Synthesis and characterization of new fully bio-based poly(acylhydrazone) vanillin vitrimers

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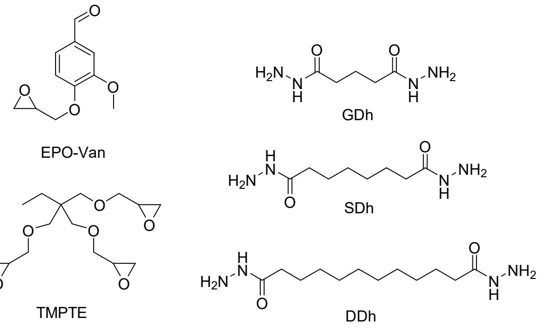
In the present century the need to recycle thermosets to reach a sustainable environment has led a huge number of researchers to develop new reshapable networked polymers. In this scenario, vitrimers, materials able to change their topology via exchange of the covalent bonds, usually activated by thermal stimulus, are attracting growing interest. They can potentially be reshaped, self-welded, repaired and recycled at high temperature without appreciable degradation [1]. These materials behave as thermosets at room temperature but becomes malleable at high temperature when the exchange reaction occurs.

In 2004, Lehn and co-workers reported the ability of acylhydrazone dynamic bonds to produce dynamers [2]. They stated that the reversibility of these linear polymers relies on the imine group of the acylhydrazone while the amide group provides hydrogen bonding like in polyamides. They not only successfully reported the synthesis of different poly(acylhydrazone)s by mixing different dihydrazides with dialdehydes but also the exchangeable behaviour of these bonds upon heating by combining the synthesized poly(acylhydrazone)s with structurally different aldehydes or dihydrazides. However, the interchange reaction between acylhydrazones in thermosets by imine metathesis has never been reported. In our study, it has been confirmed by the use of model compounds and GC analysis. This process does not require any excess of dihydrazide or the presence of any catalyst.

In recent years, products derived from renewable resources have attracted a huge interest in materials science to reduce the use of petrochemical compounds as well as to find greener synthetic routes to avoid the depletion of fossil resources. Vanillin is very interesting as a starting compound due to its phenolic and aldehyde groups that can be further modified to get the suitable functionality. Moreover, the rigid structure due to the aromatic ring provides high thermal and mechanical properties to the obtained materials. In this presentation we will describe the synthesis and characterization of a series of new bio-based poly(acylhydrazone) vitrimers. Three different dihydrazides derived from biobased glutaric, suberic and dodecandioic acids were obtained in high yields via two-step synthesis as well as the glycidyl derivate of vanillin (EPO-Van).



Scheme 1. Monomers used in the preparation of poly(acylhydrazone) vitrimers

Dihydrazides were prepared by Fischer esterification of dicarboxylic acids and further reaction with hydrazine hydrate. Dihydrazides and EPO-Van monomers were condensed to get vitrimers containing acylhydrazone dynamic covalent bonds. To increase flexibility trimethylolpropane triglycidyl ether (TMPTE) was added. Since EPO-Van has epoxy and aldehyde reactive groups, in this curing system, before epoxy-amine reaction, aldehydes react with -NH_2 of dihydrazides due to the latent character of these compounds as epoxy curing agents [3]. The dihydrazides were added in stoichiometric proportions, with an Epo-Van/TMPTE molar relation 3:1.

Cross-linked materials were successfully obtained as thin red films with high transparency. They were characterized by FTIR to confirm the complete reaction and then, they were characterized by TGA and DMTA. The materials lose 1% of weight at temperatures around 220 °C and have T_gs of 134, 113 and 100 °C for the derivatives of GDH, SDH and DDH, respectively.

To confirm the vitrimeric nature of the networked poly(acylhydrazone)s, the time and temperature dependent relaxation behaviour was investigated. The stress relaxation curves reveal that these materials are capable to rapidly relax stress, by reaching the reference relaxation value of 63% ($\sigma/\sigma_0 = 0.37$) in less than one minute at 185 °C for poly(GDH), in 1.5 min at 170 °C for poly(SDH) and in almost 3 min for poly(DDH) at 160 °C. From these experiments, it can also be calculated the time for almost total relaxation of the networks, which is reached in nearly 3.5, 5 and 10 min, respectively at 190 °C (see Table 1).

Table 1. Relaxation times at 190 °C, topology freezing temperature and activation energy for poly(acylhydrazone)s

Material	$\tau_{37\%}$ (s)	$\tau_{100\%}$ (s)	T_v (°C)	E_a (kJ/mol)	*lnA* (s)
poly(GDH)	43	200	25.2	52.5	9.90
poly(SDH)	46	300	36.8	61.4	12.45
poly(DDH)	48	600	61.7	77.2	16.20

As we can see in the table, the time to reach the relaxed state of $\sigma/\sigma_0 = 0.37$ at 190 °C slightly increases (from 43 to 48 s) on increasing the chain length of the dihydrazide. The material becomes more flexible, but the distance between acylhydrazone moieties increases and their proportion decreases, which difficult the imine metathesis.

For these materials, the T_vs calculated are much lower than their T_gs but this is a hypothetical value, since below T_g, no exchange reactions can occur because of the lack of the network's mobility. Once T_g is overpassed the exchange reaction proceeds very fast.

Their recyclability was also investigated. The temperature of the recycling process was set to 190 °C to avoid degradation. The DMTA curves of the original and recycled materials were similar, proving the possibility of recycling.

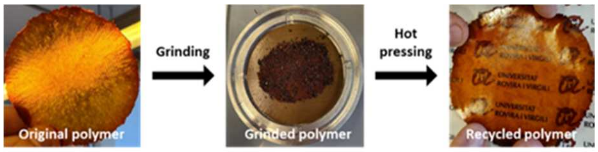


Figure 1. Photographs of the original, grinded and recycled samples of the poly(acylhydrazone)s.

To confirm the thermosetting nature of these materials they were maintained at reflux for 12 h in dichlorobenzene and above a 98.5 % in weight was recovered. However, on treating them with a 2M HCl solution/THF 8:2 mixture for 24 h at 70 °C, the starting dicarboxylic acids could be recovered, indicating that these thermosets can be hydrolysed in acidic conditions.

Self-healing characteristics were also analysed and we could prove that the longer the dihydrazide chain length the faster the self-healing ability.

Acknowledgments

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