Dynamic semicrystalline networks of polypropylene with thiol-anhydride exchangeable crosslinks

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ABSTRACT: Thermoplastic polyolefins (TPOs) crosslinked by dynamic covalent bonds (xTPOs) have the potential to be the most utilized class of polymer in the world, with applications ranging from household and automotive to biomedical devices and additive manufacturing. xTPO combines the benefits of thermoplastics and thermosets in a “single material”, and potentially avoids their shortcomings. Here we describe a new two-stage reaction extrusion strategy of TPOs with a backbone consisting of inert C-C bonds (polypropylene, PP), and thiol-anhydride, to dynamically crosslink PP through thiol-thioester bond exchange. The degree of PP crosslinking determines the rubber plateau modulus above the melting point of the plastic: the modulus at 200°C increases from zero in the melt to 23 kPa at 6% crosslinking, to 60 kPa at 20%, to 105 kPa at 40%. The overall mechanical strength of the solid xTPO plastic is 25% higher compared to the original PP, and the gel fraction of xTPO reaches 55%. Finally, we demonstrate that the crosslinked xTPO material is readily re-processable (re-cycled, re-molded, re-welded, and 3D printed).

Keywords: thermoplastic, polypropylene, vitrimer, thiol-anhydride, thiol-thioester, plastic recycling, 3D printing.

Introduction:

Thermoplastic polyolefins (TPOs) are ubiquitous in modern society. Their daily use ranges from automotive and biomedical to household applications.1-2 The production of TPO is rapidly growing and accounts for more than a half of the global plastic industry, with more than 180 million tons per annum.3 TPOs are low-cost, high-volume, re-processable, lightweight, tough, and durable materials, used in countless end-user settings.4-5 However, TPOs have many undesirable properties, such as susceptibility to creep and loss of mechanical integrity in harsh environments, such as at high temperature, in solvents, or in vivo. One of the most successful attempts to overcome TPO drawbacks is chemical crosslinking and transformation into thermosets.6-9 Crosslinked thermosets are insoluble, and used in applications demanding higher strength.9-10 However, crosslinking TPO plastics, such as high density polyethylene (HDPE) or polypropylene (PP) have challenges of their own. First, the traditional crosslinking methods rely on uncontrollable reaction methods, such as radical reaction extrusion (e.g. through peroxide7 or silane chemistry11), or the irradiation crosslinking.12 Such methods produce crosslinked polymers with random and often inhomogeneous crosslinking density. Secondly, these reaction methods require high energy input; they need to be initiated in the final mold because after crosslinking there would be no flow and injection molding possible. Critically, thermosets cannot be recycled, which is a major drawback in the modern sustainable society.13

Despite drawbacks, crosslinked TPO plastics (xTPOs) are a very important class of thermoset polymers, especially in the infrastructure industry or in biomedical devices. For example, crosslinked HDPE implants can totally eliminate osteolysis for over 10 years after hip arthroplasty.14 However, many studies have demonstrated the variation in the mechanical properties (modulus, yield stress, fatigue) of the crosslinked HDPE, directly linked to inhomogeneous crosslinking density.15-17,18 Therefore, there is a great demand for new reaction strategy to ensure the controlled homogeneous crosslinking of TPOs and allow for their re-processing post crosslinking.

A new class of crosslinked polymer networks has emerged recently to achieve an optimal balance between thermoplastic and thermoset benefits, generically named as ‘vitrimers’.19 Vitrimers, or more broadly – polymers crosslinked by dynamic covalent bonds, are chemically crosslinked polymer networks, insoluble in solvents. However, unlike thermosets, they can plastically flow under stress at high temperatures, allowing their re-processing and making a true multi-use polymer. Vitrimer or vitri-mer-like dynamic networks have proven to be useful
across wide range of proposed applications: re-processing/re-cycling thermosets,\textsuperscript{19,20} self-healing plastics,\textsuperscript{21} 3D printing,\textsuperscript{22} or programmed liquid crystalline elastomer actuators.\textsuperscript{23} In the past few years, extensive studies have described the fundamental physics and chemistry of vitrimer materials; a summary of these studies can be found in recent reviews.\textsuperscript{24-28}

Recently, xTPOs crosslinked by dynamic covalent bonds have been introduced to the field of vitrimers. Several reaction strategies, such as dioxaborolane metathesis,\textsuperscript{29,30} transesterification,\textsuperscript{31} silyl ether exchange,\textsuperscript{32} vinyllogous urethane exchange\textsuperscript{33} have been employed to produce dynamically adaptable networks from commodity TPOs. These reaction strategies have produced xTPO plastics with excellent mechanical properties, readily re-processable and recyclable, and in some cases having a shape-memory effect. Remarkably, these improvements of the mechanical properties of TPOs were achieved by adding a very small amount of crosslinking additive (less than 10 wt\%) to the initial thermoplastic. However, there has not been a systematic study of the effect of the amount of crosslinking, which ultimately influences the crystalline structure.

Here, we introduce a new reaction strategy to produce xTPO vitrimers, based on two-stage reaction extrusion of TPO, with the backbone consisting of inert C-C bonds, and thiol-anhydride to dynamically crosslink these polymer chains through thiol-thioester dynamic exchange. The first reaction stage is to functionalize TPO (e.g. PP) with maleic anhydride (MA) via radical reaction in a melt compounder. Through varying the amount of grafted MA, the crosslinking density can be controlled by reacting MA with multifunctional thiol during the second stage of the process to produce exchangeable thioester bonds.

**Experimental details:**

**Materials.** PP 3950 (melt flow rate 34 g/10 min) was donated by INEOS Olefins & Polymers USA. The relation between the melt flow rate and the molecular weight (1/MFR = GMw\textsuperscript{\alpha}, where the empirical constant G = 2×10\textsuperscript{-20} and x = 3.40 for PP) gives the estimate for its molecular weight Mw=220,400. Maleic anhydride (MA), dicumyl peroxide (DCP), pentaerythritol tetraakis (3-mercaptopropionate) (PETMP), 1,5,7-Triazabicyclo[4,4,0]dec-5-ene (TBD) and xylene were procured from Sigma Aldrich (Merck).

**Reactive Extrusion.** Thermoplastic polyolefin, TPO (such as our PP 3950) was functionalized by MA in a melt, in a 7 cm\textsuperscript{3} conical twin-screw compounder HAAKE MiniLab 3 (Thermofisher) with an integrated recirculation channel under continuous nitrogen flow. Table 1 gives the weights of each component, calculated proportionally, to achieve the same mass of the combined product in the compounder chamber (5g). PP was dried under vacuum at 80 °C for 6 h. The required amount of PP, MA (6, 20, or 40 wt\% of PP) and the peroxide initiator DCP (0.5 wt\% of PP) were introduced in the compounder through the hopper, while the rotor speed was set at 100 rpm at 180 °C. After 10 min, a small portion of the grafted MA-g-PP was extruded for ex-situ analysis of the reaction completion. Subsequently, varied amount of 4-functional thiol crosslinker (PETMP) (the molar ratio of PETM to MA is 1.25:1) and thio-transesterification catalyst, TBD (5 mol\% of thiol) was introduced into the compounder initially keeping the rotor speed at 100 rpm for an additional 10 min while maintaining the temperature of 180 °C. The axial force and the chamber pressure were followed to qualitatively understand the evolution of effective viscosity during the crosslinking reaction in the melt. The fully crosslinked xTPO network continued to be recirculated in the compounder via the plastic flow under shear stress, due to the active bond exchange.

**Gel fraction.** The gel content in the crosslinked network was measured by solvent extraction method. Single piece of sample weighing 200–500 mg was immersed in hot xylene (at 120 °C) for 24 hours, while frequently exchanging with fresh solvent. Subsequently, the insoluble part was dried and the weight measured. The gel fraction was determined as:

\[
gel content = \frac{\text{final weight}}{\text{initial weight}} \times 100 \tag{1}
\]

**Dynamic Mechanical Analysis (DMA).** DMA Q850 (TA Instrument) was employed for the measurement of thermomechanical properties. Temperature ramp of 3 °C min\textsuperscript{-1} was implemented in tensile mode on rectangular specimen with dimension =15 mm × 5 mm × 0.9 mm, at constant low frequency of \(\omega = 1\) Hz with 0.1% strain, scanning the temperatures from ambient semicrystalline state to 250-300 °C (well above the melting point).

**Differential scanning calorimetry (DSC).** Melting and crystallization transitions of neat thermoplastic and the crosslinked networks were measured in DSC4000 (Perkin Elmer). Typically, 5-10 mg of samples were vacuum dried at 80 °C for 6 h before running the temperature scan in DSC. Similar temperature profile was followed for all the samples. In the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Mass (g) & PP & MA & DCP & PETMP & TBD \\
\hline
PP 3950 & 5 & 0 & 0 & 0 & 0 \\
\hline
thiol6\% & 4.3 & 0.26 & 0.02 & 0.40 & 0.04 \\
\hline
thiol20\% & 3 & 0.65 & 0.02 & 1.00 & 0.10 \\
\hline
thiol40\% & 2.4 & 0.96 & 0.01 & 1.49 & 0.14 \\
\hline
\end{tabular}
\caption{Composition of the vitrimers, for the total final product mass of 5 g in the compounder chamber.}
\end{table}
first cycle of the temperature scan the sample was heated to 210 °C and kept isothermally for 5 min to erase any thermal history. The crystallization temperature was determined from the exothermic peak while cooling the sample to 30 °C. A second heating cycle was performed to determine melting temperature from the endothermic peak. In all the temperature scanning steps, the 10 °C min⁻¹ heating/cooling rate was used under nitrogen flow of 50 ml min⁻¹. Fraction of crystallinity was calculated by taking the ration of latent heat against the theoretical value for the fully crystalline PP: \( \Delta H_m^0 \) is 207.0 J/g.33

Mechanical experiments: Stress-to-failure and shear lab testing were done using Tinius Olen mechanical tester with 1 KN load cell. Samples were tested according to the ASTM guidelines, stress-to-failure, (ASTM D638) and lap shear stress, (ASTM D5868). All samples were tested at room temperature with displacement rate of 0.5 m/s.

3D Printing via fused filament fabrication (FFF). The 3D printing demonstration was done using Engine HR, Hyrel3D). Nothing is unusual in FFF 3D printing with thermoplastics, the challenge here is to achieve the same results with the insoluble fully crosslinked xTPO utilizing the bond exchange. Comparing with the original PP 3950, the 6% crosslinked xTPO was measured to have the melt-flow rate just ca. 4 g/10 min. Nevertheless, the continuous round filament (2.8mm in diameter) was extruded from the compounder and fitted into the 3D printer. The filament then initially connected to a print head (KR1 250, Hyrel3D), which was then loaded into a 3D printing system to be printed at 220°C, after optimizing the pressure, and speed. The control was the same FFF printing with the standard acrylonitrile butadiene styrene (ABS) thermoplastic.

Results and discussion:

In this paper, we explore the bond exchange mechanism between thioester and thiol groups, see Scheme 1, after using thiol-anhydride crosslinking reaction, see Scheme 2. In most cases in the literature,34 the method of choice to functionalize the polyethylene chains is by grafting maleic anhydride (MA) units.35-37 MA is a bi-functional monomer, widely used in the industry - mainly to produce polyesters.38 Once the reacting acidic anhydride groups are grafted to PP (Scheme 2), there are a number of reaction strategies that can be used to crosslink such functionalized polymers. In addition to the quoted literature,39 in our recent work we used bi-functional epoxy as a crosslinker:40 on reacting, the epoxy leaves the hydroxyl unit needed for subsequent transesterification. Although the epoxy-based transesterification produces crosslinking with dynamic bonds, controlling the bond exchange conditions (e.g. the amount and type of catalyst, temperature, pressure) can be challenging. As a result, epoxy-

\[
\text{O} - \text{S} \rightarrow \text{HS} - \text{C} \rightarrow \text{O} - \text{S} + \text{HS} - \text{C} 
\]

Scheme 1. Thiol-thioester bond exchange

based transesterification has strict processing condition window, otherwise this can produce crosslinked polymer with high viscosity, which ultimately blocks the extruder.

There is an important point to comment on: it is well-known that by adding a peroxide initiator, aliphatic chains (like PE and PP) can generate radicals off their -CH groups, and bond different chains together into a permanent network. In the case of MA functionalization, the peroxide creates the radical off the vinyl bond (C=C) with a much higher rate, and one can safely assume that it is MA grafting that takes place (rather than chains bonding). However, one has to be careful: adding too much peroxide will still leave a lot of chain crosslinking in addition to MA-grafting, which one has to avoid. This determines the optimal (low) concentration of DCP in our process.

We have to mention a recent paper by Wang et al.40 It is very desirable to have a one-pot reaction of

\[
\text{pp} + \text{MA} \rightarrow \text{PP-grafted-MA} 
\]

Scheme 2. The material synthesis sequence: (a) grafting of MA on PP, and (b) the reaction with 4-functional thiol crosslinker. The stoichiometric ration of 1.25 thiol bonds per 1 anhydride makes the average network topology (c), with one free thiol group to facilitate bond exchange.
functionalization and crosslinking of TPO, which is what this paper claims, by merely mixing the MA, DCP and the crosslinking groups. We must report that in many attempts we failed to achieve any similar result, which we understand by the strongly reduced reactivity of MA after its ring opens after reacting with the crosslinker first. If one needs a one-pot reaction, this has to follow the protocol of Maaz et al.\textsuperscript{41} by using a pre-made exchangeable crosslinker with e.g. maleimide ring to graft on the TPO chains. Here we choose to work with thiol reacting groups, relying on the robust and fast click chemistry of thiol-thioesters.\textsuperscript{42} A recent study by Bowman et al.\textsuperscript{43} suggested that increasing the amount of thiol functional groups lead to an increase in the rate of the bond exchange between thiol and thioester groups. That study pointed out that a polymer network with 25\% (functional mol) excess of thiol group seems to have the optimum rate of bond exchange. It also reports the relatively low activation energy of the thiol-thioester bond exchange: $E_a=100-115$ kJ/mol, which suggests a fast exchange above the melting temperature of PP. We therefore choose the concentration of reacting bonds with a slight excess of thiols over the MA (1.25:1) to enable thiol-thioester exchange with free dangling thiol groups. In our case, with the 4-functional thiol PETMP, this means that on average three out of four ‘arms’ are linking the network, while the remaining ‘free arm’ with -SH terminal is facilitating the access to bond exchange.

Table 2. Melting and crystallization temperatures, enthalpy, and the degree of crystallinity, as measured from differential scanning calorimetry (Figure 2) at heating rate of $10^\circ$/min. The last column also gives the gel fraction of the networks.

|                  | $T_m$ (°C) | $T_c$ (°C) | $\Delta H$ (J/g) | $\chi_c$ | Gel fraction |
|------------------|------------|------------|-----------------|----------|--------------|
| PP 3950          | 155        | 130        | 83.2            | 40\%     | 0            |
| thiol6\%         | 149        | 126        | 77.2            | 37\%     | 43\%         |
| thiol20\%        | 156        | 124        | 66.4            | 32\%     | 44\%         |
| thiol40\%        | 156        | 126        | 57.5            | 28\%     | 55\%         |

Figure 1. The recirculating reaction-extrusion illustrated by the compounder pressure evolution over time. After loading the thermoplastic PP, and reaching the steady-state mixing at 180°C, the MA+DCP initiator is added to the melt at $t=0$, and the grafting takes place, the reaction completed within 10 min. At $t=10$ min the PETMP+TBD catalyst is added to the melt, and the crosslinking causes a sharp rise in viscosity, until the bond exchange stabilizes the plastic deformation of the dynamic network.

Figure 2. Differential calorimetry data illustrating the melting and the crystallization transitions of the materials, indicating that the crystallization is not significantly affected by network crosslinking.

For practical applications, it is vital to have a solvent-free reaction process that is scalable. Therefore, we use a reactive process in a melt compounder to impart dynamic crosslinking onto an originally inert PP, and study its properties. This method has broad applicability for different polyolefins, polyaacrylates, and polystyrene.\textsuperscript{44} We have carried out the MA grafting in the presence of DCP initiator, and the subsequent crosslinking of MA-g-PP with thiol in the presence of TBD Catalyst, in the twin-screw extruder with recirculating channel, at 180 °C and 100 rpm, with total residence time in the compoudner of 22-25 min. To understand the processing conditions, including the optimal residence time of the reactive mixing, the process pressure was monitored, see Figure 1. The pressure measured by the sensor at the base of recirculating channel of the compounder is closely related to the shear stress applied to the mixture, which in turn has a direct relation to the effective viscosity of the plastically deformed material, since we maintained a fixed shear rate. One has to make a short comment here about the effective viscosity of a plastic solid (which is what the cross-linked vitrimer above its elastic-plastic transition...
is). This viscosity is often mentioned in the literature\(^\text{19}\), and a misunderstanding may arise—confusing the plastic flow of a vitrimer with Newtonian flow of a melt. The bond-exchange enables the plastic flow under stress, which may superficially appear similar to the linear relation between stress and strain rate, in a certain regime of applied stress and exchange rate. However, generically the plastic deformation is a different process to dissipative viscous flow. This paper is not the place for a detailed discussion of this issue, but we wished to highlight this distinction and the terminology.

The small-molecule functionalization, such as grafting MA functional groups on PP chains, does not change the overall melt viscosity. In fact, Figure 1, illustrating the pressure in the compounder that is proportional to the viscosity of the melt, shows that there is even a small decrease for the low MA-content melt, presumably because of lower entanglement of MA-g-PP chains. At the next reaction stage, the 4-functional PETMP thiol and TBD catalyst are introduced for crosslinking. Upon the addition of PETMP and TBD there is an initial drop in viscosity due to the liquid PETMP diluting the melt. The rapid rise and oscillations in the effective viscosity as the crosslinking progresses are due to the gradual mixing and homogenization of the system by the shear stress imposed by the twin-screw system. We do not observe this oscillation behavior with the thiol6\% system because the overall amount of the additives is low (see Table 1). After the compounding pressure reaches a stable plateau, determined by the crosslinking density and the rate of the bond exchange that determines the plastic flow at given temperature and stress, the extrusion of the fully crosslinked vitrimer is allowed: into a free filament, or into an injection mold.

Any multifunctional thiol or amine-based catalyst can be used in this crosslinking process. However, one should pay close attention to volatility of the desire thiol or catalyst. Herein, we have selected PETMP and TBD as an ideal crosslinker and catalyst due to their stability in a high pressure and elevated temperature environment of the compounder.

One of the intriguing aspects of crosslinking semicrystalline polymers like linear polyolefins is that the side chain functionalization does not strongly affect the crystallization transition, or the degree of crystallinity presumably because the crosslinks are able to concentrate in the amorphous regions.\(^\text{45}\) Figure 2 shows the differential scanning calorimetry (DCS) data of melting and crystallization in our networks (compared with the original neat PP 3950). Clearly adding even a substantial fraction of thiol crosslinkers does not significantly change the melting (\(T_m\)), or the crystallization temperature (\(T_c\)), see Table 2. The crystallinity fraction, \(\chi_c\), was calculated using the equation below:\(\text{46}\)

\[
\chi_c = \left(\frac{\Delta H_m}{\Delta H_0}\right) \cdot 100\%
\]

where \(\Delta H_m\) is the heat of fusion calculated from the area under the melting endotherm (the values listed in Table 2), and \(\Delta H_0 = 207\) J/g is the heat of fusion of 100\% crystalline polymer.\(^\text{33}\) In this way, we determined crystallinity fraction \(\chi_c\) given in Table 2. It is expected that the degree of crystallinity falls with the addition of flexible thiol crosslinkers, especially at high concentrations. Yet even at 40\% of MA and thiol in the system, almost a third of the material remains crystalline, which maintains exceptionally good mechanical properties of xTPO vitrimers at ambient temperatures.

The gel fraction of the crosslinked networks was measured by the standard swelling method (using xylene as solvent), and the measured values also listed in Table 2. These, and all other values in this

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**Figure 3.** Dynamic-mechanical characterization, in tensile mode at fixed strain of 0.1\% and frequency of 1 Hz, with a temperature ramp of 3\(^\circ\)/min.

**Figure 4.** (a) Tensile strength (ASTM D638), at 20\(^\circ\)C. The yield stress and the breaking stress in the crosslinked vitrimers are all higher than in the original PP3950. Vitrimer networks do not survive as large plastic deformation as the base PP, but all reach a high strain to break: photos (b, c).
table have been measured 3 times, with the error not exceeding 10% of each value. The increase in gel fraction at higher crosslinking density is expected, but the 43% gel fraction of the weakly crosslinked thiol6% system is already a very high level of network integrity. Gel fraction results are consistent with previous data obtained by several research groups.20,41

Figure 3 illustrates the dynamic-mechanical properties of these materials, in the oscillating tensile mode at a strain of 0.1% and constant frequency of 1 Hz. Unexpectedly, all of the materials, as well as the base PP thermoplastic, have approximately the same mechanical response below their melting point $T_m$, with the linear storage modulus of several hundred MPa at ambient temperature. Initially, we expected a decrease in storage modulus below $T_m$ due to insertion of the additional crosslinking bonds in the backbone of PP (that is, insertion of additional crosslinking bonds “should” lead to adverse disruption in crystalline structure).39 However, this was not the case, at least with the addition of up to 40 wt% of crosslinking additives. The results suggested that even with an addition of 40 wt% crosslinking, there were long enough polymer chains between the crosslinks that are able to form a stable and strong poly-crystalline structure. Thermoplastic PP simply melts at $T_m$, but all crosslinked vitrimers demonstrate a clear rubber plateau. The strength of crosslinked network can be related to the rubber plateau modulus, and has been the focus of recent literature.41 We find the dynamic modulus increasing in proportion to the crosslinking density: thiol6% had $E' = 23$ kPa at 200 °C, thiol20% $E' = 60$ kPa, and thiol40% $E' = 105$ kPa. The 40%-thiol vitrimer is expected to have a much higher rate of bond exchange, and indeed we start to see the rapid drop in the dynamic rubber modulus even at 1 Hz, due to the elastic-plastic transition when the temperature is raised above 230 °C. This is a dynamic effect, with competing rates of bond exchange and the imposed oscillating strain, so at the higher frequency of oscillation none of the materials would show any flow while at a much lower frequency (or at static creep) all vitrimers would flow plastically under stress, to different degrees, above $T_m$.

It comes as a positive surprise that our dynamic xTPO networks show a higher tensile strength than the original PP, while retaining a very significant ductility. Figure 4 illustrates this point showing representative curves of stress to break (ASTM D638 test), comparing with the original PP 3950. It is also unexpected that the tensile strength of xTPOs does not seem to depend on their crosslinking density. However, if we consider the DMA data in Figure 3, it is clear that the properties of xTPO in the solid semicrystalline state are essentially the same. Apparently, all we add by crosslinking the PP is a higher barrier for crystallite re-arrangement, reflected in the slightly higher yield stress – but the crosslinked network is not able to stretch to such a high tensile deformation as the original PP.

Since the vitrimer networks possess exchangeable bonds, their welding at high temperature becomes a practically relevant process. The ordinary PP thermoplastic does not bond in the solid state, and simply melts and flows above $T_m$ (Table 2). But crosslinked vitrimers retain their crosslinked shape after their crystallinity melts, and when the surface temperature is high, the two such surfaces covalently bond together under hand pressure due to the bond exchange between the two parts. We used surface flashing temperature of 210°C for 15 seconds, and then holding two surfaces together for 30 seconds, till the contact temperature drops below $T_c$. The welded plates were tested for lap shear stress (ASTM D5868), demonstrating strong bonding (Figure 5). In many cases, the substrate failure occurred instead of de-bonding, as illustrated in Figure 5c.

Having unambiguously demonstrated the crosslinked nature of our materials, and their robust mechanical properties above melting point, we then turn to exploit the dynamic nature of these vitrimer networks. The most important feature of the vitrimer is the remolding above its elastic-plastic transition. The flow in the molten state is not dissimilar to the original thermoplastic, but radically different from a permanently crosslinked thermoset. The associative bond exchange allows the material to flow.

Figure 6. 3D printing using the FFF method, comparing the standard thermoplastic, ABS filament (left) and the vitrimer with 6% thiol crosslinking (right). Scale bar =1 cm.
plastically without risking the bond cleavage (in simple terms: fracturing of the network), by altering the internal network topology under stress, while preserving the total number of crosslinks.\textsuperscript{47,48} This is demonstrated in the fused filament fabrication (FFF) 3D printing from a plastic filament, presented in Figure 6. To test the 3D printing capability, we extruded a continuous round vitrimer filament of 2.8mm diameter, which was then used in a standard FFF process in a commercial 3D printer, replacing the standard thermoplastic filament. We had to adjust the temperature and the rate of printing to reflect the much lower melt-flow rate of xTPO, but the results in Figure 6 show no difference in the printed product compared with the standard thermoplastic printing (e.g. ABS). The only difference is that the standard thermoplastic melts above $T_m$, while the vitrimer remains rubber elastic and retains its shape, so the printed object remains intact after annealing. Secondly, we tested the molding capacity: small pieces of the PP-vitrimer were fused to make a single large sample with the aid of hydraulic press at 200 °C and 2MPa for 10-20 min, and the standard injection molding was used to press a characteristic dog-bone shape shown in Figure 4b. We have verified that several re-molding cycles did not significantly affect the material properties. Despite holding permanent crosslinks, this re-molding ability of a vitrimer is in high demand since reprocessing is increasingly a prerequisite for the sustainable and affordable technologies and additive manufacturing.

Conclusions:

In summary, here we demonstrated another vitrimer system based on the commodity structural thermoplastics (PP in our case), which are ubiquitous in industry but notorious in their resistance to bonding, or any form of additive manufacturing. Also, in spite of their thermal stability, thermoplastic polyolefins can only be used below their melting temperature – and since that melting temperature is similar for different plastics – they require careful separation and purification for any meaningful recycling. The crosslinked xTPO networks allow the mechanical shape integrity high above $T_m$, and don’t mix on heating, yet due to the dynamic bond exchange they can be re-processed in the same way as the original thermoplastics. Here we introduced a different type of bond exchange: thio-ester, which offers different properties and capabilities than a more standard transesterification, and examined the role of crosslinking density, utilizing the 4-functional topology of the thiol crosslinker. It is clear that different densities of crosslinking offer different material properties, e.g. higher rubber modus above $T_m$, higher temperature of the elastic-plastic transition, or higher rate of plastic flow. The thiol6% is particularly attractive because of the low fraction of additives (and so the cost in industrial setting), while retaining the key vitrimer features.

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Author Contributions

The work was carried out, the data analyzed, and the manuscript written through contributions of all authors.

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