

Research and Development

Final Project Report

(Not to be used for LINK projects)

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Project title

Vegetable oils as polymer feedstocks: Chemical modification, materials formulation and economics

DEFRA project code

NF0513

Contractor organisation and location

University of Warwick, Coventry. CV4 7AL

Total DEFRA project costs

£ 135,132

Project start date

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Executive summary (maximum 2 sides A4)

Introduction: The high environmental burden caused by the use of non-renewable fossil based petrochemical feedstocks in the plastics industry has led to the search for vegetable oil based alternatives. The use of vegetable based feedstocks not only gives the necessary sustainability required for future plastic manufacture but also offers advantages in recycling and/or biodegradability over traditional petrochemical derived plastics. This represents an obvious step forward for both the chemical industry and oilseed producers driven by sound ecological reasons, in tandem with DEFRA's stated aim of supporting development of renewable non-food industrial materials from agricultural crops. Vegetable oils being non-toxic, biodegradable, non-polluting in water courses and relatively harmless to the environment could offer significant advantages over fossil fuel derived products. However, with very few exceptions, such oil crops still have to compete with petrochemical sources of feedstocks. Besides a competitive price, the chemical industry also wants *improved* or *new properties* from end products derived from vegetable oils. Simple replacement of existing petrochemical feedstocks on the grounds of being able to advertise that products are "derived from renewable resources" will not be a strong enough position to justify equal or inferior qualities at equal or higher prices than petrochemical equivalents. Many existing vegetable oils require chemical modification to become useful feedstocks. The cost of such modification can reduce their competitiveness, however, vegetable oils which show significant levels of functionalisation already (e.g. *Euphorbia oil*) have the potential to find significant markets and become highly competitive.

Polyurethane plastics are used globally on a scale of 9-10 million tonnes a year and include materials with diverse applications in varied This project aimed to develop economic, renewable, and novel feedstocks derived from existing UK crops (such as rapeseed) as well as evaluating the potential of other plants (such as *Euphorbia lagascae*) as renewable resources for the use in the polyurethane industry. It was possible to generate novel materials from these modified oils that have different properties to those derived from conventional petrochemical sources with possible new niche market applications.

Aims and objectives: The primary aim of the project was to evaluate and compare the potential of both rapeseed and Euphorbia oil as feedstocks for use in the polymer industry. The key business objective of the project was to compare the economics and cost effectiveness of using rapeseed or Euphorbia as the starting point for feedstock production and to compare the cost of these modified oil products with other competitor oils such as castor oil and epoxidised soyabean oil as well as existing petrochemicals. Another aim was to produce a range of materials with varied properties to encourage industrial uptake.

Main findings**Preparation of polyurethanes and comparison of materials prepared from rapeseed and euphorbia oils.**

- 1) A range of feedstocks were prepared from both rapeseed oil and euphorbia oil with the correct specifications to make polyurethane plastics.
- 2) Polyurethane films and foams were prepared from both rapeseed and euphorbia oils.
- 3) Polyurethane composites could be prepared by compression moulding from both oils with flax, or hemp as strengtheners
- 4) Cure times for polymers derived from rapeseed oil (50 minutes) were found to be slightly shorter than those from euphorbia (55 mins)
- 5) Composites derived from both oils with hemp showed better thermal stability than those without hemp (with the former degrading at approx 400 C)
- 6) Composites prepared from euphorbia are generally stiffer than those from rapeseed
- 7) Composites prepared from rapeseed generally require more energy to fracture.
- 8) Scanning electron microscopy revealed good composite adhesion properties.
- 9) Polymers derived from both rapeseed oil and euphorbia oil exhibited stability to sunlight (no decomposition over 6 months of simulated strong ultraviolet degradation).
- 10) Rapid biodegradability of rapeseed and euphorbia composites that contain hemp was found when buried in soil.
- 11) Control of biodegradability achievable by altering the level of hemp or flax used as a composite strengthener.

Economic findings

- 1) Production of feedstocks from rapeseed and euphorbia oils was financially viable and competes well in terms of price with castor oil and epoxidised soya bean oil
- 2) Production of polymers and composites from rapeseed and euphorbia oils was financially viable and competes well in terms of price with existing petrochemical based polyurethane composites and polyesters.
- 3) The cheapest method for constructing polyurethanes utilises *euphorbia lagascae* as a crop (£1.61 per kg) rather than rapeseed (£2.11 per kg)
- 4) Barriers to progress are the availability of *euphorbia lagascae* as a crop.

Thus both rapeseed and euphorbia oils have been chemically modified using a patented process to produce hydroxylated feedstocks. These feedstocks have been polymerised to make a range of polyurethanes, including materials suitable for rapid prototyping, and polyurethane foams suitable for packaging or insulation. In addition, we have incorporated UK grown fibres such as hemp, jute and flax into these materials to make composites where both the resin and the strengtheners are derived from UK indigenous crops. These composites, (produced by compression moulding) have potential as new materials for the automotive industry. A compression moulded rapeseed / hemp composite car door interior has been produced and is part of the 'eco-car' manufactured by Splendid Technologies Ltd. Other potential applications include agricultural equipment (tractors), bridge, rail and highway components, and formaldehyde free particle board. We have also fabricated disposable trays, and resin toys as example pieces (see main report). The physical properties (cure times) and mechanical properties (impact, tensile strength, strain) of both rapeseed and euphorbia resins / composites have been investigated as well as their stability to sunlight and their biodegradability/compostability profiles. The economics of the processes have also been evaluated. The estimated cheapest cost for the feedstocks synthesised from crops is that derived from *Euphorbia lagascae* oil at £1.61 per kg. This is followed by the rapeseed oil derived monomer at £2.11 per kg as a comparison the cost of preparing monomers from epoxidised soya was also investigated and found to be £2.39 per kg. Castor oil, which does not require chemical modification to be used as a monomer for the production of rigid polyurethanes, costs \$1.85 per litre (Anon e, 2003). This cost is equivalent to £1.21 per kg, using the exchange rate on 16th July 2003 and a density of 960kg/m³ (Anon a, 2003), although no costs for transport, import duties and related costs are included. *It must be noted that the analysis is for the estimated cost of producing monomers from oilseed crops, and is in no way indicative of a selling price for the feedstocks. Use of these feedstocks produced polyurethane materials*

Table 1 shows an estimate of the cost of complete polyurethane systems using feedstocks derived from oilseed crops.

Table 1: The cost of complete polyurethane systems using monomers derived from oilseed crops.

Monomer feedstock	Cost (kg)
<i>Euphorbia lagascae</i> oil	£1.54
Rapeseed oil	£1.88
Epoxidised soya oil	£2.06

By comparison, polyurethane systems derived from hydrocarbons cost between £2.50 and £9.50 of complete resin system (McCourt, 2003), whilst another common hydrocarbon origin thermoset; polyester costs approximately £2.00 per kg as of mid-June 2003 (Anon g, 2003)

Implications of the findings for future research: . Further scientific work has been highlighted: Specifically in this project it is necessary to carry out more *biodegradability studies so that it will become possible to tailor degradability to appropriate applications*. The success in the development of vegetable oil / fibre composites warrants further investigation using other UK fibre crops other than hemp. The preparation of a wider range of composites will allow a full composition/ property profile portfolio to be produced. Rape meal has been used as a renewable filler in a number of applications, it may be possible to use rape meal as a filler in our composites. Thus these materials would be truly renewable as they would contain a vegetable oil resin, a fibre reinforcer and a rape meal filler (a 3 component renewable). Variation of the amounts of these 3 components would allow for a variety of new materials to be produced. In the general area we must address the low uptake from industry of materials from renewable resources. We need a larger portfolio of materials available. *This can be addressed by exploring the use of vegetable oils in the formulation of other materials other than polyurethanes*. Lessons may be learnt from the technology of bio-diesel where uptake was slow. This technology is now more accepted and bio-diesel is often blended with conventional diesel. It is likely that the blending of renewable polymers with existing petrochemical ones will provide the industrial uptake that is required (i.e replacing only part of a material with a renewable). *Thus work involving blending of our materials with existing petrochemical derived plastics deserves attention. Apart from euphorbia lagascae there may be other plants which could be developed as crops that would furnish important raw materials for industry*. A programme to identify such potentially useful new crops will be instigated with HRI (now part of Warwick University). *In addition, although we have demonstrated that rapeseed oil can be used to prepare polymers the existing crop varieties have been bred for the food industry and not for the polymer industry. By investigating other varieties of commercially grown crops it may be possible to find varieties that are more suited for industrial materials*.

Implications of the findings for future policy

This study indicates that euphorbia oil represents a new source of potential feedstocks for the polymer industry. It highlights the necessity for research to be undertaken into the industrial uses of plants that can be later developed into potential new crops for the farming industry. Mechanisms will need to be put in place to persuade farmers to grow these new non-traditional crops if their potential is to be realised. Agronomy research into the best methods to grow these new non-traditional crops will have to be undertaken and communicated to farmers. Thus a considerable time-lag between this initial demonstration that a new crop has industrial significance and the mass growing as a crop is likely to accrue. This may be overcome if existing traditional crops (such as rapeseed) are grown. However, this research indicates that the use of such crops is more expensive and so less attractive to industry. It should be noted that the rapeseed varieties that are currently grown as crops have been bred for the food industry and not for the polymer industry. It may be possible to grow different varieties of rapeseed using existing agronomy procedures to deliver rapeseed oil which is better suited to the polymer industry. This would allow farmers to grow crops for industry with which they are already familiar.

Action to follow: We have started a company called Natural Plastics Ltd in order to exploit our technology. Licensing of the feedstock patent technology is under negotiation. We are currently acting in collaboration with Sustainable Composites Ltd who are using our euphorbia technology to prepare cable joints. Joint funding to exploit this application further is currently being sought. Negotiations with a range of company's to further bring to market this technology is ongoing.

Scientific report (maximum 20 sides A4)**Objectives**

The overall aim is to evaluate the potential of rapeseed and euphorbia oil as feedstocks for the polymer industry and to compare the materials produced from these feedstocks with those available from other sources. To be accomplished by:

- 1) Sourcing of vegetable oils.
- 2) Preparation of a range of monomer feedstocks derived from rapeseed, and *euphorbia* oil.
- 3) Use of these feedstocks in the preparation of a range of polyurethane materials
- 4) Comparison of the materials properties of polyurethanes prepared above with existing commercial derived materials
- 5) Comparison of economics / competitiveness / market opportunities of materials prepared from the above vegetable oils with existing castor oil and epoxidised soya bean oil..
- 6) To stimulate the development of LINK projects within the polymer industry.

Milestones

- 1) ADAS to source and organise supply of pilot scale quantities (circa 20 litres) of euphorbia oil
- 2) Preparation of range of feedstocks from vegetable oils
- 3) Preparation of 20 novel polyurethanes from rapeseed and euphorbia
- 4) Materials evaluation of 20 novel polyurethanes from rapeseed and euphorbia
- 5) Business report on polyurethanes
- 6) Exploitation of polyurethanes-First case study mouldings
- 7) Low environmental impact polyurethanes symposium (University of Warwick)
- 8) Final contributions: Complete economic analysis of polymer/resin production. Assessment of crude oil production costs, financial viability of crop derived oils in short and medium term as chemical feedstocks. Final report for project partners. Initiation of LINK applications. Approval of material for publication by project partners.

Introduction

In recent years the use of renewable resources has attracted the attention of many researchers as potential substitutes for petrochemicals. Attention has been focused mainly on the development of newer materials from renewable resources such as plant products. The use of vegetable oils as renewable resources for the formation of industrial materials and polymers as well as bio-lubricants is well established. Vegetable oils being non-toxic, biodegradable, non-polluting in watercourses and relatively harmless to the environment could offer significant advantages over fossil fuel derived products. However, with very few exceptions, such oil crops still have to compete with petrochemical sources of feedstocks. Besides a competitive price, the chemical industry also wants improved or new properties from end products derived from vegetable oils. Simple replacement of existing petrochemical feedstocks on the grounds of being able to advertise that products are derived from renewable resources will not be a strong enough position to justify equal or inferior qualities at equal or higher prices than petrochemical equivalents. Many existing vegetable oils (e.g. rapeseed oil) require chemical modification (e.g. epoxidation and hydroxylation) to become useful feedstocks. The cost of such modification can reduce their competitiveness, however, vegetable oils which show significant levels of functionalisation already (e.g. in Euphorbia oil) have the potential to find significant markets and become highly competitive because less chemical modification is required, (Scheme 1). In both cases, it is the potential to corner 'niche' markets, or to provide novel feedstocks or products that will determine industrial interest and uptake. The primary objective of the project was to evaluate and compare the potential of both rapeseed and Euphorbia oil as feedstocks for use in the polymer industry. The key business objective of the project is to compare the economics and cost effectiveness of using rapeseed or Euphorbia as the starting point for feedstock production and to compare the cost of the modified oil products derived from these. Another objective is to produce a range of materials with varied properties to encourage industrial uptake.

***Euphorbia lagascae* as a feedstock**

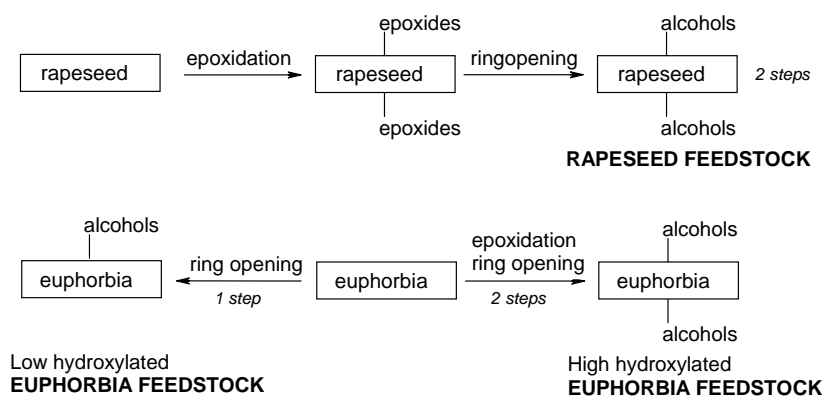
A few plant species naturally produce high quantities of fatty acids of industrial significance. *Euphorbia lagascae* has been identified from EU research programmes (VOSFA and SOCNCA) as a crop, which produces oil rich in vernolic acid, which has a number of potential uses. As vernolic acid is a fatty acid, which is naturally epoxidised, this may offer a competitive advantage over other oils such as rapeseed, soy and sunflower, which have to be chemically epoxidised as a precursor to industrial use. EC funded research has shown that it is possible to produce *Euphorbia lagascae* in the UK, with seed and oil yields of 1.1 t/h and 400 kg/ha relatively. If there is an industrial demand, then this crop could potentially be grown economically in the UK, offering an alternative cropping option to UK growers. If a viable market for naturally epoxidised oils is demonstrated, improved cropping system for *Euphorbia lagascae* cultivation could be developed to increase market yields and improvements could potentially be achieved by conventional breeding within the species or possibly by gene transfer to more agronomically adapted species. However, the public acceptance of this latter approach cannot be guaranteed.

Rapeseed oil as feedstock

Rapeseed oil the third most extensively grown crop in the UK, with about 500,000 ha was used for growing rapeseed oil in 1999. Although rapeseed oil is mostly used as cooking oil it has, in recent years increasing being used in biodegradable lubricants where the high erucic acid rape has established a niche market. Currently great interest has been in the diversification of the end uses of seed rape and one most important application where research has concentrated is in it's potential as feedstock for the manufacture of polyurethanes. Various components of the fatty acid profile of rapeseed oil are the subject of crop development and breeding efforts and enhancement of particular fatty acid components will potentially increase the value of the crop for industrial applications. Rapeseed oil is predominantly traded as a bulk oil commodity. This work is aimed at adding value to the rapeseed oil by developing novel uses for the oil in the polyurethane sector. The polyurethane market is large estimated at US \$ 2b per year in the USA alone. Applications for polyurethane are diverse ranging from foams for upholstery, shoe soles and fibre reinforced composite materials. In this work, rapeseed oil has been chemically modified producing highly hydroxylated monomers, which has been polymerised using MDI. Plant fibres mainly hemp and jute have been used in mat form as reinforcement for the MDI polymerised rape and the composites tested in tension, impact and flexure to assess their performance.

Chemical manipulation

Only castor oil (a non-indigenous crop) has gained importance as a feedstock in the polyurethane industry. Other oils often require chemical manipulation to produce appropriate feedstocks, thus rapeseed needs to be sequentially epoxidised and ring opened before an appropriate feedstock for polyurethane formation can be obtained, (Scheme 1). *Euphorbia lagascae* produces oil which is rich in vernolic acid (a fatty acid that already contains an epoxide) and thus only the second chemical step (that of ring opening) is required to furnish any desired polyurethane feedstock (low hydroxylated euphorbia). Thus the technical potential of *Euphorbia* is great. The project aimed to determine if there are any advantages (either economic or scientific) in utilising such oil as a resin as well as demonstrating the preparation of a diverse range of polyurethane resin-matrix from *Euphorbia*.



In order not to compromise the environment-friendly nature of the use of vegetable oils, methods of epoxidising and hydroxylation (see above) are required which have minimal environmental impact. Most published methods use organic solvents, however, these would need to be recycled or disposed of with the corresponding increase in the cost of the process and high environmental impact. Ring opening of the euphorbia epoxide group using phosphoric acid produced a low hydroxylated euphorbia. Additionally a high hydroxylated euphorbia could be obtained by reacting (epoxidation) the alkene group of the vernolic acid with acidified hydrogen peroxide and a catalyst. Analysis at the epoxide stage indicated that the epoxide profile was different to that in other epoxidised oils, which indicates that *euphorbia* may lead to different material properties in any consequent manufactured polymers. Ring opening in a second step then produced the high hydroxylated euphorbia, (Scheme 1)

Polyurethane formulation

Polyurethane formulations are extremely versatile, for example both thermoset and thermoplastic materials are available. Polyurethanes are made by reacting a hydroxylated monomer (at least two hydroxyl sites) with isocyanate monomer (at least two isocyanate sites) with or without a catalyst. The level of hydroxylation, molecular weight and the flexibility of the hydroxylated monomer as well as the nature of the filler/reinforcement will enable a wide range of tailored material properties for a variety of applications. The degree of hydroxylation, molecular weight and flexibility of the rapeseed and euphorbia monomer feedstocks can be controlled by altering the reaction conditions namely stoichiometry, time, temperature and concentration.. For example, it is possible to make rigid foams of the type used for packaging or pipe-insulation exhibiting excellent fire retardation properties. In general all the required parameters can be controlled to theoretically tailor any desired property in polyurethane matrix formulation.

Polyurethanes have been used for a large variety of applications from flexible foams for use as seat cushions and bedding etc. Variation in the formulation of the polyurethane produce rigid foams used for insulation and cores for structural composites. Extrusion and reaction injection moulding can process polyurethanes. Other applications include coatings, adhesives and sealants and use in rapid prototyping of pre-production/low production runs of commercial products. The production of polyurethane from

renewable source and the use of plant fibre reinforcement have not only environmental benefits but will also result in increased agricultural and industrial economies

Composite materials

Polyurethane composites prepared from modified euphorbia and rapeseed oils with plant fibres such as hemp, flax and miscanthus, have the potential to provide new materials with improved strength and flexibility compared to polyurethane derived from vegetable oils alone. We have received much industrial interest in the preparation of such composites, particularly from the automotive industry. Over the last five years, Mercedes, BMW and other automotive OEMs and first tier suppliers have partly by the usual desire for higher-weight and lower-cost materials. The other drivers for adoption of these materials are the need to be perceived as 'green' by their customer base, and to take advantage of the German interpretation of the end-of-life disposal rules that polymer composites with natural fibres do not count towards the thermal recycling quota, and can be burnt to recover energy without penalty. This is particularly important in terms of European waste disposal legislation, with its targets for recovery of end-of-life articles (in this case, scrape cars), and the consequent fate of the recovered materials, as it allows greater leeway in how the manufacturers dispose of returned end of life articles. Thus the preparation of a range of composite materials is also a prime objective of this research.

Summary of work

In this work, rapeseed oil has been chemically modified to obtain a highly hydroxylated monomer while euphorbia oil has been modified in two distinct ways to give either a low hydroxylated or high hydroxylated material (scheme 1). These monomers were polymerised using methylene diisocyanate as the cross linking agent. These polymers have then been used to produce hemp or jute fibre reinforced composite using untreated and alkalisated hemp and jute fibre. The raw materials, monomers, polymers, and composites have been subjected to analytical tests such as NMR, FT-IR, MS to study the chemical groups. Thermal characteristics were performed on the monomers, polymers and composites using the DSC and TGA analytical techniques in order to determine the extent of cure and degradation respectively. Compression moulding was used to make the composites and tests such as tensile, shear (short-beam) and impact properties were carried out to determine the mechanical properties. Scanning electron microscopy (SEM) was used to study the resin structural morphology and fibre-matrix interfacial coherence. The stability of the materials to UV and composting conditions have been determined and biodegradability studies undertaken. Economic and financial analysis has been carried out to determine the competitiveness of the materials. Links with companies have been forged in order to commercialise the results. Suggestions have been made for future work.

Methodology used and results/discussion

Chemical manipulation of vegetable oils:

Tungsten powder, hydrogen peroxide (30% w/w), orthophosphoric acid (85% w/w), adogen 464, dichloromethane, dry magnesium sulphate and sodium chloride, methylene diisocyanate (MDI) and toluene were purchased from Aldrich chemical company UK. The reactor and accessories for setting up the reaction experiment regime was bought from Aldrich Ltd.

The rapeseed and euphorbia oils were chemically modified in two stages notably *in situ* epoxidation followed by hydroxylation (to give rapeseed and high hydroxylated euphorbia feedstocks) or by ring opening of euphorbia (to give low hydroxylated euphorbia). The reactions were carried out in a heated 1 litre glass reactor fitted with a reflux condenser and equipped with a stirrer. The reactor was immersed in an oil bath regulated at the desired temperature. The reactions have been repeated on a 25 L scale using a self-contained apparatus without problems. Scale up to industrial quantities (tonnes) would require specialist pilot plant but few problems are envisaged. However, this would be likely to be the limiting step in technology transfer to the industrial sector.

A typical procedure to generate the modified oil feedstock is given below for a small laboratory scale reaction (2 stage process).

About 150 mg of tungsten powder in 0.6 ml of distilled water was placed in a reactor to which 1.26 ml of hydrogen peroxide (30% w/w) was added drop-wise. The mixture was heated at 50 °C, thoroughly stirred until a clear solution was observed (about 30 min). The solution was cooled to room temperature then 90 mg of orthophosphoric acid (85% w/w) in 1.2 ml of water was added to the solution. About 30 g of oil and 200 mg of adogen 464 were placed in a reactor stirred and heated at 50 °C. The catalyst was poured in the reactor followed by 50 ml of water. 15g of orthophosphoric acid (85% w/w) was added followed by 18 ml of hydrogen peroxide (30% w/w). The mixture was then heated at 100 °C for 6 hours. After cooling to room temperature the two layers were separated.: The top layer was dissolved in 100 ml of dichloromethane, washed with distilled water (50ml x 4) followed saturated sodium chloride solution (50ml x 3). The organic material is dried using MgSO₄ (20g) filtered and the resulting solvent was removed under vacuum (1 bar) at 80 °C. The procedure for larger scale reactions 1L-25L is somewhat modified and does not involve the use of dichloromethane solvent

Polyurethane formation using modified rapeseed oil and euphorbia oil.

Polymer resin manufacture: Two classes of polyurethane were prepared derived from either chemically modified rapeseed oil (RASOR) or euphorbia oil (EURE) and methylenebis diisocyanate. A range of materials with different stoichiometries of reagents as well as those with various fillers were prepared. FT-IR was used to study the cure characteristics of the resins by observing the change in the peak area of the hydroxyl groups during the reaction

Composite manufacture by Compression Moulding with plant fibres: Plant fibres possess surface impurities which in composites result in a weak fibre-matrix interface leading to poor mechanical properties. However, a weak interface may result in improved toughness in impact. The most common remedy to this problem is to treat plant fibres with caustic soda to remove waxy, oily surface materials and other impurities. Fibres are normally soaked in caustic soda solutions for a specified temperature and time. It is worth pointing out that alkalisation de-polymerises the native cellulose I molecular structure producing short length crystallites. Plant fibre constituents, mostly polysaccharides, which are caustic soda soluble, are removed as a consequence of alkalisation. Subsequently lignin, which is surrounded by hemicelluloses now dissolved by caustic soda, is easily extracted from the plant fibre cell wall. The removal of surface impurities, hemicelluloses and lignin exposes the cellulose hydroxyl groups enabling them to form fibre-fibre or fibre-resin hydrogen bonds. Following alkalisation fibres were used for the reinforcement and the mechanical properties determined and compared to composites produced using untreated fibres. Compression moulding produced composites. Two classes of composites were prepared using untreated and alkali treated needle punched hemp and woven jute mats as reinforcements for either rapeseed oil resin (RASOR) or euphorbia resin (EURE). Three layers of hemp were prepared weighed then hand-laid on the mould. The resin was then poured and spread on the hemp layers except the sides facing the mould. The mould was then closed and compressed at 0.6 MPa. The process was carried out at room temperature and the composite was post cured at 60 °C for ten hours.

Characterisation of modified vegetable oil feedstocks and polyurethane polymers

The feedstocks prepared above were characterised by Nuclear Magnetic Resonance (NMR), Infra-red spectroscopy (IR), Matrix Assisted Laser Desorption Ionisation-Time of Flight-Mass Spectrometry (MALDI-TOF-MS), Gel Permeation Chromatography (GPC) and Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. The polymers and composites were characterised by Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA) as well as Scanning Electron Microscopy (SEM). A range of mechanical properties (tensile and impact) were measured and electron microscopy furnished information on the micro structure.

FT-IR analysis

FT-IR analysis of the modified oil show absorbance peaks at around 3390 cm^{-1} and 3382 cm^{-1} for modified rapeseed oil, (fig 1), and modified low-OH and high-OH euphorbia oil, (fig 2) respectively due to the presence of the hydroxyl groups not observed in the spectra for unmodified oil. The FT-IR was also used to study the cure characteristics of the resins by observing the change in the peak area of the hydroxyl and carboxyl groups during the reaction for, which a sample spectra of hydroxylated euphorbia oil, hydroxylated rapeseed oil and their respective 50min cured resin are shown in (fig 3). The remaining peak observed after the cure implies that not all the hydroxyl groups are utilised in the reaction after 50 minutes of reaction. It was observed that the change in the peak area of the hydroxyl groups is proportional to the extent of cure of the resins. Similar results were obtained with hemp fibre reinforced resins; however, in this case the peak observed after 50 minutes of reaction is attributed to the presence of the amine groups (Chao *et al.*, 1998), which is produced by the traces of water in the fibres.

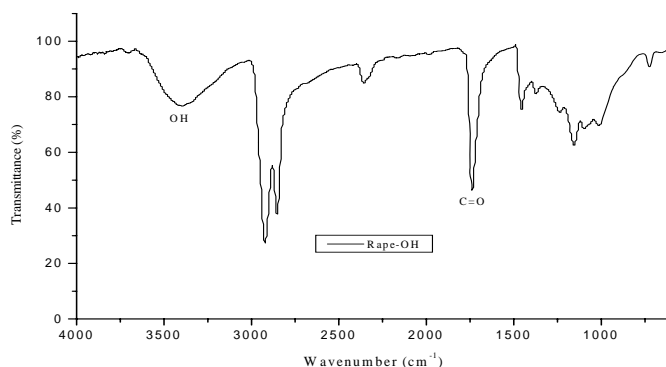


Fig. 1 IR of modified rapeseed oil

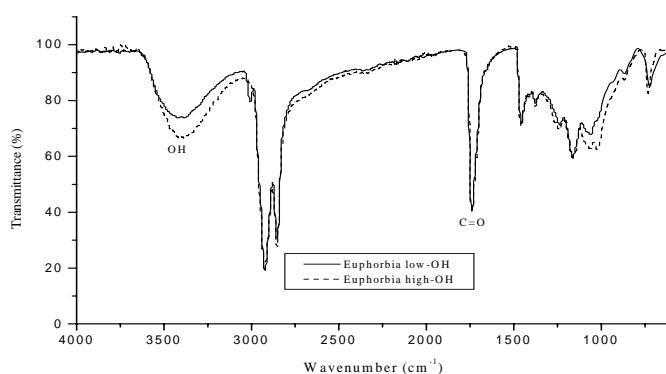


Fig. 2. IR of modified low hydroxylated and high hydroxylated euphorbia

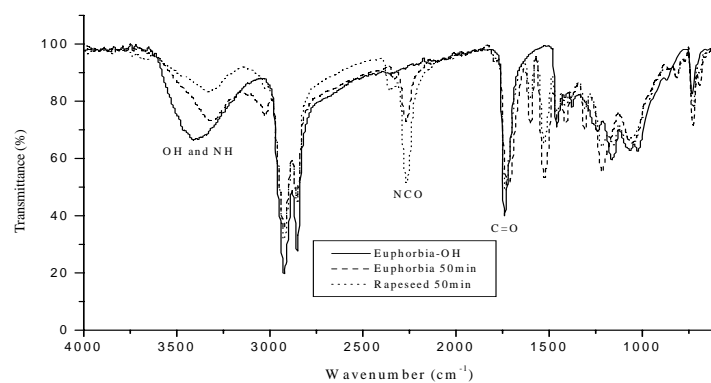


Fig 3. IR spectra of 50 min cured rapeseed and euphorbia oil

Fig. 4a plots the change in the level of the hydroxyl groups in the EURE and RASOR polymers while fig 4b shows the decreasing level of the isocyanate (NCO) with respect to time of cure. The change in hydroxyl groups and that of NCO is calculated using :

$$\alpha = \left(\frac{H_i - H_f}{H_i} \right) \times 100$$

Where α is the change in hydroxyl groups (%), H_i is the initial amount of arbitrary units of hydroxyl groups and H_f is the final amount of arbitrary units of hydroxyl group obtained using FT-IR technique.

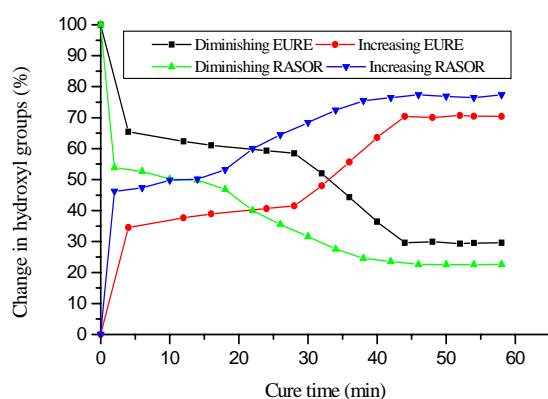


Fig. 4a

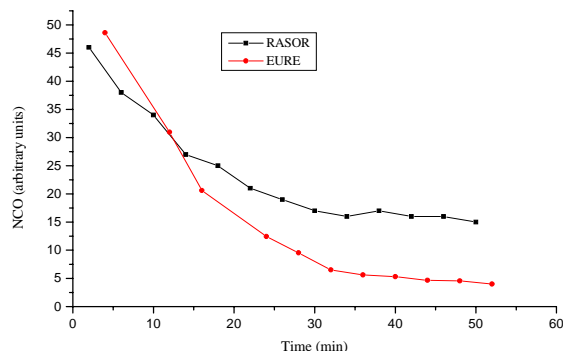
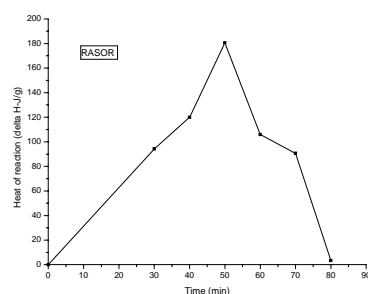


Fig. 4b

The observed change in hydroxyl groups (fig 4a) and the decrease in the NCO groups (fig 4b) imply that the OH and NCO groups are participating in the MDI polymerisation reaction as expected.

Differential scanning calorimetry (DSC) analysis: Samples of polymers weighing between 5-10 mg were placed in an aluminium capsule and sealed. A Pelkin Elmer Pyris 1 DSC equipped with thermal analysis modules was operated in a dynamic mode with a heating scheme of 20-300 °C and heating rate of 10 °C/min. in a nitrogen environment purged at around 25 ml/min. The DSC thermograms of the first run of the hydroxylated rapeseed oil shows a small exothermic peak at around 160 °C, which is not observed during the second run indicating the decomposition of the solvent and some low molecular weight materials. Hydroxylated euphorbia also shows an exothermic peak at 160 °C similar to that of hydroxylated rapeseed oil. This indicates the decomposition of chemical compounds present in the two materials. The thermograms of the polymers were also analysed for any changes in the behaviour of the materials. Isothermal mode was performed on a mixture of the hydroxylated oils and MDI to study cure characteristics. Rapeseed polyurethane resins shows an optimum cure time at 50 minutes while for euphorbia resins the time is slightly longer (55 minutes). Fig 5 shows a typical cure curve for MDI polymerised rapeseed (RASOR).

Fig 5



Isothermal cure characteristics of MDI polymerised rapeseed resin (50°C, 180 J/g)

Thermal Gravimetric Analysis: The loss in mass as a function of temperature of the materials was determined by using a Pelkin Elmer TG7 equipped with thermal analysis controller TAC 7/DX. Samples weighing between 5-10 mg were placed in a crucibles in a furnace and heated in nitrogen between 40-800 °C at a rate of 10 °C/min. In general both the rapeseed and euphorbia oils show the same trend (Fig 6 (a) and (b)). Hence, the starting natural oils degrade at a higher temperature than either of the chemically modified oils and the simple MDI polyurethane resins. However, both the rapeseed and euphorbia hemp composites show increased heat stability. This implies the fibre reinforcement improves the thermal stability of the neat polyurethane resin in both cases. Step analyses of the polymer thermograms were performed and the results are shown in Fig 7a and fig 7b. Fig 7a shows a higher thermal stability of RASOR at temperatures below 300 °C compared to hemp-RASOR composite. It also shows the degradation temperature of RASOR of 425 °C with a 26.5% delta mass loss while the degradation temperature of hemp-RASOR composite is 525 °C with

delta mass loss of 22.07%. The higher degradation temperature and lower mass loss of hemp-RASOR composites implies that the addition of hemp fibre improves the thermal stability of the material. At higher temperatures hemp-RASOR composite has more residual materials than RASOR. EURE and hemp-EURE polymers exhibit similar thermal properties (Fig 7)

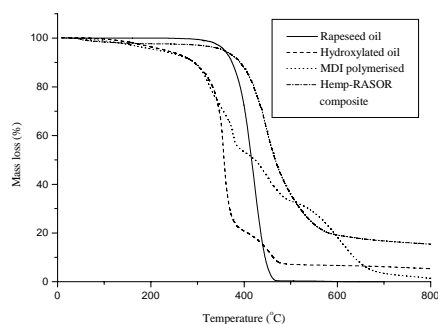


Fig 6 (a)

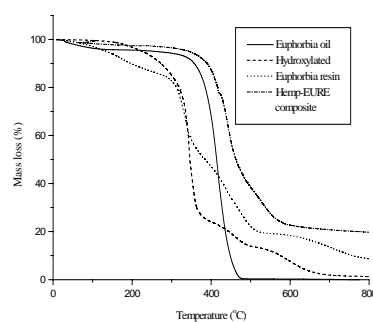


Fig 6(b)

Fig. 6 Thermograms of (a) rapeseed, (b) euphorbia resin derived materials as a function of temperature

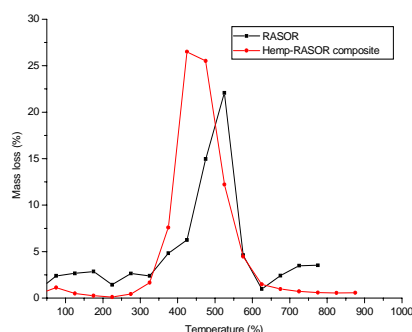


Fig 7 (a)

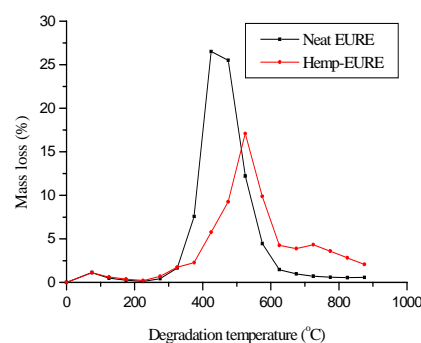


Fig 7 (b)

Fig. 7. Degradation of (a) neat rapeseed resin (RASOR) and hemp-RASOR composite and (b) neat euphorbia resin (EURE) and hemp-EURE composite obtained using the TGA technique

Table 1 shows that hemp reinforcement increases the onset degradation temperature. Hydroxylated euphorbia (high-OH), EURE (low-OH), hemp-EURE (high-OH), rapeseed oil and RASOR exhibit two degradation temperatures while EURE (high-OH) and rapeseed oil exhibits three degradation temperatures. The observed second and third degradation temperatures are believed to be due to the presence of dimer and trimer components of the resin producing higher molecular weight materials that exhibit higher thermal stability than low molecular weight compounds. It also means that new chemical compounds are produced as the materials undergo heat degradation. Table 1 also shows that the addition of reinforcements increases the thermal stability of the resins except for the hemp-EURE (low-OH) composite. The understanding of the degradation temperature provides a limiting temperature of a material for processing and in end use applications to avoid catastrophic failure of the materials.

Table 1: The degradation temperatures of resins, modified resins, polymers and composites

Material	Onset (T_{on} , °C)	Degradation (T_d , °C)		
		1	2	3
Euphorbia oil	360.8	417.0	-	-
Euphorbia low-OH		417.0	-	-
Euphorbia high-OH		343.1	457.3	-
EURE low-OH		372.3	503.0	-
EURE high-OH	240.0	436.9	547.6	747.7
Hemp-EURE low-OH		395.4	-	-
Hemp-EURE high-OH		439.4	536.7	-
Rapeseed oil	305.1	359.3	470.8	651.9
Rapeseed oil-OH	371.4	399.0	-	-
RASOR		423.26	528.9	-
Hemp-RASOR	409.3	448.4	-	-

Tensile properties: The tensile testing of rectangular laminated composites were carried out according to ASTM D 3039-82 using an Instron tensile testing machine Model 4303 with installed computer programme. The machine was run at a crosshead speed of 5 mm/min.

Impact properties: The impact strength was determined using the pendulum impact testing machine provided with different operating hammer weights. The choice of the operating weight depends on the expected impact strength of the composites. ASTM D 256-92 applied for simple beams Charpy-type test was used. This is a test standard for plastic materials with or without fibre reinforcement. The specimens were un-notched. Impact loads were applied at a point in direction of the fabric plane.

Fig. 7 shows representative stress-strain curves for untreated and alkalis hemp-RASOR and hemp-EURE composites. An initial linear trace of the curve is observed for both composites followed by an inflexion zone, which indicates the elastic and plastic nature of the materials. It is observed that there is a lower failure strain for the untreated low-OH EURE hemp composites. The diagram shows the non-linear matrix dominated behaviour of the composites. It is known that fibre ends in the composite cause increased levels of elongation in the fibre-matrix interface of adjacent fibres. This causes breakdown at the interface when there is insufficient fibre-matrix adhesion and matrix elongation at break (Mehan and Schandler, 2000). The greater the fibre content and the shorter the fibres, the greater the number of fibre ends present to introduce such flows. So while on one hand the fibres have a reinforcing effect they also have a fracture-generating effect at the interface of adjacent fibres (Keller, 2003). Ashbee (1993) reports that the non-linearity of the curves is due to plastic deformation of the matrix and is more significant with alkali treated than untreated fibre bundles. In this work the plant fibres used as reinforcements were chemically treated using caustic soda to confirm Ashbee's observation and this is seen in Fig. 7 and in Table 1. However, the low stiffness observed for alkalis hemp-RASOR composites is attributed to the damage to the cell wall caused by caustic soda, suggesting that lower concentration might cause less damage and provide better higher stiffness. The distribution of the fibre lengths in the composites and waviness caused by compression moulding can also influence the shape of the curve since the load taken up by the fibres decreases as the strain increases.

Fig. 7a

Fig. 7b

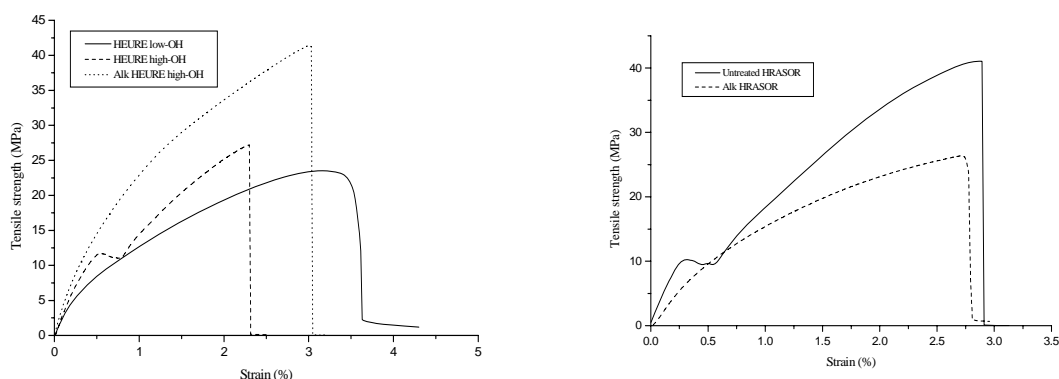


Fig. 7: Stress-strain curves of untreated and alkali treated (a) hemp-EURE and hemp-RASOR composites

The inflexion observed for untreated hemp-EURE (high-OH) and hemp-RASOR composites is an artefact of the testing machine. A range of tests (not all shown above) were carried out and the results are shown in Table 2. The tensile strength and Young's modulus (stiffness) of untreated hemp-RASOR composites are higher by 41%, 31.62%, 10.68% and 38.67% than that of untreated hemp-EURE (low-OH), untreated hemp-EURE (high-OH), alkali treated hemp-EURE (high-OH) and alkali treated hemp-RASOR composite respectively. The lower tensile properties exhibited by untreated hemp-EURE is due to the low level of hydroxylation of the monomer thus providing minimal reactive sites. The lower values for alkali treated hemp-RASOR are caused by the damage to the cell wall caused by caustic soda.

Table 2 shows fibre volume fractions of approximately between 19% and 24% exhibiting tensile strength of approximately between 23 MPa and 56 MPa and impact strength of between 7 kJ and 19 kJ. These values are quite reasonable for the amount of fibre content and densities exhibited. Wool *et al.*, (2000) obtained similar ranges of mechanical properties for vegetable fibre reinforced plant-based resin-matrices.

The lower tensile properties exhibited by untreated hemp-EURE compared to untreated hemp-RASOR composites is most likely due to the level of hydroxylation which is likely to be higher on modified rapeseed than modified euphorbia, which implies that more controlled monomer synthesis is important. However, alkalisation seems to improve the mechanical properties of hemp reinforced EURE by 20.93% with respect to that of untreated hemp-RASOR composite. Figs. 8 and 9 shows the tensile strength, Young's modulus of untreated and caustic soda treated hemp reinforced EURE/RASOR composites respectively.

Table 2: Mechanical properties of untreated and alkali treated hemp mat and woven jute reinforced composites

Composite type	Fibre volume fraction (%)	Tensile strength (MPa)	Young's Modulus (GPa)	Composite density (Kg/m ³)	Impact strength (kJ/m ²)	ILSS (MPa)
HEURE-low-OH	21.05	22.91 (1.06)	2.31	649.55	18.81 (2.17)	3.12
HEURE-high-OH	18.89	26.56 (1.85)	2.78	625.07	7.03 (1.13)	3.49 (0.45)
HRASOR	19.92	38.84 (2.21)	3.40	697.09	9.25 (1.21)	3.88 (0.45)
AHEURE-high-OH	20.39	34.69 (3.76)	3.13	675.46	9.15 (1.64)	4.73 (0.76)
AHRASOR	19.20	23.82 (2.96)	2.35	633.16	10.47 (2.01)	3.81 (0.43)
JEURE-high-OH	23.77	55.52 (2.60)	4.26	658.59	10.60 (2.27)	4.95 (0.43)
JRASOR	23.74	46.38 (3.37)	3.89	704.93	13.70 (1.95)	3.99 (0.82)
AJEURE-high-OH	22.69	26.76 (2.23)	2.52	663.34	8.33 (0.88)	3.45 (0.45)
AJRASOR	22.70	26.84 (1.60)	2.61	655.23	13.34 (1.78)	3.55 (0.66)

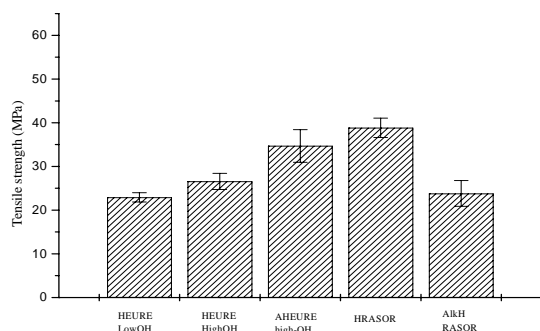


Fig. 8

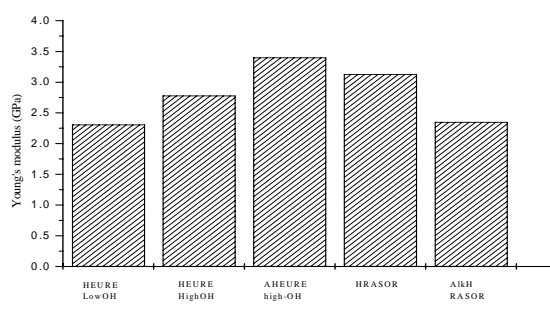


Fig. 9

Figs. 10 and 11 show the tensile strength and Young's modulus of untreated and caustic soda treated woven jute reinforced EURE/RASOR composites respectively. The property trends for the alkalised fibre reinforced composites is not the same due to the damaging effect caustic soda has on the cell wall and it is noticeably seen with the woven jute mats (Fig. 10 and 11). The severe damage on the fabric is due to the entrapping of the caustic soda solution between the interlacing yarns and within the yarn structure.

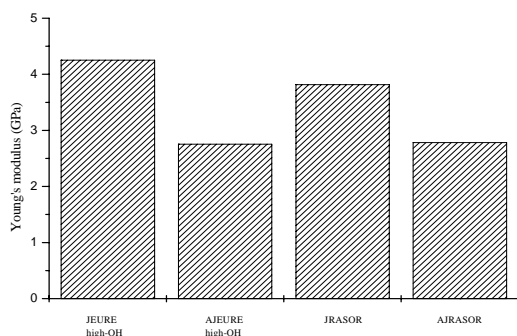


Fig. 10

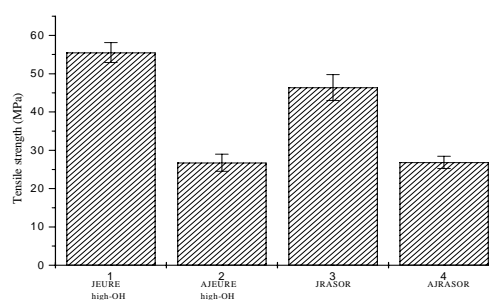


Fig. 11

Impact properties

Figure 12 shows the impact energy of the hemp fibre reinforced composites while Figure 13 shows the impact energy of woven jute fibre reinforced composites. The impact energy of low-OH EURE hemp composite is the highest followed by alkalisated hemp-RASOR composite, untreated hemp-RASOR and alkalisated hemp-EURE (high-OH) and untreated hemp-EURE (high-OH) composites respectively implying that low-OH EURE hemp composites require more energy to break.

Alkalisiation increases the impact strength of hemp reinforced composites it has a decreasing effect on the woven jute reinforced composites as observed in Fig. 12 and Fig. 13 respectively

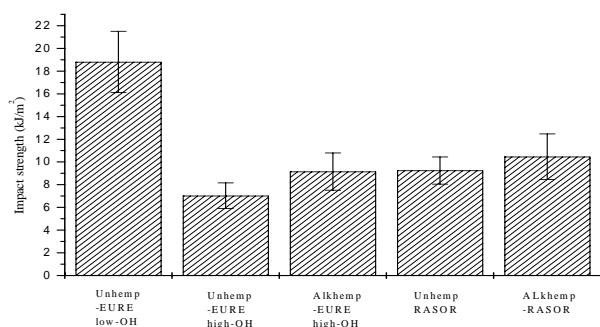


Fig. 12

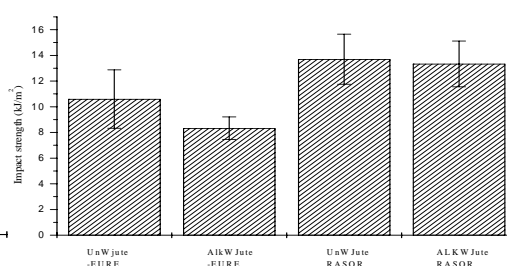


Fig. 13

Inter-laminar shear strength by short beam flexure

Results for short beam interlaminar shear tests are shown in Table 2 for non-woven hemp and woven jute composites. Although flexural tests do not provide basic design data, their use is often justified on the basis that the material is subjected to flexure loading in actual service. This is a valid argument if the span length to material thickness ratio is similar at laboratory and industrial applications. Otherwise, the failure mode in service may be different than obtained in the laboratory testing, and the comparison is not valid. The short beam shear test provides reasonable inter-laminar shear strength (ILSS) values but does not provide shear stiffness or shear strain information (Adams, 2000). It is for this reason that the stiffness and strain to failure for short beam interlaminar shear have not been determined in this work. Fig. 14 shows the ILSS of untreated and alkalisated hemp composites and Fig. 15 shows the ILSS of untreated and alkalisated woven jute composites respectively.

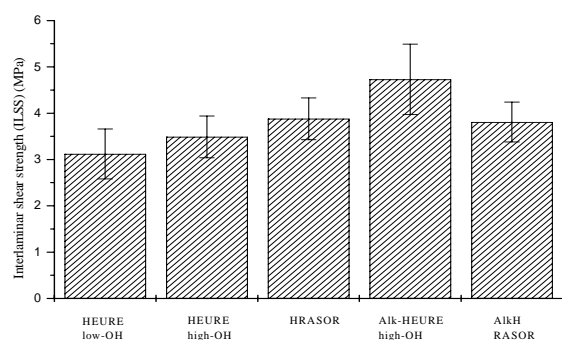


Fig. 14

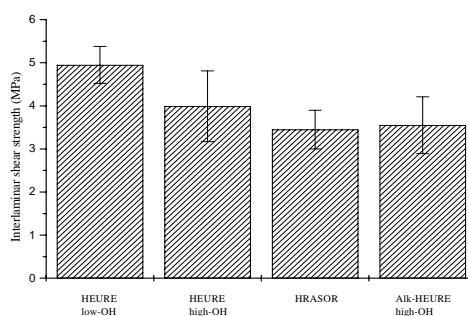


Fig. 15

The trends for shear strength is similar to the trends for the tensile strength of hemp fibre reinforced EURE/RASOR composites. Since shear strength is closely a measure for the strength of the matrix plus the interphase, it is logical to imply that the values for the shear strength would represent more or less the tensile strength of the neat matrices.

SEM analysis: Scanning electron microscopy was used to study the fractured surfaces of the neat resin-matrices and composite samples. Prior to the analysis the samples were coated with Au/Pd alloy by means of a Polaron Sputtering apparatus. The scanning electron microscope analysis of the tensile fractured neat RASOR and hemp-RASOR composite were performed and the micrographs are shown in Fig 16a and Fig 16b respectively. The neat RASOR (Fig. 16a) shows a brittle fracture topography similar to those obtained by synthetic thermoset resin matrices. The arrow shows a void caused by volatile gaseous materials produced by polycondensation reaction. Figure 16b shows the fracture topography of the hemp-RASOR composite. Again the matrix exhibits a brittle fracture and the composite shows a coherent hemp fibre-matrix interface. Fig 17a and 17b shows the tensile fracture topography of EURE and hemp-EURE composite respectively for comparison. EURE (Fig.17a) exhibits a brittle fracture with a

smaller void. Generally all alkalis fibre reinforced composites show cleaner fibre surface implying surface impurities have been removed following alkalisation. It also observed that following alkalisation a more coherent fibre-matrix interface is attained. Further observation reveals that pull out fracture profile is seen in all cases implying a coherent fibre-matrix interface. Untreated hemp-resin composites show a more incoherent interface and more brittle failure of the matrix than the alkali treated hemp fibre composite. The fibre bundle texture of alkalis hemp mat is friable and weak compared with untreated hemp fibre bundles. Evidence of the fibrils being 'torn apart', thereby splitting the hemp fibre bundles, can be observed in the fracture surface of the alkalis mat composites. Alkalis fibre bundles show more fibril splitting because of the reduction in lignin and hemicelluloses content, which has been extracted by caustic soda. The fibrils, which have been torn away from the fibre bundles, show signs of considerable plastic deformation especially in alkalis fibre mat composites (Ashbee, 1993 and Sanadi *et al.*, 1986). In plant fibres, fracture of the fibrils occurs at stress concentrations usually at the weakest points of the micro-fibrils. The fracture of micro-fibrils in plant fibre reflects the composite nature of the fibres and fibre bundles.

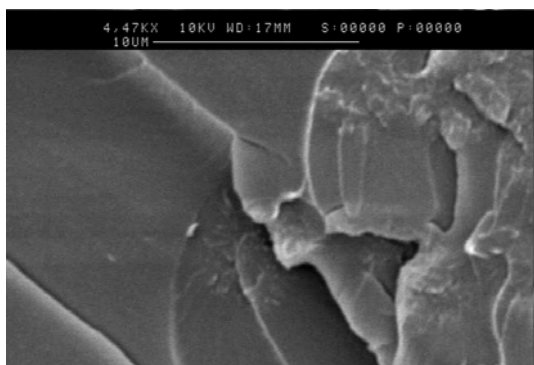


Fig 16a

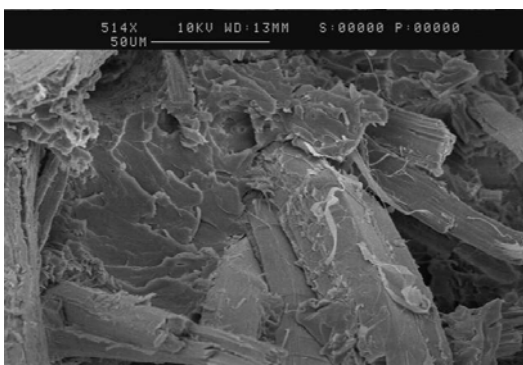


Fig 16b

Fig. 16: SEM micrographs of tensile fractured (a) neat RASOR and (b) hemp-RASOR composite

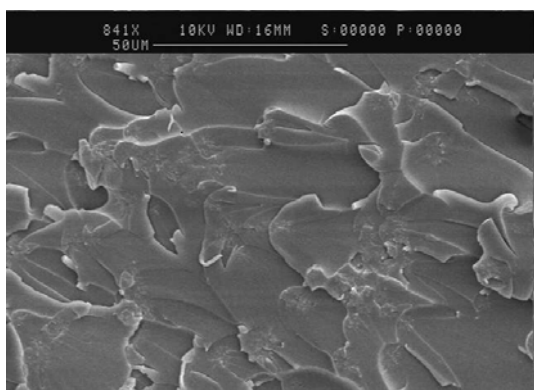


Fig 17a

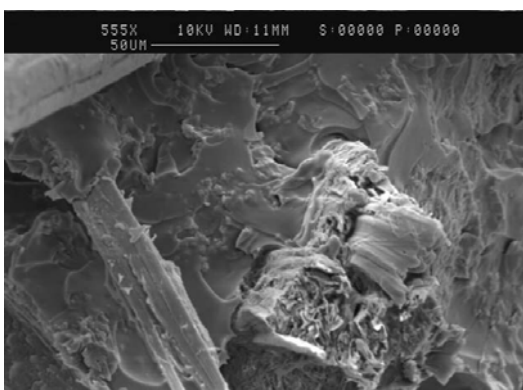


Fig 17b

Fig. 17: SEM micrographs of tensile fractured (a) neat EURE and (b) hemp-EURE composite

The resin at the fibre-matrix interface of alkali treated hemp fibre bundle composites shows matrix shear hackles where the matrix transfers stress to the fibre bundles. The shear hackle indicates more plastic flow of the matrix implying that plasticisation has occurred due to the presence of the aliphatic nature of the triglycerides. Sanadi *et al.*, (1986) made similar observations on sunn hemp reinforced polyester composites. This shows that resin curing continues after composite manufacture.

This study indicates that these natural plant fibres cannot be treated along the same lines as the homogeneous carbon and glass fibres. The various fracture mechanisms of the fibres in the composite observed using the SEM are fibril pull out, plastic flow of the lignin-hemicelluloses matrix, plastic deformation of the fibrils, fibre splitting and fracture diversion at the fibril-fibril interface

Biodegradability and weather stability

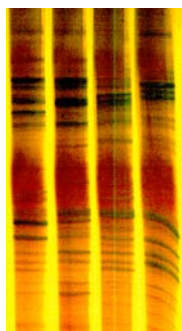
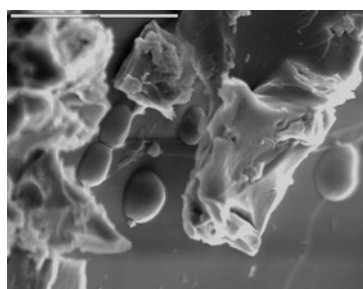
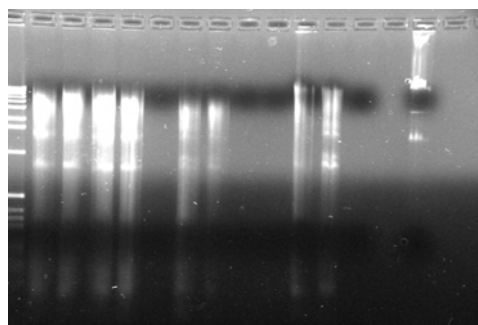
In order for industrial uptake of new materials to be successful it is necessary to prepare them not just economically with the correct properties but to also determine their stability and biodegradability. Stability to sunlight was assessed by irradiating all four of the polymer classes using ultraviolet light in a weatherometer (simulating 6 months of strong sunshine). No evidence of major decomposition was detected (by IR spectroscopy).

Preliminary work involving the biodegradability of the four polymer classes has been undertaken by burying the ground polymers in soil. Bags of the size 6 x 6 cm were prepared using nylon mesh with pore size 20 μm which allows free access of bacteria and fungi to buried material but restricts access of any bigger micro fauna to eliminate any losses of buried material due to movement of such organisms or its contamination with soil. Two bags of each polymer were recovered after three weeks, with the two remaining bags

recovered after 6 weeks of incubation in the soil. One bag of each polymer was dried and used to establish weight loss of the polymer, the second one was used for extraction of DNA from colonizing microflora and for electron microscope studies. Universal bacterial primer pairs P2 – P3¹⁵ and F984GC-R1378¹⁶ were used for PCR amplification, PCR products were analysed using denaturing gradient gel electrophoresis (DGGE).¹⁵ A small amount of each polymer recovered was fixed by 5% glutaraldehyde, dried, fixed on aluminium stubs, gold-coated and observed under scanning electron microscope. Measurements of weight loss indicate high biodegradability of resin/hemp composite polymers (hemp-RASOR, hemp-EURE) with half of the buried amount of each polymer being degraded after just 6 weeks (Table 3). Little weight loss of from the resin polymers (RASOR, EURE) indicates low biodegradability. In fact no DNA was recovered from RASOR and EURE resin polyurethanes indicating very low microbial degradation (runs 6 and 9, fig 20). However, SEM confirmed the presence of bacterial and eukaryotic colonization (yeast cells in fig 19) but the density of population was below the limit used for the DNA isolation technique in fig 20). DGGE band pattern (Fig. 18) using primer pair P2-P3 demonstrate presence of more than 20 dominant bacterial degraders for the hemp-composites. Some differences in diversity of bacterial colonizers on each polymer (represented by different position of bands on DGGE gel) can be detected. In conclusion, the composite materials with hemp are much more rapidly biodegraded than the non composite polymers. It should be possible to control biodegradability by altering the hemp ratio of the materials.

Sample	Weight loss after 6 weeks [%]
Euphorbia polyurethane (EURE)	15.2
Rapeseed polyurethane/hemp composite (hemp-RASOR)	52.2
Euphorbia polyurethane/hemp composite (hemp-EURE)	50.3
Rapeseed polyurethane (EURE)	12.4

Table 3

1 2 3 4
Fig 18.round structures = yeast
Fig 19

1 2 3 4 5 6 7 8 9

Fig 20

1= 3 weeks hemp-EURE
2= 3 weeks hemp-RASOR
3= 3 weeks hemp-EURE
4= 3 weeks hemp-RASOR

1 = ladder DNA, 2-5 = soil DNA,
6 = microflora DNA from EURE
7 = microflora DNA from hemp-RASOR
8 = microflora DNA from hemp-EURE
9 = microflora DNA from RASOR

Economic Analysis.

Introduction

The cost of monomers derived from *Euphorbia lagascae* has been estimated and compared with the estimated cost of monomers derived from rapeseed oil and epoxidised soya oil. These estimated costs were then be compared with castor oil and cashew nut shell liquid (CNSL), two other plant origin thermosetting resins.

Assumptions used in the calculations

There are a number of assumptions used in the calculations. The assumptions were used for a number of reasons; the first of which is that no accurate data was available, the second reason is that by including some factors into the analysis, such as inflation, unneeded complexity would have been added to the analysis. The assumptions used in the analysis are listed below.

- The economic analysis is based on the monomer being produced on a pilot scale. It has been assumed that the pilot plant for the production of monomers has already been built and its cost amortised. Thus any calculation will not include a cost apportioned to the construction and upkeep of a pilot plant.
- It is assumed that the pilot plant produces on a batch scale and produces 100 metric tonnes of monomer per year. The plant operates 5 days per week for 50 weeks per year; therefore the monomer is produced at a rate of 400kg per day.
- The water used in the reaction(s) is assumed to be softened water supplied directly by a utility, which is estimated to cost £1 per cubic metre, equivalent to £1 per tonne. Whilst this cost is negligible, it has been included in the economic analyses.
- The brine used in the final stage(s) of the reaction(s) is assumed to be manufactured on site using a brine generator and the water mentioned previously, and it is assumed that the brine generator cost has already been amortised. It is assumed that the brine used will be a super saturated solution containing 30% sodium chloride (salt), and the cost of the salt is set at £75 per tonne. Thus, the cost of brine used in the calculations is £18.10 per tonne.
- It is envisaged that the largest additional cost are for the electricity used to heat the material during reaction. The amount of energy required to increase 400kg of oil from room temperature (20°C) to 100°C, is 57.6MJ, assuming a specific heat capacity for the oil of 1.8kJ/kg K, the specific heat capacity of castor oil (Anon a, 2003). This is a safe assumption to make as crop and plant origin oils have a specific heat capacity in the range of 1.6 kJ/kg K (sesame oil) to 1.97 kJ/kg K (olive oil and soya oil). Assuming that the specific heat capacity of the oil is not affected by the addition of the various compounds, the heat is transferred without loss and the heating takes one hour, then the amount of power required would be 1.6kWhr. Electricity costs 4.43p per kWhr (Anon b, 2003), thus the price required to heat the oil for Stage Two (see Figure 1) of the rapeseed monomer reaction would be 7.1p, a negligible cost compared to the cost of the materials if the reaction is to produce 400kg of monomer. Of course any heating would not take place without some thermal and electrical losses, and maintaining the material at temperature over the course of the reaction would also require electrical input due to thermal losses. It would be difficult to calculate the amount of energy required to heat and maintain the materials during the reaction without first knowing the design of the pilot plant, thus a different way of including these costs must be used. This will be discussed later.
- The calculations assume that 80% of the dichloromethane (by volume) is recycled. This has a large affect upon the monomer cost.
- Labour costs are also difficult to calculate without having detailed knowledge of the plant design and layout in addition to the level of automation used in the plant. Therefore, a different method of accounting for labour costs must be used and this is discussed later.
- Several of the prices in this document were calculated from prices in other currencies. The exchange rates used in the work were obtained from Oanda (www.oanda.com) on 16th July 2003, and the exchange rate for the Euro used in the calculations is €1.42 to £1, for US dollars the exchange rate used in the calculations is \$1.59 to £1, and the exchange rate for the Indian rupee used in the calculations was R74.6 to £1.
- In order to account for other costs in the process that are difficult to calculate, i.e. labour and electricity, a factor will be included for each process, and this factor will take the form of a percentage of the material costs. For the more complex process; the derivation of monomers from rapeseed oil, a factor of 30% will be used, whilst for the less complex process; the derivation of monomers form *Euphorbia lagascae* oil and epoxidised soya oil a factor of 20% will be used. The author suggests that this is a realistic assumption to use as the labour content of the monomer is likely to be low, and, as detailed previously the electricity required to heat the process is relatively economical.

Costs of rapeseed, epoxidised soya bean, castor and euphorbia oil based monomer feedstocks.

The estimated cheapest cost for the monomers synthesised from crops is that derived from *Euphorbia lagascae* oil at £1.61 per kg. This is followed by the rapeseed oil derived monomer at £2.11 per kg with the epoxidised soya at £2.39 per kg. Castor oil, which does not require chemical modification to be used as a monomer for the production of rigid polyurethanes, costs \$1.85 per litre (Anon e, 2003). This cost is equivalent to £1.21 per kg, using the exchange rate on 16th July 2003 and a density of 960kg/m³ (Anon a, 2003), although no costs for transport, import duties and related costs are included. It must be noted that the analysis is for the estimated cost of producing monomers from oilseed crops, and is in no way indicative of a selling price for the monomers.

Costs of rapeseed, epoxidised soya bean, and euphorbia based polymers and comparison with hydrocarbon origin materials

To produce a thermosetting resin system using monomers synthesised from oilseed crops requires the addition of a diisocyanate (e.g. MDI or TDI) at a rate of one part diisocyanate to two parts monomer. MDI costs between €1950-2050 per tonne as of January 2003 (Anon f, 2003), taking the average cost (€2000) and converting it using the exchange rate on 16th July 2003 gives a diisocyanate cost of £1.41 per kg. Table 4 shows the cost of complete polyurethane systems using monomers derived from oilseed crops.

Table 4: The cost of complete polyurethane systems using monomers derived from oilseed crops.

Monomer feedstock	Cost (kg)
<i>Euphorbia lagascae</i> oil	£1.54
Rapeseed oil	£1.88
Epoxidised soya oil	£2.06

By comparison, PU systems derived from hydrocarbons cost between £2.50 and £9.50 of complete resin system (McCourt, 2003), whilst another common hydrocarbon origin thermoset; polyester costs approximately £2.00 per kg as of mid-June 2003 (Anon g, 2003) From Table 6, it can be determined that all of the oilseed derived monomers are estimated to be able to compete in terms of cost with the hydrocarbon origin thermoset resins. There exist other 'natural' thermosetting resins, one of these mentioned previously; castor oil would cost approximately £1.28 per kg of complete resin system, whilst cashew nut shell liquid (CNSL) would cost £1.00 per kg of complete resin system based on large quantities (Tucker, 2003).

Composite costs

In this section the estimated cost of composites (i.e. glass reinforced plastic or GRP) produced from the oilseed crop monomers is estimated as this would be a typical use of a rigid thermoset polyurethane resin such as those produced from Euphorbia oil or rapeseed oil. If a 'natural' resin is to be used, it follows that the reinforcement used in the composite should be 'natural' in origin too. Fig. 21 shows the tensile strength of selected synthetic and natural fibres.

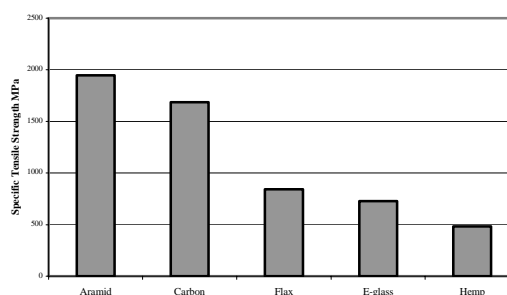
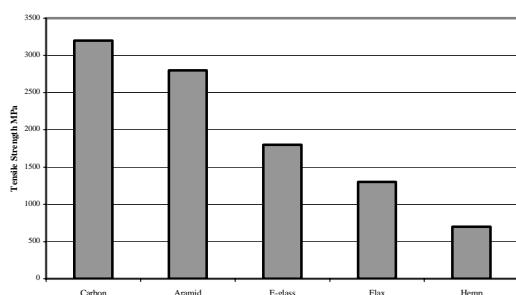


Fig. 21: Tensile strengths of synthetic and natural fibres

Fig. 22: Specific tensile strengths of synthetic and natural fibres

Adapted from: Robson (1993), Garcia-Jaldon (1998), Shim (2001), Baley (2002).

From Fig. 21 it can be determined that the two natural fibres, flax and hemp, have lower tensile strengths than the three synthetic fibres; carbon fibre, aramid (e.g. kevlarTM and twaronTM) and E-glass fibres. Whilst this is an issue when tensile strength is measured, as the synthetic fibres are clearly superior to the natural fibres, if the weight of the material is taken into account, natural fibres can compete with the lower strength synthetic fibres. Such a measurement is called specific strength and Livingston-Smith (1945), states that the specific strength of a material is the strength divided by the density, and Fig. 22 shows the specific strength of selected synthetic and natural fibres. From Fig. 22 it can be determined that the lighter natural fibres see a relative increase in strength when compared with the heavier synthetic fibres. This allows flax to have a higher tensile strength on a weight-to-weight basis than E-glass fibres, although the finished hemp composite, whilst weighing the equivalent (if not slightly less) of an E-glass composite will be bulkier due to the inclusion of the lower density natural fibres. This means that, at least hypothetically, hemp fibre/oilseed crop derived resin system composites can compete in terms of technical performance with GRP made using a polyurethane resin matrix and E-glass fibre reinforcement. Whether they can compete economically is a different issue. It can be determined however that the material cost of 'natural' composites fabricated from hemp fibres and oilseed crop origin resins is very similar, with the cheapest resin system (*Euphorbia lagascae* origin polyurethane) providing the cheapest material costs. In terms of processing costs, all materials would require the same processing route, thus, the critical factors impacting the cost of these materials are the costs of materials. Hydrocarbon origin PU with E-glass reinforcement composites would undergo the same processing regimen as the 'natural' composites, and these have a material cost of £2.57 per kg, assuming a fibre cost of €3.8 per kg (Kandachar, 2002) which is equivalent to a cost of £2.82 per kg using the exchange rate of 16th July 2003, and a matrix (PU resin system) cost of £2.50 per kg (McCourt, 2003). Therefore, in terms of cost, there is little to choose between 'natural' composites and those that utilise a hydrocarbon origin PU with E-glass.

Environmental impact

There are a number of problems with the current end of life disposal routes for products manufactured from thermoset polymers. Thermoset polymers, once cured, are notoriously difficult to recycle. This is due to the curing mechanism being chemical and is generally irreversible. Thermoset composites such as Sheet Moulding Compound (SMC) and Bulk Moulding Compound (BMC) can be recycled at end-of life, and the process to perform this is to grind the scrap and then add to virgin material at levels of up to 20% (Maxwell, 1994). Other thermoset composite materials such as Glass Reinforced Plastic (GRP) are much more troublesome to recycle. The polymer matrix can be broken down through the use of hydrolysis and the long fibre recovered and utilised in 'cascade' recycling, although hydrolysis technology is not being realised on a large scale (Maxwell, 1994). Cascade recycling involves the comminution of the fibres into shorter lengths, which can then be utilised as reinforcing fibres for injection moulding compounds. The options that are available for the disposal of thermoset components are currently the same options that are available for the disposal of most discarded items; incineration and landfilling, and unfortunately the majority of polymeric waste is currently being landfilled (McCrum, 1997). Polyurethanes from oilseed crops partially solve the problems of the finiteness of oil reserves and the environmental impact caused by the disposal of plastics at the end-of life as the feedstocks used in their manufacture is of a sustainable origin.

No data is available for the environmental impact of polyols produced from oilseed crops as they have not been calculated using a life cycle analysis (LCA) technique, and this in itself would be a labour intensive task. By comparison, data for the environmental impact of polyurethanes from hydrocarbon sources has been published. The production of polyols for polyurethanes results in the use of approximately 1.9kg of hydrocarbons, used as both feedstock and fuel, per 1kg of polyol and the emission of 3.1kg of carbon dioxide per 1kg of polyol in addition to numerous aerial and water emissions (Boustead, 1999). Whilst no LCA data is available for polyols from oilseed crops, it is highly likely that a reduction in hydrocarbon use would be witnessed in addition to CO₂ being mitigated as the crops sequester carbon dioxide over the growth cycle resulting in lower environmental impact. Empirical data would be required to prove or disprove this argument, and work would also be needed to quantify the emissions directly attributable to the process and the by-products of the process.

Economic conclusions

From this analysis it appears that the production of polyols from both *Euphorbia lagascae* oil and rapeseed oil is financially viable and the plastic materials compete well in terms of price with hydrocarbon origin polyols, polyurethanes and composites. The cheapest method of producing polyols from oilseed crops is estimated to be through the use of *Euphorbia lagascae* oil at an estimated cost of £1.61 per kg, whilst the estimated cost of rapeseed oil derived polyol is higher at £2.11 per kg due to the increased processing costs. The barriers to progress are the availability of *Euphorbia* oil in large quantities and the technical viability of scaling up the production, although economically the material appears to be very viable. Further work is needed to quantify the environmental impact, not only of production of the material, but also of the disposal of the material at end of life and the cost of oil extracted from *Euphorbia lagascae*.

Have the Objectives been met?

We believe that all the objectives of the project have been met. A brief justification of this statement is listed after each objective.

- 1) *Sourcing of vegetable oils:* Successfully sourced from ADAS. Euphorbia oil was obtained in 30-40 litres. As no home-grown source of *Euphorbia lagascae* was available during the course of the project, the decision was taken to import seed from the USA and to crush in the UK. Therefore, c. 320kg of crude Euphorbia seed was purchased from Dr Richard Roseburg at Oregon State University. The nature of some of these samples was fairly impure, and four of the five batches were contaminated with husk and other dry plant material giving c. 120kg of pure seed. Despite the reported high seed oil content, the high level of extraneous plant matter and with the relatively small batch size studied, oil yield was very low under cold pressing conditions. Thus, there was difficulty in obtaining an oil of adequate quality and quantity from this source. In order to proceed with experimental work, 40 litres of oil was sourced from a commercial supplier in Europe, and with this, we were able to satisfy the requirements of the project experimental work. The decision was taken to halt further processing of the imported seed. Moreover, due to the air freight costs, and the high tariff paid on importation (of this relatively small batch of seed), the costs are not applicable to commercial extraction. However, it should be noted that a sample of the imported material is still available at Springdale Crop Synergies, and is to be used in further demonstration and commercial work.
- 2) *Preparation of a range of monomer feedstocks derived from rapeseed, and euphorbia oil.* A range of monomer feedstocks with various levels of hydroxylation were obtained from both euphorbia oil and rapeseed oil. The extent of derivatisation and the properties of the monomers were determined by using a range of techniques. Monomers were synthesised in 5 kg batches. Three main types of monomers were produced, notably rapeseed monomer, low hydroxylated euphorbia monomer and high hydroxylated euphorbia monomer.
- 3) *Use of these feedstocks in the preparation of a range of polyurethane materials:* The different monomer feedstocks obtained from objective 2 were polymerised with MDI using a variety of catalysts and conditions to produce a range of oil resin polyurethanes. In addition a library of composite materials consisting of the resins with renewable reinforcers consisting of hemp or jute fibres were prepared. Fibres prepared by utilising either a caustic wash or with no such a wash were used in composite manufacture.
- 4) *Comparison of the materials properties of polyurethanes prepared above with existing commercial derived materials:* All materials prepared in objective 3 were rigorously tested using TGA, DSC, impact, tensile, and SEM analysis. A limited range of materials were investigated for biodegradability and weatherability. A full comparison of the properties of both rapeseed and euphorbia derived materials is given in the preceding sections
- 5) *Comparison of economics / competitiveness / market opportunities of materials prepared from the above vegetable oils with existing castor oil and epoxidised soya bean oil.* A 16 page report on the above was commissioned and received by Dr. Mark Johnston and is available as an appendix to this report, however the main findings are listed above under the economics section.
- 6) *To stimulate the development of LINK projects within the polymer industry:* We have fostered links with Sustainable Composites Ltd and MoVirgo Ltd, two SME companies in Cornwall interested in marketing our technology. We are currently investigating joint funding mechanisms (potentially LINK) to bring the technology to market with these companies. In addition we presented our work at a symposium at the University of Warwick in July 2003 (sponsored by DEFRA). We have also set up a company, Natural Plastics Ltd, in order that we ourselves can market our technology. Springdale are currently using euphorbia lagascae seed provided to them during this research in a demonstration project.

Implications of the findings for future research: .

Further scientific work has been highlighted: Specifically in this project it is necessary to carry out more *biodegradability studies so that it will become possible to tailor degradability to appropriate applications*. The success in the development of vegetable oil / fibre composites warrants further investigation using other UK fibre crops other than hemp. The preparation of a wider range of composites will allow a full composition/ property profile portfolio to be produced. Rape meal has been used as a renewable filler in a number of applications, it may be possible to use rape meal as a filler in our composites. Thus these materials would be truly renewable as they would contain a vegetable oil resin, a fibre reinforcer and a rape meal filler (a 3 component renewable). Variation of the amounts of these 3 components would allow for a variety of new materials to be produced. In the general area we must address the low uptake from industry of materials from renewable resources. We need a larger portfolio of materials available. *This can be addressed by exploring the use of vegetable oils in the formulation of other materials other than polyurethanes*. Lessons may be learnt from the technology of bio-diesel where uptake was slow. This technology is now more accepted and bio-diesel is often blended with conventional diesel. It is likely that the blending of renewable polymers with existing petrochemical ones will provide the industrial uptake that is required (i.e replacing only part of a material with a renewable). *Thus work involving blending of our materials with existing petrochemical derived plastics deserves attention. Apart from euphorbia lagascae there may be other plants which could be developed as crops that would furnish important raw materials for industry*. A programme to identify such potentially useful new crops will be instigated with HRI (now part of Warwick University). *In addition, although we have demonstrated that rapeseed oil can be used to prepare polymers the existing crop varieties have been bred for the food industry and not for the polymer industry. By investigating other varieties of commercially grown crops it may be possible to find varieties that are more suited for industrial materials*.

Conclusion and relevance to industry and NF05: A range of materials from rapeseed oil and euphorbia oil have been prepared and analysed. Properties of materials produced differ depending upon the type of oil used. It is not appropriate to conclude that one source of oil is better than the other however as different properties will be required for different applications. Fibre composites of resins give superior properties to resins alone with the degree of fibre added effecting the biodegradability of the materials as well as the mechanical properties. The full cost benefit analysis of the procedures is currently being undertaken. The increased range of materials available from this project will broaden the portfolio of potential industrial applications of materials from renewables which should lead to an increased value added market for fibres and oil crops in the UK agricultural sector. The project is clearly addressing the scientific and technical objectives of NF05. In particular it has identified Euphorbia lagascae as a potential new crop for renewable materials production, and is investigating economic ways of producing new chemical feedstocks and polymers from UK crops.

Technology Transfer:

The Faraday Plastics Partnership has given us access to a national database of companies working with polymers. It is part of the role of the partnership to bring together the results of academic research and potential end users, by developing programmes of research conducted from the viewpoint of SME's and their supply chains and is based upon a funding model that encourages their active involvement. We (via Dr. N. Tucker) have been disseminating our results to the Partnership members who will be able to gain access to our technology. In addition, technology is being transferred through SusCompNet, a network of industry and academia funded via the EPSRC (Engineering and Physical Sciences Research Council).

Publications and other dissemination from this project.

Three academic publications have been submitted.

- 1) Mwaikambo, LY, Clark AJ and Tucker, N: Mechanical properties of hemp fibre reinforced euphorbia composites, submitted in Composites Science and Technology Journal (2003)
- 2) Mwaikambo, LY, Clark, AJ and Tucker, N: Mechanical properties of hemp fibre reinforced rapeseed composites, submitted in Journal of Applied Polymer Science, (2003)
- 3) Mwaikambo, LY, Clark, AJ and Tucker, N: Mechanical properties of jute fibre reinforced composites, submitted in Macromolecular Engineering, (2003)

The work has been presented by oral presentations at :

- 1) EcoComp 2003 workshop, Queen Mary's University of London, 1-2 September 2003.
- 2) Review of DEFRA funded research on renewable industrial materials, University of Wawick, 16th June 2003
- 3) SusCompNet 3 conference , Swansea University, 11th July 2002,.

By poster or stands at:

- Royal Agricultural Show, Stonleigh, July 2002
SusCompNet 3 conference , Swansea University, 11th July 2002,.

Articles have appeared in Farmers Weekly, the Financial Times and news bulletin sheets.

**Project
title**

Vegetable oils as polymer feedstocks: Chemical modification,
materials formulation and economics

**DEFRA
project code**

NF0513
