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VANILLIC ACID: A NATURAL AROMATIC BUILDING BLOCK FOR THE DESIGN OF NEW COPOLYMERS WITH TUNABLE PROPERTIES

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INTRODUCTION

Today the interest of the scientific community towards bio-based polymers is notable increasing [1]. In particular, the development of aromatic bio-based polymers represents a great challenge to substitute traditional petro-derived materials [2] and to overcome limits in thermal and mechanical properties generally found in aliphatic bio-based materials.

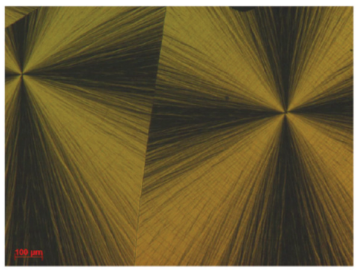
Inside the NoAW H2020 European project, the possibility of extracting aromatic building blocks from agricultural waste has been investigated and the attention has been focused on vanillic acid. It is present in a low amount in different natural resources and can be also derived from lignin, one of the main by-products of the chemical wood processing.

The aim of this study is therefore to investigate the possible exploitation of vanillic acid as a building block for the production of new series of copolymers with tunable properties according to their chemical structure.

RESULTS AND DISCUSSION

Vanillic acid is characterized by a low reactivity of the phenolic group and, then, a preliminary modification of the original chemical structure is necessary to increase the reactivity of the molecule towards polymerization. In this work, vanillic acid has been treated with ethylene carbonate: a polymer (PEV) characterized by Mn=5000, melting temperature of 264°C and a very high level of crystallinity has been obtained [1]. PEV crystallizes in Maltese cross spherulites, which can reach a remarkably large size and a high degree of perfection, as shown in Figure 1.

The polymer is characterized by a high brittleness and, thus, the copolymerization can be a very fruitful way to improve the mechanical performances of the material. The selected comonomer was the ω-pentadecalactone, a molecule derived by original source.



Figures 1 – Morphology of the PEV after isothermal crystallization at 216°C.

The syntheses have been carried out in one pot and two stages: different comonomer amounts have been used to prepare the new PEV-P15 copolymers, according to Figure 2.

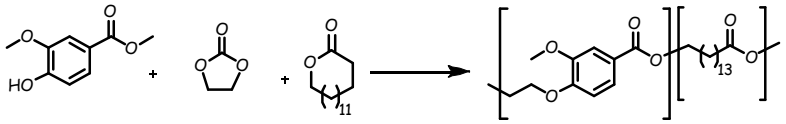


Figure 2 – Synthetic pathway to prepare the new PEV-P15 copolymers

In the final polymer, it is notable that the chemical structures of the two monomers are substantially different, the EV units being aromatic and stiff, whereas the P15 units bear a flexible long aliphatic chain.

The obtained copolymers are characterized by properties that gradually vary as a function of the composition, as reported in Table 1. In particular, the crystalline structure of PEV prevails at compositions varying from 100% PEV to 40/60 PEV-P15, with a melting temperature that decreases from 264 to 178°C. On the other hand, the 20/80 PEV-P15 copolymer is able to crystallize in the crystalline structure of P15, with a melting temperature of 82°C. The crystallinity is high in all the samples.

Accordingly, the processability of PEV is favored by the presence of the P15 co-units and the mechanical performances result improved.

Table 1 – Chemical composition and thermal properties of the PEV-P15 copolymers

sample	mol % PEV	mol % P15	Tc (°C)	ΔHc (J/g)	Tm (°C)	ΔHm (J/g)
PEV	100	-	165	65	262	86
PEV/P15 80/20	70	30	166	41	229	42
PEV/P15 60/40	60	40	104	27	184	27
PEV/P15 40/60	40	60	12 -103	4-29	33-178	11-32
PEV/P15 20/80	17	83	69	92	82	99
P15	-	100	79	85	95	93

Hence, the final properties of these new materials can be easily tuned by modifying the ratio between the two components. This approach constitutes a promising route for using vanillic acid as a platform of aliphatic-aromatic structures that can match the properties of petroleum-based traditional polyesters.

References

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