Prior to the ample supply of low cost petrochemicals, plant oils were used extensively as binders for paints and coatings. The utility of plant oil triglycerides as coating binders stems from the unsaturated fatty acid esters that provide a means to crosslink the liquid plant oil into an insoluble film by simply exposing the thin film of oil to the atmosphere. The crosslinking mechanism is a complex free-radical process, referred to as autoxidation, and involves abstraction of bis-allylic hydrogen atoms by singlet oxygen present in the atmosphere [1-4]. Since the concentration of bis-allylic hydrogens is critical to the autoxidation process, only plant oils with relatively high levels of linoleic and linolenic fatty acid esters are useful, such as linseed, tung, poppy seed and walnut oil.

Plant oils such as these are referred to as ‘drying oils.’ Soybean oil (SBO), which is the plant oil currently produced in the highest volume in North America, is referred to as ‘semi-drying’ since it is capable of autoxidising to a cured film, but the time required to do so is too long to be useful for paints and coatings. The crosslinking mechanism is a complex free-radical process, referred to as autoxidation, and involves abstraction of bis-allylic hydrogen atoms by singlet oxygen present in the atmosphere [1-4]. Since the concentration of bis-allylic hydrogens is critical to the autoxidation process, only plant oils with relatively high levels of linoleic and linolenic fatty acid esters are useful, such as linseed, tung, poppy seed and walnut oil.

Alkyd resins are polyester oligomers containing fatty acidester residues that enable crosslinking via autoxidation as well as aromatic moieties that function to increase glass transition temperature (Tg) [5]. Increasing the Tg with aromatic monomers allows the coating film to become dry-to-touch with little to no crosslinking required. With alkyd coatings, especially those based on soybean oil, chemical resistance is generally limited and develops slowly with time. Besides enabling curing via autoxidation, the unsaturation in plant oils has also been used to incorporate other functional groups into the triglyceride. For example, epoxy groups can be easily introduced into unsaturated plant oils by oxidising the unsaturation to epoxy groups using, for example, peracetic acid as the oxidant [6, 7]. From the epoxy-functional plant oil, other functional groups can be incorporated using epoxy ring-opening reactions, such as ring-opening with acrylic acid to produce an acrylate-functional material or ring-opening with methanol to produce a hydroxy-functional material. Acrylate-functional plant oils are useful for the production of radiation-curable coatings, and hydroxy-functional ones for polyurethane coatings [8-11].

Metal-based catalysts have been developed to increase the overall rate of autoxidation. Examples of these catalysts, referred to as driers, include carboxylates based on metals such as cobalt, manganese, iron, vanadium, lead and zirconium. Even with an optimised drier package, the curing rate of drying oils is often undesirably long for many coating applications. This problem can be at least partly attributed to the high molecular mobility of plant oil triglycerides. This means that a substantial level of autoxidation is required to produce a film that can be touched and handled without affecting the appearance or damaging the coating. To overcome this issue, alkyd resins were developed.

**Alkyds and their modifications outlined**

Alkyd resins are polyester oligomers containing fatty acid ester residues that enable crosslinking via autoxidation as well as aromatic moieties that function to increase glass transition temperature (Tg) [5]. Increasing the Tg with aromatic monomers allows the coating film to become dry-to-touch with little to no crosslinking required. With alkyd coatings, especially those based on soybean oil, chemical resistance is generally limited and develops slowly with time. Besides enabling curing via autoxidation, the unsaturation in plant oils has also been used to incorporate other functional groups into the triglyceride. For example, epoxy groups can be easily introduced into unsaturated plant oils by oxidising the unsaturation to epoxy groups using, for example, peracetic acid as the oxidant [6, 7]. From the epoxy-functional plant oil, other functional groups can be incorporated using epoxy ring-opening reactions, such as ring-opening with acrylic acid to produce an acrylate-functional material or ring-opening with methanol to produce a hydroxy-functional material. Acrylate-functional plant oils are useful for the production of radiation-curable coatings, and hydroxy-functional ones for polyurethane coatings [8-11].

**Novel technology yields highly unsaturated polymers**

The authors have developed a polymer technology based on plant oils that allows the production of linear polymers with fatty acid ester side chains [12]. The technology involves the production of vinyl ether monomers from either the plant oil triglyceride or alkyl esters derived from a plant oil using simple base-catalysed transesterification.

Figure 1 provides a schematic describing the production of a vinyl ether monomer from SBO using methyl soyate as the plant oil-based component. This particular monomer is 2-(vinyl oxy) ethyl soyate (2-VOES). By using the appropriate polymerisation system, a living polymerisation was produced for this monomer using a cationic polymerisation mechanism.
Since the reactivity of the vinyl ether double bond is much higher towards relatively stabilised carbocations than that of the internal double bonds derived from SBO, all of the unsaturation derived from the SBO is preserved in the polymer. This unsaturation can then be utilised to produce coating films either directly or by derivatisation to other functional groups. The value of various plant oil-based polymers such as these for coating applications is outlined below.

Figure 2 illustrates the difference in molecular architecture between SBO and poly(2-VOES). While SBO possesses three fatty acid esters per molecule, poly(2-VOES) possesses tens to hundreds of fatty acid esters per molecule. Due to the dramatically higher number of allylic hydrogens per molecule associated with poly(2-VOES), the extent of radical coupling reactions needed to reach the gel point is much lower for poly(2-VOES) than for SBO. A marked difference in tack-free time was obtained when a drier package was added to coatings derived from poly(2-VOES) and SBO. Even with an autoxidation catalyst, it took 40 hours – almost two days – for SBO to convert from a liquid film to a tack-free film at ambient conditions. In contrast, poly(2-VOES) became tack-free in 6.1 hours [13, 14]. This result clearly shows the benefit of increasing the number of fatty acid ester groups per molecule by converting the SBO to a polymer.

Purified monomer yields colourless polymer

As discussed above, prior to the petrochemical revolution, most paints were mixtures of a drying oil and pigments. While these paints and coatings have been largely replaced with petrochemical-derived coatings, plant oil-based paints are still used by many artists. Linseed oil in particular possesses a relatively high concentration of linolenic acid esters that allow curing without the addition of a drier. Its significant drawback is the strong yellow colour of the oil, which is problematic for the production of white or pale coloured paints [15]. It was demonstrated that essentially colourless poly(2-VOES) can be produced by simply purifying 2-VOES by vacuum distillation prior to polymerisation. Figure 3 provides a comparison of the colour of poly(2-VOES) derived from vacuum distilled 2-VOES to linseed oil. White paints were prepared from both linseed oil and the colourless poly(2-VOES) and the appearance and drying time determined. Figure 4 shows the difference in colour between the two paints produced using rutile titanium dioxide as the white pigment. The image displayed in Figure 4 clearly shows that the coating derived from the colourless poly(2-VOES) was essentially a pure white, while that derived from linseed oil was clearly an off-white that appears more a beige or cream colour than pure white. With regard to drying time, the linseed oil-based paint took 316 hours to become dry-to-touch, while the poly(2-VOES)-based paint only took 26 hours. It should be noted that neither the poly(2-VOES)-based paint nor the linseed oil based paint contained a drier to catalyse the curing process. It is very interesting that poly(2-VOES) cures quite fast even without a drier package.

Copolymerisation extends range of properties

A major advantage of this plant oil polymer technology is that copolymerisation can be utilised to dramatically change polymer thermal, physical, and mechanical properties.
properties. Since cured films of poly(2-VOES) possess Tgs below 0 °C, it was of interest to investigate the use of copolymerisation to increase the Tg of cured films. Two comonomers were initially investigated, namely, cyclohexyl vinyl ether (CHVE) and menthol vinyl ether (MVE) [16, 17]. The cycloaliphatic pendent groups associated with these monomers were expected to substantially increase both polymer Tg and coating film Tg.

Figure 5 displays the tangent delta response obtained from dynamic mechanical analysis for films cured at ambient temperature. As can be seen, the Tg of the cured networks increased with increasing comonomer content.

Figure 6 shows the variation in solvent resistance for the same films. The coatings derived from the copolymers were found to have somewhat lower solvent resistance than the coating based on poly(2-VOES), which can be attributed to the lower crosslink density of the copolymer-based films stemming from the lower concentration of fatty acid ester pendant groups.

Polyols for PU coatings give high crosslink density

As discussed initially, the unsaturation in plant oils can be utilised to incorporate other functional groups that provide alternative curing chemistries. For example, polyurethane coatings were produced by converting a poly(2-VOES) sample to a polyol [HO-poly(2-VOES)] by first epoxidising the double bonds of poly(2-VOES) with peracetic acid and then ring-opening the epoxy groups with methanol.

Polyurethane clear coatings were produced from the HO-poly(2-VOES) by simply solution blending the polyol with an isocyanate (isophorone diisocyanate trimer) and casting films from the solution. For comparison purposes, a polyol from SBO (HO-SBO) was also produced and an analogous coating produced.

As shown in Figure 7, the crosslinked network from the HO-poly(2-VOES) provided a higher Tg and a substantially higher storage modulus in the rubbery plateau region. The higher storage modulus in the rubbery plateau region is indicative of a higher crosslink density.

The higher crosslink density associated with the use of the HO-poly(2-VOES) can be attributed to the higher number of tertiary carbon atoms per gram of material, as illustrated in Figure 8. In addition to the urethane bonds formed during curing, these tertiary carbon atoms also serve as crosslinks in the fully cured network.
Biopolymers

Versatile chemistry for high quality coatings

The plant oil-based polymer technology described here possesses several attributes with respect to coating applications. Compared to drying oils and alkyd resins, the higher functionality (i.e. double bonds and allylic hydrogens) per molecule results in faster curing by autoxidation. Also, due to the tertiary carbon atoms present in its backbone, relatively high crosslink densities can be achieved. Since these plant oil vinyl ether monomers can be vacuum distilled, colourless monomer can be produced. It was demonstrated that polymerisation of the colourless monomer produces colourless polymer due to the mild conditions of the polymerisation process. The production of a colourless polymer is very important for the production of white and other pale-coloured coatings. Probably the most important attribute of this technology is the ability to utilise copolymerisation to tailor polymer properties. Copolymerisation has been used to increase the Tg of the plant oil-based polymers and to impart water-dispersibility or solubility to the polymer. Due to the living nature of the polymerisation, block copolymers can also be produced with other vinyl ether monomers. While the unsaturation present in the plant oil-based polymers can be directly utilised to produce crosslinked films through autoxidation, the unsaturation can also be derivatised to other functional groups to provide other curing/crosslinking mechanisms.

ACKNOWLEDGEMENT

The authors thank the Department of Energy (grant DE-FG36-08GO088160), United States Department of Agriculture/National Institute of Food and Agriculture (grant 2012-38202-19283), United Soybean Board, National Science Foundation (grants IIA-1330840, IIA-1355466, and IIP-1401803), and North Dakota Soybean Council for financial support.

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