RECENT ADVANCEMENTS IN THE DEVELOPMENT OF MATERIALS AND PRODUCTS FROM RENEWABLE RESOURCES

M. van der Zee, E. Pras, J. van Haveren, R. van Tuil

ATO, Business unit Renewable Resources, Department Polymers, Composites, and Additives, P.O. Box 17, NL-6700 AA Wageningen, the Netherlands.

1. ABSTRACT

Natural materials, i.e. renewable resources, are a versatile and very promising class of materials. Natural materials, either polymeric or not, often exhibit properties that can not be achieved with synthetic materials. Natural rubber, for example is still used for high performance tyres like aeroplane- and truck tyres since it outperformes synthetic materials like EPDM. ATO successfully performs developments in collaboration with industry leading to novel, innovative outlets for materials from natural origin. Examples of topics that receive considerable attention are polymer additives, adhesives, coatings and bioplastics.

Bioplastics - i.e. thermoplastic polymers from renewable resources - have been available on the market for a long time but have failed to gain a significant market share so far. As a main reason, one can identify the unfavourable cost/performance ratio as compared to that of conventional petroleum based materials. Together with industrial partners, ATO works on the initiation of a breakthrough in the use of polymers from renewable resources by increasing the cost/performance ratio. The number of commercial applications for bio-based polymers can be increased when products are developed that utilise the advantageous properties of this type of materials. Examples of such properties that can be obtained with biobased materials are: a) excellent gas barrier properties (comparable with EVOH); b) straight forward processability into foam materials (without chemical blowing agents); c) biodegradability; d) anti-static properties; e) hydrophilic behaviour (therefore these materials are potentially good water-absorbent materials); f) excellent matrix material for encapsulation of natural ingredients (fertilisers, flavours etc.); and g) abundance and low cost.

In this paper, examples are presented of recent advancements in the development of materials and products from renewable resources utilising one or more of these unique specific functionalities of natural feedstocks. The first example shows results in the field of sustainable additives for the plastic processing industry. A second shows the progress that has been made in the bioplastics area.

2. INTRODUCTION

For a long time, most industrial products such as chemicals, pharmaceuticals, clothing, fibres, colorants, and packaging were made from natural resources. Since the relatively recent discovery of oil and the corresponding development of the oil based chemistry, petroleum derived chemicals have replaced these biobased products to a large extent. However, recent developments are raising the prospects that natural derived resources again will be a major contributor to the production of industrial products.

Raw materials from natural origin present an enormous potential for the production of polymers, plastics and related chemicals with unique properties. Natural resources offer an exceptional variety of chemical building blocks for the design of materials with a strong added value to synthetic materials. At the same time, environmental, health and safety concerns are intensifying the interest in agricultural and forestry resources as alternative feedstocks.

ATO successfully performs developments in collaboration with industry leading to novel, innovative outlets for materials from natural origin. ATO continues to be naturally inspired in order to bridge the gap and explore the synergy between materials, products and technologies from synthetic and natural origin.

In this paper, some examples of recent advancements in the development of materials and products from renewable resources are presented. In the first example results are shown in the field of sustainable additives for the plastic processing industry. A second shows the progress that has been made in the bioplastics area.

3. RESULTS AND DISCUSSION

3.1 Polymer additives

Polymer additives are used in huge amounts either to enable processing of plastics or to modify or enhance the properties of a given material. Examples are heat stabilisers, UV stabilisers, flame retardants, colorants, plasticisers, and processing aids like lubricants, etc. A number of the additives currently used in plastic processing, are under environmental constraints. Colorants, heat stabilisers, and flame retardants frequently contain heavy metals that may cause environmental and health problems. Also the potential of bioaccumulation and suspected (eco)toxicity of some of the currently used plasticisers (Scholz *et al.,* 1997), has prompted legislators to express caution with regard to their widespread use. Although there is much controversy about whether this will be proven true or not, industry is responding by looking for more environmentally friendly colorants, heat stabilisers, flame retardants and plasticisers. This has led to the initiative to develop environmentally friendly, biobased additives for use in conventional petroleum based polymer processing. Naturally, these biobased alternatives must meet the technical demands and it must be demonstrated that they do no cause negative effects from the environmental point of view. Research activities are currently focussed on the development plasticisers and stabilisers for PVC, heat stable colorants and pigments, and flame retardants.

Almost 90% of all plasticisers presently used for plasticizing PVC are phthalate derivatives. Diethylhexyl phthalate (DOP) and Butyl benzyl phthalate (BBP) are the most commonly used. However, these phthalates are at present under suspicion of bioaccumulating in the environment (Scholz *et al.,* 1997). Furthermore, studies have shown that they may have ecotoxic and possibly even carcinogenic effects, and their use is now under discussion. In some countries, their application in toys for children and food packaging has been banned. Current alternatives, however, do not meet the required technical specifications or not economically viable.

Recently, a novel route was developed at ATO for the production of a range of alternative plasticisers based on carbohydrates and (fatty) acids derived from natural feed stocks. Patents have been filed on their production and application (Luitjes and Janssen, 1999), and at the moment their use is explored in co-operation with industrial partners. The technical performance properties can be modified by altering their chemical composition. As shown in Figure 1, these biobased alternative plasticisers can easily compete with the phthalate based compounds considering their performance and in some cases (transmittance, haze) clearly outperform DOP and BBP.

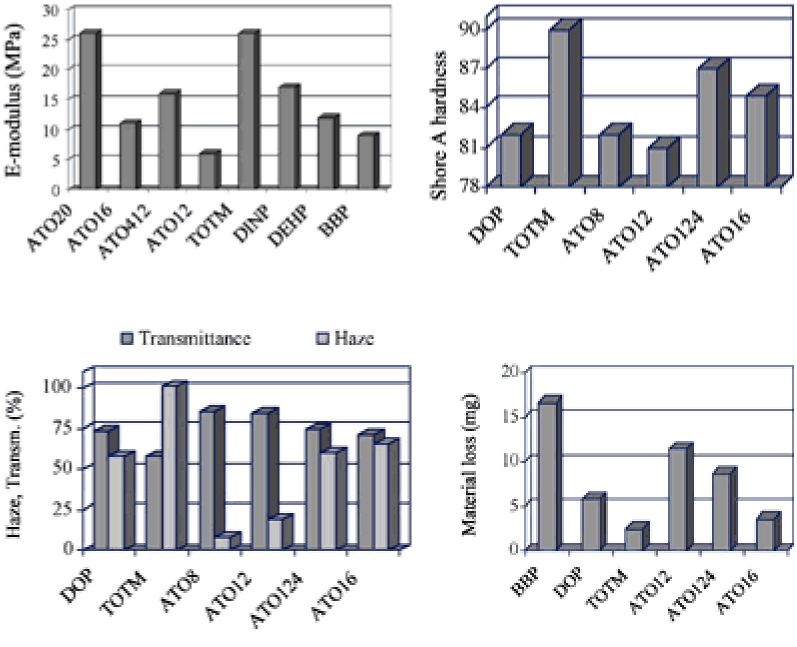

Figure 1. Properties of PVC plasticised with phthalate based and alternative biobased plasticisers;
(A) E-modulus, (B) Shore A hardness, (C) Optical properties and (D) Fogging data.
Plasticiser content is in all cases 45 phr.

The environmental fate of the alternative biobased plasticisers is currently being investigated, but considering the raw materials and the production process, no major problems are anticipated.

From the examples presented here, it is concluded that renewable materials can be the starting materials for the synthesis of sustainable additives for thermoplastic resins.

3.2 Bioplastics

Over the last 10 years various plastics have been developed from renewable resources (Coombs and Hall, 2000; Mangan, 1992). They may be divided into three main categories based on their origin and production.

- Category 1:?Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose and proteins like casein and gluten.
- Category 2:?Polymers produced by classical chemical synthesis using renewable biobased monomers. A well known example is poly(lactic acid), a polyester polymerised from lactic acid monomers. The monomers themselves are produced via fermentation of carbohydrate feedstock.
- Category 3:?Polymers produced by micro-organisms or genetically modified bacteria. To this date, this group of biobased polymers consists mainly of the poly(hydroxy alkanoate)s.

The fundamental repeating chemical units of the biobased materials described so far are identical to those of a significant group of the conventional petroleum based plastics. In its broadest sense, polysaccharides, which possess repeating acetal functionalities, can be regarded as the naturally occurring analogues of the synthetic polyacetals. Proteins (with a repeating peptide functionality) can be compared to the synthetic polyamides whilst poly(lactic acid) is merely an example of the diverse group of polyesters (Carraher, 1981). Clearly, however, the gross physical and chemical properties of native biobased materials and their synthetic counterparts are quite different and this is a feature of additional chemical functionality inherent in biobased materials. It can be expected that, following processing and product development of biobased materials, resulting properties should equal or outperform those of the conventional alternatives. However, such processing and product development is not always trivial and is unlikely to be cost effective in all cases.

It is not surprising, therefore, that the current applications of biobased plastics seek not to emulate the properties of conventional plastics, but to capitalise on inherent biodegradability. Biobased plastic applications are currently targeted towards compostable, single-use, disposable, short life packaging materials, service ware items, disposable non-wovens and coatings for paper and paperboard applications.

However, the possible products made from renewable resources cover a broader range. As mentioned before, most biobased materials exhibit some unique specific properties, which may make them especially suitable in certain applications. Examples of these properties are:

- Excellent gas barrier properties
- Straight forward processability into foam materials (without chemical blowing agents)
- Anti-static properties
- Hydrophilic behaviour. Therefore these materials are potentially good water-absorbent materials.
- Excellent matrix material for encapsulation of natural ingredients (fertilisers, flavours etc.)
- Abundance and low cost

Recent activities at ATO with respect to product development from renewable resources have focussed on utilising these specific properties, of course taking into account the economics of the production process as well as the environmental issues from raw materials production unto after use disposal options. As an example, some results are presented on the development of multi-layer (barrier) films for applications such as food packaging.

In many food applications, both a water vapour barrier as well as a gas barrier is required. No single biobased polymer can fulfil both these demands. In this case the use of co-extrusion can lead to laminates which meet the objectives. A range of melt-processable starch grades were developed for extrusion in co-operation with Avebe (currently on the market as Paragon®). Some of the properties of these materials are presented in Table 1.

Properties (at 60% RH, 23 °C)	***Sheet grade*** **SE 1500**	***Film grade*** **SE 1620**
Modulus (MPa)	2400	1500
Strength (MPa)	34	25
Strain at break (%)	30	46
T_g (°C)	80	52
Density (kg/m^3)	1350	1330

Table 1 Properties of Paragon® SE grades

Subsequently, the co-extrusion technology was developed for manufacturing multi-layer films and sheets from these polymers. Several stages of research can be identified in this phase:

- Choice of the materials to be used; definition of the layer sequence
- Optimisation of the adhesion between layers
- Optimisation of the rheology of the different layers

Satisfactory adhesion between the coating and the base material was established by developing Paragon® tie-layers. It proved possible to produce 2-5 layer blown film or flat sheets which can be transformed and sealed like conventional films. The films can have tailor made barrier properties (for carbon dioxide, oxygen and/or water), transparency, and biodegradability. In this way starch based materials can provide cheap alternatives to presently available gas barrier materials like EVOH and PA6.

The biobased barrier laminates are currently tested in realistic application trials such as the packaging of bread, cheese and vegetables. Preliminary results show that the multi-layer films used for cheese packaging exhibit perfect handling on vacuum forming machinery. Sensory evaluation of the cheese packed for 1 month in the biobased film was comparable to that packed in conventional film. This was attributed to the low water permeability and the low oxygen permeability of the used packaging films. Figure 2 shows the oxygen permeability of two novel biobased films for cheese packaging compared to that of the conventionally used film, i.e. a commercially available PE/PA6 laminate.

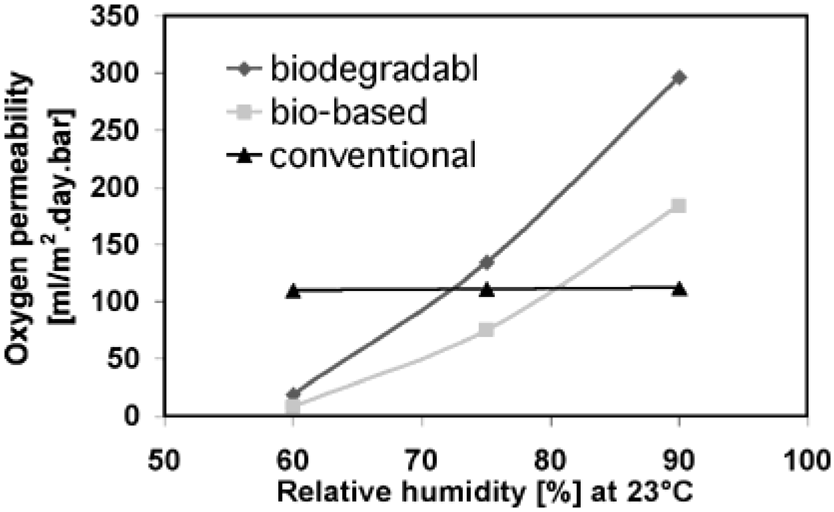

Figure 2.
Oxygen permeability of biobased multi-layer films and a commercially available PE/PA6 laminate film.

Paragon® based packaging films also significantly reduced the relative humidity in the head-space of packed vegetables. Furthermore, realistic chain trials demonstrated that the use of biobased laminates significantly reduced the fogging and quality loss of mushrooms. This was attributed to its high carbon dioxide/oxygen permeability ratio and its low water barrier (as shown in Figure 3).

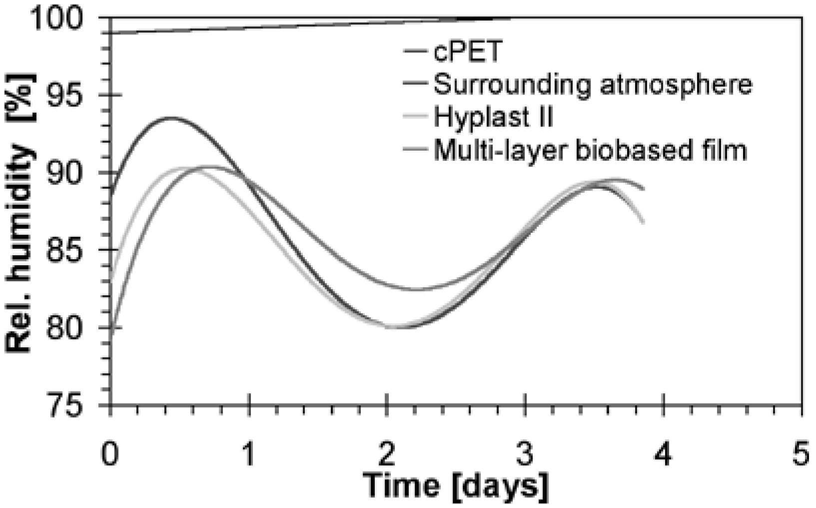

Figure 3.
Relative humidity inside a mushroom packaging of made of cPET, Hyplast II and a biobased multi-layer film compared to the surrounding atmosphere.

For bioplastics, future developments will focus on films, foams and green monomers. By making use of unique properties of natural materials, new markets can be identified. Nevertheless, the complete life-cycle of a product should be considered; a bioplastic based product should offer an advantage during production, during use, or in the disposal phase. Both price, performance, and environmental aspects should always be kept in mind.

4. CONCLUSIONS

The examples given above, have demonstrated that renewable resources can be very interesting and versatile starting materials. The trend is to focus more on their specific properties and functionalities. The properties of natural materials make them suitable not only to produce bioplastics, but also to develop applications in the field of e.g. coatings, adhesives, controlled release and additives for the plastic processing industry. The development of industrial applications for these materials is ongoing and will produce numerous applications in the future.

5. AKNOWLEDGEMENTS

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