WILEY

Online Proofing System

1. Corrections should be marked with the Adobe Annotation & Comment Tools below:

Online Proofing System

Filename : smj_2167_review.pdf

Please add your comments and click Publish Comments so that other reviewers can automatically see them.

SMJ2167

Strategic Management Journal

Strat. Mgmt. J., **0**: 000–000 (2013)

Published online EarlyView in Wiley Online Library (wileyonlinelibrary.com) DOI: 10.1002/smj.2167

Received 11 May 2012; Final revision received 19 June 2013

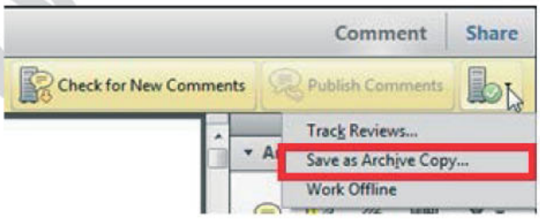
AQ1

COMPETITION-DRIVEN REPOSITIONING

RICHARD D. WANG* and J. MYLES SHAVER

2. To save your proof corrections, click the ‘Publish Comments’ button. Publishing your comments saves the marked up version of your proof to a centralized location in Wiley’s Online Proofing System. Corrections don’t have to be marked in one sitting – you can publish corrections and log back in at a later time to add more.

3. When your proof review is complete we recommend you download a copy of your annotated proof for reference in any future correspondence concerning the article before publication. You can do this by clicking on the icon to the right of the ‘Publish Comments’ button and selecting ‘Save as Archive Copy…’.



4. When your proof review is complete and you are ready to send corrections to the publisher click the ‘Complete Proof Review’ button that appears above the proof in your web browser window. Do not click the ‘Finalize/Complete Proof Review’ button without replying to any author queries found on the last page of your proof. Incomplete proof reviews will cause a delay in publication. **Note: Once you click ‘Finalize/Complete Proof Review’ you will not be able to mark any further comments or corrections.**

Firefox, Chrome, Safari Users

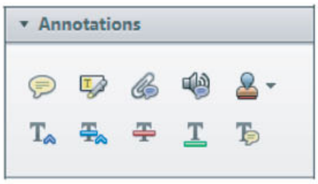
If your PDF article proof opens in any PDF viewer other than Adobe Reader or Adobe Acrobat, you will not be able to mark corrections and query responses, nor save them. To mark and save corrections, please follow these instructions to disable the built-in browser PDF viewers in Firefox, Chrome, and Safari so the PDF article proof opens in Adobe within a Firefox or Chrome browser window.

USING e-ANNOTATION TOOLS FOR ELECTRONIC PROOF CORRECTION

WILEY

Once you have Acrobat Reader open on your computer, click on the Comment tab at the right of the toolbar:

This will open up a panel down the right side of the document. The majority of tools you will use for annotating your proof will be in the Annotations section, pictured opposite. We've picked out some of these tools below:

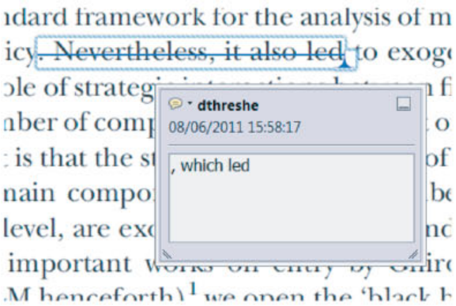


1. Replace (Ins) Tool – for replacing text.

Strikes a line through text and opens up a text box where replacement text can be entered.

How to use it

- Highlight a word or sentence.
- Click on the Replace (Ins) icon in the Annotations section.
- Type the replacement text into the blue box that appears.

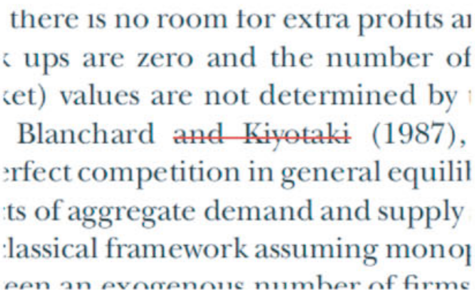


2. Strikethrough (Del) Tool – for deleting text.

Strikes a red line through text that is to be deleted.

How to use it

- Highlight a word or sentence.
- Click on the Strikethrough (Del) icon in the Annotations section.

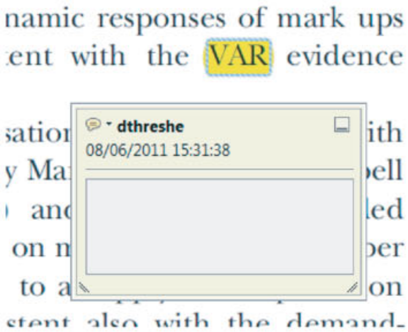


3. Add note to text Tool – for highlighting a section to be changed to bold or italic.

Highlights text in yellow and opens up a text box where comments can be entered.

How to use it

- Highlight the relevant section of text.
- Click on the Add note to text icon in the Annotations section.
- Type instruction on what should be changed regarding the text into the yellow box that appears.

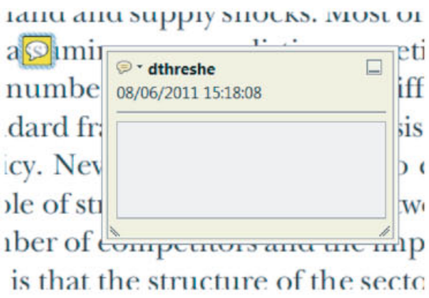


4. Add sticky note Tool – for making notes at specific points in the text.

Marks a point in the proof where a comment needs to be highlighted.

How to use it

- Click on the Add sticky note icon in the Annotations section.
- Click at the point in the proof where the comment should be inserted.
- Type the comment into the yellow box that appears.

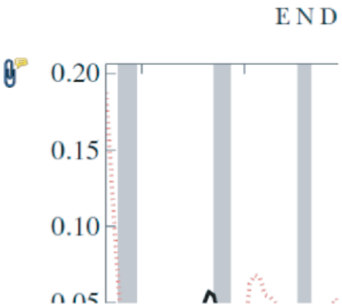


5. Attach File Tool – for inserting large amounts of text or replacement figures.

Inserts an icon linking to the attached file in the appropriate pace in the text.

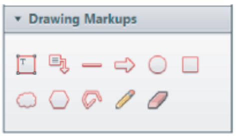
How to use it

- Click on the Attach File icon in the Annotations section.
- Click on the proof to where you'd like the attached file to be linked.
- Select the file to be attached from your computer or network.
- Select the colour and type of icon that will appear in the proof. Click OK.



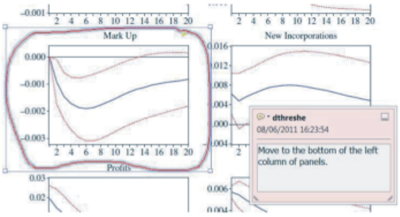
6. Drawing Markups Tools – for drawing shapes, lines and freeform annotations on proofs and commenting on these marks.

Allows shapes, lines and freeform annotations to be drawn on proofs and for comment to be made on these marks.



How to use it

- Click on one of the shapes in the Drawing Markups section.
- Click on the proof at the relevant point and draw the selected shape with the cursor.
- To add a comment to the drawn shape, move the cursor over the shape until an arrowhead appears.
- Double click on the shape and type any text in the red box that appears.



dthreshe
08/06/2011 16:23:54
Move to the bottom of the left column of panels.

Received: 10 April 2015 Revised: 20 August 2015 Accepted article published: 7 October 2015

DOI 10.1002/pi.5033

Recent developments in plant oil based functional materials

Mirna A Mosiewicki and **Mirta I Aranguren** *

Abstract

The increasing interest of academic and industrial sectors in the use of bio-based materials mirrors the overwhelming need for replacing, as much as possible, petroleum derived chemicals, reducing the negative environmental impact derived from their usage. Vegetable oils fulfill this goal extremely well, because of their worldwide availability, large volume production at comparatively low prices and versatility of the modifications and reactions in which they can participate to produce a large variety of different monomers and polymer precursors. Further reactions of these chemicals can lead to very different types of final materials with varied applications. It is because of this remarkable versatility that many review articles have appeared during the last few years; many of them have dealt with the various routes for vegetable oil modification and options for polymer synthesis, whilst others were dedicated to the analysis of the properties of the derived materials, generally focusing on structural properties. In this review, we focus on the capabilities of vegetable oils to be modified and/or reacted to obtain materials with functional properties suitable for use in coatings, conductive or insulating materials, biomedical, shape memory, self-healing and thermoreversible materials as well as other special functional applications.

Keywords: plant oils; vegetable oils; bio-resins; bio-based polymers; functional properties; smart materials

INTRODUCTION

Plant oils have found very different and diverse uses in history, not just as food ingredients but also as industrial chemicals such as paint solvents, varnishes and lubricants or polymer modifiers. However, it has been during the last few years that they have received renewed and growing attention from the areas of energy and new materials. Since it became obvious that there was a need to find alternatives for replacing or reducing the consumption of petroleum, due to its non-renewable nature and dwindling reserves, the use of vegetable oils in the production of biofuel has increasingly gained importance. The final disposal of products formulated with synthetic polymeric materials is also a big concern that contributes to widening the use of bioresources beyond the narrow range to which they were confined during the second half of the last century. It became equally apparent that plant oils could contribute to replacing petroleum as a source for polymers aimed at different applications. Because of their special characteristics, not only replacements of fuel based polymers can be envisioned, but also novel materials with particular properties.

Vegetable oils consist of triglyceride molecules, esters of glycerol and fatty acids, whose structure (chain length, content and amount of unsaturation and the presence of other chemical groups) depends on the plant source. Because of the variety of potentially reactive groups present in their structure they can be chemically modified giving a response to the need for different types of bio-based reactants. As a result, the number of publications focusing on polymers based on plant/vegetable oils has seen an increasingly fast growth since the 1990s. In these past two decades, important contributions have been made by different research groups around the world to the synthesis of polymer precursors and resins from plant oils, and several review papers and books gather these advances.[1–10] The work has covered the synthesis of bio-based polyurethanes, crosslinked polymers, plant oil based composites, as well as monomers and additives for different formulations. Although a review on vegetable oil based polymeric composites has recently been published,[11] there are not many papers that condense the latest advances in the use of vegetable oils for the formulation of materials with functional applications. A literature search shows that the most frequent approach has been the study of the structural bulk properties of these materials, but other properties have also attracted the interest of researchers. In particular (as could be expected from the old tradition of using oils in paints and varnishes), coating and thin film applications have been considered, in which hardness, glossiness and scratching resistance are properties of paramount importance. However, other functional properties have been examined depending on the envisioned purpose, from insulators and foams to biomedical applications.

Considering the above, this work is focused on reviewing the use of plant oils for the production of materials for non-structural and functional applications such as coatings, adhesives, electrically insulating or conductive materials, biomedical applications, smart or responsive polymers and other specialty formulations.

---

* *Correspondence to: Mirta I Aranguren, Institute of Research in Materials Science and Technology (INTEMA) and Facultad de Ingeniería, Universidad Nacional de Mar del Plata – National Scientific and Technical Research Council (CONICET), Argentina. E-mail: marangur@fi.mdp.edu.ar*

Institute of Research in Materials Science and Technology (INTEMA) and Facultad de Ingeniería, Universidad Nacional de Mar del Plata – National Scientific and Technical Research Council (CONICET), Argentina

Mirna Alejandra Mosiewicki (PhD INTEMA, Argentina, and postdoctoral student at the University of Alabama, USA) is Professor at the Universidad Nacional de Mar del Plata and researcher at the Ecomaterials Group (INTEMA). Her research interests are polymers, composites and nanocomposites from biomass and materials with functional properties. She is coauthor of 38 international papers and five book chapters.

Mirta Inés Aranguren (PhD, University of Minnesota, USA) is Professor at the Universidad Nacional de Mar del Plata and head of the Ecomaterials Group (INTEMA). Her research interests are polymers, composites and nanocomposites based on biomass. She has received IFS and TWAS grants, an IFS award and a Guggenheim Fellowship. She is co-author of more than 100 international articles and several book chapters.

PLANT OILS AND ROUTES OF CHEMICAL MODIFICATION

Much work has been realized during the last two decades to produce monomers, polymer precursors and resins from vegetable oils. The triglyceride molecules are triesters of glycerol and fatty acids with chain lengths of *ca* 14–20 C atoms, but most frequently 18 C atoms. These chains can be saturated or contain 1–3 unsaturations, conjugated or not. Besides, some naturally occurring fatty acid chains contain special chemical groups, such as hydroxyl or epoxy groups. Because of their different chemical structures, relatively low cost and geographical availability around the world, plant oils constitute very versatile resources for the formulation of novel polymeric materials.

Vegetable oils can be chemically modified through epoxidation to be further reacted with anhydrides or isocyanates, or they can be cationically polymerized or modified using olefin metathesis, thiol-ene addition etc.[1,3,5,8,12] Probably, epoxidation is the most frequent modification (including cases where the oxirane ring is opened to synthesize biopolyols), but also ozonolysis (of the original oil, the constituent fatty acids or other derived molecules) is applied to obtain chains with end chemical groups (such as primary hydroxyls) by cleavage of the original chain.[13]

FUNCTIONAL PROPERTIES AND APPLICATIONS

Coatings

The use of vegetable oils in the synthesis of protective or decorative coatings offers a wide range of possibilities through the tailoring of plant oils and their derivatives to suit requirements for different applications. A recent publication[14] has focused on this specific purpose. As in the case of structural materials based on plant oils, functional materials are also frequently polyurethane (PU) or epoxy based formulations, and this is particularly true in the case of coatings. Besides, combinations with other polymers or addition of nanoparticles have been considered in order to improve the quality of the coatings. For example, Lu and Larock[15] prepared a hybrid coating through the emulsion polymerization of combined latexes of a soybean-based waterborne polyurethane (WBPU) and methyl methacrylate/butyl acrylate copolymer. The combination of the two polymers dispersible in water allowed the development of extended interactions between the copolymers, such as grafting of acrylics onto the WBPU and interpenetration of the two polymers, leading to improved thermal and mechanical properties. Thus, the Young's modulus, tensile strength and elongation at break of the PU film were 154 MPa, 8.8 MPa and 200%, respectively. On the other hand, although the hybrid latex film (75 wt% acrylic) showed values of 537 MPa and 16.9 MPa for the first two properties, the content of the bio-PU was much reduced in this formulation. Regarding the elongation at break, it showed a maximum of 365% at 50 wt% acrylic content, which may be desirable depending on the envisioned application.

Chaudharia *et al.*[16] also worked with PU coatings but incorporating nanoparticles of titanium dioxide. The PU was based on a polyetherimide based on neem seed oil (a non-edible oil with large production in India and used mainly in medicinal applications) and bisphenol A, which were reacted with MDI (4,4′-diphenylmethane diisocyanate). The nanocomposite coatings contained 0–4 wt% of vinyltriethoxysilane modified nanoparticles. Drying time, an important property for coating applications, was observed to diminish as the content of modified TiO_2 increased from 0 to 3 wt%, but it increased again at 4 wt% of the oxide. As in the previous example, all the coatings were flexible, and additionally they showed good resistance toward acids, alkalis and xylene. In the present case, although gloss increased with the content of TiO_2, other properties (such as impact resistance and hardness) improved only up to a nanoparticle concentration of 2–3 wt%, decreasing at higher contents. This observation was explained by the increased difficulty of dispersing the nanoparticles at high concentrations, a usual problem in nanocomposites.

As mentioned above, another frequent modification is epoxidation, and several products are commercially available. Tsujimoto *et al.*[17] used epoxidized soybean (ESO) and linseed oils (ELO) together with two silanes (3-glycidoxypropyltrimethoxysilane (GPTMS) and 2-(3,4-epoxycyclohexyl)- ethyltrimethoxysilane (ECTMS)). The preparation resulted in nanostructured coatings that presented domains rich in organics and inorganics (silica), the latter produced by condensation of the silanes that acted as reinforcements in these formulations. A comparison of the properties of the sets of films prepared from the two oils is a good example of the effects of the oil chemical structure on the final product properties. Thus, the polymers prepared with ELO resulted in harder coatings, in perfect agreement with the higher oxirane content of the ELO with respect to ESO, which led to a higher degree of crosslinking of the network based on ELO and consequently a higher glass transition temperature T_g of the nanocomposite film. As expected, the generated inorganic phase led to improved mechanical properties (Young's modulus 210 MPa for the unmodified ESO coating, and 620 MPa and 830 MPa for the samples containing 20 wt% of GPTMS and ECTMS, respectively). Gloss and hardness were also much improved: a gloss value of *ca* 100 measured at 60 °C compared to the tacky unfilled coating, and a hardness value of 27 N mm^{-2} for the 20 wt% ECTMS-ESO sample compared to only 9 N mm^{-2} for the unmodified ESO coating. Because of the nanosize of the organic and inorganic domains, and the good dispersion obtained through covalent interfacial bonding, the films were highly transparent (at least up to 20 wt% silane) as determined using UV – visible spectroscopy.

Coatings are generally applied to fulfill a protective function with respect to the supporting material; in some cases, specific functions are also incorporated. On this line of thought, Lu *et al.*[18] utilized a soybean oil to improve the barrier properties of a hygroscopic packaging material made from nanofibrillar cellulose. To achieve this goal, they produced base films from mixtures of the nanocellulose and beeswax latex (10 wt% on a dry basis), and added a coating made of an epoxidized soybean oil (AESO) and 3-aminopropyltriethoxysilane. Films of 10 g m^{-2} were coated to achieve different thicknesses (corresponding to 1, 3 and 5 g m^{-2}). The application of the barrier material resulted in the reduction of water vapor transmission from 5088 g m^{-2} in 24 h (38 °C, 90% RH) to 188 g m^{-2} (equal conditions) for a coating weight of 5 g m^{-2}. Because of the combination of additives selected, the nanocomposite films became very hydrophobic (the contact angle changed from 67.3° to 106.5° respectively for the microfibrillated cellulose film and the film containing beeswax with the thickest coating). As the base material was a cellulosic film, it had high flexibility, and additionally the coating contributed to improving thermal stability and transparency. This last observation has also been reported in other work – when a polymer is added to fill any possible porosity of a nanocellulose film, with a consequent reduction of light scattering.

The dielectric properties of these materials were studied by other authors who worked on PU coatings for insulation.[19] Hyperbranched PUs were synthesized from castor oil or the monoglycerides of castor oil by reaction with toluene diisocyanate and incorporation of butanediol and polycaprolactone as diols.[19] The coating made from castor oil was better suited as a dielectric material than the coating synthesized from the monoglyceride, presenting a higher dielectric constant. On the other hand, the PU made from the monoglyceride had slightly better mechanical and scratch properties and higher gloss than the PU obtained from the castor oil, which is related to the different structure of the resulting PU networks. However, chemical resistance in distilled water and in aqueous solutions of HCl (5 v/v%), NaOH (10 w/v%) and NaCl (10 w/v%) was high and quite similar for the two types of PUs. Also, a study on the dielectric properties and insulation potential of a bio-PU was reported by Petrović *et al.*[13] They used ozonolyzed bio-polyols (soybean and canola oils) to formulate PUs with a wide range of final properties (from those of a rigid plastic to hard rubber-like behavior) governed by the density of crosslinking and the content of dangling chains.

Certainly, corrosion protection is a much esteemed function of coating films. For example, Alam and Alandis[20] used potentiodynamic polarization tests in different corrosive media to investigate the corrosion resistance of a coating deposited on mild steel and prepared from a polyetherimide resin based on an amide from corn oil and catechol, further reacted with isophorone diisocyanate.[20] Different weight percentages of isocyanate were used, and it was found that the highest hardness was reached at 35 wt% of isocyanate; higher concentrations in the formulation reduced the property, which was explained by the excess of isocyanate leading to secondary reactions. The good flexibility of the films was related to the alkyl chains of the oil, a characteristic also present in previous examples and that can be traced to the dangling chains present in networks based on vegetable oil polymers. In most cases, reactive groups are located in the middle of the fatty acid chains (as a result of the modification of the original unsaturation of the triglyceride), and a short dangling chain results when these groups react. On the other hand, polar groups in the PU structure led to good adhesion to the metal. In addition to good scratch hardness and impact resistance, the material showed a corrosion rate of 1.377 × 10^{-2} mm year^{-1} in HCl solution (3.5 wt%) and 2.359 × 10^{-3} mm year^{-1} in NaCl solution (5 wt%), conferring good protection thanks to the crosslinked structure of the coating. TGA showed that the coatings could be safely used up to at least 250 °C.

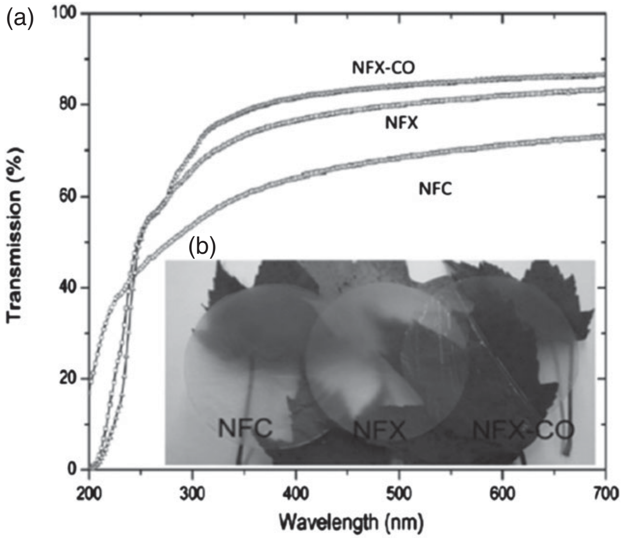


Figure 1. (a) SEM pictures of the produced films: NFC corresponds to the cellulose film, NFX to the film produced with the added beeswax and NFX-CO to the NFX films with the vegetable oil coating. (b) UV – visible transmission spectra of the films. Adapted from reference 18. Reproduced with permission.

Adhesives

Plant oils have been used as raw materials for synthesizing a wide variety of polymers that found application as adhesives, with PU being one of the most frequently used, especially when wood is the substrate. As is well known, the hydroxyl groups in the wood can react with the isocyanate component of the PU formulation, contributing to the excellent substrate – polymer bonding observed in these materials. One example of a PU adhesive system for wood bonding produced from potato starch/natural oil based polyester polyol and toluene 2,4-diisocyanate was reported by Desai and co-workers.[21] They found that the shear strength of the vegetable oil based PU adhesive was higher than that of commercially available adhesives for wood joints with an optimum NCO/OH ratio of 1.3. These PU adhesives presented good resistance to cold and hot water, although with moderate resistance to acids and weak resistance to alkali. It was also reported that, as the hydroxyl value of the polyol increased, bond strength increased due to formation of a more highly crosslinked structure, an observation that was confirmed by Somani *et al.*[22] who produced a PU adhesive by reacting a castor oil derivative and several glycols (ethylene glycol, diethylene glycol and triethylene glycol) with isocyanate adducts. These authors also used an NCO/OH ratio of 1.3 and reported that adhesives made from castor oil based polyol with shorter glycol segments gave adhesives with shear strength higher than that found for the commercially available wood adhesives used for comparison.

A more recent work with adhesives based on PUs was reported by Kong *et al.*[23] They synthesized a bio-based poly(ether ester)

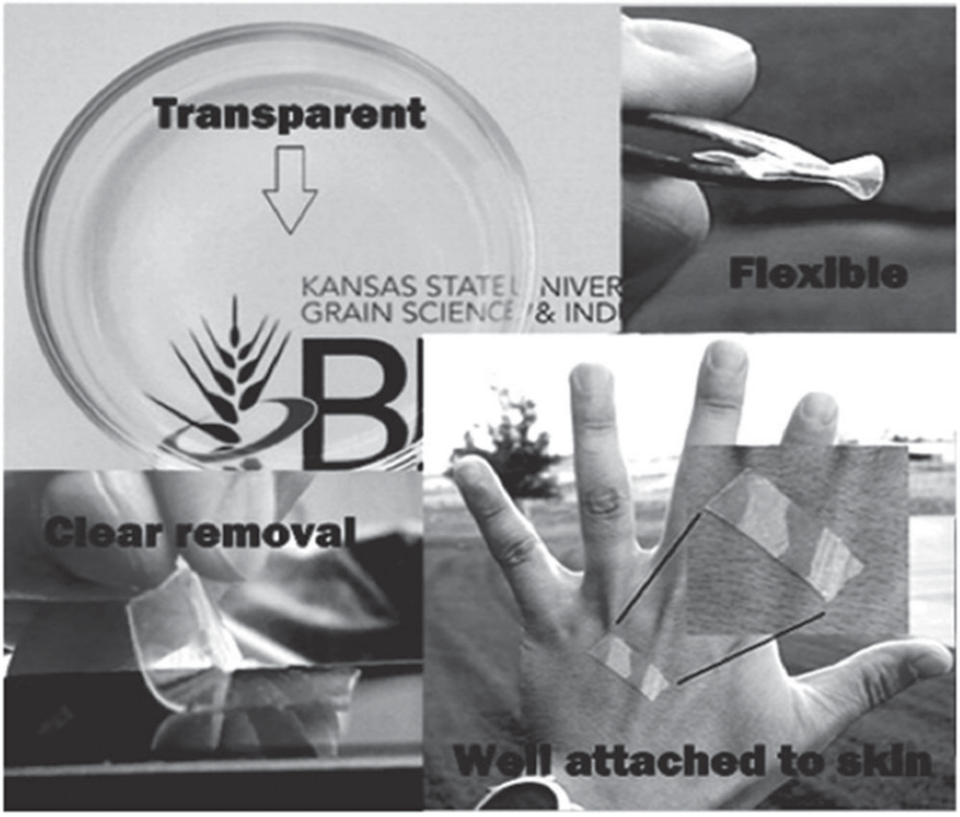


Figure 2. Images illustrating the characteristics of the ESO derived films. From reference 24. Reproduced with permission.

polyol from canola oil containing primary and secondary functional groups via epoxidation of canola oil and further reaction by ring-opening with 1,3-propanediol, for the subsequent preparation of PU adhesives. The authors reported similar adhesive properties of the bio-based system compared to those of commercial adhesives in terms of lap shear strength and overall chemical resistance to cold water, acid and alkali. The general observation from the previous work is that high NCO/OH ratios lead to high performance. This effect is related to the fact that free isocyanate can react with the wood improving the wood adhesive properties, because of the higher crosslinking density that leads to a higher rigidity and strength of the adhesive bonds.

Some plant oil systems have been effective in the preparation of pressure-sensitive adhesives. Kollbe Ahn *et al.*[24] used fast curing formulations based on ESO and from a mixture of ESO with dihydroxyl soybean oil (DSO), in both cases polymerized with the addition of H_3PO_4 to form a network with phosphoric ester and ether crosslinkages. The films had a low thermal expansion coefficient, which was 14.08 ppm K^{-1} for the ESO derived material, compared with that of glass (8.5 ppm K^{-1}) and that of flexible plastics (approximately 50 ppm K^{-1}). The modulus of the polymer was too low to produce self-standing films, so it was characterized as a coating on a substrate instead. On the other hand, it had excellent transparency, comparable to that of glass (even better than glass at a wavelength of about 300 nm) (Fig. 2). DSO was added to the formulation as tackifier and the adhesion to a glass substrate was tested, resulting in an adhesive with slightly higher peel strength than some commercial adhesives for reusable sticky note papers, at least during 10 stick-and-peel repetitions.

The preparation and characterization of urethane acrylate pressure-sensitive adhesives based on palm oil were discussed by Mahmood and co-workers.[25] The molecular structure of the diisocyanate compounds and hydroxyl acrylate monomers tended to determine the molecular weight and hence viscosities of the final products made from the urethane acrylate prepolymers, but had no direct effects on the properties of the UV curable coatings and adhesives. Comparatively, competitive adhesives from epoxidized camelina oil (a highly unsaturated oil) were also used in UV curing formulations.[26]

The performances of adhesives prepared from palm oil and from jatropha oil have been compared in the work of Aung *et al.*[27] Jatropha oil based adhesive (PU made from a polyol prepared by hydroxylation and alcoholysis or epoxidation) exhibited better shear strength adhesion to solid wood and plywood compared to palm oil based adhesives as well as overall resistance to chemicals (response to hot water, acid and alkali). The differences were explained by the higher content of unsaturations of the jatropha oil and the presence of natural gums.

Thermal insulation

One important market for vegetable oil derived materials is foamed polymers and composites, including foams for thermal insulation mostly prepared from PU and epoxy formulations.

As an example of epoxy formulations applied to the construction industry, an epoxidized tall oil (40–50 wt%) was utilized in a mixture with different proportions of clay, fly ash and rice husk ash.[28] The authors found that the different composites prepared from these raw materials had relatively low thermal conductivity, varying from 0.537 to 0.256 W m^{-1} K^{-1}, with increasing values as the amount of clay increased in the composite material and decreasing as the concentrations of the epoxidized oil and the flash ash increased. It is important for the application to notice that the reported values are in the same range as (in some cases lower than) the thermal conductivity of conventional cement block with perlite (0.427 W m^{-1} K^{-1}). The prepared material can be a replacement for standard plaster and it can be sawed, drilled or milled, with the advantage of a lower density and for some samples much lower thermal conductivity.

On a different approach, low conductivity foams based on vegetable oils have been considered by different authors.[29–34] For example, two different polyester polyols were prepared from castor oil by alcoholysis of the oil with glycerol or pentaerythritol and further esterification with phthalic anhydride.[30] PU rigid foams were further produced by crosslinking with a polyaryl polymethylene isocyanate. The properties of the bio-based foams were comparable to foams prepared from commercial polyesters: densities in the range 37–38.5 kg m^{-3}, thermal conductivities of 0.021 – 0.023 W m^{-1} K^{-1}, compression strengths (10% compression strength in the parallel direction relative to the foaming rise) of 173–199 kPa and similar dimensional stability compared to commercial formulations. Besides, the thermal stability was better for the bio-based foam, and was further improved with the addition of a flame retardant (ammonium polyphosphate, APP). Characterization by cone calorimetry showed a significant decrease of the heat release rate, total heat release and mass loss for the samples with added APP. Additionally, the improvements were more noticeable for the two bio-derived polyester polyols due to the presence of the phthalic rings.

Foamed PU composite materials with similar low densities (apparent density *ca* 40 kg m^{-3}) were prepared with a rapeseed oil based polyol by addition of a low percentage of vegetable fibers.[31] The replacement of 30% of a petrochemical polyol by rapeseed oil based polyol led to more and smaller cells, with a consequent increase in the apparent density and thermal conductivity of the foams. One interesting result of this work is the confirmation of the relation between compression strength and apparent density of the foams. Addition of fibers above 5 wt% led to a lower apparent density; similarly longer fibers (1.2 – 2 mm instead of 0.5 mm) added in the composites at a fixed concentration resulted in foams of lower relative density. The short fibers could accommodate better in the cell strouts than long fibers, causing less damage and distortion of the foam structure and consequently leading to higher compressive strength.[31]

Rapeseed oil based rigid foams of high apparent density (*ca* 300 kg m^{-3}) were prepared by the same group.[32] In this case, after epoxidation and ring opening, a further step of esterification with triethanolamine was performed that led to different hydroxyl contents and different reactivity. As in the case of low density foams, the compression strength was improved with the addition of 5 wt% fibers (flax in this work). In particular, the authors found that the use of vegetable oils led to reduced hydrophilicity of the materials.[32]

Transesterification with triethanolamine has also been used to prepare rigid PU foams from castor oil filled with wood flour.[33] It is interesting to mention the results of the TGA. When comparing the experimental derivative signal and a prediction calculated from the curves of the PU and the wood flour, large differences were observed that were related to the strong interactions that were developed in these systems. Thus, a char value higher than the calculated value was one of the consequences of these interactions.[33] Also a higher than predicted char value was determined by TGA of a tung oil (TO) based rigid PU foam filled with rice husk ash having a high silica content[34] that also contributed to the inorganic residue.

Smart polymers

Shape memory polymers

Among the functional properties of polymers, some are related to the behavior of smart materials that have autonomous responses to ambient changes. In particular, materials that show shape memory behavior have a sensitive response (change of shape) to external stimuli such as temperature, pH, humidity, light and electricity. Among the shape memory materials, thermoresponsive polymers have gained enormous attention because of their good processability, low cost and high recovery ability at relatively low temperature.[35–38] They are capable of fixing a transient shape and recovering their original dimensions when heated above a switching temperature, T_{switch}. For shape memory polymers this temperature is usually the glass transition temperature T_g or the melting temperature T_m of one of the phases in multiphase polymers, and it is higher than the application temperature. The permanent shape is fixed in the material through chemical or physical crosslinks that are stable in the conditions of application.[39] These materials, responsive to changes in environmental conditions, have found use in actuators, smart fabrics, heat shrinkage tubes for electronic packaging, and biomedical devices.

One of the first reports on shape memory polymers using vegetable oils is due to Li and Larock.[40] This work presented the development of shape memory polymers using cationic copolymerization of regular soybean oil (SOY), low saturation soybean oil and/or conjugated low saturation soybean oil with styrene (St) and divinylbenzene (DVB), initiated by boron trifluoride diethyl etherate or related modified initiators. The type of soybean oil employed affected the shape memory properties of the resulting polymers. The reactivity toward cationic polymerization was shown to increase with the concentration of double bonds and particularly with the concentration of conjugated double bonds. For SOY concentrations exceeding 50%, the resulting polymer had a low T_g and behaved like a regular elastomer.[41] Introducing DVB in the formulation, the degree of crosslinking was increased and consequently the T_g values of the resulting polymers. This also had an effect on other properties of the materials: the deformability was reduced, the ability of the polymers to fix temporal deformations was enhanced (from 23% to 100% at room temperature) and complete shape recovery was obtained for all the specimens. Similar results were reported by Meiorin *et al.*[42] on cationically polymerized TO with partial replacement of St by DVB. As in the previous case, the T_g of the samples increased, which was related to the more rigid crosslinking structure generated by this comonomer. This allowed T_{switch} to be changed from 25 °C to 40 °C.[42]

TO is naturally suited to be cationically polymerized because it is formed by a high percentage of α-eleostearic acid (80% – 85%) that has three conjugated unsaturations per chain, readily reactive under the proper temperature and catalysis conditions. Hard elastomers prepared from this oil and St presented shape memory behavior with high capabilities of fixing the temporary shape and recovering the initial one, and also displayed high damping quality.[43] The properties of the copolymers can be related to the degree of crosslinking, the length of St homopolymer sequences and the mobility of the dangling chains in the crosslinked network. These materials can exhibit shape memory behavior in a low temperature range. Figure 3 shows the shape recovery of a bar shaped sample containing 70:30 wt% of TO and St and initially deformed at a temperature above T_g to adopt a curly temporary shape. The series of images shows the recuperation of the deformed sample after being immersed in hot water (40 °C) to recover the original bar shape after 40 s.

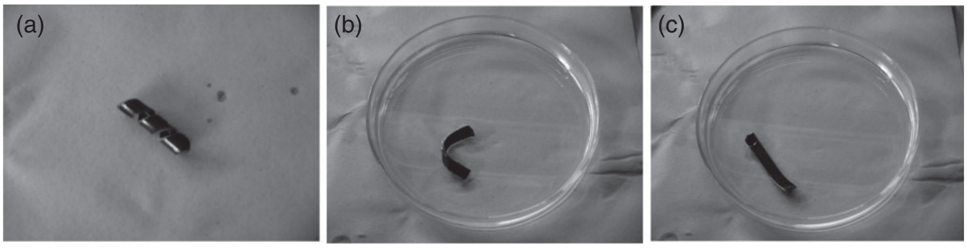


Figure 3. Shape recovery of a TO/St sample initially deformed at a temperature above T_g to adopt a curly shape. Temporary shape before heating and recovery (a), and after 20 s (b) and 40 s (c) in hot water. From reference 43. Reproduced with permission.

The partial replacement of St by DVB did not have disadvantageous effects on the good damping properties of the copolymers with 50 wt% TO and different ratios of St or DVB; however, the shape memory properties were only obtained with low DVB contents (up to 10 wt%).[42] The thermal mechanical cyclic tests showed that the recovery force increased with the crosslinking density (higher DVB content), as well as the fixity ratio, while the recovery ratio decreased with the DVB content in the copolymer.

Although not frequently mentioned, these materials suffer chemical aging because vegetable oil can be oxidized in contact with air. The reactions that are responsible for rancidity in vegetable oils occur when unsaturations are present, which may be the case if unreacted double bonds remain after the network formation. Meiorin *et al.*[44] have evaluated the changes with time of the properties of the TO copolymers mentioned above. The action of atmospheric oxygen produced chemical changes in these polymers, affecting their glass transition temperature and consequently increasing the switch temperature for the shape memory behavior. These authors have reported and compared the shape memory properties of recently prepared and aged (2 years after preparation) samples of TO/St copolymers. The change in glass transition temperature of the copolymers with time (aging) allowed T_{switch} to be increased from 25 to 40 °C with St contents of 50–70 wt%. Aged samples with 50–60 wt% St could be cyclically stretched at 40% strain (at 40 °C), showing high fixity and recovery values (100% for the 60 wt% St sample). Higher elongations could also be reached with fixity ratios higher than 99.4% and recovery ratios higher than 84.4% in all cases.

The replacement of St by a vegetable oil derived monomer (methyl ester of TO obtained by transesterification of the oil with methanol) in the cationic polymerization with TO was also investigated.[45] All the materials obtained presented good mechanical damping capacity, but addition of DVB (10 wt%) was necessary to obtain shape memory behavior at low T_{switch} (25 °C).

Other polymerizations are also possible and have been used. A bio-based polymeric material from ESO and poly(L-lactic acid) (PLLA) has also been reported to show shape memory behavior.[45] PolyESO/PLLAs were synthesized by acid-catalyzed curing of ESO in the presence of PLLA. PLLA was scarcely reacted with ESO during the reaction and was dispersed in the ESO based polymer network. A sample polyESO/PLLA (50/50 wt%) was shown to maintain a temporary shape at 20 °C, with a T_{switch} of 80 °C and complete recovery of the original shape. At a higher temperature ($T > T_g$(PLLA)), the polyESO/PLLA is easily deformed because both the ESO polymer and PLLA are in a rubbery state. After the subsequent cooling (20 °C), PLLA becomes glassy, and the temporary shape is fixed with the internal stress of the ESO based polymer network. Upon reheating above T_{switch}, the PLLA chains regain mobility and the sample recovers the original shape by action of the entropic elasticity of the ESO based polymer network. The addition of the PLLA is required to achieve good shape memory properties (recovery was higher than 90% in all cases), since the ESO homopolymer is too brittle to be conveniently deformed. Moreover, strain fixity decreased as the PLLA content decreased because of the increase in inner stresses of the ESO network. Repeated cycling was possible, and recovery was observed even after five cycles.

Polymers are mostly used in modified formulations or in the form of composites in order to tailor the material properties, and in more recent times different nanofillers have been incorporated into the polymer matrices with this objective. Saralegi *et al.*[47] have investigated the effect of the addition of cellulose nanocrystals on segmented thermoplastic PU shape memory properties. Particularly interesting is the fact that these PU composites were synthesized by adding cellulose nanocrystals in the first step of polymerization (thus being able to react at the same time as the other OH components of the reactive mixture) and that a castor oil based diol and a cornsugar based chain extender were used. The bionanocomposites presented two main transitions – the melting events of the soft and hard phases, responsible for shape fixity and shape recovery, respectively. The neat PU presented poor shape memory properties, with low recovery ratios (*ca* 50%), but the addition of cellulose nanocrystals led to an increase of the hard phase crystallinity; thus more physical network points took part in molding the permanent shape and a significant improvement was observed in the shape recovery (*ca* 100% for the second cycle) with $T_{switch} = 60$ °C. In all cases, the capacity of the soft segments to act as switching segments was retained for several cycles.

Self-healing and recyclable thermoreversible materials

Among the smart materials, self-healing materials have gained much attention in the last few years because of their structurally incorporated aptitude to mend damage caused by mechanical usage over time. The formation of microcracks during service in structural materials is a critical problem in polymers and composites. The development and coalescence of microcracks can lead to catastrophic failure of the materials, reducing their lifetimes.[48] A material that intrinsically corrects damage caused by normal usage can reduce the costs of industrial processes, because of the longer part lifetime, the reduction of inefficiency caused by degradation and the reduction of costs incurred by material failure.

In this area of work,[49] 'green' self-healable polymer networks have been obtained by the reaction of an initial emulsion of an aqueous solution of citric acid in ESO, using the protons derived by the citric acid dissociation in water as a catalyst of the epoxy–acid reaction. The initial system was an emulsion, but it became a homogeneous and transparent polymer network after curing. The reaction was initiated by the protonation of epoxy groups followed by the attack of carboxylate groups (epoxy–acid reaction) or water molecules (hydrolysis of epoxy groups). Residual COOH groups underwent esterification reactions with OH groups at high temperatures. The transesterification reactions of hydroxyester groups at high temperatures are the reactions responsible for stress relaxation and self-healing in the material without the addition of any extrinsic catalyst. These reactions could also enable the recycling of parts by milling followed by compression molding at 160 °C.

Mendability and thermoreversible polymerization for recycling have also been the focus of a series of papers based on vegetable oils and/or derived monomers bearing furan moieties.[50–55] Some of these polymers can also be used as coatings/adhesives that can be removed by heating the polymer. Furan heterocycles were attached through thiol-ene click chemistry and subsequent Diels–Alder polycondensation of the furan moiety with complementary maleimide moieties at a temperature *ca* 65 °C. Linear, branched and crosslinked polymers were produced by the adequate selection of modified plant oils, or derived monomers and comonomers. The authors showed that links formed from these furan moieties are thermoreversible, recovering the starting monomers or other monomeric structures (depending on the initial formulation) through a retro Diels–Alder reaction when they are heated above *ca* 100 °C. The acid derivative of the pyrolysis of castor oil (10-undecenoic acid) was used as the basic raw material to attach the furan moiety in the work of Vilela *et al.*[51–53] A TO was directly used to produce a Diels–Alder adduct by reaction with bismaleimides (the vegetable oil functioning as a diene).[55] However, the thermoreversibility was not observed in this material, although it was observed when the Diels–Alder reaction was performed on a derived precursor obtained from the aminolysis of the oil with excess furfuryl amine. The Diels–Alder susceptible sites are the furan moiety and the unsaturations of the fatty acid amide formed. The authors give a step forward by using bismaleimides with different structures in an attempt to tailor the flexibility of the final material (the highest rigidity related to the use of an aromatic bismaleimide). Not all the formulations presented thermoreversibility but only those with retro Diels–Alder involving the furan moiety.

Magnetic properties

As already mentioned, the incorporation of small percentages of nanoparticles can change the material properties, depending on the nanoparticle characteristics and allowing the development of new applications.

Specifically, magnetite particles (Fe_3O_4) incorporated into polymers could potentially induce a response in the material on the application of magnetic fields. This would allow new responsive mechanisms to be generated to activate particular behaviors in these polymers. In particular, under an alternating magnetic field, the particles could produce heat, triggering the response of shape memory polymers, or incorporate magnetic properties to an originally diamagnetic polymeric matrix, widening the field of applications. Although several papers related to shape memory polymers and magnetic nanoparticles have been published recently,[56] the use of bio-based polymers for this type of material offers environmental advantages, although this is still a scientific and technological challenge. This was the motivation behind the addition of magnetite nanoparticles (MNPs) (1 and 9 wt%) to a TO/St copolymer (50/50 wt%).[57] MNPs were synthesized by the method of alkaline coprecipitation, followed by coating with oleic acid in order to make their surfaces hydrophobic and improve their compatibility with the polymeric matrix. To characterize the static magnetic properties, isothermal magnetization curves as well as zero-field cooling/field cooling measurements were performed and the results showed that both nanocomposites presented superparamagnetic behavior. From the results of the 1 wt% sample, a very narrow distribution in size of these nanoparticles (in the composite) was inferred, as well as absence of particle–particle agglomeration and inter-particle interactions in the nanocomposites. The results obtained for the 9 wt% MNP sample indicated an increase in dipolar interactions between nearby nanoparticles. The sample with 1 wt% MNP presented shape memory properties denoting a response governed exclusively by the polymer matrix.

Electrical properties

The development of more environmentally friendly base materials is also growing in the production of electronic devices such as printed circuit boards (PCBs). High electrical resistance, low dielectric constant and low dielectric loss are desirable properties for PCB applications.[58] While there are many different types of base materials for PCBs, they all contain resin systems, as well as reinforcements and additives/modifiers. Dimensional stability at different temperatures is important to maintain good adhesion between copper lines and the supporting composite. Although different systems and material combinations have been reported,[59–62] most commercial PCBs consist of glass fiber cloth reinforced epoxy composites because of the good combination of mechanical and electrical properties.

An unusual combination was proposed by Zhan and Wool,[63] who have worked on the development of greener composite materials for PCBs using soybean oil resins, chicken feathers and E-glass fibers that could potentially replace the traditional E-glass/epoxy composites. The phthalated acrylated soybean oil (PAESO) was prepared from AESO. The flame retardancy of the PCB was achieved by halogen-free melamine polyphosphate and diethylphosphinic salt. The volume and surface resistivity of the composites were in the range required for PCB insulation materials.[64] The dielectric relaxation of the composites was controlled by the polymer. At high frequencies, the rotational motion of the molecules had a delay behind the electric field,[65] which led to a decrease of the dielectric constant as the frequency increased. The addition of flame retardants incorporated higher polarity and the dielectric constant comparatively increased. However, the dielectric losses were very close to 0.02, which is a typical value for commercial PCB materials.[64] Although the evaluation of various properties of the bio-based PCBs showed comparable values to traditional materials, some of the properties, like peel strength, still needed to be improved in order to use these biocomposites as alternative materials for PCBs.[66] Figure 4(a) shows a PCB made from chicken feather fibers and soybean oil resins. The circuits on the board are trans-impedance amplifiers for an eight-channel photodiode array. Figure 4(b) shows a bio-based PCB mounted with electronic components and used for a telephone.

On the other hand, a polymer material complexed with salt may show ionic conductivity, giving the opportunity for the development of solid-state electrochemical devices for energy storage such as rechargeable batteries, photoelectrochemical cells, supercapacitor and electrochromic windows.[67] A photoelectrochemical solar cell is an electrochemical device that can generate electrical and electrochemical energy upon absorption of light by one or more of the electrodes. It is generally composed of a photoactive semiconductor electrode (either n- or p-type) and a metal counterelectrode, which are immersed in suitable redox electrolytes.[68,69] Bio-based PUs have also been used to develop a photoelectrochemical cell as solid polymer electrolyte with lithium iodide (LiI)

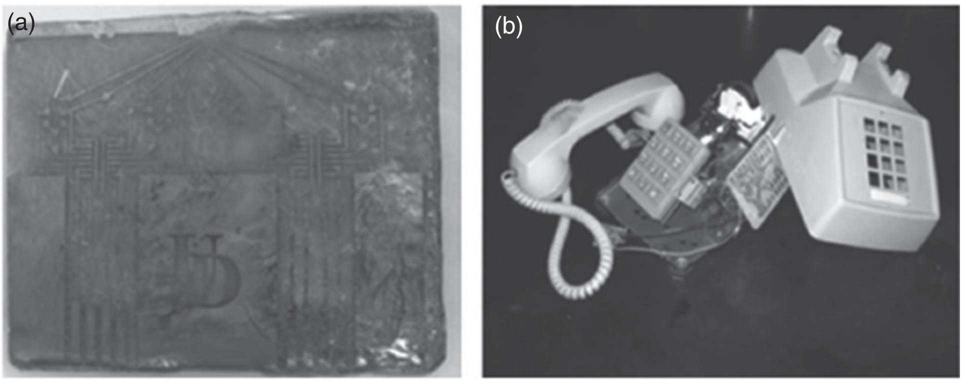


Figure 4. Bio-based printed circuit boards. (a) A printed circuit board made from feather fibers and soybean oil resin. The circuits on the board are trans-impedance amplifiers for an eight-channel photodiode array. (b) A bio-based printed circuit board mounted with electronic components and used in a telephone. From reference 63. Reproduced with permission.

as the conducting material.[70] In the initial stage, the PU prepolymer was prepared via a prepolymerization technique by reacting palm kernel oil based monoester-OH (PKO-p) and 2,4′-methylene diphenyl diisocyanate (2,4′-MDI). The PU electrolyte film was then prepared by inclusion of varying amounts of LiI via a solution casting technique. The formation of urethane linkages and the chemical interaction/complexation between segmented PU and lithium ions from the salt were confirmed by the attenuated total reflectance Fourier transform IR technique and TGA. The ionic conductivity increased with the addition of 25 wt% LiI, resulting in a high conductivity (7.6×10^{-4} S cm^{-1}) while reducing the crystallinity of the PU, as revealed by XRD. A dye-sensitized solar cell made from this composite showed a photovoltaic effect (electricity was generated under incident light), which is promising for the development of photoelectrochemical cells from bio-based polymer/electrolyte.

Conductive polymers have also been combined with vegetable oils to obtain functional materials with different electrical conductivities in the range of antistatic materials. An interpenetrated polymer network (IPN) (50/50) of poly(methyl methacrylate) (PMMA) and a castor oil based PU was filled with polyaniline (PANI) to take advantage of the electrical conductivity of the PANI, while improving the film forming capability and the homogeneity of the resulting composite films and their mechanical properties.[71] A toluene diisocyanate castor oil prepolymer was mixed sequentially with MMA, an initiator and different amounts of PANI. Finally, the catalyst and the crosslinker were added and the mixture was poured and heated for the polymerization reaction to proceed. Mechanical properties improved with respect to the neat IPN (PU/PMMA) when the content of PANI was above 2.5 wt%, which was explained by the reinforcing effect of PANI, including the formation of H-bonds between NH in PANI and NHCOO in the PU/PMMA IPN. On the other hand, at concentrations above 12.5 wt% the material became brittle. Although PU/PMMA was not an electrical conductor (10^{-14} S cm^{-1}), a rapid growth of the property was observed above 2.5 wt% PANI, and antistatic properties were reached for the sample with 7.5 wt% PANI (1.36×10^{-7} S cm^{-1}).

Biodegradable and biomedical polymers

The applicability of biodegradable polymers as biomaterials provides a thrust in developing new biocompatible polymers for various applications. Their usage in the biomedical field has gained importance because of their degradation in physiological conditions inside the human body.[72] As temporary implants, it is expected that they stay intact until the healing process is complete and subsequently that they degrade and are excreted from the body as waste products.[73] Vegetable oil derived material can also be produced in the form of drug carriers as in anticancer drug delivery systems.[74] The applicability of the polymer depends on its mechanical, physical and surface properties, with biodegradation playing a crucial role in determining the application of the polymers for a specific function inside the human body.

Biodegradable aliphatic polyesters are the most frequently chosen materials for *in vivo* applications due to their degradability and biocompatibility.[75–77] When placed in aqueous medium, the easily cleavable ester bonds of the polymer hydrolyze, generating short chain oligomers and/or monomers. However, the biodegradation process of aliphatic polyesters such as polylactic acid, poly(glycolic acid), poly(lactic-*co*-glycolic acid) and polycaprolactone may last from months to years.[75,78]

Comparatively short periods of biodegradation were reported for castor oil based polyesters synthesized by a catalyst free melt condensation reaction between two different diacids and castor oil with D-mannitol.[79] The polymer was a soft material with a hydrophilic surface whose *in vitro* degradation in phosphate buffer saline solution at physiological conditions required 21 days for completion. Interestingly, the rate of degradation could be tuned by varying the synthesis conditions.

Other chemical structures have been investigated, some of them used in the formulation of composites and with biodegradable characteristics. In particular, vegetable oil based biodegradable advanced materials with hyperbranched architecture have drawn tremendous attraction in recent years. Das *et al.*[80] carried out the synthesis of sunflower oil modified hyperbranched polyurethane (HBPU) and linear polyurethane (LPU) by using toluene diisocyanate, poly(ε-caprolactone), butanediol and monoglyceride of oil. Pentaerythritol (a multifunctional monomer) was incorporated in the formulation of the HBPU and, as a result of the different chemical structure, advantageous results were reported for this system. Most final properties were found to be higher for HBPU than LPU: scratch hardness (4.7 kg *versus* 4.3 kg), tensile strength (23.18 MPa *versus* 18.9 MPa), elongation at break (750% *versus* 700%), and also higher thermal stability (onset of degradation at 250 °C *versus* 239 °C) and biodegradability (broth culture using *Pseudomonas aeruginosa* and *Bacillus subtilis* strains).

Specifically in the biomedical field, in recent years vast progress has been made in the development of tissue and organ substitutes.[81–84] As already indicated for general implants, when

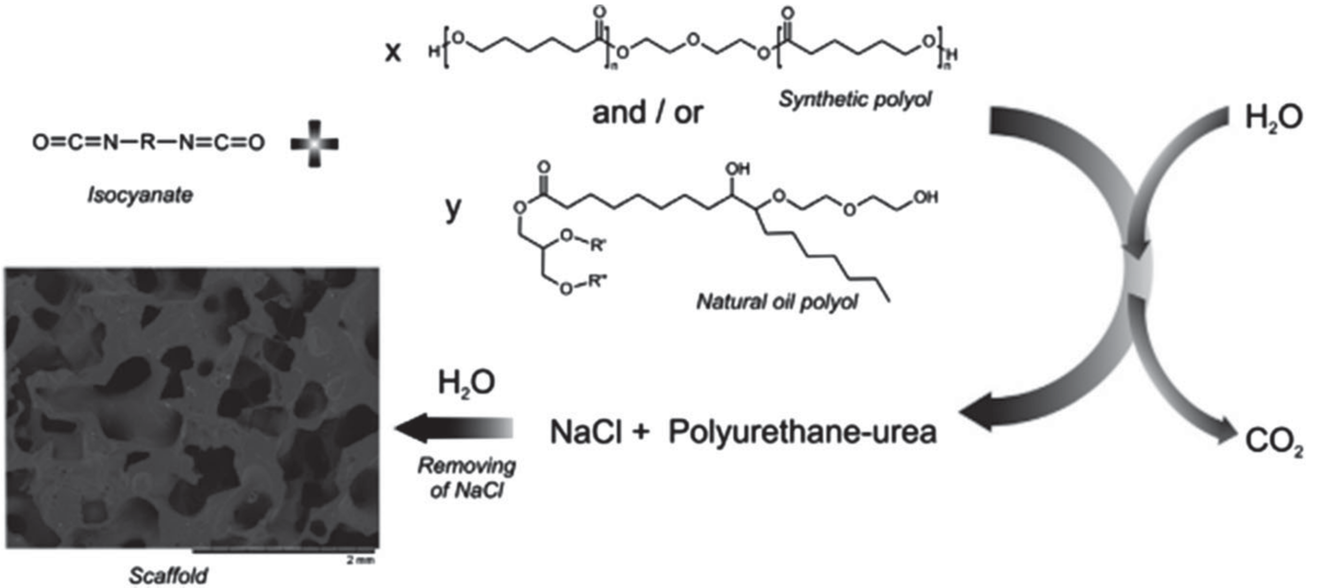


Figure 5. Scaffold formation processes. From reference 89. Reproduced with permission.

the natural regeneration of damaged tissues is not viable[85] a possible solution is to install an artificial scaffold in the damaged area to facilitate the regeneration process.[86] Scaffolds help to ensure the agglomeration of cells into tissues, affecting their shape and mobility whilst also providing mechanical support.[83,87,88] After fulfilling its purpose, the implant should undergo gradual degradation to be replaced by natural tissue without negatively impacting the human body.[87]

Porous PU-urea substrates have been used to fulfill the requirements of a scaffold for bone tissue cultures using rapeseed oil based and poly(ε-caprolactone) diols in various weight ratios.[89] The materials were produced using hexamethylene diisocyanate, distilled water as a chain extender and sodium chloride particles as porogens. PU synthesis was performed using a prepolymer method in mass. The scaffold formation process is shown in Fig. 5.The capability of varying porosity by changing the compositions of the reaction mixtures and the results of studies of bioactivity and degradation in simulated body fluid supported their potential use as substrates for bone tissue cultures.

AQ13

The role of PUs in biomedical applications is particularly important; Bakhshi *et al.*[90] have prepared PUs from soybean oil derived polyols containing different bio-active groups. Polyols (obtained from ESO through reaction with sodium azide and further cycloaddition with alkynes or reaction with methyl iodide) were used in the formulation of PUs, using isophorone diisocyanate in tetrahydrofuran. Free standing films and aluminium coatings were prepared to investigate the properties of the materials obtained. The intended application of the polymers was their use as coatings for biomedical implants and devices, and for that reason hardness, adhesion strength as well as biocidal properties and biocompatibility were investigated. Polyols containing triazole groups led to high hardness, but with relatively low adhesion strength and hydrophilicity, a property that is necessary for interacting with cells. Mouse fibroblast cells in contact with the PUs showed good viability (60% – 110%, quantified through the optical density of the sample compared with positive and negative control samples), while films containing quaternary amine salts showed moderate biocidal action. The addition of polyethylene glycol (PEG) as an additional source of hydroxyls in the PU formulation resulted in improved hydrophilicity and biocidal action of the films, but with reduced cytocompatibility.

PU prepolymers (based on castor oils and PEG) were reacted with amines through terminal epoxy groups for use in biomedical implants and tissue engineering.[91] Again, the aim was to obtain tunable biodegradation for which the ratio of castor oil or PEG in the final formulation allowed the hydrolytic degradation rate and mechanical properties of these materials to be controlled. The authors also reported non-toxic behavior and good cytocompatibility with fibroblast cells.

As has been considered in other applications, nanofillers/fibers have been added to different bio-based polymers. To maintain the biodegradable character of the polymer component while improving the mechanical properties, Gao *et al.*[92] introduced cellulose nanocrystals (CNCs) from *Eucalyptus globulus* in a biocompatible WBPU based on castor oil/PEG. The CNCs were obtained by the usual sulfuric acid method. The nanocomposites showed significant improvement in tensile strength and Young's modulus (5.43 to 12.22 MPa and 1.16 to 4.83 MPa, respectively). As has been reported by other authors,[93] CNCs favored the hard segment – soft segment microphase separation of the WBPU, which in this case led to shifts of the soft segment glass transition temperature ($T_{g,s}$) and the hard segment melting temperature ($T_{m,h}$) towards higher temperatures.

Zinc oxide (ZnO) nanoparticles have also been used as reinforcements in nanocomposites based on an ESO and the bioactivity and antimicrobial activity against food-borne pathogens of the derived materials were investigated.[94–96] Fourier transform IR spectroscopy revealed the existence of strong ESO – ZnO hydrogen-bonding interactions. The studies also showed that the nanoparticles acted as mass transport barriers, reducing water absorption and gas permeability and leading to higher thermal stability. Significant improvements in the mechanical properties were also attained due to ZnO reinforcement, with only a small reduction of the material stiffness and strength after exposure to several cycles of steam sterilization or to simulated body fluid at body temperature. Extraordinary reductions in the coefficient of friction and wear rate were detected under both dry and simulated body fluid conditions, confirming the potential of the reinforcing nanoparticles for also improving the tribological performance of the oil-based polymer. The nanocomposites displayed antimicrobial action against human pathogenic bacteria with and without UV illumination, which increased progressively with the ZnO content.[95,96]

FINAL COMMENTS

In general, the direct use of triglycerides or modified triglycerides produces polymer networks with heterogeneous molecular structure resulting from the reactivity and location of the reactive groups in the molecule. Because of this characteristic and the presence of dangling chains, the glass – rubber transition covers a wide range of temperatures. If the reactivity is low, the reactions are slow or incomplete. When this is the case, the aging of the samples due to the action of oxygen in the surrounding air must be investigated, and this is particularly important in thin films and coatings.

Because of this drawback, many modifications or derived monomers have been proposed to obtain primary or end-chain chemical groups, as well as combinations with other polymers (blends, copolymers, IPNs) or reinforcement with microparticles, nanoparticles and fibers in order to achieve better hardness and modulus, reduced tackiness or higher gloss and transparency.

Many different examples have been presented of more specific, functional and non-traditional applications of polymers derived from plant oils, from smart to biomedical materials. The low electrical conductivity of most polymers is also a characteristic of vegetable oil based polymers, but this property has been widely varied by tuning the formulation of the final material by combination with other insulating components or, in contrast, electrical conductors. Mendability, self-healing and thermoreversibility and recyclability are also new added functionalities that offer great potential for extended uses and greener applications.

Biodegradability or biocompatibility depend on the overall formulation, but plant oils have been shown to be an excellent starting point to regulate this property while balancing other requirements such as mechanical properties.

The use of vegetable oils is therefore a versatile tool that offers the possibility of tailoring the right chemical or polymer according to the specific need and allowing us to benefit from its availability, capability of forming films/coatings or self-standing parts, versatility to vehiculize different functional agents and possibility of affecting or being affected by biological agents.

ACKNOWLEDGEMENTS

The authors wish to thank the Universidad Nacional de Mar del Plata (UNMdP), the National Research Council for Science and Technology (CONICET) and the Ministry of Science and Technology (MINCyT) from Argentina for their financial support. Thanks are also due to Dr Jorge Froilán González for his help in the final revision of the paper.

REFERENCES

1 Li F and Larock RC, in *Natural Fibers, Biopolymers, and Biocomposites*, ed. by Mohanty AK, Misra M and Drzal LT. CRC Press, Taylor & Francis, Boca Raton, FL, Ch. **23** (2005).
2 Wool RP, in *Bio-based Polymers and Composites*, ed. by Wool RP and Sun XS. Elsevier Academic, Boston, MA, Chs 4 and 5 (2005).
3 Lu Y and Larock RC, *ChemSusChem* **2**: 136–147 (2009).
4 Petrović ZS, *Polym Rev* **48**: 109–155 (2008).
5 Xia Y, Quirino RL and Larock RC, *J Renew Mater* **1**: 3–27 (2013).
6 Desroches M, Escouvois M, Auvergne R, Caillol S and Boutevin B, *Polym Rev* **52**: 1 (2012).
7 Belgacem MN and Gandini A, in *Monomers, Polymers and Composites from Renewable Resources*, ed. by Belgacem MN and Gandini A. Oxford University Press, Oxford, Ch. 3 (2008).
8 Montero de Espinosa L and Meier MAR, *Eur Polym J.* **47**: 837–852 (2011).
9 Seniha Güner F, Yagč Y and Tuncer Erciyes A, *Prog Polym Sci* **31**: 633–670 (2006).
10 Gandini A and Lacerda T, *Polymers from Plant Oils*. Springer, Shawbury, UK (2015).
11 Mosiewicki MA and Aranguren MI, *Eur Polym J* **49**: 1243–1256 (2013).
12 Vilela C, Rua R, Silvestre AJD and Gandini A, *Ind Crops Prod* **32**: 97–104 (2010).
13 Petrović ZS, Zhang W and Javni I, *Biomacromolecules* **6**: 713–719 (2005).
14 Alam M, Akram D, Sharmin E, Zafar F and Ahmad S, *Arabian J Chem* **7**: 469–479 (2014).
15 Lu Y and Larock RC, *Biomacromolecules* **8**: 3108–3114 (2007).
16 Chaudharia A, Gitea V, Rajputa S, Mahulikara P and Kulkarniba R, *Ind Crop Prod* **50**: 550– 556 (2013).
17 Tsujimoto T, Uyama H and Kobayashi S, *Polym Degrad Stabil* **95**: 1399–1405 (2010).
18 Lu P, Xiao H, Zhang W and Gong G, *Carbohydr Polym* **111**: 524–529 (2014).
19 Thakur S and Karak N, *Prog Org Coatings* **76**: 157–164 (2013).
20 Alam M and Alandis NM, *Ind Crop Prod* **57**: 17–28 (2014).
21 Desai SD, Patel JV and Sinha VK, *Int J Adhes Adhes* **23**: 393–399 (2003).
22 Somani KP, Kansara SS, Patel NK and Rakshit AK, *Int J Adhes Adhes* **23**: 269–275 (2003).
23 Kong X, Liu G and Curtis JM, *Int J Adhes Adhes* **31**: 559–564 (2011).
24 Kollbe Ahn B, Kraft S, Wang D and Sun XS, *Biomacromolecules* **12**: 1839–1843 (2011).
25 Mahmood MH, Baharom SN, Tajau R, Salleh MZ, Mohd Dahlan KZ and Ismail RC, *J Nucl Relat Technol* **1**: 47–58 (2004).
26 Kim N, Li Y and Sun XS, *Ind Crop Prod* **64**: 1–8 (2015).
27 Aung MM, Yaakob Z, Kamarudin S and Abdullah LC, *Ind Crop Prod* **60**: 177–185 (2014).
28 Balo F, *Energy Build* **86**: 161–175 (2015).
29 Hu YH, Gao Y, Wang DN, Hu CP, Zhu S, Vanoverloop L et al., *J Appl Polym Sci* **84**: 591–597 (2002).
30 Zhang M, Pan H, Zhang L, Hu L and Zhou Y, *Ind Crop Prod* **59**: 135–143 (2014).
31 Kuranska M and Prociak A, *Compos Sci Tech* **72**: 299–304 (2012).
32 Kuranska M, Prociak A, Kirpluks M and Cabulis U, *Compos Sci Tech* **75**: 70–76 (2013).
33 Mosiewicki MA, Dell'arciprete GA, Aranguren MI and Marcovich NE, *J Compos Mater* **43**: 3057–3072 (2009).
34 Ribeiro da Silva V, Mosiewicki MA, Yoshida MI, Coelho da Silva M, Stefani PM and Marcovich NE, *Polym Test* **32**: 438–445 (2013).
35 Nakayama K, *Int Polym Sci Technol* **18**: T43–T48 (1991).
36 Ping P, Wang W, Chen X and Jing X, *Biomacromolecules* **6**: 587–592 (2005).
37 Knight PT, Lee KM, Chung T and Mather PT, *Macromolecules* **42**: 6596–6605 (2009).
38 Julich-Gruner KK, Löwenberg C, Neffe AT, Behl M and Lendlein A, *Macromol Chem Phys* **214**: 527–536 (2013).
39 Wei ZG, Sandstrom R and Miyazaki S, *J Mater Sci* **33**: 3743–3762 (1998).
40 Li F and Larock RC, *J Appl Polym Sci* **84**: 1533–1543 (2002).
41 Nielsen LE and Landel RF, *Mechanical Properties of Polymers and Composites*, 2nd edn. Marcel Dekker, New York (1994).
42 Meiorin C, Aranguren MI and Mosiewicki MA, *J Appl Polym Sci* **124**: 5071–5078 (2012).
43 Meiorin C, Aranguren MI and Mosiewicki MA, *Polym Int* **64**: 735–742 (2012).
44 Meiorin C, Mosiewicki MA and Aranguren MI, *Polym Test* **32**: 249–255 (2013).
45 Meiorin C, Aranguren MI and Mosiewicki MA, *Eur Polym J* doi:10.1016/j.eurpolymj.2015.01.005 (2015).
46 Tsujimoto T and Uyama H, *ACS Sustain Chem Eng* **2**: 2057–2062 (2014).
47 Saralegi A, Gonzalez ML, Valea A, Eceiza A and Corcuera MA, *Compos Sci Tech* **92**: 27–33 (2014).
48 Yuan YC, Yin T, Rong MZ and Zhang MQ, *Express Polym Lett* **2**: 238–250 (2008).
49 Altuna F, Pettarin V and Williams R, *Green Chem* **15**: 3360–3366 (2013).

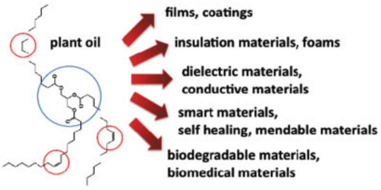
50 Gandini A, *Progr Polym Sci* **38**: 1–29 (2013).
51 Vilela C, Cruciani L, Silvestre AJD and Gandini A, *Macromol Rapid Commun* **32**: 1319–1323 (2011).
52 Vilela C, Cruciani L, Silvestre AJD and Gandini A, *RSC Adv* **2**: 2966–2974 (2012).
53 Vilela C, Silvestre AJD and Gandini A, *J Polym Sci A Polym Chem* **51**: 2260–2270 (2013).
54 Gandini A, Lacerda TM and Carvalho AJF, *Green Chem* **15**: 1514–1519 (2013).
55 Lacerda TM, Carvalho AJF and Gandini A, *RSC Adv* **4**: 26829–26837 (2014).
56 Puig J, Hoppe CE, Fasce LA, Pérez CJ, Piñeiro-Redondo Y, Bañobre-López M et al., *J Phys Chem C* **116**: 13421–13428 (2012).
57 Meiorin C, Muraca D, Pirota KR, Aranguren MI and Mosiewicki MA, *Eur Polym J* **53**: 90–99 (2014).
58 Treichel H, Withers B, Ruhl G, Ansmann P, Wurl R, Muller C et al., Low dielectric constant materials for interlayer dielectrics, in *Handbook of Low and High Dielectric Constant Materials and Their Applications – Materials and Processing*, ed. by Nalwa HS. Academic Press, San Diego, CA (1999). AQ21
59 Kelley EJ. Introduction to base materials, in *Printed Circuits Handbook*, ed. by Coombs CF. McGraw-Hill, New York (2007). AQ22
60 Goosey M and Poole M, *Circuit World* **30**: 34–39 (2004).
61 Ehrler S, *Circuit World* **28**: 38–45 (2002).
62 Santillo D and Johnston P, *Environ Int* **29**: 725–734 (2003).
63 Zhan M and Wool RP, *Composites A* **47**: 22–30 (2013).
64 *IPC 4101B – Specification for Base Materials for Rigid and Multilayer Printed Boards*. IPC (2002). AQ23
65 Smyth CP, *Annu Rev Phys Chem* **17**: 433–456 (1966).
66 Murphy J, *Plast Addit Compound* **3**: 16–20 (2001).
67 Armand MB, Chabagno JM and Duclot M, Poly-ethers as solid electrolytes, in *Fast Ion Transport in Solids. Electrodes and Electrolytes*, ed. by Vashitshta P, Mundy JN and Shenoy GK. North Holland, Amsterdam (1979). AQ24
68 Sharon M, The photoelectrochemistry of semiconductor/electrolyte solar cells, in *Encyclopedia of Electrochemistry, Semiconductor Electrodes and Photoelectrochemistry*, ed. by Bard AJ, Stratmann M and Licht S. Wiley-VCH, Weinheim (2002). AQ25
69 Wei D, *Int J Mol Sci* **11**: 1103–1113 (2010).
70 Su'ait MS, Ahmad A, Badri KH, Mohamed NS, Rahman MYA, Azanza Ricardo CL *et al.*, *Int J Hydrogen Energy* **39**: 3005–3017 (2014).
71 Jeevananda T and Siddaramaiah, *Eur Polym J* **39**: 569–578 (2003). AQ26
72 Saad B, Neuenschwander P, Uhlschmid GK and Suter UW, Int J *Biol Macromol* **25**: 293–301 (1999).
73 Xue L and Greisler HP, *J Vasc Surg* **37**: 472–480 (2003).
74 Wong HL, Rauth AM, Bendayan R, Manias JL, Ramaswamy M, Liu ZS *et al.*, *Pharm Res* **23**: 1574–1585 (2006).
75 Gunatillake PA and Adhikari R, *Eur Cells Mater* **5**: 1–16 (2003).
76 Edlund U and Albertsson AC, *Adv Polym Sci* **157**: 67–112 (2002).
77 Lee SH, Kim BS, Kim SH, Choi SW, Jeong SI, Kwon IK *et al.*, *J Biomed Mater Res A* **66**: 29–37 (2003).
78 Marois Y, Zhang Z, Vert M, Deng X, Lenz R and Guidoin R, *J Biomed Mater Res* **49**: 216–224 (2000).
79 Sathiskumar PS and Madras G, *Polym Degrad Stabil* **96**: 1695–1704 (2011). AQ27
80 Das B, Konwar U, Mandal M and Karak N, *Ind Crop Prod* **44**: 396– 404 (2013).
81 Mi HY, Salick MR, Jing X, Jacques BR, Crone WC, Peng XF *et al.*, *Mater Sci Eng* **33**: 4767–4776 (2013).
82 Vacanti JP and Langer R, *Lancet* **354**: S32–S34 (1999).
83 Kaznica A, Joachimiak R, Drewa T and Drewa G, *Med Biol Sci* **21**: 9–14 (2007).
84 Gogolewski S, *Injury* **31**: 28–32 (2000).
85 Williams D, *Mater Today* **7**: 24–29 (2004).
86 Dorati R, Colonna C, Genta I, Modena T and Conti B, *Polym Degrad Stab* **95**: 694–701 (2010).
87 Wang Y, Liu L and Guo S, *Polym Degrad Stab* **95**: 207–213 (2010).
88 Miao S, Sun L, Wang P, Liu R, Su Z and Zhang S, *Eur J Lipid Sci Technol* **114**: 1165–1174 (2012).
89 Zieleniewska M, Auguscik M, Prociak A, Rojek P and Ryszkowska J, *Polym Degrad Stabil* **108**: 241–249 (2014).
90 Bakhshi H, Yeganeh H, Mehdipour-Ataei S, Solouk A and Irani S, *Macromolecules* **46**: 7777–7788 (2013).
91 Yeganeh H and Hojati-Talemi P, *Polym Degrad Stabil* **92**: 480–489 (2007).
92 Gao Z, Peng J, Zhong T, Sun J, Wang X and Yue C, *Carbohydr Polym* **87**: 2068– 2075 (2012).
93 Auad ML, Contos VS, Nutt S, Aranguren MI and Marcovich NE, *Polym Int* **57**: 651–659 (2008).
94 Díez-Pascual AM and Díez-Vicente AL, *Appl Mater Interfaces* **6**: 17277–17288 (2014).
95 Burt SA, *Int J Food Microbiol* **94**: 223–253 (2004).
96 Santin M and Ambrosio L, *Rev Med Devices* **5**: 349–358 (2008).

Contents

Published online in Wiley Online Library:
(wileyonlinelibrary.com) DOI 10.1002/pi.5033

Review

Vegetable oils can be modified/reacted to obtain competitive or innovative materials for coatings, conductive or insulating materials, biomedical, shape-memory, self-healing materials and other special functional applications.



Mirna A Mosiewicki and Mirta I Aranguren *

QUERIES TO BE ANSWERED BY AUTHOR

IMPORTANT NOTE: Please mark your corrections and answers to these queries directly onto the proof at the relevant place. DO NOT mark your corrections on this query sheet.

Queries from the Copyeditor:

AQ1. Please confirm that given names (red) and surnames/family names (green) have been identified correctly

AQ2. Please confirm the short title or provide another one, 50 characters maximum.

AQ3. Please check the strength of headings throughout.

AQ4. Please confirm the spelling.

AQ5. Please check the rewording.

AQ6. Please confirm.

AQ7. Lu et al. is not reference 18. Please check.

AQ8. How is this different from ESO?

AQ9. Please insert a mention of Fig 1 in the text.

AQ10. Do you mean “struts”? If not please clarify.

AQ11. Please confirm α-eleostearic acid meant.

AQ12. Please check the rewording.

AQ13. Is anything missing here?

AQ14. Please give the chapter titles.

AQ15. Please give the chapter titles.

AQ16. Please give the page range.

AQ17. Please give the chapter title.

AQ18. Are there any further details – volume and page numbers?

AQ19. Reference “46” is not cited in the text. Please indicate where it should be cited; or delete from the reference list and renumber the references in the text and reference list.

AQ20. Ref 46 isn’t mentioned in the text. Please insert a mention or delete the reference and renumber the following references.

AQ21. Please give the page numbers.

AQ22. Please give the page numbers.

AQ23. Please give the location of IPC.

AQ24. Please give the page numbers.

AQ25. Please give the page numbers.

AQ26. Please give the initials for Siddaramaiah.

AQ27. Please confirm the author’s name.