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Thermosetting (bio)materials derived from renewable resources: A critical review

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ABSTRACT

This review presents the recent advances in the synthesis, properties and applications of thermosetting materials derived from renewable resources. Thermosetting materials are highly cross-linked polymers that are cured or set using heat, or heat and pressure, and/or light irradiation. This leads to high-performance products for industry due to their high modulus, strength, durability and resistance towards thermal stress and chemical attacks as provided by their high cross-linking density. Within this contribution, a special emphasis was made on a broad-brush approach over the potential opportunities and drawbacks concerning the use of renewable feedstock in the design of some commonly used networks such as phenolics, epoxy, polyester and polyurethane resins. Thereby, the utilization of renewable resources is discussed as a novel and appropriate sustainable feedstock rather than as a substitute for petroleum-based thermosetting materials.

Contents

1. Introduction

Thermosetting resins (or thermosets) play an important role in industry due to their high flexibility for tailoring desired ultimate properties, leading to their high modulus, strength, durability, and thermal and chemical resistances as provided by high cross-linking density [1–5]. Owing to their high cross-linking density, thermosetting resins are,

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however, inherently of low impact resistance, and cannot be reshaped after curing/polymerization [6,7]. In order to extend to more high-performance industrial applications, such as civil infrastructure and transportation [8–10], a variety of fillers such as continuous or chopped fibers (glass, carbon, aramid or natural fibers) are often added to the resin to form composite materials. These thermosetting-based composites are currently prepared using manual lay-up and spray-up as techniques. The manual lay-up involves setting a fibrous fabric on a one-sided and open mold, and then spreading the resin over the mold with a manual roller across the fabric. In the latter, polymer and chopped glass fibers (on the order of a few cm) are spread with an air-assisted gun on a one-sided mold. Since an open mold is used in both processes, the final-net shape cannot be readily controlled. Another drawback is an undesirable release of volatile organic compounds (VOC) during the curing process. For better dimensional accuracy and safer work conditions, liquid composite molding processes are therefore preferred. In this respect, a pre-polymeric and liquid resin is injected (or compressed) into a closed mold containing a fibrous preform. The mold is then heated, and the resin cures/polymerizes into a cross-linked network, entrapping the fibers. As an alternative, pre-impregnation of fabrics with the pre-polymeric resin may be carried out. In that case, curing/polymerization are generally activated by heat in an autoclave after compressing the mixture into a closed mold. Thermosetting-based composites parts (so-called profiles) with a constant cross-sectional shape may be manufactured through a continuous technique, so-called pultrusion. The continuous process consists of impregnating a fiber as a reinforcing material into a resin bath, and then passing the impregnated fiber towards a shaping die where the resin is subsequently cured. Filament winding is another way to continuously manufacture hollow composite parts (such as pipes and vessels). After impregnation in resin bath, fiber yarns are continuously conveyed to a rotating mandrel. By comparison with thermoplastic polymer composites in which fibers are inserted in a polymer melt, followed by forming the composite to the desired shape at an elevated temperature, the use of a thermosetting resin provides better impregnation, and to some extent better reactivity with fillers during the curing processes, leading to finer morphological structures. Surprisingly, although thermosets were among the earliest polymeric materials, their continuing development is sometimes overlooked with respect to thermoplastics [11].

Recent years have witnessed an increasing demand on natural products in industrial applications for environmental issues, waste disposal, and depletion of non-renewable resources [12–16]. Renewable resources can provide an interesting sustainable platform to substitute partially, and to some extent totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values [17,18]. In non-food applications, the most widely applied renewable resources include plant oils, polysaccharides (mainly cellulose and starch), and proteins [19]. Plant oils are now being considered as the most important renewable raw materials for the production of bio-based polymer materials [20]. Plant oils are triglycerides (triesters of glycerol with long-chain fatty acids) with varying composition of fatty acid depending on the plant, the crop, the season, and the growing conditions [21]. The molecular parameters affecting the physical and chemical properties of plant oils are the stereochemistry of the double bonds of the fatty acid chains, the degree of unsaturation, and the length of fatty acids. However, the degree of unsaturation mostly remains the key-parameter of plant oils. As expressed by the iodine value, plant oils can be classified into drying oils (iodine value higher than 130), semi-drying oils (iodine value between 90 and 130), and non-drying oils (iodine value lower than 90). Other types of fatty acid functionalities (e.g., epoxy, hydroxyl, cyclic and furanoid groups) are available as well [22]. In industrial practice, drying oils are most frequently used to form resins due to their high ability for autoxidation, peroxide formation, and subsequent radical polymerization, as currently applied in paint and coating formulations [22–24]. Recent reviews have focused on the development of cross-linked plant oils and their derivatives for thermosetting applications such as coating and resins [25–28]. Thermal or cationic (co)polymerization of these plant oils with styrene or divinylbenzene is usually carried out to obtain thermosetting (bio)materials, ranging from elastomers to rigid and tough plastics, depending on the stoichiometry, the type of plant oils, and the (co)monomers [29,30]. Recently, new value-added applications have been obtained for (nano)composites derived from these plant oil-based thermosetting polymers [31–33].

In addition to plant oils, other raw renewable materials of interest in the design of bio-based thermosetting materials include lignin and proteins due to their vast abundance and high functionality [28,34]. Lignin is the second most abundant naturally occurring macromolecule amidst cellulose and plant oils. Due to its phenolic nature, lignin has been considered as a promising substitute for phenol in phenol–formaldehyde-based resins. Thermo-chemical conversion of lignin is carried out to enhance its reactivity for reactions with formaldehyde. In non-food applications, the use of plant proteins like soy proteins and wheat gluten may be also a promising way to produce thermosetting (bio)materials with a large range of applications. For example, plant proteins are considered to be ideal templates for biomaterials as temporary replacement implants due to their ease of processability, adhesion to various substrates, and surface-active properties. For any processing technique, the processing of proteins involves heat-treatment leading to cross-linked systems. In some cases, a suitable cross-linker is added in order to control the cross-linking density for the protein-based systems.

During the past decades, the explosive growth of biotechnology has been extended to organic polymer chemistry [35]. The reasons for this trend include the recognition of the rapidly increasing capabilities of biotechnology, the demonstrated ability of microorganisms to supplement existing chemistry synthesis technology, and the desire to create new polymer materials with improved performances [35–39]. There is of course increasing awareness of the need for green chemistry in chemical industries. For example, high-content cardanol, by-product derived