, which is necessary for implementation on an industrial scale. This part presents a techno-economic analysis, it is a method of analyzing the economic performance of an industrial process, product, or service. TEM is useful throughout the technology development lifecycle. When considering new ideas, innovators can use the technique to assess economic feasibility and potential. The individual techniques used in TEM, which include process modeling, equipment sizing, and economic calculations. This chapter demonstrates how the integration of different analysis methods optimizes the process and shows its potential for largescale use and the realistic evaluation of cost structures.

# 7.1. Process Failure Mode Effects Analysis

The PFMEA or Process Failure Mode and Effects Analysis is a cause-effect analysis of potential product failures including the risk factor: the goal of the PFMEA is the systematic identification of defects and their elimination or minimization of the risk of their occurrence and an increase in the detection of nonconformities during the production process, which translates into cost reduction, increased quality level and increased customer satisfaction. The method consists of the following steps:

- 1. Formation of a team with a foreman and possibly an expert
- 2. Identification of product/process components
- 3. Developing a list of possible defects
- 4. Indication of possible consequences of the developed bugs
- 5. Identification of the possible causes of the mistakes
- 6. Estimate the P number, or probability of occurrence, of each error based on reports, knowledge, and experience.

PFMEA analysis is performed for permanent magnetic material recycling process. A production test run is conducted on a prototype laboratory line. The aim of this study is to identify possible manufacturing errors/defects at the process design stage. To this end, 100 test specimens (500 specimens according to the scheme shown in Figure 7.1. and 500 specimens according to the scheme after the necessary process modifications, Figure 7.1.) are produced using the prototype production line.



Figure 7.1. Technological approach of recycling of magnets - extrusion process of magnetic compound (1) Storage of electronic waste WEEE; (2) Dismantling of multi-material systems (dismantling of magnets from motors in WEEE); (3) Thermal demagnetization (temperature above the Curie temperature); (4) Mechanical grinding in a protective atmosphere; (5) Homogenization of the composition - aggregate from magnetic materials and polymer (at the temperature of plasticization of the binder); (6) Composite blend extrusion and granulation; (7) Injection molding; (8) Magnetization, (9) Packaging - protection against the atmosphere; (10) Storage and transport.

The evaluation and quality control of the specimens is based on microscopic analysis and measurements using calipers and templates. During the analysis, attention is paid to the distribution of the particles in the composite and the structure of the material - only samples with pronounced surface changes and spalling are considered defective. Geometry and symmetry are taken into account in the accuracy control. Only specimens with significant deformations and cracks are considered defective. Due to the principles of process management and improvement, a process PFMEA is performed. As it is known, the FMEA method is the most often used method of process examination at the initial design stage, before beginning of serial production, therefore, it precedes value stream design. Due to its universality and easy application FMEA is adapted in quality assurance standards and ISO 9000 and especially in standards used in automotive industry (ISO/TS 16949, QS 9000, VDA 6.1, AVSQ and EAQF) (*Kapustka K., Ziegmann G., Klimecka-Tatar D., Nakonczy S. 2020*). According to the procedure of the PFMEA method, errors/process malfunctions are assigned the following indicator values presented in Table 19:

Dating	Souoritu	Probability of	Probability of	
Katilig	Severity	occurrence	detection	
10	Extremely borordous	Extremely high (>1 in	Abcoluto un containte	
10	Extremely nazardous	2)	Absolute uncertainty	
9	Hazardous	Very high (1 in 3)	Very remote	
8	Vorwhigh	Repeated failures (1 in	Domoto	
	veryingn	8)	Remote	
7	High	High (1 in 20)	Very low	
6	Modorato	Moderately high (1 in	Low	
	WOULDALE	80)	LOW	
5	Low	Moderate (1 in 400)	Moderate	
4	Very low	Quite low (1 in 2k)	Moderately high	
3	Minor	Low (1 in 15k)	High	
2	Very minor	Remote (1 in 150k)	Very high	
1	None	Nearly impossible	Almost certain	

Table 19 The value scale of indicators used in PFMEA analysis of recycling of magnet process

Based on the values of SOD indicators the Risk Performance Number (RPN) is determined:

$$RPN = S \cdot O \cdot D \tag{42}$$

Where: S - severity, O - probability of occurrence, D- probability of detection.

Parameters as severity (S), probability of o occurrence (O) and probability of detection (D) are determined in accordance with requirements of PN-EN IEC 60812: 2018, based on observations and tests carried out on one production batch. Simplified

138

evaluation data are represented in Table 19. As is known, if RPN>120, the corrective actions need to be taken. At the prototype phase, as is the case in this work, it is possible to make changes in the technology and eliminate critical steps. Most importantly, it is possible to determine the suitability of the process, identify critical points, and implement preventive measures. Magnets in the first stage must be separated from WEE and demagnetized. The first stage of magnet separation has been automated for hard disk drives and electric motors. Table 20 shows the characteristics and evaluation of the three most dangerous malfunctions occurring during the magnet recycling process (Figure 7.1.).

	ormance ber N		0	
8	Risk Perfe Num RP	40	15(	15
7	Probability of detection D	H	Ŋ	1
9	Probability of occurrence 0	6	m	ო
5	Potential causes	Insufficient homogenization of ingredients (uneven distribution of scraps/powder particles and polymer binder)	Cracks, holes, voids, chipping, delamination	Lack of proper adhesion between the powder particles and the polymer binder
4	Severity S	10	10	ю
ю	Potential effects of irregularities	Isotropy of magnetic properties - classification as incompatible product	Non- permanent magnetic properties- waste	Failure to meet dimensional requirements
7	Potential irregularities	Uneven distribution of magnetic particles in the composite	Materials non heterogeneous	Inappropriate shape of the finished product
1	Process	Recycling	g of permanent mag	nets

Table 20 The PFMEA analysis of recycling of magnets according to preliminary designed process (Figure 7.1)
As it is easy to see, in the three indicated errors/irregularities are characterized with RPN significantly exceeded the value of 120. This means that it is absolutely necessary to introduce corrective actions that will allow to prevent these errors/irregularities occurrence. The proposed corrective actions are:

1. After the operation (3) demagnetization, an additional special control is introduced – preliminary control of the chemical composition of magnetic materials (3A) and segregation in terms of the content of rare earth elements (3B).

2. After the operation (4) mechanical milling in a protective atmosphere, a sieve selection (4A) is introduced, the aim of which is to extract the fraction of powder particles in certain sizes. For further processing, it is suggested to the use fractions with a sieve diameter  $50 < d < 200 \mu$ m, while the powder particles with  $d \sim 50 \mu$ m would be finally used in a 3D printer, and the powder particles with  $d > 200 \mu$ m should be sent for regrinding.

3. After the operation (7) injection molding, and additional (7A) special control is introduced. Depending on the final requirements of the process, it is possible to introduced: microscopic tests, (quantitative analysis of structural component, including analysis of homogenization of the composition, distribution of magnetic particles), mechanical tests (Brinell hardness test, bending compression strength test), surface geometry tests (e.g. analysis of roughness parameters).

4. After the operation (8) magnetization, an additional product release control (8A) is introduced – magnetic tests, which enable the classification of material into the selected range of magnetic properties. Changes in the course of the process are presented in the Figure 7.2.



Figure 7.2. Technological approach of recycling of magnets process - magnetic compound with polymer extrusion process (magnetic filler and particles obtained from WEEE): (1) Storage of electronic waste WEEE; (2) Dismantling of multi-material systems (dismantling of magnets from motors in WEEE); (3) Thermal demagnetization (temperature above the Curie temperature); (3A) Preliminary control of the chemical composition of magnetic materials; (4) Mechanical grinding in a protective atmosphere; (4A) Sieve selection; (5) Homogenization of the composition - aggregate from magnetic materials and plastic (at the temperature of plasticization of the binder); (6) Composite blend extrusion and granulation; (7A) Special control (7) Injection molding; (8) Magnetization; (8A) Product release control; (9) Packaging - protection against the atmosphere; (10) Storage and transport.

ø	Risk Performance Number RPN	720	540	200
٢	Probability of detection D	ω	9	œ
ų	Probability of occurrence O	σ	6	Ŋ
Ŋ	Potential causes	Insufficient homogenization of ingredients (uneven distribution of scraps/powder particles and polymer binder)	Cracks, holes, voids, chipping, delamination	Lack of proper adhesion between the powder particles and the polymer binder
4	Severity S	10	10	N
m	Potential effects of irregularities	lsotropy of magnetic properties - classification as incompatible product	Non-permanent magnetic properties- waste	Failure to meet dimensional requirements
Ю	Potential irregularities	Uneven distribution of magnetic particles in the composite	Materials non heterogeneous	Inappropriate shape of the finished product
1	Process	Recycling of perm	anent maş	gnets

Table 21 The PFMEA analysis of recycling of magnets according to improved process (Figure 7.2.)

### 7.2. VSD – Value Stream Design

Value stream design is a method developed by Toyota for optimizing process flows. The basis of value stream design is the representation and evaluation of material and information flows. The value stream represents the flow of all value-adding and nonvalue-adding activities of a product. The value stream method supports a production in its ability to material flow, products, and information flow through process chains, quickly with waste reduction and at high of quality. The fundamental underlying idea of value stream design in the avoidance of waste in a production process, directing the focus of production optimization on cost reduction, i.e., economic efficiency. The term "waste" as such, however, already specifies that costs may not be cut at the expense of performance, but that only those costs may be eliminated which are not related to any immediate benefits to the customer, which the customer has paid for. Overproduction, stockpiling, and transport are the three types of waste relating to waste in the production procedure, the first two of which are the gravest types of waste we know apart from the production of rejections. These are particularly clearly visible in the value stream analysis, the potential of which explicitly points out these two types of waste: The operator balance chart identifies waste caused by badly balanced production processes and their usually entailing overproduction. The timeline reveals waste resulting from long lead times and their resulting excess inventories (Kapustka K., Ziegmann G., Klimecka-Tatar D., Nakonczy S. 2020). The value stream depiction helps localize the respective causes within the production. In the following, the eight types of waste are going to be discussed in detail in Table 22.

#### Table 22 Eight types of waste

Types of waste	Reason and solution
Overproduction	This may be caused by selective overcapacities and/ or production processes poorly balanced with a view to capacities, or cycle times, respectively. The value stream design is responsible for the designing of a processing logic in which each process produces only what the subsequent process needs and not until it is needed.
Stockpiling	One could well argue that storage costs are a reasonable price to pay for inventories which assure the consistent operation of a production. Consistent improvement of the production may thus be pursued by consistent reduction of the inventory levels.
Conveyance	The first reason is an organization: Interruptions of partially processed orders may increase the transport effort. Conveyance effort can be almost totally avoided by consistent value stream- oriented factory planning, a smoothly flowing production and suitable spatial arrangement of the production processes in the factory, supported by clearly marked retrieval areas for material.
Waste in production processes	Incidental activities such as the grasping of a tool, the clamping of a part into a fixture, the switching on or adjusting of machines. These resource- related support processes are of value-decreasing effect, entailing costs without raising the value of the product.



A process for recycling magnetic materials is presented using the VSD method. This project is based on the information and analysis carried out in the first part of this work. Thanks to a detailed analysis of the individual processes, a general scheme of a recycling line for polymer-based magnets is presented. The implementation of the presented recycling line in a company already involved in the recycling of electrical equipment will require a low investment. Thanks to the detailed planning and analysis of the individual parameters, including optimization, this project can be implemented directly in the company.

#### 7.3. Results of Value Stream Analysis

Kaizen is a methodical concept and a holistic philosophy, according to which a stepby-step optimization of a product or workflow is aimed for. It is not just about the actual waste (muda). Rather, it is also about the avoidance of non-uniformity (mura) and the elimination of inappropriateness (muri). Figure 7.3. shows the current state, with the upper part of the graph representing the flow of information. It starts at the individual order (from the right side) then the order comes to the information exchange in the plant and there to a raw material supplier. The current state also shows the material flow, starting from the supplier through the warehouse where the magnets are manually transported by employees to the hall to operation 1: the **pre-treatment** (demagnetization) - at the same time the control for chemical analysis of the material is performed. After pre-treatment and control, the magnets are transported by forklift truck to operation 2: pulverization. Then the proper processing of the compound in the extruder begins, here the plastic is mixed together with magnetic powder. The material is processed under appropriate parameters such as temperature, torque, filler and volume fractions. The compound is granulated in the next phase and at the same time the quality control of the product is processed. If the homogenization meets the requirements, then the product can be delivered for the next step operation 3: injection molding. During injection molding, different molds can be produced, depending on the order. The process must consider the parameters mentioned: nozzle temperature, mold temperature, injection pressure, injection speed, holding pressure and holding pressure time, depending on the part dimensions. The processing parameters are saved to be available for further batches of products. After the magnets are produced in the desired shape, magnetization is performed. At the end, the product is transported to packaging and prepared for delivery to the customer. It should be noted that the times of the value-adding operation in the production cycle and the machining times with the machine are not required for the process, because a design with a completely new process is presented here.



Figure 7.3. Current state VSM for the recycling process of permanent magnets

Based on the visualization of the process, it is found that many aspects caused the Figure 7.4. shows the current state with indicated areas that need improvement first. The suggested improvements in Figure 7.4. relate to three types of waste:

**1. Stockpiling**: material that is not currently being used. Obviously, a certain amount of stock is necessary to avoid unnecessary interruptions in production, but there is the possibility of reduction through the application of the just-in-time method, based on perfect synchronization with suppliers.

**2. Processing**: Unnecessary movements of the material can result from a poor organization of the process and the non-use of the available technical tools. It is proposed to change the demagnetization process and to use the permanent magnetic chuck during the material transport on the conveyor belt. These measures will save the time and large part of energy in the whole process.

**3. Motion:** All moments when employees are idle represent a loss to the process. The inability to continue the operation is caused by the absence of tools or materials in the workplace. For this, the 5S method (sort, systematize, clean, standardize, self-discipline) is implemented to organize the workplace and its environment in such a way that waste can be significantly reduced there and employees find a positive working environment.

**4. Conveyance**: The weekly delivery of materials will reduce stocking and therefore any defects that occur during production will be detected and repaired in real time. Weekly deliveries will also provide a better material flow and improve process control. This will also reduce weekly unloading times and material placement times. By planning consistently on a weekly basis, you can improve production flow and reduce unnecessary costs.

**5.** Order and management processing: The better order management system coordinated with storage makes it possible to plan the work on a weekly basis for the entire production. There is no need a continuous manager control of technology, which does not add any value to the product. Thanks, a better organization of work, introduction of weekly standards and a preventive plan in case of error or sudden change, control will become unnecessary and production employees will be able to handle such situations on their own.



Figure 7.4. The current state with proposals to improve of the analyzed production process

With the end of the value stream mapping, the value stream analysis is far from finished. On the basis of the value stream mapping the potential for improvement of the production process can be identified.

1. The basis for this is a comparison of the performance of the individual production processes, which indicates the quality of the layout of the machines, both in relation to each other and to the demands of the customers. On the basis of the comparative overview with corresponding level of capacity utilization, it can be determined how to achieve a consistent productivity of the production process with respect to customer waiting times.

2. In addition, selective immediate improvement measures can be initiated in the case of easily recognizable process weaknesses without initiating major conceptual changes.

Figure 7.5. shows the value stream flow map of the analyzed production process taking into account the introduction of the proposed changes, which relate not only to the flow of the streams, but also to the implementation of the order (order acceptance, planning, scheduling and quality management). The main focus is placed on quality, as the consideration of intermediate stops due to costs increases.

The method of moving material from the storage is changed. In many areas of the process, it is suggested that the project manager check inventory status (at process entry) and after process exit. Monitoring at the input of the process would streamline the process of necessary material purchase and weekly planning, while monitoring at the output of the process would allow to obtain information about the deviations in the process. The operation magnetization is modified in terms of the number of operations, which would create the introduction of a production loop that would eventually eliminate the bottleneck of the process. Magnetization is performed directly and specifically in the injection molding process. An additional employee would assist in packaging the finished products on a pallet, which would significantly reduce the processing time associated with inspection. Thanks to the introduced changes, it would be possible to significantly save the time of material flow and energy in the whole process.

To improve the process, it is possible to use different approaches. Which are based on identifying root causes and indicating which processes events, changes in settings, raw material properties, etc. affect the product quality and process efficiency. The value stream design therefore is a tool to initiate and evaluate changes in the process.



Figure 7.5. Future state VSM for the recycling process

152

#### 7.4. Summary

The Process Failure Mode and Effects Analysis (PFMEA) and Value Stream Analysis (VSA) provided a wider picture of the designed process and highlighted its weaknesses. Thanks to the logical application of improvement tools such as KANBAN, SMED, 5S, etc., the process has been optimized and the individual steps have been improved in order to reduce material waste and decrease the time of each step. By applying these optimizations and the parameters analyzed in the thesis, it is possible to implement the process on an industrial scale. However, the cost-effectiveness of this process is, at present, only feasible for companies that are already recycling electrical equipment or producing new rare earth magnets. The combination of this process with automatic dismantling will slowly enable the maximum recovery of magnets in the shortest possible time. This is a necessary condition for the process to be economically profitable. However, it should be noted that at present the interest in recycling rare earth magnets is too low. Only political changes will make it possible to develop this field more rapidly and effectively and to become less dependent on Chinese suppliers.

In further studies, it is necessary to take into account the environmental elements and to carry out a full life-cycle assessment (LCA). It is necessary to analyze carbon dioxide during production as well as water consumption.

## CONCLUSION

In the present work, the influence of irregular shaped NdFeB microparticles on the polycrystalline polypropylene (PP) has been studied. A systematic procedure for the recycling of neodymium magnets is developed, allowing their re-use in combination with the polymer matrix. The influence of the filling level and particle geometry on the obtained flow and conversion properties profile as well as the polymer structure and functional properties of the compounds are analyzed.

Standard neodymium magnets, which are destined for recycling from Waste of electrical and electronic Equipment (WEEE), are used for the study. Magnetic powder is produced under argon shielding gas and particles are qualified according to size. The mixtures are prepared with different ratios of magnetic powder, from 30 Vol.% to 70 Vol.% in steps of 10 Vol.%. The extruded powder together with the polymer at determined content is mixed with the thermoplastic matrix using a laboratory kneader. The blends produce is then molded in a conventional injection molding process. In order to evaluate the conversion properties, the materials are characterized in terms of bonding behavior, flow behavior and magnetic properties. The flow characteristics and structural properties of the compounds and the structural properties of the thermoplastics are presented.

Injection molded parts are analyzed for their thermal and magnetic properties. The results are discussed on the basis of existing mathematical models. The profile of the properties of particle- filled thermoplastics is mainly influenced by the degree of filling both in the melt and in the solid region. In the case of solids, the degree of filling, the particle size distribution, the geometry and the composition of the hard magnetic particles used have a decisive influence. Significant changes in properties due to particle-particle interactions occurred at a filling level of 30 Vol.%. Furthermore, the dependence of processing and material properties on compound viscosity is shown in the results.

Analysis of the maximum packing density at a spherical particle size distribution showed a good agreement with the maximum fill rate that can be processed in injection molding. In compounding, the minimum kneading time can be derived from the torque curve in the laboratory kneader. It must be remembered that neodymium magnet particles are highly flammable in an oxygen atmosphere. The flow properties of the melt flow in the injection molding process have been determined by rheological studies. It has shown that the flow properties of the thermoplastic material, the degree of filling and the geometry of the particles have a significant influence on the material flow. An increase in the filling ratio, irregular shape and residual magnetization significantly affects the parameters under consideration. At medium and high filling factors, particle-particle interfaces in the flow structure have been analyzed for extrusion-molded samples which indicate the formation of conductive pathways and associated residual magnetization resulting in particle contact.

As expected, the melt viscosity increased as the filling ratio increased. However, the yield point is formed at low shear rates ( $\gamma \rightarrow 0$ ).

The molar mass distribution of PP has been slightly moved towards low molar masses as a result of processing in the mixing and injection molding process. The crystallization degree of PP is not significantly affected by the particles, but the steady decrease in melting point with increasing filling degree showed an increase in the proportion of narrow crystalline lamellae. The glass transition temperature tended to be linear in both calorimetry (DSC) and thermal analysis (TGA). Furthermore, the addition of particles led to linear increase in the thermal stability of PP. This effect is enhanced with decreasing average particle size.

The presented effect of residual magnetization on the material flow shows that it has influence on the technological processes and allow to control them using magnetic force. It is possible to orientate the magnetic particles by using already low magnetic forces. Therefore, the useability of magnets produced in this way is increased considerably. In this project, the magnets made using the presented methods are applied again to electric motors in e-bikes with satisfactory results.

# OUTLOOK

The subject presented in this thesis indicates a wide application in the industry but requires continuous improvement. On the basis of analyses and observations made, further actions are proposed.

According to the results, the polymer matrix reduces the magnetic properties of the magnets produced, creates a barrier that can be replaced by another polymer. This idea focuses on the use of a matrix based on thermosensitive polymers. Thanks to the use of such a polymer, the energy demand resulting from the delivery of high temperature is reduced. Another advantage is the possibility to remove the matrix after the molding process. Thermosensitive polymers are also soluble in liquid solutions. The choice of the right polymer is of course dependent on the application. Another route that opens further possibilities is to use a 3D printer to apply the magnetic layer only where these properties are necessary for optimal product performance. This allows for a reduction in material and a more economical use of such a valuable rare earth material.

Another important method that can be used for the fragmentation of magnets is electrohydraulic fragmentation. The use of this method allows for the fragmentation of larger magnets, e.g., electric motors from magnets without affecting their magnetic properties. The technology is based on shock waves which are generated by pulsed high voltage spark discharges. The shock waves propagate through the surrounding carrier medium and hit the material. The short but very intense mechanical impacts preferably attack weak spots within the material: microscopic phase or grain boundaries. Fragmentation by means of shock waves offers the possibility of breaking down magnets quickly and disproportionately, especially in case of thick products.

However, in order to realize all these scenarios, a greater interest in recycled magnetic materials is required. This, however, leads to major policy changes that must be undertaken. The prediction of another crisis is not a prophylactic consideration. Only further research on this topic will allow Europe to be independent from the Chinese market.

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160

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# APPENDICES

Appendix A - Nomenclature

Appendix B - Common Terms

Appendix C - Curriculum Vitae
# Appendix A

#### Nomenclature

$$\begin{split} \eta * (\omega), \cdot \textit{Complex viscosity} \\ (\phi m) \cdot \textit{Maximum packing fraction} \\ \eta s \cdot \textit{Viscosity of the solvent/filling} \end{split}$$

[

 $[\eta] \cdot Intrinsic viscosity$ 

Δ

 $\Delta \cdot Delta$ 

#### 7

 $\nabla \cdot$  Hamilton differential operator

## Α

 $A_r \cdot Aspect ratio equal to d_{max}/d_{min}$ aPP · Atactic polypropylene

#### В

B  $\cdot$  Magnetic flux density (magnetic induction) T, Magnetic induction [T]

 $B_p \cdot Magnetic induction for flocculation into secondary minimum [T]$ 

BH<sub>max</sub> · Maximum energy product [J/m<sup>3</sup>]

 $_{B}H_{C} \cdot Flux$  density coercivity, field at which B = 0

 $B_r \cdot Remanent magnetic induction [T]$ 

С

 $\begin{array}{l} C_p \cdot \textit{Heat capacity} \\ C_3H_6 \cdot \textit{Cyclopropane} \\ \text{CIP} \cdot \textit{Cold isostatic pressing} \\ \text{CLAHE} \cdot \textit{contrast limited adaptive histogram equalization} \\ \text{CO}_2\text{H} \cdot \textit{Carboxylic acid} \\ \text{CO-NH} \cdot \textit{Group in amides} \end{array}$ 

D

 $\begin{array}{l} D \cdot \textit{Diameter of the particle} \\ D_{ro} \cdot \textit{rotary diffusivity} \\ De \cdot \textit{Deborah number} \end{array}$ 

Ε

*E*<sub>A</sub> · *Anisotropy energy emu · Magnetic moment emu/g · Mass magnetization* 

G

 $G' \cdot storage modulus$  $G'' \cdot loss modulus$ 

## Η

H · Magnetic field strenght (intensity) [A/m]
H<sub>A</sub> · Anisotropy field
HCl · Hydrochloric acid
H<sub>d</sub> · Demagnetizing field [A/m]
HD · Hydrogen decrepitation, hydrogen decrepitation
HDDR · The hydrogenation, disproportionation, desorption and recombination

Ι

iPP · Isotactic polypropylene

## J

J  $\cdot$  Magnetic polarization [T] J<sub>r</sub>  $\cdot$  Remanent polarization [T]

#### Κ

K<sub>1</sub> · *Leakage factor* k<sub>b</sub> · *Boltzmann constant; 1,380649\*10<sup>-23</sup>J/K* 

L

 $\label{eq:Lorentz} \begin{array}{l} L \cdot Lenght \ of \ the \ particle \\ LOT \cdot \ Low-oxygen \ technology, \ low-oxygen \ technology \\ LREE \cdot \ Light \ Rare \ Earth \ Elements \end{array}$ 

#### М

$$\begin{split} M \cdot Magnetization \\ m_{T,norm} \cdot thermoplastic mass fraction \\ m_{C} \cdot compound output mass \\ m_{F} \cdot filler mass \\ M_{s} \cdot Saturation magnetization [A/m] \\ MFR \cdot Melt Flow Rates \\ MOFe_{12}O_{18} \cdot Hexagonal ferrites where M is a metal in a positive oxidation state \\ MRIs \cdot Magnetic Resonance Imaging \\ M_{s} \cdot Magnetization vector \end{split}$$

Ν

N<sub>d</sub> · Demagnetization factor NdFeB · Neodynium Iron Boron NdH2 · Neodymium Hydride NMRs · Nuclear Magnetic Resonance Spectroscopy

Р

*p* · aspect ratio according to the axis of symmetry
PA · Polyamide, Polyamide
PFMEA · Process Failure Mode Effects Analysis
PP · Polypropylene, Polypropylene

## Q

 $Q \cdot volumetric$  flow rate of compound melt

## R

RE · Rare earth REE · Seltene Erden-Elemente REO · rare earth oxide rPP · Recycled Polypropylene

## S

s · extra stress tensor SEM · Scanning microscopy analysis sPP · Syndiotactic polypropylene SPS · Spark plasma sintering Т

 $\begin{array}{l} T \cdot \textit{Temperature, torque, kinetic energy} \\ t_c \cdot \textit{Relaxation time} \\ t_p \cdot \textit{Time of observation} \\ TGA \cdot \textit{Thermogravimetric analysis} \\ T_m \cdot \textit{Melt temperature} \end{array}$ 

#### U

u · Velocity vector

#### V

VSD · Value Stream Design

#### W

WEEE · Waste of Electrical and Electronic Equipment

## X

XRD · X-ray diffraction patterns

#### Ζ

ZHOFP · Zhenghai Oxygen-Free Process

## Г

 $\dot{\gamma} \cdot Shear strain rate [s^{-1}]$ 

Η

 $\begin{array}{l} \eta_{C} \cdot \textit{Viscosity of the dispersal phase} \\ \eta_{D} \cdot \textit{Viscosity of the dispersal phase} \\ \eta_{sp} \cdot \textit{Specific viscosity} \\ \eta\text{-phase} \cdot \textit{Paramagnetic phase} \end{array}$ 

#### Λ

 $\lambda$  · Represents the ratio of viscosities of dispersed phase and continuous phase

### М

 $\begin{array}{l} \mu_0 \cdot \textit{Magnetic permeability of vacuum (4\times107 H/m)} \\ \mu_m \cdot \textit{Relative magnetic permeability of particle} \end{array}$ 

#### Т

 $\tau \cdot Shear \ stress [Pa]$ 

#### Φ

 $\varphi\cdot \textit{Phi},$  Hard magnetic phase  $\Phi\cdot\textit{Concentration}$  degree of filling phase

#### Ψ

 $\Psi \cdot Electric flux$ 

# **Appendix B**

### **Common Terms**

Agglomeration  $\cdot$  the act or process of collecting in a mass.

- Amorphous polymers · type of polymer that has a seemingly random and coiled molecular structure and does not immediately melt when heated.
- **Brownian motion** *the erratic random movement of microscopic particles in a fluid, as a result of continuous bombardment from molecules of the surrounding medium.*

**Compounding**  $\cdot$  *the process of combining two materials.* 

- **Coercivity** · the resistance of a magnetic material to changes in magnetization, equivalent to the field intensity necessary to demagnetize the fully magnetized material.
- **Curie temperature** · *temperature at which certain magnetic materials undergo a sharp change in their magnetic properties.*
- **Deborah number** · used in rheology to characterize the fluidity of materials under specific flow conditions.
- **Demagnetization**  $\cdot$  removing the magnetic field from an object.
- Filler  $\cdot$  a substance added to a product (as to increase bulk, weight, viscosity, opacity, or strength).
- **Heavy metals** · metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb).
- **Injection molding**  $\cdot$  *the shaping of rubber or plastic articles by injecting heated material into a mold.*
- Loss modulus  $\cdot$  the loss modulus (*G*") (viscous response) is a measure of the energy dissipated or lost per cycle of sinusoidal deformation.
- **Magnetic anisotropy**  $\cdot$  the dependence of any magnetic property of a material on the direction in which it is measured.

- **Magnetic field**  $\cdot$  a region around a magnetic material or a moving electric charge within which the force of magnetism acts.
- **Magnetization** · the vector field that expresses the density of permanent or induced magnetic dipole moments in a magnetic material.
- **Particles** a small, localized object to which can be ascribed several physical or chemical properties, such as volume, density, or mass.
- **Permanent magnets** · materials that retain their magnetic properties after having been exposed to a magnetic field. They are found in a great variety of materials used in a significant and increasing number of industrial and commercial applications.
- **Polymer matrix**  $\cdot$  a material consisting of a composite made stronger by adding fibers or particles to it.
- **Rare earth elements** (**REE**) · consist of 17 elements: Sc, Y and the lanthanoids La–Lu. *Their magnetic and luminescent properties make them essential components of digital and low carbon technologies.*
- **Rare earth oxides**  $\cdot$  readily formed from rare earth elements as they are typically very reactive with oxygen in the ambient atmosphere.
- $\mathbf{Recycling} \cdot \mathbf{the} \ \mathbf{process} \ \mathbf{of} \ \mathbf{converting} \ \mathbf{waste} \ \mathbf{materials} \ \mathbf{into} \ \mathbf{new} \ \mathbf{materials} \ \mathbf{and} \ \mathbf{objects}.$
- **Remanence** · the magnetic flux that remains in a magnetic circuit after an applied magnetomotive force has been removed.
- **Residual magnetism**  $\cdot$  the amound of magnetization left behind after removing the external magnetic field from the circuit.
- **Rheological properties**  $\cdot$  the properties of materials that govern the specific way in which these deformation or flow behaviors occur.
- **Rheology** the branch of physics that deals with the deformation and flow of matter, especially the non-Newtonian flow of liquids and the plastic flow of solids.
- Sauter diameter · defined as the diameter of a sphere that has the same volume/surface area ratio as a particle of interest. Originally developed by German scientist, J. Sauter in the late 1920s.

- Semi-crystalline polymers · type of compound with a highly ordered molecular structure. With a sharp melting point, semi-crystalline polymers remain solid until it absorbs a specific amount of heat.
- **Storage modulus**  $\cdot$  *elastic storage modulus (G') is the ratio of the elastic stress to strain, which indicates the ability of a material to store energy elastically.*
- $Upcycling \cdot reuse$  (discarded objects or material) in such a way as to create a product of higher quality or value than the original.
- **Viscoelastic behavior**  $\cdot$  a combination of elastic and viscous behavior where the applied stress results in an instantaneous elastic strain followed by a viscous, time-dependent strain.
- Viscosity  $\cdot$  a measure of a fluid's resistance to flow.

# Appendix C

# **Curriculum Vitae**

#### Personal information

Name	Katarzyna Joanna Kapustka
Date of birth	October 20 <sup>th</sup> 1990
Nationality	Polish
Education	
since 02.2018	<b>PhD candidate</b> , Clausthal University of Technology, Clausthal Centre for Material Technology, Germany
2016 - 2017	<b>Master student</b> , Clausthal University of Technology, Material Engineering and Material Science, Germany
2014 - 2017	Master student, Production Management and
	Production Technology, Czestochowa University of Technology, Poland
2011 - 2015	<b>Dual Study student,</b> Material and Dental Engineering, A.
	Meissner Dental Engineering University, Poland

# Work experience and scholarships

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Since 02.2018	Scientific Researcher, Project: Recycling von magnetischen
	Materialien aus Generatoren von Windkraftanlagen,
	Elektromotoren und Elektronikschrott. Clausthal University of
	Technology, Germany
2017 - 2018	Scientific trainee, Project: Recycling von magnetischen
	Materialien, Clausthal University of Technology, Germany,
	scholarship funded by Deutsche Bundesstiftung Umwelt
2016 - 2017	Scientific trainee, Clausthal University of Technology,
	scholarship funded by Erasmus+
2015	Research Assistant, Poland
2014 - 2013	Dental Technician, Poland
2013 - 2010	Self-employme
Awards	
2015-2017	Scholarship for the best students of the University of
	Czestochowa, Poland

2014-2016	Scholarship of Ministry of Science and Higher Education of
	Poland
2012-2015	Scholarship for the best students of the A. Meissner Dental
	Engineering
2014, 2013	1 <sup>st</sup> award during Academic Champion in Swimming, Poland

#### Conferences

Participation in:

- 5 international conferences
  - a) First author of 3 and co-author of 5 oral presentations
  - b) First author of 4 and co-author of 10 posters
- 4 national conferences
  - a) Co-author of 2 oral presentations
  - b) First author of 3 and co-author of 3 posters.

# Appendix D

## List of publications

#### Publications with peer review process

- Kapustka K., Ziegmann G., Klimecka-Tatar D., Nakonczy S. (2020). Process management and technological challenges in the aspect of pernament magnets recycling - the second life of neodymium magnets, *Manufacturing Technology*, DOI: 10.21062/mft.2020.098.
- Kapustka K., Ziegmann G., Klimecka-Tatar D., Ostrega M. (2020). Identification of health risks from harmful chemical agents - review concerning bisphenol A in workplace, *Production Engineering Archives*, DOI: 10.30657/pea.2020.26.10.
- Kapustka K., Ziegmann G., Klimecka-Tatar D. (2019). The Management and Potential Risk Reduction in the Processing of Rare Earths Elements, *System Safety: Human-Technical Facility- Environment*, DOI: 10.2478/-2019-0010.
- Kapustka K., Klimecka-Tatar D. (2018). Value Streams Mapping in the Implementation of Process Innovations – in the Case of Single–Unit Production, *Multidisciplinary Aspects of Production Engineering*, DOI: 10.2478/mape-2018-0082.
- Kapustka K., Ziegmann G., Klimecka-Tatar D. (2017). Technological and ecological safety in aspect of chemical properties of recycled neodymium magnets – electric motors and hard disk, *Production Engineering Archives*, DOI:10.30657/pea.2017.17.08.
- Kapustka K., Ziegmann G., Sdrenka S., Elwert T., Klimecka-Tatar D. (2017). Microscopic characteristic of Nd-Fe-B magnets structure - magnets recovered from electric motors, *Archives of Engineering Knowledge* Vol. 2, Issue 1 (2017) 39-41.
- Kapustka K., Klimecka-Tatar D. (2016). Innowacyjne procesy druku 3D analiza ryzyka wdrożenia innowacji w branży stomatologicznej, Oficyna Wydawnicza Stowarzyszenia Menedżerów Jakości i Produkcji, ISBN 978-83-63978-35-8 (in Polish)
- Kapustka K. (2015). Drukowanie 3D zębów, czyli wpływ innowacji na rynek stomatologiczny, Inżynieria Stomatologiczna *Biomateriały ISSN* 1644-0420 (in Polish)
- Kapustka K., Klimecka-Tatar D. (2015). Postęp innowacyjnych technologii druku 3d, a medycyna/protetyka = Development of Innovative 3d Printing Technologies in Medicine/Prosthetics, Inżynieria stomatologiczna - biomateriały. Nowoczesne materiały i technologie, stosowane, ISBN:978-83-9382612-4 (in Polish)

- Kapustka K., Hajduga M. (2015). Cooperation with dentist technician. How to take the dental impression properly, Zabrze 2015, *Aktualne Problemy Biomechaniki*, s.111-116.
- Kapustka K., Hajduga M. (2014). The internal structure of the weld in orthodontic wires connections, *TPS Twoj Przeglad Stomatologiczny*, s.97-98.
- Kapustka K., Hajduga M., Was-Solipiwo J. (2014). The recent timberline changes in the Tatra Mountains: A case study of the Mengusovská Valley (Slovakia) and the Rybi Potok Valley (Poland). Geographia Polonica 88(2), 71-83.
- Kapustka K, Hajduga M. (2014). Safe number of additives melted steel alloys prosthetic without affecting formation metalosis, *Innovations in Biomedical Engineering-IiBE*.
- Kapustka K., Hajduga M. (2014). Wybrane sposoby połączenia drutów ortodontycznych, Inżynieria stomatologiczna biomateriały : teoria, praktyka, doświadczenie/Rajmund Orlicki, Dorota Klimecka-Tatar, s.55-64. (in Polish)

#### Conference proceeding with peer review process

- Kapustka K., Ziegmann G., Sdrenka S., Elwert T., Klimecka-Tatar D. (2018). Problems in waste management in the aspect of the secondary use of plastics from WEEE, *MATEC Web of Conferences 183*, 01011 (2018) QPI 2018.
- Kapustka K., Ziegmann G., Sdrenka S., Elwert T., Klimecka-Tatar D. (2017). Recycling von magnetischen Materialien, *42 Statusseminar Lenzen*.
- Kapustka K., Ziegmann G., Klimecka-Tatar D., Sdrenka S. (2017). The combination of NdFeB type magnetic powder with polymer as a functional material recycled from electric motors, Metal 2017: 26<sup>rd</sup> International Conference on Metallurgy and Materials.
- Kapustka K., Ziegmann G., Klimecka-Tatar D. (2017). Recycling von Magnetischen Materialien, Fachkolloquium "Umweltschutz im 21. Jahrhundert", Julius-Kühn-Institut, Quedlinburg.
- Kapustka K., Klimecka-Tatar D., Wawrzynek K. (2015) Drukowanie 3D zębów, czyli wpływ innowacji na rynek stomatologiczny = 3D Printing Teeth, That Influence Innovation in Dental Market, XVI Międzynarodowa Konferencja Naukowa "Inżynieria Stomatologiczna - Biomateriały". Ustroń.
- Kapustka K., Hajduga M. (2014). Corrosion changes of the weldable nitinols (NiTi) in an environment of physiological liquids, Metal 2014: 23rd International Conference on Metallurgy and Materials: conference proceedings, Brno, Česká Republika, 21-23.5.2014.