Influence of the use of Renewable Compatibility Agent Wood Plastic Composite (WPC)

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Abstract: The growing interest in using recycled and natural materials in the application of new composites in recent years implies ecological, economic and versatility benefits. Wood plastic composite (WPC) are considered very attractive materials, as they allow the use of polymers of recycled or virgin origin, associated with forestry by-products. The present work aims to investigate the influence on the mechanical, thermal and morphological resistance of WPC, using oleic acid and glycerol as renewable coupling agents. Composites were also prepared with a commercial compatibility agent in its formulation - maleic anhydride grafted polypropylene (MAPP) - under the same conditions. The composites were prepared in a single-screw extruder, with fixed contents of 5% sawdust with 95% virgin polymer, of this total, 2% were coupling agents: MAPP, oleic acid or glycerol, according to the desired composition. To be evaluated as changes in mechanical properties, tensile and impact strength tests were performed on specimens obtained through the injection molding process. The fracture surfaces of specimens tested in tensile tests were examined using images generated by scanning electron microscopy. The thermal stability of the composites was also investigated by thermogravimetric analysis. The use of glycerol and oleic acid improved the mechanical properties of the composite. An increase in tensile strength is observed when glycerol is added in composite. As for impact strength, the addition of glycerol or oleic acid was around 58% higher in impact strength when compared to without coupling agent. Glycerol and oleic acid are renewable, low-cost alternative to be a potential substitute for the commercial coupling agent MAPP, especially when the main requirement is to obtain better impact resistance properties.

Keywords: Oleic acid, glycerol, natural fiber, coupling agent, mechanic properties.

1. INTRODUCTION

In order to minimize environmental problems in the world, techniques for developing environmentally friendly materials are becoming increasingly common [1]. In this context, polymeric composite materials reinforced with natural fibers have received great attention due to the numerous advantages that natural fiber can offer, such as low density, low cost, sustainability and non-toxicity [2, 3]. Thermoplastic composites reinforced with wood waste, called wood plastic composite (WPC), have received attention from many researchers.

Studies carried out indicate that the use of cellulosic fibers or wood residue as reinforcement or filler in thermoplastic composites has the potential to replace conventional wood. In addition to the benefit of reusing waste, other advantages can be listed, such as: greater resistance to humidity and environmental deterioration; resistance to pests and insects; can be extruded into profiles with different shapes; have better dimensional stability; resistance to warping and cracking, among other advantages. Due to its benefits, WPC is considered a promising material. In the area of civil and automobile construction, the use of polymer-wood composite materials has been highlighted. The combination of extruded polyethylene, polypropylene and polyvinyl chloride with wood residue form profiled products for floors, window and door frames and automotive components. The combination of these two materials provides lightness, versatility and low cost [4].

On the other hand, the use of natural fibers generates some disadvantages when used as filler or reinforcement in polymeric composites, such as compromised mechanical performance, high moisture absorption; processing temperature limitation and incompatibility with most common thermoplastics. However, most of the problems related to the use of fibers in thermoplastic composites are due to the incompatibility of the hydrophilic groups present in the natural fiber structure with the hydrophobic group present in the olefinic polymer [5]. This mixture will result in low interfacial interaction and poor adhesion, which characterizes the material as having low mechanical properties [6].

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For a composite with interaction and good properties it is necessary to obtain an uniform mixture [5]. The use of coupling agents is the most popular technique for the production of WPC, mainly due to its rapid production, in addition to being a convenient and attractive method, in the sense that it can facilitate the preparation steps by directly melting the mixture of the natural fiber with the thermoplastic polymer [7, 8]. As for the renewable coupling agents, glycerol is a by-product derived from the production of biodiesel, whose production in Brazil is higher than its consumed volume, even though it is an industrially versatile product, therefore, its application in composites would present an alternative to use part of the crude glycerol produced [9]. Oleic acid comes from vegetable oils, is renewable, biodegradable and non-toxic [10].

Another important aspect is that a good part of WPC applications is directed to deck manufacturing, in this context impact resistance is the crucial mechanical property, as it is a common practice for children to run and jump on decks. Therefore, achieving good impact resistance properties is a necessary condition to avoid failure [11]. However, the production processes of commercial coupling agents can generate environmental impact, are expensive and toxic [12]. In this context, this work compares the influence on impact resistance and thermal stability of oleic acid and glycerol composites as a renewable coupling agent with one commercial maleic anhydride grafted polypropylene coupling agent (MAPP).

2. MATERIALS AND METHODS

2.1. Materials

Polypropylene (PP) with a flow rate of 8 g/10 min is marketed by Braskem, the interfacial agent MAPP (498-NA-MB) with MFI (g/10 min): 10.0 - 20.0 and density (g/cm³): 1.2 - 1.4 marketed by the company Cristal Master (Joinville, Santa Catarina). Oleic acid was marketed by Vetec Química (Rio de Janeiro, Brazil) and glycerol was produced in the process development laboratory during the production of biodiesel [13] and used without any treatment (FURB, Blumenau). The wood residue from the furniture industry was in sawdust format, with a varying particle size from 0.34 mm to 2.38 mm.

2.2. Methods

2.2.1. Composite Preparation

Prior to the extrusion process, the sawdust and polymer pellets were oven dried for 24 h at a temperature of approximately 70 ºC. After this step, the wood residue and PP were manually mixed at room temperature with each renewable coupling agent, oleic acid and glycerol. A composite with MAPP was also manually mixed with wood residue and PP at room temperature before the extrusion process to compare with composites with renewable coupling agents. All composites were prepared with 5% sawdust, 95% virgin polymer and of this total, 2% were coupling agents. The composites were processed in a single-thread extruder from the Eco Soluções brand. The temperature profile was zone (1) 185 ºC, zone (2) 190 ºC, zone (3) 195 ºC. The extruded composites were pelletized and dried at 70 °C for 24 h. For the preparation of the specimens, the composites were injected in an AX Plásticos bench injection molding machine, model AXINJET. The temperature used in the pipe was 195 ºC for composites and polymers. The mold temperature was 80 ºC and the applied pressure was 0.6 MPa.

2.2.2. Mechanical Properties

The tensile tests were performed according to ASTM D638 method at tensile speed of 5 mm/min, using the INSTRON brand machine, model EE 08. Izod impact strength was measured in accordance with the ASTM D256 method with 2.7 J pendulum does not using notched. Each mechanical test value was calculated as the average of at least five independent measurements. In addition, statistical analysis was performed. The significant differences between means were verified by the Tukey test ($p<0.05$).

2.2.3. Thermogravimetric Analysis

Approximately 5 mg of each sample was used. The equipment used was the model DTG-60, Shimadzu brand with a flow of 100 [mL/min] of Argon. The TGA was carried out under conditions 20 to 600 ºC with a heating rate of 20 ºC min^{-1}.

2.2.4. Morphological Analysis

The morphology of the composites was examined using a scanning electron microscope Tescan, VEGA3. Before performing the analysis, the fracture surface of the of specimens tested in tensile tests were metallized with gold.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties

Figure **1** show the tensile and impact strength of composite materials. According to this data, when

MAPP was added to polymer virgin/sawdust (PV/s) composite, the interface between sawdust and polypropylene formed a connection that improved the tensile strength, from 28.43±0.56 to 30.80±0.24. There are several studies that address the effects caused by the addition of MAPP in WPC. Its effectiveness is the result of the graft ratio, MAPP molar mass and its processing. As discussed earlier, MAPP interacts with fiber and matrix creating a bond between them, and consequently improving interfacial adhesion, but often also promoted better dispersion of fillers in the polymer matrix volume important in better mechanical properties of the WPC [14, 15]. The addition of oleic acid in composite are not statistical significantly different in comparison with the PV/s composite (29.22±0.90), this can be explained because natural oil becomes less polar as the carbon chain increases and oleic acid has 18 carbons in its structure, which results in weaker intermolecular interactions, reducing mechanical properties [16].

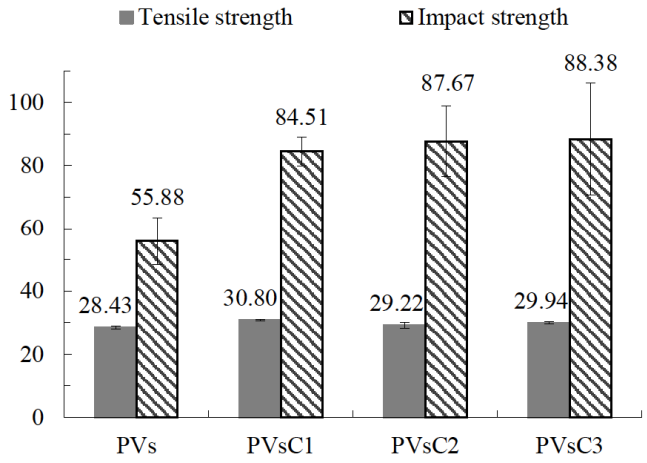

Figure 1: Values of tensile strength and (b) impact strength of composite materials PVs; PVsC1; PVsC2; PVsC3 (PV: polymer virgin; s: sawdust; C1: MAPP (maleic anhydride-grafted polypropylene); C2: oleic acid; C3: glycerol).

The increase in tensile properties to 29.94±0.44 when glycerol (C3) is added in composite compared with the composite without coupling agent can be attributed to the corresponding increase (in molar amounts) of acidic aliphatic organics present in glycerol, causing an increase in the coupling effect [17]. Figure **1** also presents that the impact strength of the composites with coupling agent (MAPP, oleic acid, and glycerol) increase the impact resistance compared with the composite without coupling agent.

The impact force is related to the functional resistance of the material to the dissipation of cracks from the weakest point of the composite, this point being the connection between the lignocellulosic material and the polymer [12]. The increasing impact resistance of composites with the addition of oleic acid and glycerol resulted in no improvement in the adhesion between a natural fiber and the polymer, causing a better charge distribution between them. Possibly this good interaction was promoted using renewable coupling agents, which were responsible for promoting a delay in the initiation and propagation of cracks in the matrix, which result is an increase in the impact resistance of the composite.

The highest impact strength was 88.38±17.75 for the composite with 2% by weight of glycerol, followed by the composite with oleic acid and the MAPP, 87.67±11.07 and 84.51±4.55, respectively. The resistance to the composite without coupling agent was 55.88±7.56. The presence of the coupling agent was responsible for promoting interfacial adhesion between the wood residue and polypropylene.

Mohanty *et al*. [18] studied four types of modifications in polypropylene (PP) composites reinforced with sisal fiber, such as: alkali, cyanoethylation, addition of a coupling agent commercially known as Epolene (G-3015) and Hostaprime (HC5) belonging to the group of MAPP. When HC5 and G-3015 were added, the improvement in tensile strength values was more pronounced, up from 49.6% for G-3015 and 50% for HC5. Impact strength increased by about 32.6% using G-3015 and 57.5% when HC5 was added. On the other hand, cyanoethylation and alkaline treatment were less efficient compared to the results obtained in composites with the coupling agents G-3015 and HC5. The authors concluded that the gain in mechanical properties by the addition of MAPP (HC5 or G-3015) can be explained by the coupling between the hydroxyl groups of the fibers and the anhydride groups of MAPP, thus forming an ester bond. The presence of the MAPP coupling agent improved the interaction of PP with the sisal fiber, which contributes to the stress transfer from the matrix to the fiber.

3.2. Thermogravimetric Analysis

The TGA and DTG curves for composites with and without coupling agents are shown in Figure **2**. The individual behavior of each coupling agents in the composite, it is considered that an initial weight loss (Ti) is the temperature at which a sample lost 5% of weight. The presence of MAPP in the composite presented a lower thermal stability among the treated

composites, which indicates that the chemical nature of this product, especially the presence of oxygen, favored the decomposition process and reduced residue content compared to composites without the addition of coupling agents [19].

Although the behavior of the thermogravimetric analysis curves showed a similar behavior for all samples, the expected thermal behavior for the composites was the presence of at least two stages of thermal degradation (seen in the DTG). The composite containing natural fiber was expected to present at

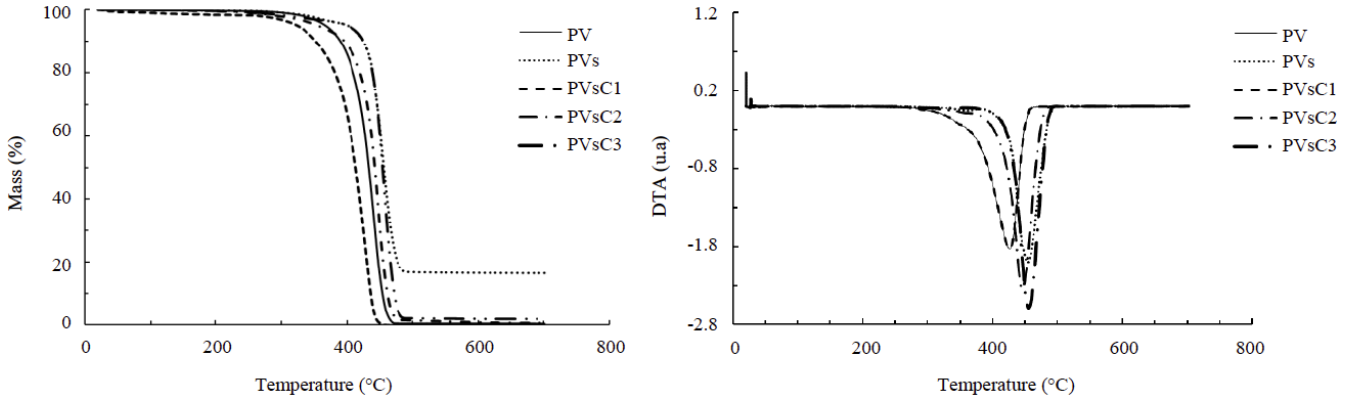

Figure 2: Thermogravimetric and derivative thermogravimetric curves for the composites studied PVs; PVsC1; PVsC2; PVsC3 (PV: polymer virgin; s: sawdust; C1: MAPP (maleic anhydride-grafted polypropylene); C2: oleic acid; C3: glycerol).

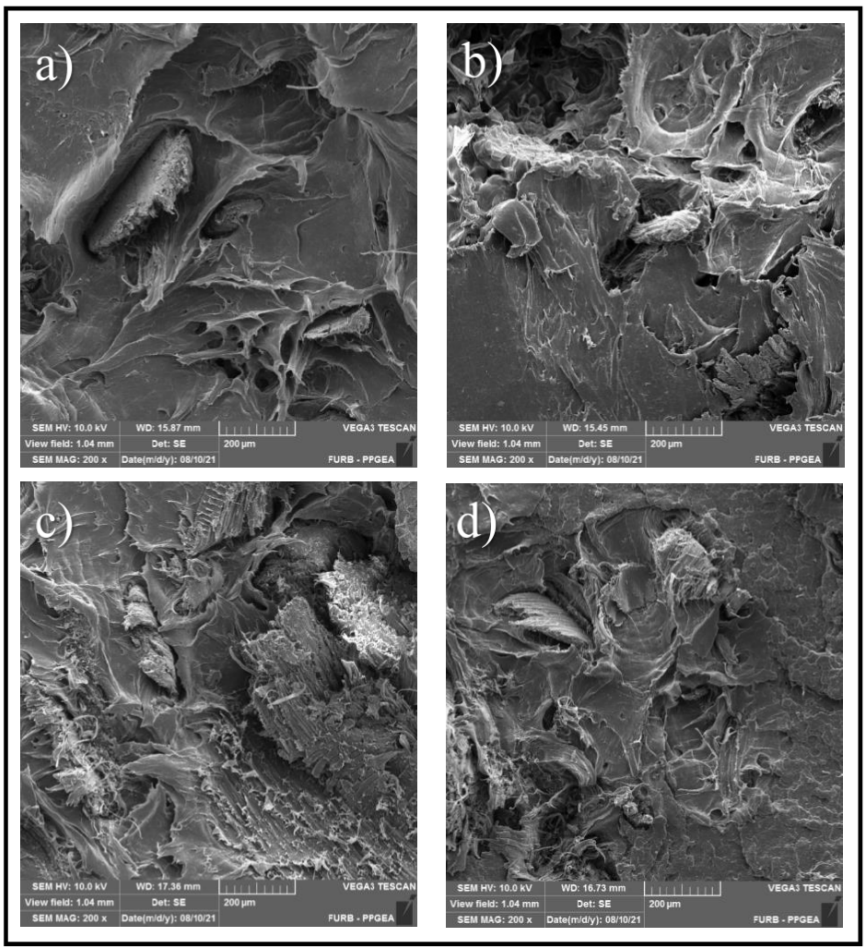

Figure 3: Scanning electron microscopy micrographs for (**a**) PVs (**b**) PVsC1 (**c**) PVsC2 and (**d**) PVsC3 (magnification x 500, scale 100 µm) (PVs; PVsC1; PVsC2; PVsC3 (PV: polymer virgin; s: sawdust; C1: MAPP (maleic anhydride-grafted polypropylene); C2: oleic acid; C3: glycerol).

least two evident degradation peaks as described by Poletto [8], where the first peak with lower temperatures (220 °C and 370 °C), which would be associated with the degradation of cellulose, hemicellulose and lignin, and the second degradation peak would involve thermal degradation mainly of polypropylene at temperatures between 370 °C and 500 °C. However, the peaks were restricted to the peaks of thermal degradation of polypropylene. This behavior may be the result of most of the composite, 95% by weight, being filled with polymer and only 5% by weight of dust or sawdust, leading to the thermal behavior being predominantly characteristic of polypropylene.

3.3. Morphological Analysis

As for the distribution of fibers in the composite, in Figure **3**, when analyzing their dispersion, it is possible to notice that the fibers are not evenly distributed in the matrix, which is evident by its loose piece.

Thus, it can be concluded that the sawdust dispersed in the matrix did not have sufficient adhesion and dispersion to promote reinforcement, which is evident by its detachments after the tensile test, as this weak adhesion easily leads to complete disbonding of the sawdust from the matrix on the surface of the fracture [20, 21].

Composites with oleic acid and glycerol show that a natural fiber is incorporated into the matrix. This shows that the sawdust is strongly embedded in the recurrent polypropylene of aggregation improvement by adding renewable coupling agents, improving the adhesion between the fiber and the matrix [20].

4. CONCLUSIONS

The use of glycerol and oleic acid improves the interfacial adhesion between the wood residue and the polypropylene matrix. Consequently, the use of glycerol and oleic acid improved the mechanical properties of the composite. Based on the results of this work, the addition of glycerol resulted in greater impact strength when compared to oleic acid. The improvement promoted by oleic acid was similar with the results when MAPP was added to its feed, although it is worth mentioning that MAPP is a commercial compatible agent used in industrial applications to produce WPC products.

Therefore, the use of glycerol and oleic acid in composites becomes a potential substitute for the commercial coupling agent MAPP when the main requirement is to obtain better impact resistance properties, as they represent a low-cost alternative and are renewable.

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REFERENCES

[1] Mothé CG, Araujo CR. Caracterização térmica e mecânica de compósitos de poliuretano com fibras de Curauá. Polímeros Ciência e Tecnol 2004; 14: 274-278. https://doi.org/10.1590/S0104-14282004000400014

[2] Oliveira TÁ, Teixeira A, Mulinari DR, Goulart SAS. Avaliação do uso de agente compatibilizante no comportamento mecânico dos compósitos PEBD reforçados com Fibras de Coco Verde. Cad UniFOA 2017; 5: 11-17. https://doi.org/10.47385/cadunifoa.v5.n14.1008

[3] Poletto M. Compósitos termoplásticos com madeira – uma breve revisão. Rev Interdiscip Ciência Apl 2017; 2: 42-48.

[4] Correa CA, Fonseca CNP, Neves S, Razzino CA, Hage Jr., E. Compósitos termoplásticos com madeira. Polímeros 2003; 13: 154-165. https://doi.org/10.1590/S0104-14282003000300005

[5] Albinante SR, Pacheco ÉBAV, Visconte LLY. Revisão dos tratamentos químicos da fibra natural para mistura com poliolefinas. Quim Nova 2013; 36: 114-122. https://doi.org/10.1590/S0100-40422013000100021

[6] Beckermann GW, Pickering KL. Engineering and evaluation of hemp fibre reinforced polypropylene composites: Fibre treatment and matrix modification. Compos Part A Appl Sci Manuf 2008; 39: 979-988. https://doi.org/10.1016/j.compositesa.2008.03.010

[7] Lu JZ, Wu Q, Negulescu II. Wood-fiber/high-densitypolyethylene composites: Coupling agent performance. J Appl Polym Sci 2005; 96: 93-102. https://doi.org/10.1002/app.21410

[8] Poletto M. Maleated soybean oil as coupling agent in recycled polypropylene/wood flour composites: Mechanical, thermal, and morphological properties. J Thermoplast Compos Mater 2019; 32: 1056-1067. https://doi.org/10.1177/0892705718785707

[9] Leonel EC, De Faria EH, Pimentel RC, Nassar EJ, Ciuffi KJ, Dos Reis MJ, Calefi PS. Aproveitamento da glicerina proveniente da produção de biodiesel na obtenção de híbrido de caulinita para adsorção de Cr 3+. Quim Nova 2012; 35: 1407-1411. https://doi.org/10.1590/S0100-40422012000700022

[10] Lathi PS, Mattiasson B. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. Appl Catal B Environ 2007; 69: 207-212. https://doi.org/10.1016/j.apcatb.2006.06.016

[11] Yeh SK, Hsieh CC, Chang HC, Yen CCC, Chang YC. Synergistic effect of coupling agents and fiber treatments on mechanical properties and moisture absorption of

polypropylene-rice husk composites and their foam. Compos Part A Appl Sci Manuf 2015; 68: 313-322. https://doi.org/10.1016/j.compositesa.2014.10.019

[12] Younesi-Kordkheili H, Pizzi A. Ionic liquid-modified lignin as a bio-coupling agent for natural fiber-recycled polypropylene composites. Compos Part B Eng 2020; 181: 107587. https://doi.org/10.1016/j.compositesb.2019.107587

[13] Suota MJ, Simionatto EL, Scharf DR, Motta V, Moser D, Oliveira LB, Pedroso LR, Wisniewski Jr. A, Wiggers VR, Botton V, Meier HF. Avaliação de características de biodieseis de fontes alternativas submetidos a condições de armazenagem diferenciada. Quim Nova 2018; 41: 648-655. https://doi.org/10.21577/0100-4042.20170222

[14] Cantero G, Aitor A, Mugika F, Angel V, Mondragon I. Mechanical behavior of wood/polypropylene composites: effects of fibre treatments and ageing processes. J Reinf Plast Compos 2003; 22: 37-50. https://doi.org/10.1177/0731684403022001495

[15] Kajaks J, Kalnins K, Uzulis S, Matvejs J. Physical and Mechanical Properties of Composites Based on Polypropylene and Timber Industry Waste. Cent Eur J Eng 2014; 4: 385-390. https://doi.org/10.2478/s13531-013-0172-z

[16] Poletto M. Natural oils as coupling agents in recycled polypropylene wood flour composites: Mechanical, thermal and morphological properties. Polym Polym Compos 2020; 28: 443-450. https://doi.org/10.1177/0967391119886941

[17] Animpong MAB, Oduro WO, Koranteng J, Ampomah-Benefo K, Boafo-Mensah G, Akufo-Kumi K, Tottimeh GO, Amoah JY. Coupling effect of waste automotive engine oil in the preparation of wood reinforced LDPE plastic composites for panels. South African J Chem Eng 2017; 24: 55-61. https://doi.org/10.1016/j.sajce.2017.01.004

[18] Mohanty S, Nayak SK, Verma SK, Tripathy SS. Effect of MAPP as coupling agent on the performance of sisal-PP composites. J Reinf Plast Compos 2004; 23: 2047-2063. https://doi.org/10.1177/0731684404041711

[19] Bento LS, Silveira MRS, Santana MC. Estudo das propriedades termo-mecânicas de madeira plástica com diferentes especies de pó de madeira, in: Anais Do 10o Congresso Brasileiro de Polímeros 2009.

[20] Pang AL, Ismail H, Abu Bakar A. Eco-friendly coupling agenttreated kenaf/linear low-density polyethylene/poly (vinyl alcohol) composites. Iran Polym J English Ed 2018; 27: 87-96. https://doi.org/10.1007/s13726-017-0588-z

[21] Santos EF, Moresco M, Rosa SML, Nachtigall SMB. Extrusão de Compósitos de PP com Fibras Curtas de Coco: Efeito da Temperatura e Agentes de Acoplamento. Polímeros Ciência e Tecnol 2010; 20: 215-220. https://doi.org/10.1590/S0104-14282010005000036

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