New radiation curable oligomers with high renewable carbon content for coating and 3D-printing applications

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Abstract

Non-renewable resources such as natural gas and oil are limited in availability. Consequently, substantial efforts are being expended to develop alternative technologies for the manufacture of industrial chemicals which utilize renewable raw materials.

Due to the avoidance of VOC emissions and low energy consumption, radiation curing is already recognized as a sustainable technology. With the use of radiation curable materials based at least partially on renewable raw materials, end-users can develop new formulations with improved carbon footprints and therefore achieve a higher level of sustainability.

Here, we report the successful fabrication of new acrylic oligomers with a renewable content ranging from 56 to 81%. The extraordinary mechanical properties of these new resins in the targeted coating and 3D-printing applications will be discussed.

1. Introduction

Consumers are increasingly interested in products based on renewable raw materials that they perceive as healthier, more natural and having a positive environmental impact. In Europe, the use of renewable resources is also being driven by the European Commission's measures to cut CO2 emissions and to support the bioeconomy; similar programs exist in other regions. According to the Lead Market Initiative (LMI) of the European Commission (2007)[1], products based on renewable raw materials (RRM) are seen as one of the most promising future trends. The use of RRM as a feedstock for the production of resins, plastics, chemicals and other bio-based products can save petrochemical resources and reduce negative impacts on the environment. It can also support the agricultural sector, and lead to innovations in, for example, biomaterials or bio-based chemicals.

From an environmental point of view, renewable raw materials for chemical synthesis are considered on the one hand to reduce environmental impacts of the use of petrochemical resources, e. g. by fewer greenhouse gas emissions. On the other hand, the benefits of using renewable raw materials for chemical industry might be challenged by land use competition and land use change due to the worldwide increasing demand for biomass on food and fodder and for bioenergy/biofuels.

Several bio-based raw materials can be used in the production of bioplastics.[2], [3] Most of them are made from sugar – either derived from cane or beet. Recently there has been a heated debate regarding the use of crops for applications other than for food or feed. Will there be enough for everyone, amid a growing global population? Statistically, agricultural land dedicated to growing crops for bioplastics worldwide is minimal - it accounted for less than 0.02% in 2017 - and it’s expected to stay this way for many years.

Nevertheless, the use of next generation (or alternative) carbohydrates as a biomass source for bioplastics is currently being explored.[4] Unlike first generation feedstocks, such as sugarcane or sugar beet, next generation feedstocks are not intended for human consumption and therefore present a valuable potential additional feedstock source. Promising materials include bagasse, corn stover, wheat straw and wood chips – from agricultural by-products and waste streams.

In this paper, two new UV-curable oligomers based on regrowable raw materials are introduced: RCX 18-843, a mono-functional aliphatic acrylate with a regrowable content of 81% and RCX 19-193, a di-functional aliphatic urethane acrylate with a regrowable content of 56%. Remarkable characteristics of these two oligomers are shown for their rheological and thermal behavior, and for their mechanical properties.

2. Experimental

The two new oligomers RCX 18-843 and RCX 19-193 were produced according to a proprietary synthesis method owned by RadLab AG. The regrowable carbon contents of these oligomers were calculated from the regrowable carbon contents of the employed raw materials. Rheological measurements were carried out with a Rheotest RN 4 rheometer using a cone plate (cone 20mm) oscillation method and a temperature ramp from 20-80°C. Mettler Toledo DSC 3+ was used for the investigation of the thermal behavior of the cured products using a temperature ramp from -70°C to 150°C at 10 K/min. For the UV-cure of the oligomers, a Fusion VPS 6 I601 (240W/cm) UV lamp and 0.5% photoinitiator (GENOCURE* LTM) were used. 3D-prints with the two new products were carried out on a DLP printer from Totem with a 385 nm LED lamp and with a slicing thickness of 100µm. Mechanical properties were measured with a Zwick ProLine 10 kN using the ASTM D638-14 standard test method for tensile properties of plastics.[5]

3. Results and Discussion

3.1. Rheological behavior

At room temperature (25°C), the viscosity of RCX 18-843 has a viscosity of 200 Pa*s while RCX 19-193 is solid. When warmed-up, both products show a significant viscosity drop with small temperature increase, not typical for acrylate resins. Most resins decrease in viscosity when heated, but compared to standard Urethane Acrylates the decline of the viscosity is much steeper. (Figure 1)

Such a rapid viscosity drop with moderate temperature increase is an interesting feature for applications like hot melt adhesives or Toray inks where, typically, low viscosity is desired and a mild preheating can be applied.

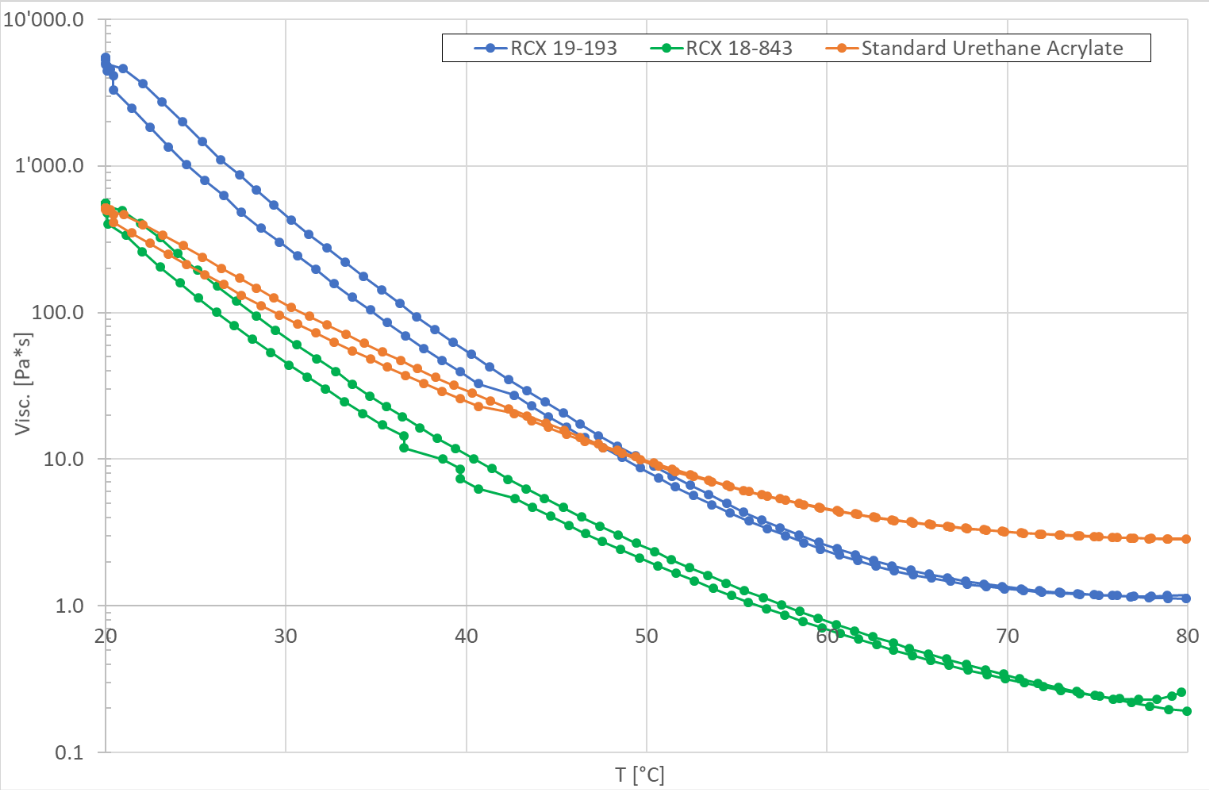

Figure 1: Temperature dependence of the viscosity of the two oligomers RCX 18-843 and RCX 19-193 in comparison to a standard urethane acrylate. Viscosity on the y-axis is on logarithmic scale.

3.2. Thermal properties

Investigations of the thermal properties of the two oligomers RCX 18-843 and RCX 19-193 by using Differential Scanning Calorimetry (DSC) show sharp glass transitions for both products. (Figure 2). The glass transition temperature (T_g) for RCX 18-843 is just above room temperature at 28°C and the T_g of RCX 19-193 at 67°C. This means both oligomers have a glass transition temperature positioned in a desirable temperature window for many applications, e.g., powder coatings, hot melt adhesives and coatings for deep drawing.

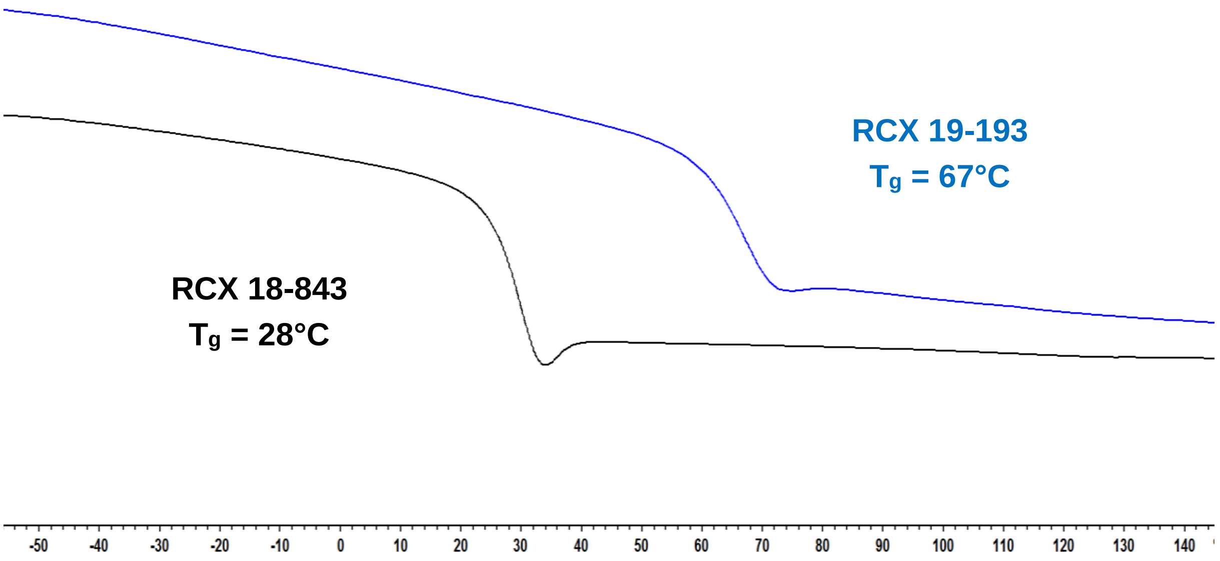

Figure 2: DSC curves of RCX 18-843 (black) and RCX 19-193 (blue)

3.3. Mechanical properties

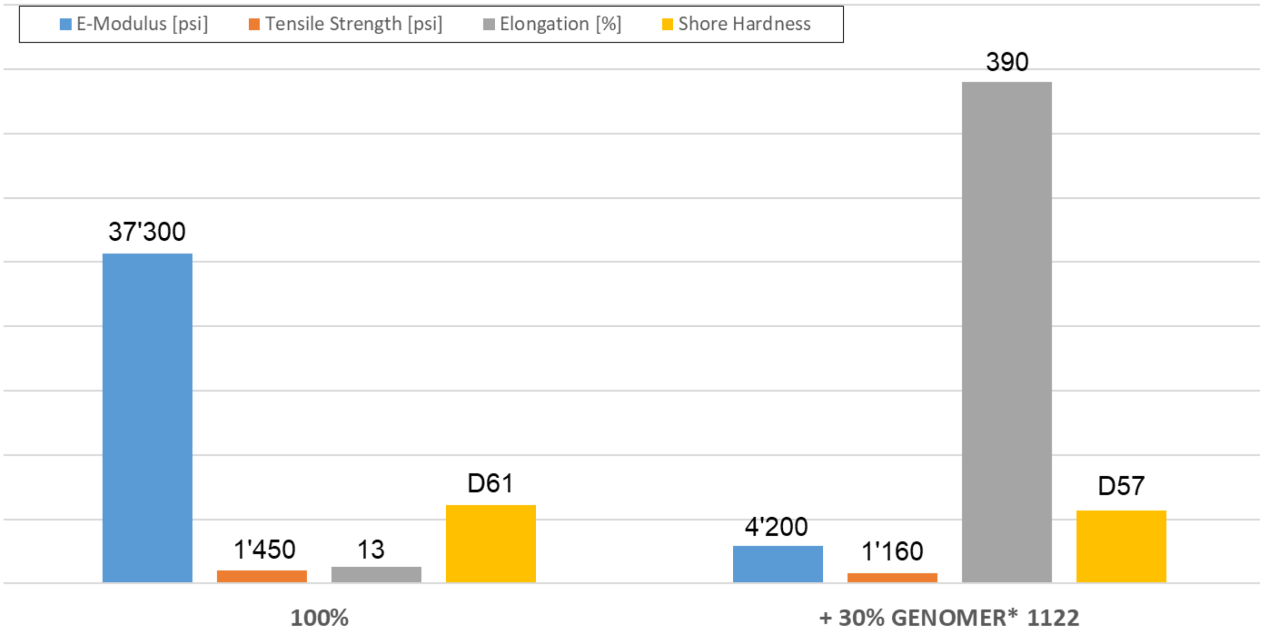

Figure 3: Mechanical properties of RCX 18-843 cured under UV-lamp in neat conditions (100%, left side) and diluted with 30% GENOMER* 1122 (right side).

RCX 18-843 after curing under the UV-lamp neat (100%) is very stiff and brittle. The E-Modulus is quite high but tensile strength and elongation are very low. (Figure 3).

RCX 18-843 diluted with 30% GENOMER* 1122 (a flexible aliphatic urethane acrylate monomer) shows improved mechanical performance. While the elongation rises to almost 400% the E-modulus decreases but does not collapse completely. Tensile strength stays low, which is common for mono-functional acrylates. Hardness of the neat cured RCX 18-843 and the 30% GENOMER* 1122 dilution of RCX 18-843 are almost the same.

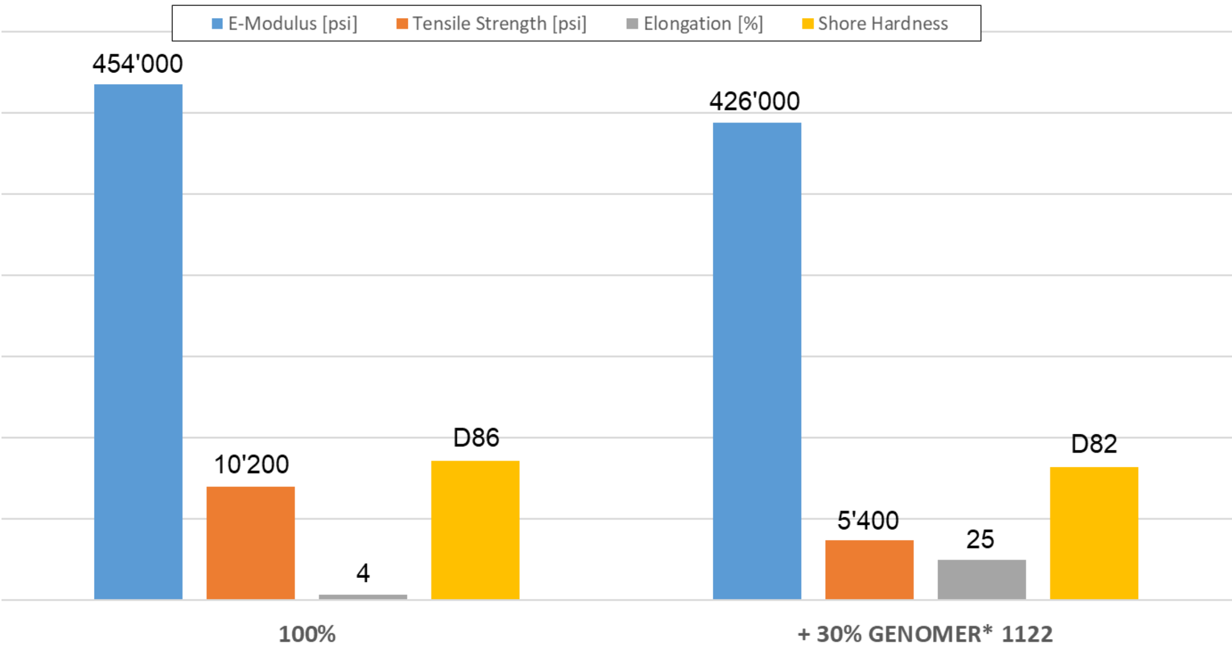

Figure 4: Mechanical values of RCX 19-193 cured under UV-lamp in neat conditions (100%, left side) and diluted with 30% GENOMER* 1122 (right side).

E-Modulus of RCX 19-193 UV-cured neat is very high, more than 435'000 psi. And even diluted with 30% of the flexible monomer GENOMER* 1122, the E-modulus is almost at this value. (Figure 4) Tensile strength drops almost ~50% from the 100% RCX 19-193 to the diluted version. The undiluted RCX 19-193 shows almost no elongation, by adding the flexible monomer GENOMER* 1122, the elongation goes up to 25%. Hardness is for the undiluted as well as for the diluted version of RCX 19-193.

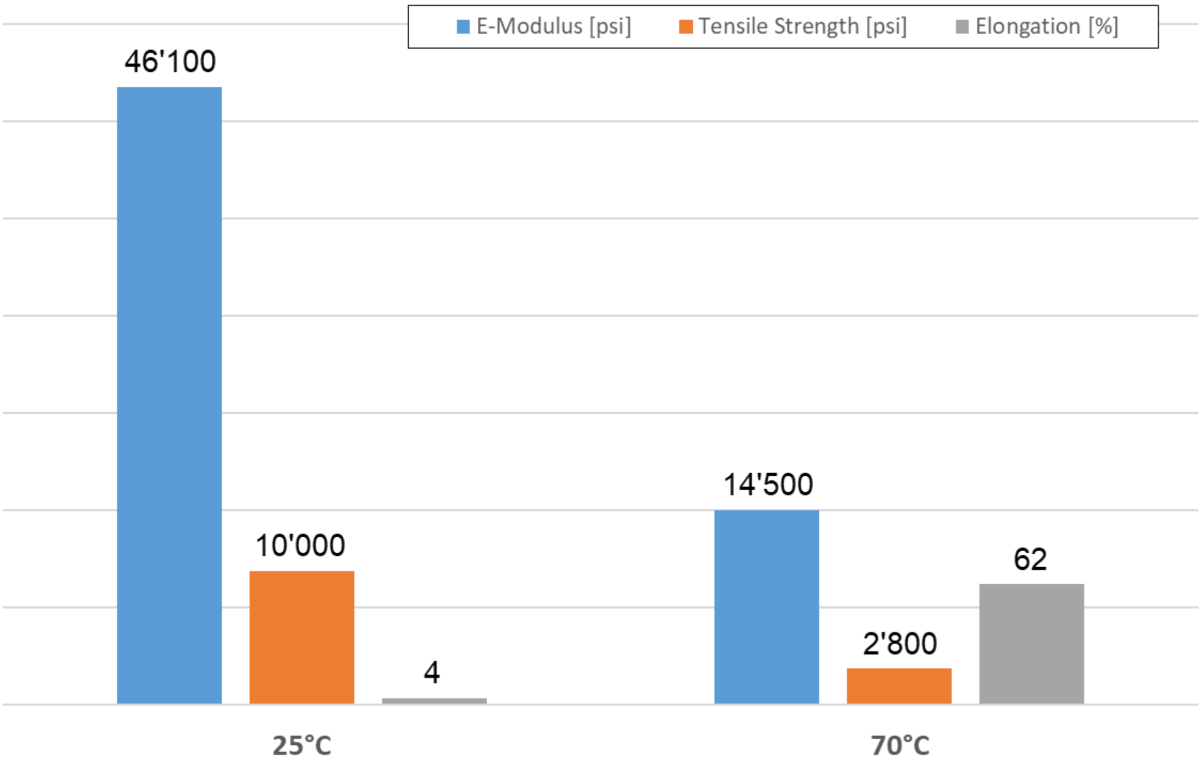

Figure 5: Temperature dependency of mechanical values of RCX 19-193.

Measurements of the mechanical properties of RCX 19-193 at elevated temperatures showed another outstanding behavior. For most urethane acrylate resins, E-modulus and tensile strength completely fail at temperatures above 60°C. But RCX 19-193 exhibits at 70°C still remarkably good values for E-modulus and tensile strength. (Figure 5) Elongation increases from nearly zero at room temperature to over 60% at 70°C.

3.4. Shape Memory Effect

Shape memory effect is a *thermoplastic* phenomenon, in which a material recovers its original size and shape when heated above a certain characteristic transformation temperature.[6] While investigating the mechanical performance of RCX 19-193 at varying temperatures, the thermoplastic shape memory of UV-cured test samples of RCX 19-193 diluted with 30% GENOMER* 1122 were observed (Figure 6).

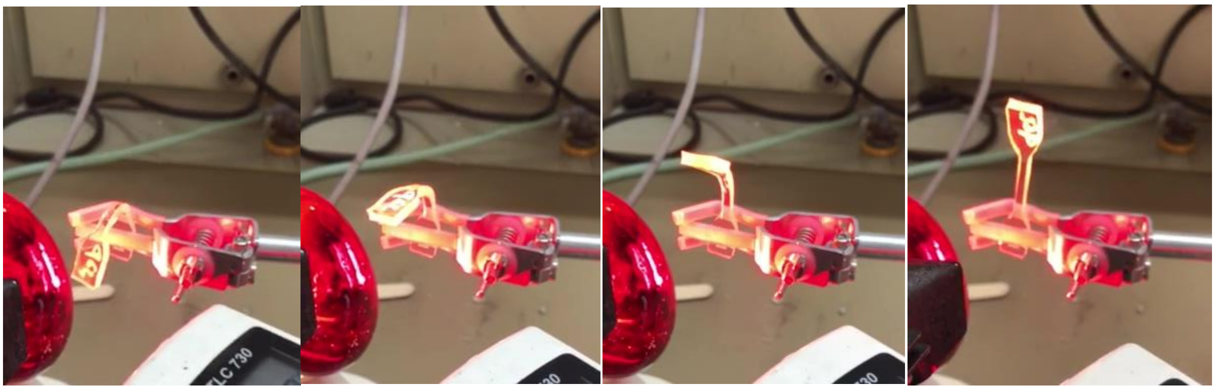

Figure 6: Sequence of still images of a video documenting the shape memory effect of a UV-cured test sample of RCX 19-193 diluted with 30% GENOMER* 1122.

4. Conclusions

Two new UV-curable oligomers RCX 18-843 and RCX 19-193 with high regrowable content (81% and 56%) were introduced. These oligomers show some very remarkable features, both in their neat form and diluted with 30% of GENOMER* 1122 monofunctional aliphatic urethane acrylate. Both oligomers exhibit a significant viscosity drop with small temperature increase and a sharp glass transition in a useful temperature window. Compositions of RCX 19-193 with 30% GENOMER* 1122 are very tough, even at elevated temperatures, and show a thermoplastic shape memory effect.

These properties open potential applications for these oligomers, i.e. coatings for deep drawing, 3D-printing, hot sealing, hot melt adhesives, Toray inks, powder coatings and overprint varnishes.

5. References

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