

Natural Thermosets

Biologically Degradable Plastics made of Gelatine and Natural Fibres

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Biologically degradable plastics [1, 2] are of increasing interest because of environmental aspects and due to their durability. Recently numerous biodegradable polymeric materials have been found that can be made industrially based on renewable raw materials or on fossil materials. Practically all available biologically degradable plastics show thermoplastic behaviour, while biologically degradable thermosetting polymers have hardly been described and have not yet achieved any importance.

An interesting raw material for biologically degradable plastics is gelatine,

For the first time natural thermosetting polymers can be made from gelatine-linseed oil blends. As composite materials with natural fibres they can compete in their mechanical characteristics with conventional thermosetting polymers and are problem-free biologically degradable.

which possesses good mechanical characteristics as a biopolymer. The main problem is in its high sensitivity to moisture, which already more than 100 years ago was handled by cross-linking the peptide chains. For this after shaping the gelatine was treated in an aqueous formaldehyde bath. This was time consuming, complicated and expensive. At the time the months-long hardening of the formaldehyde containing gelatine products made production of materials with well-defined characteristics very difficult. The necessary large surplus of cross-linking material and the thus unavoidable content of free formaldehyde decreased the biological degradability of such materials substantially. In addition, they sometimes gave off formaldehyde during use.

Later on it has become possible to manufacture cross-linked materials based on gelatine that have the characteristics of conventional thermosetting polymers without impairing their biological degradability through modification of the gelatine or through the use of additives. To achieve this new possibilities for hardening and for decreasing water absorption were investigated by making blends of gelatine and linseed oil.

Gelatine

Gelatine is made in different ways from collagen, which belongs to the group of fibrous proteins that in mammals comprises about 30 wt.-% of the entire protein content [3]. Gelatine is a polypeptide

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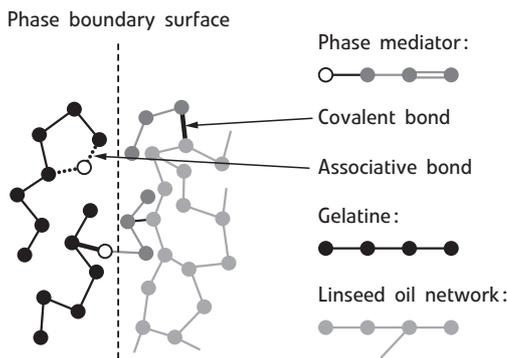


Fig. 1. Schematic representation of the phase boundary surface of gelatine and linseed oil with phase mediator

similar in its structure in principle to the polyamides. The reactivity of the gelatine is due to free functional groups of the amino acids in the structure of the gelatine, of which in particular the hydroxy, carboxy and amino groups are easily transformed chemically.

Different gelatine chains can be linked together and cross-linked with highly functional reagents such as dicarboxylic acids or dialdehydes as well as polyacids or polyphenolic substances. Products with substantially reduced water absorption are developed thusly. However, their biological degradability is frequently strongly reduced.

In order to reduce water absorption in the very hydrophilic gelatine, apart from cross-linking there is the possibility of building in hydrophobic cross-linkable components. In order not to impair their biological degradability, natural oils can be used, for instance the polyunsaturated or poly-functional triglycerides known to be drying oils. The molecular growth initiated by autoxidation leads to products that cannot be melted and which mostly cannot be dissolved in organic solvents. They are used as film formers in oil paints, lacquers and varnishes and in addition are already long known as bonding agents and used technically.

Gelatine Blends

As the already mentioned cross-linking of the gelatine does not lead to sufficient water resistance and additionally reduces biological degradability, other methods have to be found to make a thermosetting material out of gelatine. Here there is the possibility of a combination of blending and cross-linking. The gelatine is made less sensitive to moisture through incorporation of linseed oil whereby the blend is compatibilised using a phase mediator and the linseed oil is bound both physically and chemically to the gelatine.

Cross-linking is then achieved mainly by autoxidation of the unsaturated groups in the linseed oil, whereby two finely dis-

tributed polymer phases with different physical characteristics and different chemical structures develop, so that one can speak of multi-phase blends. The problem here is to achieve sufficient phase contact between the hydrophilic gelatine and the hydrophobic linseed oil to get as

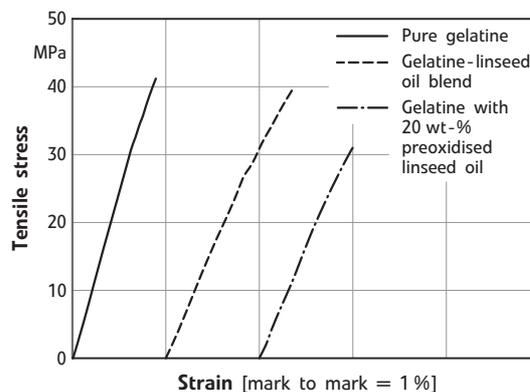


Fig. 2. Tensile stress-strain curves of pure gelatine and of gelatine blends with 20 wt-% pre-oxidised linseed oil (lecithin content 5 wt-%) (hardened at 170 °C)

good a distribution of the linseed oil as possible in the gelatine (Fig.1). For the partial binding of the pre-oxidised linseed oil acid groups can be introduced through maleic acid anhydride. This takes place in a way similar the production of alkyd resins.

The use of vegetable lecithin as phase mediator is simpler, by which is meant fatty substances derived mainly from oil seedlings. Vegetable lecithin can be cross-linked with the linseed oil through its unsaturated fatty acid residues. If linseed oil is mixed with 5 wt-% lecithin it can be easily emulsified in a 30 wt-% aqueous gelatine solution. Fine distributions develop in this way, from which well homogenised lents can be obtained after drying in air flow at ambient temperature.

The mechanical characteristics of unfilled gelatine blends give valuable information on their internal structure. A comparison of the tensile strength of pure untreated gelatine and that of gelatine blends gives information about the stability of the phase boundary surfaces and

the degree of cross-linking of the linseed oil.

Each component contributes to the mechanical characteristics if the phase boundary surfaces are stably connected by the phase mediator. Untreated gelatine pressed to make sample test specimens gives tensile stress-strain curves and brittle failure typical of pure thermosetting polymers (Fig. 2). A mixture of linseed oil and gelatine without phase mediators in the cross-linked state behaves in a way similar to untreated gelatine. However, for very small break elongation the breaking stress is clearly lower than the values for pure gelatine. From this it must be concluded that the linseed oil polymer does not bind across the boundary surfaces to the gelatine. Thus the mechanical characteristics are largely determined by the gelatine.

In contrast, if a phase mediator such as lecithin and an oxidative cross-linking accelerating catalyst such as manganese naphthenate are added, then the tensile stress-strain curve of the cross-linked sample test specimen is steep. However, it has a higher elongation at break. The phase boundary surfaces are stabilised by the phase mediator so that both the gelatine and the linseed oil polymer contribute to the mechanical stability. The values of the tensile strength, the elongation at break and the elastic modulus almost correspond to those of a typical phenolic resin (Fig. 3).

Composite Materials

Gelatine-linseed oil blends have high brittleness just like conventional thermosetting polymers. This is not necessarily a disadvantage, as with other reaction resins, if they are combined with reinforcing materials. In order not to lose the advantage of the biological degradability of the matrix, vegetable fibres and cellulose are used for this purpose, which as re-

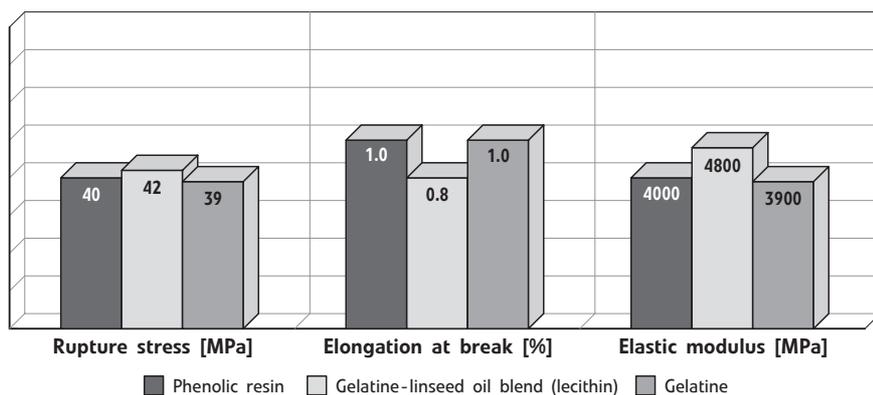


Fig. 3. Mechanical characteristics of gelatine-linseed oil blends and of phenolic resin

newable raw materials support the sustainability concept. Flax fibres are particularly good candidates since they are made from the same plant as linseed oil.

Thus gelatine-linseed oil blends can be made into composite materials. After adding about 35 mm long fibres at 70 °C, before solidifying the product is rolled to prepregs or extruded to a strand. The prepregs can be dried in air flow while the extruded strand can easily be granulated after solidifying and likewise dried in air flow. Thus is obtained an even distribution of the fibres in the matrix, which adheres firmly to the fibres after pressing at 160 °C.

Scanning electron microscopic (SEM) pictures (Fig. 4) show that after breaking, the flax fibre bundles in pure gelatine (A) show no adhesion of the fibre. In contrast, in gelatine-linseed oil blends there is obviously a linkage of the fibres to the matrix (B). During breakage this causes many small tears in a way similar to the way a sort of craze formation is generated in high impact strength thermoplastics. The impact strength is increased through transformation of thermal energy into heat.

Mechanical and Physical Characteristics

The high elastic modulus of the unfilled brittle resin together with the still higher elastic modulus of the reinforcement material leads to a further increase in the rigidity. The elastic modulus depends only weakly on the fibre length of the reinforcement material. However, as previously mentioned, the impact strength of gelatine-linseed oil blends is substantially increased by embedding about 35 mm long flax fibres.

In many ways the described composite materials based on gelatine are equivalent

to conventional products or even improve on them. Only the maximum water absorption of gelatine blends is clearly higher. The mechanical characteristics correspond approximately to a polyester resin reinforced with 20 mm long glass fibres (40 volume%). However, the elastic modulus of this resin is somewhat higher because of the larger modulus of the glass fibres.

On the other hand, a great advantage of composite materials based on natural fibres is their lower density compared to products reinforced with glass fibres. The density amounts to about 1,4 g/cm³ and is thus about 25% under that of moulded parts made of polyester resin reinforced with glass fibres with same fibre content.

Biological Degradability

Experimental tests were planned according to the proposed DIN 54900 in order to make a convincing evaluation of the biological degradability of the described composites. In the laboratory tests the biological degradation was investigated by determining the amount of carbon dioxide production in water compared to the maximum possible CO₂ production. The decomposition characteristics in conventional composting were evaluated in practice-relevant composting experiments. The quality of the compost is substantially increased since the nitrogen content of the composites is as high as in some fertilisers. Because it is in the form of amino acids bound in the gelatine it is very easily accessible for most organisms.

To measure the biological degradation by aerobic micro-organisms the test material was mixed with an inoculation medium consisting of activated sludge, agitated and ventilated with CO₂-free air.

The CO₂, which forms during the biological reduction, is bound to barium hydroxide and measured afterwards by titration with hydrochloric acid.

Test disks of composite materials reinforced with flax fibres and cellulose based on gelatine showed their good rotting characteristics in a conventional compost (Fig. 5). No differences could be determined between compost made of the described gelatine composites with flax or cellulose and compost without composite material. Thus the biological degradability of thermoplastic materials based on gelatine is proven without doubt in accordance with DIN 54900. The tested materials fulfil all required criteria or even clearly exceed them.

Conclusion

For the first time biologically degradable thermosetting polymers can be made from gelatine-linseed oil blends with suitable phase mediators. They can compete as composite materials with likewise degradable natural fibres with conventional thermosets with respect to their mechanical characteristics. The thus constituted products are problem-free biologically degradable and support the sustainability concept.

If they are classified as biological waste according to DIN 54900 the new fibre reinforced composites should be economically profitable despite the somewhat higher price of the gelatine compared to conventional thermosets.

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Fig. 4. REM picture of flax fibre bundles in pure gelatine (A) and in a hardened gelatine-linseed oil blend with 20 wt-% linseed oil and 42 wt-% flax

Fig. 6. Composting natural fibre-strengthened gelatine-linseed oil blends