Relazione scientifica finale sul PROGRAMMA DI RICERCA STM 2015

"Ecocomposites based on biopolyesters and fillers from renewable resources"

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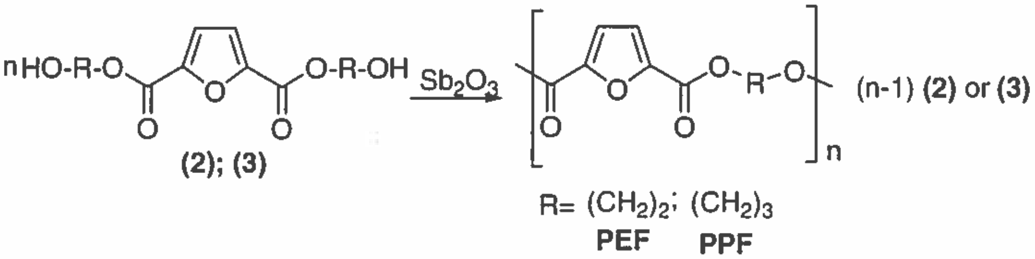
During the stay of Prof. Gandini in Genova a thorough discussion took place with the members of the CNR-ISMAC research group involved in the STM Program regarding the most salient aspects of the proposed collaboration with Grenoble INPG-Pagora research Lab related to the short program outlined in the STM 2015 documents.

The discussion above mentioned was fruitful sustained by a cycle of seminars (for a total of 20 hours) that Prof. Gandini gave at ISMAC Genova on *"Polymers and Composites from Renewable Resources"* and a seminar (of about 2 hours) at ISMAC Milano on *"Polymers from Renewable Resources: Macromolecular Materials for the XXI Century"*. Given the great and global interest of the proposed topics and the internationally recognized scientific excellence of Prof. Gandini, said seminars gathered a good numbers of researchers, post-docs and students, not only from ISMAC, but also from other CNR Institutes, Research Institutions and Universities.

The topics selected to be carried forward in collaboration with INPG-Pagora of Grenoble and involving various researchers from ISMAC Genova and Milano, as well as some others from University of Genova, were selected also on the basis of the expertise on polyester synthesis[1] and development of ecocomposite materials[2] of the Italian counterpart involved in this STM program, as well as of previous experience of collaboration with Prof. Gandini.[3]

Following are the relevant topics which were selected.

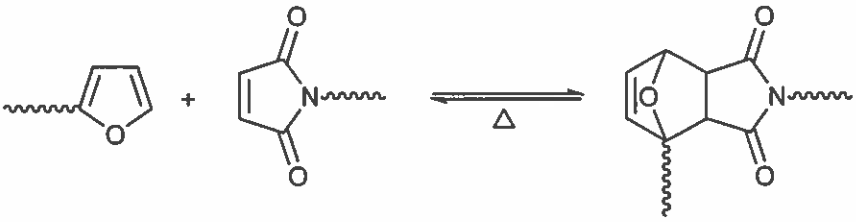
1- Given the recent upsurge of interest from both academia and industry on polyesters incorporating the 2,5-furandicarboxylate (since the corresponding diacid has now become a biobased chemical commodity derived from hydroxymethylfuraldehyde), and particularly PEF (the member prepared from ethylene glycol, representing the biobased counterpart of PET),[4] it was remarked that this relatively abundant literature did not reflect any study on the preparation of composite materials based on these polyesters.



All indications are that this new family of polymers based for most part on renewable resources will reach technological applications within a short period of time (as an example, the Coca-Cola Company has launched a joint venture to produce plastic bottles for soft drinks made of PEF). It seems therefore quite profitable to consider the possibility of carrying out preliminary research within the present STM program based on the elaboration and characterization of composite materials in which the matrix would be a choice of the furan polyesters, as such or in conjunction with other biobased monomers like lactic and succinic acid, and the reinforcing elements would include renewable resources, such as nanocellulose fibers (both in the form of nanofibrillated strands and nanocrystal wiskers), wool fibers, lignin powder, and chitin nanofibers, as well as starch nanocrystals. The fact that all these fillers are characterized by a high polarity, should facilitate their bulk incorporation into the matrices, particularly in the case of polyesters with relatively short methylene sequences. The interest of this approach stems, first and foremost, from the possibility of improving the mechanical properties of the polyesters, but also from similar enhancement related to both barrier and thermal performances. Concerning the respective contribution of the two laboratories, given the specificity of their research priorities within the general area of biopolymers, the role of CNR-ISMAC would concentrate on the optimized synthesis of the polyesters (including copolyesters) and their thorough characterization, but also to providing wool and lignin fillers and complement the assessment of the physical properties of the ensuing composites, e.g. morphological and morphometric observations and pyrolysis tests. As for the Pagora laboratory, its role would mostly concentrate on the elaboration and characterization of the composites and the furnishing of the polysaccharide nanofillers. It is obvious that this separation of research activities does not imply a sharp divide, since many of the most specific aspects associated with all these operations would be often shared and/or compared in terms of achieving the most meaningful results.

2- Whereas, as mentioned in the previous point, furan polyesters are witnessing remarkable surge of interest, the corresponding polyamides have received very little attention as regards the use of 2,5-furandicarboxylic acid as the comonomer, except a study on Kevlar-like material.[5] Indeed, much work had been conducted on furan polyamides based on the use of a difurandicarboxylic acid[6] when the availability of the former diacid was very poor. This surprising lack of studies opens the way to the intervention of the two laboratories aimed at filling the gap, because there is no obvious reason that would dissuade researchers from tackling this topic. Although aliphatic-aromatic polyamides do not represent materials as commercially important as the corresponding polyesters, the possibility of their furan counterparts displaying original properties and hence potential applications cannot be excluded. Various diamines would be studied including both aliphatic and cycloaliphatic structures. The approach to this second topic would proceed exactly with the same construct as discussed above for the polyesters, with the important difference that we would be dealing here with almost entirely new materials and composites.

3- The furan heterocycle displays the typical dienic character encountered in the click Diels-Alder (DA) reaction and a considerable amount of research has been published in the last decade concerning the synthesis and/or chemical modification of polymers bearing this ring using maleimide moieties as dienophile complements.[4,7]



This work includes typical linear and non-linear polycondensations involving monomers with the two complementary DA functions and crosslinking operations using polymers with the same pendant functions. The interest of this approach resides on the unique features related to the thermal reversibility of the adduct formation between furan and maleimide within a reasonable range of temperatures (forward reaction prevailing up to about 60°C and backward regeneration from about 110°C). In other words it becomes readily possible to recycle any of these macromolecular structures at the end of their life cycle, as well as to prepare self-mending materials.[4,7] In the present context, the presence of the furan moiety along both the polyester and polyamide chains provides a straightforward possibility to prepare crosslinked materials bearing this important thermal reversibility by simply using a bismaleimide as the bridging molecule. This complementary study will therefore be carried out on both matrices and composites discussed above in view of highlighting the important complementary green connotation associated with polymer recycling, here through decrosslinking. The fact of preparing and characterizing polyester and polyamide networks represents an additional aspect to the overall research program, since such materials are not commonly studied.

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