



PROJECT REPORT No. OS47

LOW-COST SYNTHESIS AND
EVALUATION OF POLYMERS
PREPARED FROM OILSEED RAPE
AND *EUPHORBIA LAGASCAE* OILS

I: PROJECT AT UNIVERSITY OF WARWICK

II: PROJECT AT MID-KENT
COLLEGE

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LAGASCAE OILS**

I: PROJECT AT UNIVERSITY OF WARWICK

by

Dr ANDREW CLARK

University of Warwick, Coventry, Warwickshire, CV4 7AL

II: PROJECT AT MID-KENT COLLEGE

by

Dr RICHARD HIGNETT* AND PROFESSOR BRIAN KEENE*

Mid-Kent College, Horsted, Chatham, Kent, ME5 9UG

* Now deceased

This is the final report of two projects:

I: Project at University of Warwick

This two year project started in September 1998 and was funded by a grant of £80,634 from HGCA (project no 1507).

II: Project at Mid-Kent College

This two year project started in July 1995 and was funded by a grant of £61,580 from HGCA (project no 1505) and £10,000 from John L Seaton and Co. Ltd., Hull.

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I: PROJECT AT UNIVERSITY OF WARWICK

Abstract

The high environmental burden caused by the use of non-renewable petrochemical-based feedstocks for the chemical and polymer industries has led to the search for vegetable oil-based alternatives. Despite this, only castor oil (a non-UK indigenous crop), has gained importance as a feedstock in the polyurethane industry. Polyurethanes are used globally on a scale of around 7 million tonnes a year and this is rising at a rate of about 1 million tonnes a year.

The main aims of this project were thus to widen industrial demand for agricultural oilseed derived products from UK sources, primarily by demonstrating that oils such as rapeseed can be used as chemical feedstocks to make polyurethanes and replace existing petrochemicals and castor oil. However, oils such as rapeseed do not contain the necessary chemical functionality (hydroxyl groups) required to be useful as polyurethane feedstocks and so it is necessary to introduce such functionality by low-cost chemical manipulation. We have shown that it is possible to prepare a range of feedstocks containing both epoxide (required for epoxy resin formation) and hydroxyl groups (required for polyurethane formation) on a 25-litre scale. By careful control of the reaction it is possible to control the level of functionality introduced into the feedstock. In this way, it is possible to prepare a range of polyurethane products with differing properties, such as rigid packaging foams, flexible elastomers and rigid polyurethane. In addition the new feedstocks can be used to replace castor oil in a variety of polyurethane formulations.

In bulk chemical markets these renewable feedstocks must compete in price with existing petrochemical sources (as well as castor oil) and at current costs this is unlikely. However, the real advantage of these feedstocks is their potential to corner 'niche' markets as opposed to 'bulk' chemical markets. We are currently working very closely with a variety of chemical companies to develop further these 'niche' markets. For example, we are currently evaluating the feedstocks in critical civil applications such as binders to stabilise ballast on rail track and environmental coatings in marine applications (estimated feedstock level of 6000 tonnes per annum for only two of many 'niche' applications).

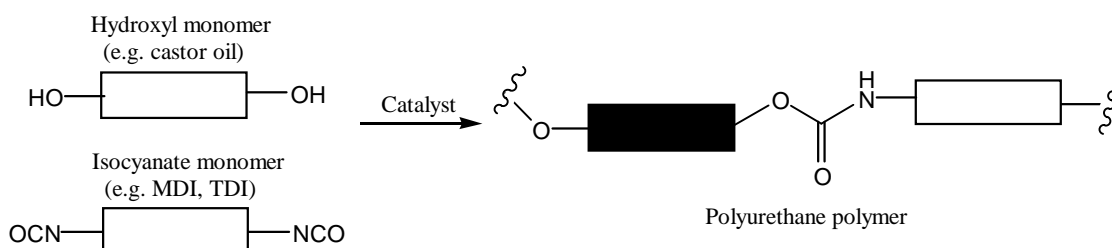
Based upon the results from this HGCA-funded study we (in collaboration with agronomists from ADAS, materials scientists from the Warwick Manufacturing Group, an economist from Warwick Business Ventures and a variety of chemical companies), have received MAFF funding to explore the development of these niche markets for the future.

Summary

Background and aims

The high environmental burden caused by the use of non-renewable petrochemical-based feedstocks has led to the search for vegetable oil-based alternatives. This represents an obvious step forward for both the chemical industry and oilseed producers driven by sound ecological reasons, in tandem with the Ministry of Agriculture Fisheries and Food's stated aim of supporting development of renewable non-food industrial materials from agricultural crops. Despite this, only castor oil (a non-indigenous crop), has gained importance as a feedstock in the polyurethane industry. Castor oil is rich in ricinoleic acid (a fatty acid that contains the hydroxyl group). This is important because polyurethanes are prepared by the reaction of hydroxylated monomers. Polyurethane products themselves made up more than \$2 billion in sales in the United States in 1991 and these products are an important contributor of the UK economy as well. Polyurethanes have been used for a large variety of applications, such as flexible foams for use as seat cushions and bedding. Variation in the formulation of polyurethanes produces rigid foams used for insulation and cores for structural composites. Polyurethanes may also be processed by extrusion and reaction injection moulding. Other applications include coatings, adhesives and sealants and use in rapid prototyping of pre-production/low production runs of commercial products. Modern rapid prototyping often uses polyurethane materials produced from castor oil. 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 a isocyanate monomer (at least two isocyanate sites) with or without a catalyst or a filler or reinforcement (Scheme 1). 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. However, unlike castor oil, indigenous oilseeds such as rapeseed do not contain the hydroxyl functionality required to be useful in polyurethane formulation. Thus to exploit these oilseeds the desired

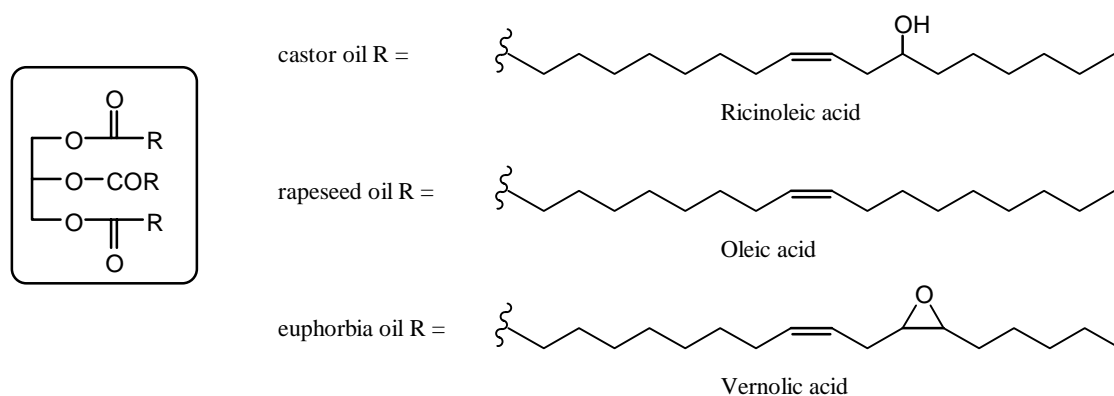


Scheme 1

hydroxyl functionality must be introduced by chemical manipulation.

The main aims of this project were to widen industrial demand for agricultural oilseed derived products from UK sources, primarily by demonstrating that oils such as rapeseed can be chemically modified and used as feedstocks and thus replace existing petrochemicals and castor oil in the preparation of polyurethanes. Thus the stated objective in the original proposal was to *‘prepare and characterise a variety of new industrial feedstocks derived from rapeseed oil, and to demonstrate that these feedstocks can be used to prepare a range of industrially and technologically important polymers’*. The results of this project were also to be *‘disseminated to interested and industrial parties with a view to more general evaluation and commercialisation’*

Fig. 1 Main R groups in common triglycerides



Rape as a feedstock

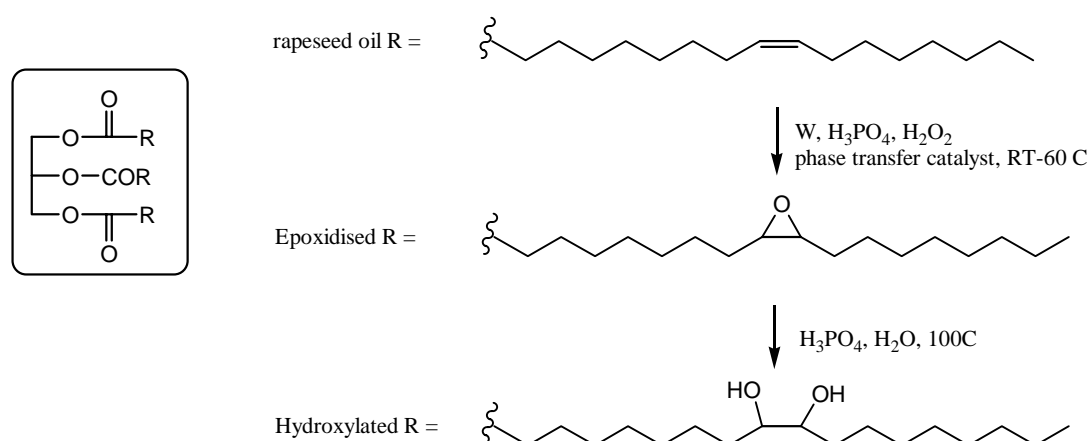
Oilseed rape is the third most extensively grown crop in the UK, with over 500,000 ha grown in 1999. Financial support (area aid payments) for oil crops under Agenda 2000 reform are dropping from current rates of £354/ha in 2000, down to £241/ha in 2002. This is putting increasing pressure on profitability for UK oilseed growers of what is a valuable break crop from cereals. Depending on the scale of development and industrial uptake, development of alternative uses for rapeseed oils, would give greater financial stability to UK oilseed growers, and greater market diversity. Rapeseed oil is predominantly used directly as a cooking oil, but increasingly industrial markets are developing. Rapeseed oil has been developed as a biodegradable lubricant, and High Erucic Acid Rape (HEAR) has established a niche market in this area. Various components of the fatty acid profile of oilseed rape 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 uses. Rapeseed oil is predominantly traded as a bulk oil commodity. This work sought to add value to rapeseed oil by developing novel uses for the oil in the polyurethane sector. The

polyurethane (PU) market is large (\$2billion per annum in USA - figures for UK not available) and applications are diverse ranging from foams for upholstery, shoe soles and structural composite matrices

Methods/chemical manipulation

As previously stated, oils such as rapeseed or linseed require chemical manipulation to produce appropriate feedstocks for polyurethane synthesis, thus rapeseed needs to be sequentially epoxidised and ring opened before an appropriate feedstock for polyurethane formation can be obtained (Fig 2). In order not to compromise the environment-friendly nature of the use of vegetable oils, methods of epoxidising and hydroxylation 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.

Fig. 2 Showing how main R groups react



We used Venturello's catalyst Q₃PO₄[W(O)(O₂)]₄ (where Q is a phase transfer catalyst), in the presence of hydrogen peroxide to transpose rapeseed and linseed oils into epoxidised products (by-product water, Fig 2). The reaction can be achieved without the use of a solvent, as the catalyst is able to dissolve in both the water and oil phases as long as the reaction is properly emulsified. The catalyst itself can be prepared from tungsten powder, hydrogen peroxide and phosphoric acid followed by the addition of a phase transfer catalyst such as adogen 464 (methyltrialkyl (C8-C10) ammonium chloride). The catalyst can be prepared *in situ* or extracted in a solvent and stored until needed. During the course of this work we discovered that we could control the degree of epoxidation, by altering the reaction conditions (namely stoichiometry, time, temperature and concentration). If the reaction was

carried out at high temperature some opening and polymerisation of the material occurred. However, if the reaction was run at room temperature or below 60°C then the epoxides could be isolated fairly pure. Reaction times varied from a few hours at 100°C to a few days at room temperature. We could easily scale the reaction up to a 15-20 litre scale. The catalyst could be recovered at the end of the reaction, thus avoiding contaminating waste. Attempts to prepare solid supported catalysts which could be much more easily reclaimed by filtration after the reaction were unsatisfactory. While supported catalysts could be prepared they showed disappointing rates of activity. In collaboration with Dr. Nick Tucker in the Warwick Manufacturing Group we tested a range of the epoxides as monomers in epoxy resin formation. All reactions were disappointing, indicating that this class of epoxide monomer is unlikely to be successful in the epoxy resins market.

We next investigated the ring opening reactions of the epoxides to give the desired hydroxyl monomers suitable for polyurethane formation. This was accomplished by acid-catalysed ring opening of the epoxides. Fairly harsh conditions were required (50% phosphoric acid) at 100°C. Again by varying a whole range of conditions we could prepare a range of feedstocks with different degrees of flexibility and hydroxyl content. In order to prepare a range of polyurethane materials a whole spectrum of monomers containing a range of hydroxyl groups was prepared and reacted with a variety of diisocyanates (TDI and MDI) to produce a range of materials. For example, it was possible to make rigid foams of the type used for packaging or pipe insulation exhibiting excellent fire retardation properties. In addition, in collaboration with the companies Envirofoam, Hyperlast and Adhesives and Sealants we found that we could also easily produce a range of flexible elastomers and rigid polyurethanes of potential industrial significance. Thus we could control all the required parameters necessary to theoretically tailor any desired property in polyurethane matrix formulation. We tested the thermal stability of a range of the polyurethane materials and compared the results with those derived from castor oil. Results indicated that polymers derived from the rapeseed process were harder to degrade and were stable to higher temperatures than their castor oil derived counterparts.

Integral to our research was the ability to characterise the feedstocks by a variety of state-of-the-art analytical techniques at the University of Warwick. By far the most important technique that allowed us to characterise the complicated feedstock mixtures was Matrix Assisted Laser Desorption Ionisation-Time of Flight-Mass Spectrometry (MALDI-TOF-MS), a technique which is now finding favour routinely in the characterisation of a range of triglyceride mixtures. In addition the use of Gel Permeation Chromatography (GPC) and high field Nuclear Magnetic Resonance (NMR) was also essential. This allowed us to accurately determine the course of our reactions and thus optimise them further.

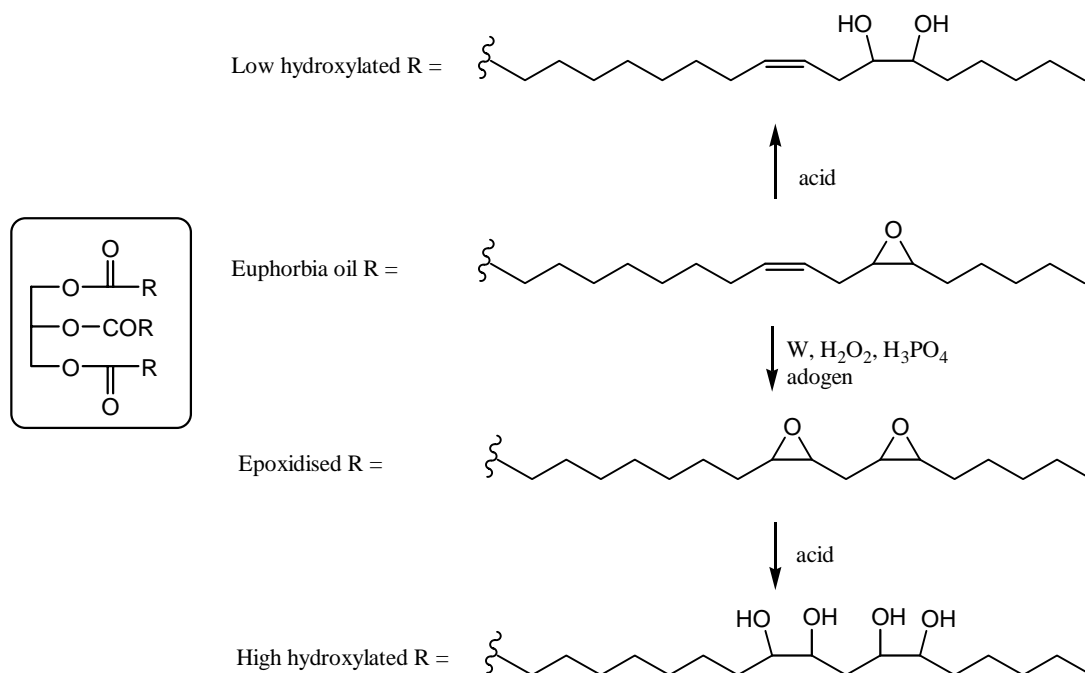
In bulk chemical markets these renewable feedstocks must compete in price with existing petrochemical sources (as well as castor oil) and at current costs this is unlikely. The procedure is unlikely to lead to a replacement for castor oil in current bulk markets. However, the real advantage of these feedstocks is their potential to corner 'niche' markets as opposed to 'bulk' chemical markets due to the ability to tailor their hydroxyl content. We are currently working very closely with a variety of chemical companies to develop further these 'niche' markets. For example, we are currently evaluating the feedstocks in critical civil applications such as binders to stabilise ballast on rail track and environmental coatings in marine applications (estimated feedstock level of 6000 tonnes per annum for only two of many 'niche' applications).

Evaluation of Euphorbia oil as a feedstock and ongoing research

Many existing UK indigenous vegetable oils require chemical modification (e.g. we have just seen that rapeseed and linseed require two chemical steps: epoxidation followed by ring opening) to produce the hydroxylated feedstocks which can be used in the polyurethane industry. This added expense may reduce their competitiveness as replacements to petrochemical feedstocks. It should be possible to generate novel materials from these modified oils that may have different properties to those derived from conventional petrochemical sources with possible new niche market applications. However, vegetable oils which show significantly high levels of "exotic" functionalisation already (e.g. *Euphorbia lagascae* oil is rich in vernolic acid, a fatty acid that contains an epoxide, fig 1) have the potential to find significant markets due to the lesser degree of chemical modification required to furnish the desired feedstocks. Whereas rapeseed requires two chemical steps to produce an appropriate hydroxylated feedstock, *euphorbia* requires only one (that of ring opening). In addition, because the ring opening step is normally by far the cheapest of the two chemical steps, this makes *euphorbia* oil a particularly attractive raw material. To our knowledge there has been no in depth study into the use of *euphorbia* oil as a feedstock for the polyurethane industry until now.

In collaboration with ADAS (M. Froment, D. Turley, S. Cook) we also undertook a feasibility study into the chemical manipulation of *euphorbia* oil to give feedstocks for polyurethane production. Because *euphorbia* requires minimal low cost chemical manipulation to produce desirable monomer feedstocks it may provide significant advantages in terms of economics of feedstock production. Consequently ring opening of *euphorbia* using aqueous acid (phosphoric acid) produced a hydroxylated monomer (termed by us "low hydroxylated *euphorbia*") which we demonstrated could be used to make simple polyurethanes. Although *euphorbia* already contains epoxide groups it also contains alkene groups which can be further functionalised.

Fig. 3 Preparation of high and low hydroxylated *Euphorbia*



Hence, we also reacted *euphorbia* at these alkene positions to introduce further hydroxyl groups to produce a "high hydroxylated *euphorbia*". Analysis at the epoxide stage indicated that the epoxide profile was different to that in other epoxidised oils (e.g. epoxidised rapeseed) which indicates that *euphorbia* may lead to different material properties in any consequent manufactured polymers. We prepared a range of polyurethane products produced from the high and low hydroxylated *euphorbia* but have yet to compare their materials properties with those derived from rapeseed or linseed oils.

In the MAFF/EC funded VOSFA project (contract AIR2 CT93-1817) and the EC funded SONCA (contract ECLAIR AGRE CT90-0039) project a range of oilseed crops was evaluated for their potential use in industrial applications. Although *Euphorbia lagascae* is not yet a commercially grown UK crop it was identified as producing an oil of interest to the lubricants, plasticisers, and coatings sectors. Within the VOSFA project this crop was successfully grown in southwest England. As a follow on from VOSFA, an ongoing EC funded Concerted Action, co-ordinated by ADAS, is evaluating existing information on *E. lagascae*. Data is being collated on crop performance and production, oil extraction and industrial applications of *Euphorbia* and barriers to commercialisation. Results indicate that typical seed yields are on average 1-1.3 t/ha (although the yield was somewhat underestimated due to dehiscence). Seed oil content was high (48-52%), and the vernolic acid side-chain content of the oil ranged from 58-67%. Indehiscent genotypes have been developed to get over the seed shattering problem, thus there is potential to increase the harvestable yield.

Dissemination of results and further funding

We have disseminated the results of this HGCA sponsored work in a number of ways. We were recently invited to submit a paper by Prof. F. Gunstone on our chemistry to the journal 'Lipid Technology'. This has now appeared in print (November 2000, page 129). We are currently preparing another invited paper to the RSC Journal 'Green Chemistry'. We have also given seminars at the 'Oilseed Rape Pipeline' seminar organised by ACTIN at UMIST in June 1999 where a large number of industrialists were present, and at the concerted action workshop on 'the development of *Euphorbia lagascae* as a new oil crop within the European Community' (FAIR-CT98/4460) at Cambridge in March 2000. We have been invited to speak in March 2001 at another ACTIN sponsored conference on renewable resources. A number of academic and industrial collaborations of relevance to this work have arisen as a direct consequence of speaking at these conferences.

As a consequence of the results obtained from this HGCA sponsored research we have been able to successfully bid for a MAFF grant (£135K) to work on the further development of this technology. This grant will be used to fund a large team comprising of 5 industrial companies, two agronomists (D. Turley, M. Froment from ADAS), myself (Principal Scientist and team leader-Chemist), two materials scientists from the Warwick Manufacturing Group (Dr. N. Tucker) and the Warwick Advanced Technology Centre (polymer testing - Dr. R. Cain) and an economist (from Warwick Business Ventures). With this team we believe that we have the appropriate mix of expertise, not only to investigate the chemistry and materials formulation of a range of potential products, but also the personnel to investigate the potential market/economics of the process and the breeding and agronomy issues.

Conclusions

A process for converting unsaturated oils into hydroxylated materials suitable for the preparation of polyurethanes has been developed. Attempts to prepare epoxy resins from epoxidised materials was unsuccessful. The hydroxylation process does not require chemicals that are particularly hazardous, flammable or volatile, and produces materials at a cost that is likely to be comparable to castor oil. It is unlikely to be used as a castor oil substitute, because the cost per tonne would need to significantly undercut castor oil for companies to invest money in reformulation and investment into new equipment.

On the positive side a great deal of control of the hydroxyl content is possible. Hence the number of possible uses is broadened with respect to castor oil and therefore it would be used for new rather than existing applications. Consequently, we are currently examining the use of modified rapeseed in a number of industrial applications in collaboration with Hyperlast and Adhesives and Sealants Ltd. More exciting is the possibility that potential new crops such as *Euphorbia lagascae* produce oils that already contain epoxide functionality, thus

cutting out the most expensive stage of the chemical manipulation. Ring opening of the *euphorbia* oil can be accomplished very cheaply and provides another useful feedstock with very high potential to make 'niche' polyurethanes. The potential for the development of *Euphorbia* as a UK crop is currently being evaluated by other groups. The recent establishment of a MAFF funded consortium of agronomists, chemists, material scientists and economists (headed by myself) should ensure that any possible market opportunities from this work and related work is efficiently and readily exploited.

Technical Report

Introduction

The use of non-renewable fossil fuels for chemical feedstocks causes large environmental problems for the polymer industry. Renewable resources such as vegetable oils (rapeseed and linseed) offer a non-toxic, non-polluting potentially biodegradable alternative, with attendant manufacturing benefits for the chemical industry. The use of vegetable oils as renewable resources for the formation of industrial materials and polymers as well as bio-lubricants is well established.^{1,2} Renewable vegetable oils which are 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. In addition, the quality requirements of oils used in the polymer industry is often high. 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. Of the different vegetable oils only castor oil (rich in ricinoleic acid – a hydroxylated monomer) has gained industrial importance in the polymer industry. In particular it has found use as a hydroxylated feedstock to make polyurethanes.³ Polyurethanes are made by reacting a hydroxylated monomer (at least two hydroxyl sites) with a isocyanate monomer (at least two isocyanate sites) with or without a catalyst or a filler or reinforcement, (scheme 1). 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. However, unlike castor oil, indigenous oilseeds such as rapeseed do not contain the hydroxyl functionality required to be useful in polyurethane formulation. Thus to exploit these oilseeds the desired hydroxyl functionality must be introduced by chemical manipulation by epoxidation followed ring opening.^{4,5}

The polyurethane industry alone is a large and diverse business accounting for seven million tonnes of production per annum, covering a range of applications in infant and mature market sectors.⁶ When no longer required, the products are typically dumped in landfill sites. However, in our opinion, the true potential for the use of UK indigenous oilseed crops in the polymer industry (in particular the polyurethane industry) has not been realised. We wished to combine the use of vegetable oils with polyurethane and perhaps epoxy resin production to make potentially biodegradable novel materials for the chemical industry.

Aims and objectives of original proposal

We will prepare and characterise a variety of new industrial feedstocks derived from rapeseed oil. We will demonstrate that these feedstocks can be used to prepare a range of industrially and technologically important polymers and the results will be disseminated to interested industrial parties with a view to more general evaluation and commercialisation. These objectives were to be achieved by:

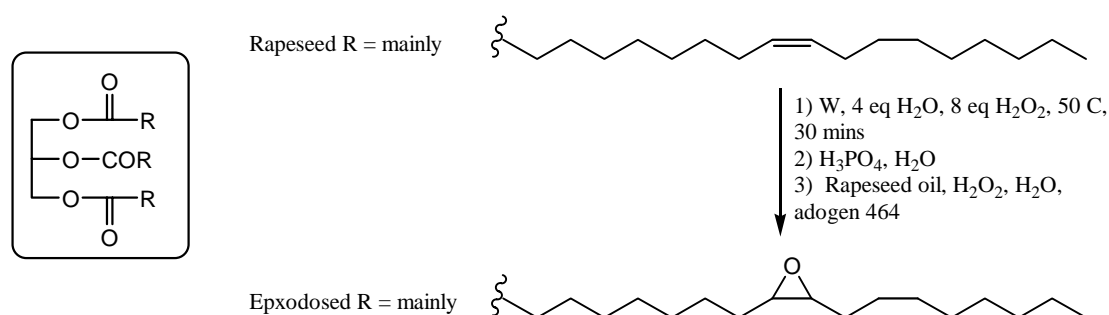
- 1 Chemical manipulation of rapeseed oil (by hydroxylation and epoxidation) and rigorous characterisation of the resulting feedstocks using state-of-the art equipment at Warwick
2. Fine-tuning of the hydroxylation and epoxidation technology to optimise the range of monomer feedstocks available from rapeseed to give materials with properties identified by consultation with industrial users
- 3 Development of lower-cost ‘environmentally friendly’ alternative catalysts (solid supported) to prepare monomer feedstocks
- 4 Scale up of monomer feedstock production and demonstration of their use in the preparation of polyurethanes, polyesters, polyethers and epoxy resins.
- 5 Organisation of a symposium to disseminate results to industrial collaborators and other interested parties to encourage further evaluation and commercialisation of the developed methodology.

Materials and methods, results and discussion

We used Venturello’s catalyst $\text{Q3PO}_4[\text{W}(\text{O})(\text{O}_2)]_4$ (where Q is a phase transfer catalyst), in the presence of hydrogen peroxide to transpose rapeseed and linseed oils into epoxidised products (by-product water, Fig 4).⁷ The reaction can be achieved without the use of a solvent, as the catalyst is able to dissolve in both the water and oil phases as long as the reaction is properly emulsified. The catalyst itself can be prepared from tungsten powder, hydrogen peroxide and phosphoric acid followed by the addition of a phase transfer catalyst such as adogen 464 (methyltrialkyl (C8-C10) ammonium chloride). The catalyst can be prepared *in situ* or extracted into an organic solvent such as dichloromethane and stored until needed but typically it was added directly to the reaction mixture. Reaction times varied from a few hours at 100°C to a few days at room temperature. We could easily scale the reaction up to a 15-20 litre scale. The use of alternative catalysts based upon molybdenum were also

examined but were not so efficient. During the course of this work we discovered that we could control the degree of epoxidation, by altering the reaction conditions (namely stoichiometry, time, temperature and concentration). If the reaction was carried out at high temperature some opening and polymerisation of the material occurred however if the reaction was run at room temperature or below 60°C then the epoxides could be isolated fairly pure. We also examined test reactions using the procedure on commercial triolein in order to compare the results with those from rapeseed. A typical procedure is as follows. Tungsten powder (9.9g) is heated at 50°C in water (40ml) and hydrogen peroxide (80 ml) for 30 minutes. Then phosphoric acid (5.9g) in water (80ml) is added with stirring. Then rapeseed oil (2Kg), water (3L), 30% hydrogen peroxide (1L) and Adogen 464 (14g) is added and the mixture stirred at 50°C until the disappearance of the alkene signals monitored by NMR.

Fig.4 Preparation of epoxides of rapeseed oil

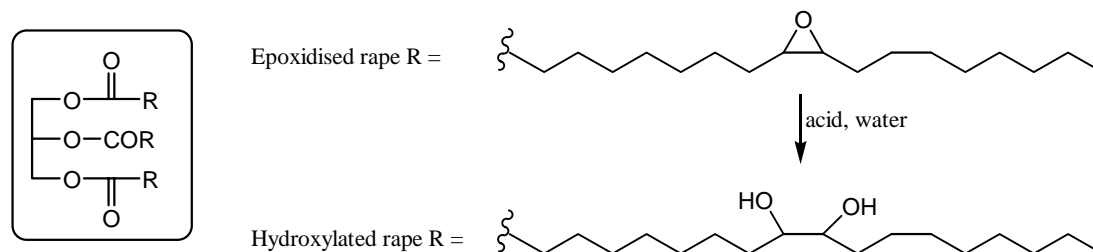


The effect of a range of different phase transfer catalysts was investigated however no difference in reactivity was observed for the range studied. We analysed the epoxide products using Matrix Assisted Laser Desorption Ionisation-Time of Flight Mass Spectrometry (MALDI-TOF)⁸⁻¹² which clearly indicated the degree of epoxide functionality, Fig. A (appendix A). In addition we able to follow the rate of the reaction by both 1H 400MHz Nuclear Magnetic Resonance (NMR) and 13C NMR. This data also confirmed the disappearance of the olefinic groups

With epoxides in hand we investigated the ring opening of the epoxides to give the required diols. We initially investigated the ring opening under acid catalysis with phosphoric acid. Fairly harsh conditions were required (50% by weight phosphoric acid with respect to natural oil, 100°C and vigorous stirring). This transformation was found to be more easily accomplished in organic solvents such as THF with much lower temperatures and less acid required. However, using this protocol there were problems associated with recovering the desired polyols from the solvent and in the disposal of the acidic waste; in contrast by using the aqueous phosphoric acid procedure the product was easily separated from the acidic

phase by washing with water. Using this protocol it was also possible to reclaim the Venturellos catalyst.

Fig.5 Preparation of hydroxylated rapeseed oil



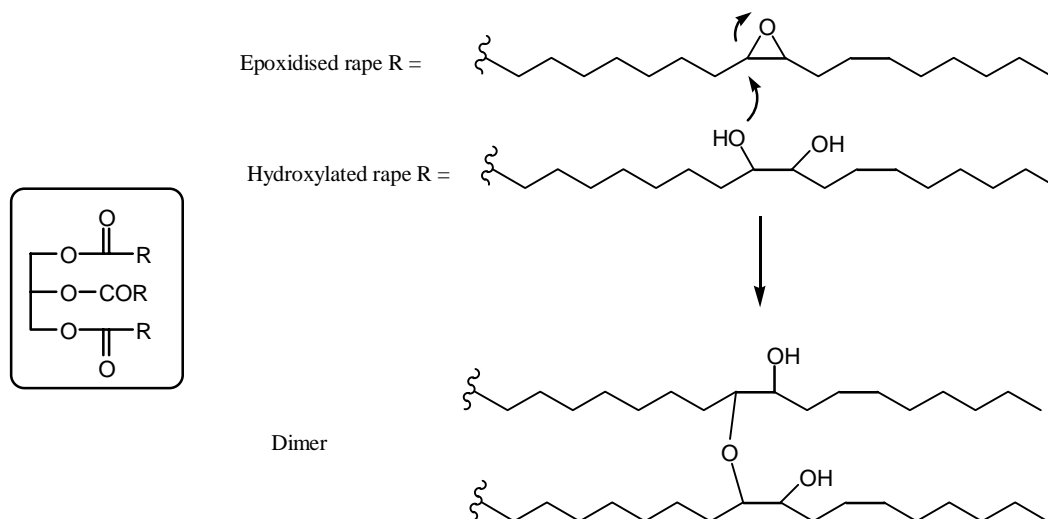
We then investigated the effect of concentration of phosphoric acid as well as the effect of using different temperatures ranging from 100°C to room temperature. The reactions occurred under all conditions but while the reaction was over in less than 90 minutes at 100°C it took over a day at room temperature to fully ring open. Others acids such as toluene sulphonic acid, hydrochloric acid and sulphuric acid were also investigated as replacements to phosphoric acid. Ring opening with hydrochloric acid produced among other products undesirable chlorohydrins. We also investigated the effect of a solid supported acid resin (Amberlyst 15) upon the ring opening reaction. It was hoped if successful the ease of recycling and work-up of the reaction would make the process very competitive, however we observed no reaction at all under a variety of conditions with this system.

We also investigated the ring opening reaction in the presence of water soluble nucleophiles such as 5-aminopentan-1-ol, 3-aminopropan-1-ol, 1,4-butyndiol, 1,4-butenediol, 1,3 propandiol and ethylene glycol. In this way it was possible to prepare a range of hydroxylated monomer with different flexibilities and functionalities.

The hydroxylated monomers were analysed by NMR, Infrared (IR), MALDI-TOF (Fig. B, Appendix A), and Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry (FTICR-MS) (Fig. C, Appendix A), as well as by Gel Permeation Chromatography (GPC) (Fig. D, Appendix A). Interestingly, we discovered that not only were the desired hydroxylated monomers produced but also a mixture of dimers, trimers and oligomers of the initial monomer feedstocks were detected. This can be seen plainly in the FTICR and GPC data. Hence, in addition to the expected ring-opening reaction with water, the intermolecular reaction show in figure 6 can also occur. The reaction seems to produce the same profile of polymeric products over a fairly wide-range of acid concentrations and reaction temperatures. Long reaction times or very high concentrations of acid do however result in cleavage of one or more of the fatty acid side chains attached to the central glycerol, with the end result being

complete hydrolysis of the triglyceride. While changing the acid concentration did not seem to be particularly efficient at generating different precursor's it does show that the process is a robust one with a high degree of reproducibility.

Fig 6 Dimerisation of rapeseed oil through intermolecular ring opening



In order to optimise the process still further we investigated carrying out both the epoxidation and ring-opening reaction in one pot without isolation of the intermediate epoxides. While this was successful using 50% weight for weight of phosphoric acid if lower concentrations were used (such as 1%) the reaction stopped at the epoxidation stage.

We could easily scale the successful reactions up to a 15-20 litre scale. The catalyst could be recovered at the end of the reaction thus avoiding contaminating waste. Attempts to prepare solid supported catalysts which could be much more easily reclaimed by filtration after the reaction were unsatisfactory. While both tungsten and molybdenum catalysts could be immobilised onto Amberlyst-27 (Analysis indicated 3.5%-3.9% functionalised by metal) the reaction did not produce epoxide even after 4 days at elevated temperature. The use of solid supported phase transfer catalysts also failed to mediate the reaction. The use of other oxidation sources such as bubbled oxygen gas as alternatives to hydrogen peroxide also failed.

Use of feedstocks to make epoxy resins and polyethers.

As polyether formation was partly observed to occur during the ring opening process we did not investigate this much further, however attempts to take the epoxide feedstocks and develop them in epoxy resin formulations was undertaken in collaboration with Dr. Nick Tucker in the Warwick Manufacturing Group. While we tested a range of the epoxides as

monomers in epoxy resin formation all the reactions were disappointing indicating that this class of epoxide monomer is unlikely to be successful in the epoxy resins market. No successful epoxy resin formulation could be produced.

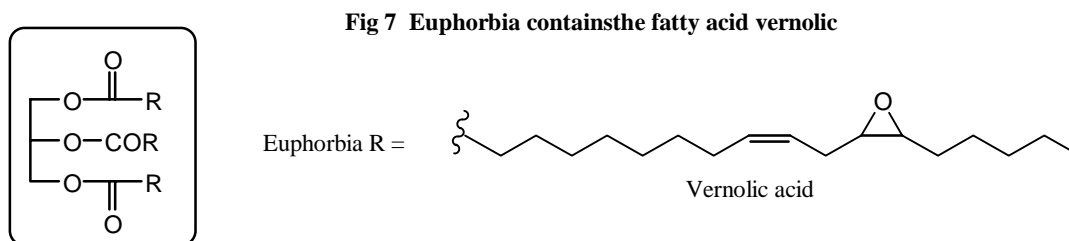
Use of feedstocks to polyurethanes

The reaction of a diol with a diisocyanate to give polyurethanes is often carried out in the presence of a catalyst (normally a tertiary amine or dibutyltin dilaurate). If the hydroxy monomer has more than two hydroxyl groups then cross-linking of the polymers can occur. The most commonly used diisocyanates are toluene diisocyanate (TDI) and methylene di-*p*-phenyl diisocyanate. For a given polyol-diisocyanate system, the higher the OH content of the polyol, the greater the degree of cross-linking and hence the more rigid the polyurethane formed. Conversely, the longer the diol component, the more flexible the polyurethane formed. By altering the hydroxyl content of the feedstocks it was possible to prepare both very flexible elastomers and very rigid polyurethanes (with Adhesives and Sealants and Hyperlast Ltd). It was also possible to use the highly hydroxylated materials in the preparation of rigid lightweight foams (in collaboration with Envirofoam Ltd). The materials properties of a range of polymers prepared using dibutyltin dilaurate as catalyst in the presence of fillers such as sand and molecular sieves were analysed by a range of techniques including differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Polymers prepared from highly functionalised feedstocks (rape and *euphorbia* based -see later) showed better thermal degradation properties than those prepared from castor oil. (Fig. E-F, Appendix A). Difficulties arose if the monomer hydroxyl content was low. In some formulations there was a problem with oily exudate from the polymers. While this is not desirable in most applications it may prove useful in the preparation of 'drawn' polyurethanes, (acting as own lubrication in the drawing process) and this is currently under investigation.

Evaluation of Euphorbia oil as a feedstock and ongoing research

Many existing UK indigenous vegetable oils require chemical modification (e.g. we have just seen that rapeseed and linseed require two chemical steps: epoxidation followed by ring opening) to produce the hydroxylated feedstocks which can be used in the polyurethane industry. This "added expense" may reduce their competitiveness as replacements to petrochemical feedstocks. It should be possible to generate novel materials from these modified oils that may have different properties to those derived from conventional petrochemical sources with possible new niche market applications. However, vegetable oils which show significantly high levels of "exotic" functionalisation already (e.g. *Euphorbia lagascae* an oil that is rich in vernolic acid a fatty acid that contains an epoxide, fig 7) have

the potential to find significant markets due to the lesser degree of chemical modification required to furnish the desired feedstocks.

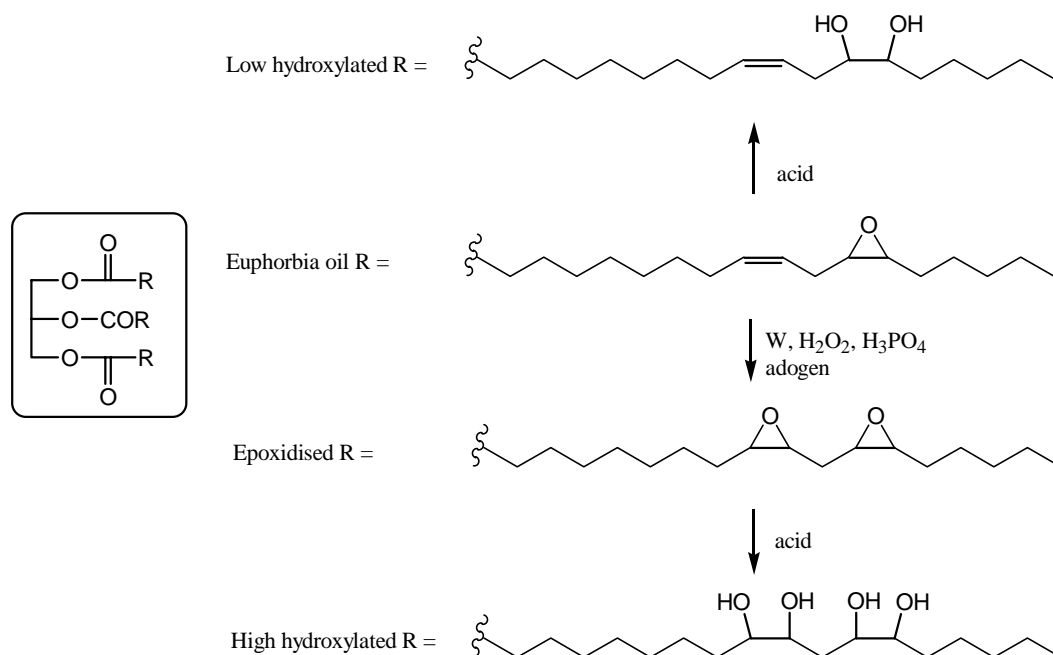


For example, whereas rapeseed requires two chemical steps to produce an appropriate hydroxylated feedstock *Euphorbia* requires only one (that of ring opening). In addition because the ring opening step is normally by far the cheapest of the two chemical steps this makes *euphorbia* oil a particularly attractive raw material. To our knowledge there has been no in depth study into the use of *euphorbia* oil as a feedstock for the polyurethane industry up until now.

In collaboration with ADAS (M. Fremont, D. Turley, S. Cook) we also undertook a feasibility study into the chemical manipulation of *euphorbia* oil to give feedstocks for polyurethane production. As stated previously, because *euphorbia* requires minimal low cost chemical manipulation to produce desirable monomer feedstocks it may provide significant advantages in terms of economics of feedstock production. *Euphorbia* oil was analysed by IR, ^1H and ^{13}C NMR and MALDI-TOF-MS (Fig. G Appendix A). Consequently ring opening of *euphorbia* using aqueous acid (phosphoric acid) produced a hydroxylated monomer (termed by us "low hydroxylated *euphorbia*") which we demonstrated could be used to make simple polyurethanes. Although *euphorbia* already contains epoxide groups it also contains alkene groups which can be further functionalised.

Hence, we also reacted *euphorbia* at these alkene positions to introduce further hydroxyl groups to produce a "high hydroxylated *euphorbia*". Analysis at the epoxide stage indicated that the epoxide profile was different to that in other epoxidised oils (e.g. epoxidised rapeseed) which indicates that *euphorbia* may lead to different material properties in any consequent manufactured polymers (Fig. H, appendix A). We prepared a range of polyurethane products produced from the high and low hydroxylated *euphorbia* (Fig. I, Appendix A) but have yet to compare their materials properties with those derived from rapeseed or linseed oils.

Fig. 8 Preparation of high and low hydroxylated *Euphorbia*



In the MAFF/EC funded VOSFA project (contract AIR2 CT93-1817) and the EC funded SONCA (contract ECLAIR AGRE CT90-0039) project a range of oilseed crops were evaluated for their potential use in industrial applications. Although *Euphorbia lagascae* is not yet a commercially grown UK crop it was identified as producing an oil of interest to the lubricants, plasticisers, and coatings sectors. Within the VOSFA project this crop was successfully grown in southwest England. As a follow on from VOSFA, an ongoing EC funded Concerted Action, co-ordinated by ADAS, is evaluating existing information on *E. lagascae*. Data is being collated on crop performance and production, oil extraction and industrial applications of *Euphorbia* and barriers to commercialisation. Results indicate that typical seed yields are on average 1-1.3 t/ha (although the yield was somewhat underestimated due to dehiscence). Seed oil content was high (48-52%), and the vernolic acid side-chain content of the oil ranged from 58-67%. Indehiscent genotypes have been developed to get over the seed shattering problem, thus there is potential to increase the harvestable yield and develop a new UK crop. If the chemical manipulation can compete in cost with existing feedstocks then this crop could have great potential for the future.

Dissemination of results and further research/funding as a consequence of this project

We have disseminated the results of this HGCA sponsored work in a number of ways. We were recently invited to submit a paper by Prof. F. Gunstone on our chemistry to the journal 'Lipid Technology'. This has now appeared in print (November 2000, page 129, Appendix

B). We are currently preparing another invited paper to the RSC Journal 'Green Chemistry'. We have also given seminars at the 'Oilseed Rape Pipeline' seminar organised by ACTIN at UMIST in June 1999 where a large number of industrialists were present, and at the concerted action workshop on 'the development of *Euphorbia lagascae* as a new oil crop within the European Community' (FAIR-CT98/4460) at Cambridge in March 2000, (Appendix C). We have been invited to speak next March at another ACTIN sponsored conference on renewable resources. A number of academic and industrial collaborations of relevance to this work have arisen as a direct consequence of speaking at these conferences.

As a consequence of the results obtained from this HGCA sponsored research we have been able to successfully bid for a MAFF grant (£135K) to work on the further development of this technology. This grant will be used to fund a large team comprising of 5 industrial companies, two agronomists (D. Turley, M. Fremont from ADAS), myself (Principal Scientist and team leader-Chemist), two materials scientists from the Warwick Manufacturing Group (Dr. N. Tucker) and the Warwick Advanced Technology Centre (polymer testing-Dr. R. Cain) and an economist (from Warwick Business Ventures). With this team we believe that we have the appropriate mix of expertise to not only investigate the chemistry and materials formulation of a range of potential products, but also the personnel to investigate the potential market/economics of the process and the breeding and agronomy issues. In particular we will be examining the differences in cost of developing feedstocks from rapeseed oil and euphorbia oils. In addition we will be examining the materials properties of polymers prepared from these two feedstocks.

A key objective of the newly funded project will be to identify the acceptability and exploitation potential of the materials. In addition to the performance of the materials produced and assessed, the potential for environmental improvement will be a central component of the acceptability of such materials for industrial uptake and consumer utilisation. This work will be undertaken by an experienced Business Development Manager (BDM) based in Warwick Ventures, a new unit established by the University of Warwick to exploit research generated by the university.

The initial work of the BDM will concentrate on the input of those industries who have already indicated their support for the project (Hyperlast, Fleming Polymer Testing and Consultancy, Bical, JB Plant Fibres, and Adhesives and Sealants Ltd) and will include an assessment of the acceptability of the materials in terms of cost and suitability for a range of applications as specified by the industrial partners. In addition, the environmental benefit of these materials over those produced by conventional protocols will be quantified (e.g. crop production regimes, reduction in use of toxic chemicals in the production of oils etc.). If costs of production are higher than conventional processes, an assessment of the level of premium acceptable for the provision of materials derived from such renewable resources will be made.

Following this baseline survey, the potential for uptake of these materials to a wider industrial base will be investigated.

The outputs of this objective will be:

- (i) A full cost/benefit analysis for each of the oils in terms of procedure, time and consumables costs.
- (ii) Quantification of the benefits of each approach in terms of environmental protection
- (iii) Identification of an acceptable premium for the provision of renewable/biodegradable materials A list of potential users of the materials and a schedule for exploitation if appropriate.

In addition The Faraday Plastics Partnership will give the project consortium 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 addressing the issues SME's face and based upon a funding model that encourages their active involvement. We will disseminate our results to the Partnership members who will be able to gain access to the technology. In the same way our results will be disseminated *via* the Alternative Crops Technology Interaction Network who will also be able to contact industrial partners of relevance.

Conclusions

A process for converting unsaturated oils into hydroxylated materials suitable for the preparation of polyurethanes has been developed. Attempts to prepare epoxy resins from epoxidised materials was unsuccessful. The hydroxylation process does not require chemicals that are particularly hazardous, flammable or volatile, and produces materials at a cost that is likely to be comparable to castor oil. It is unlikely to be used as a castor oil substitute, because the cost per tonne would need to significantly undercut castor oil for companies to invest money in reformulation and investment into new equipment.

On the positive side a great deal of control of the hydroxyl content is possible, hence the number of possible uses is broadened with respect to castor oil and therefore it would be used for new rather than existing applications. Consequently, we are currently examining the use of modified rapeseed in a number of industrial applications in collaboration with Hyperlast and Adhesives and Sealants Ltd. More exciting is the possibility that potential new crops such as *euphorbia lagascae*, which produce oils that already contain the epoxide functionality, can be used as feedstocks thus cutting out the most expensive stage of the chemical

manipulation (that of epoxidation). Ring opening of the *euphorbia* can be accomplished very cheaply and provides another useful feedstock with very high potential to make 'niche' polyurethanes. The potential for the development of *euphorbia* as a UK crop is currently being evaluated by other groups. The recent establishment of a MAFF funded consortium of agronomists, chemists, material scientists and economists (headed by myself) should ensure that any possible market opportunities from this work and related work is efficiently and readily exploited.

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Appendix A Fig. A

MALDI spectra of epoxidised rapeseed clearly showing the level of epoxidation

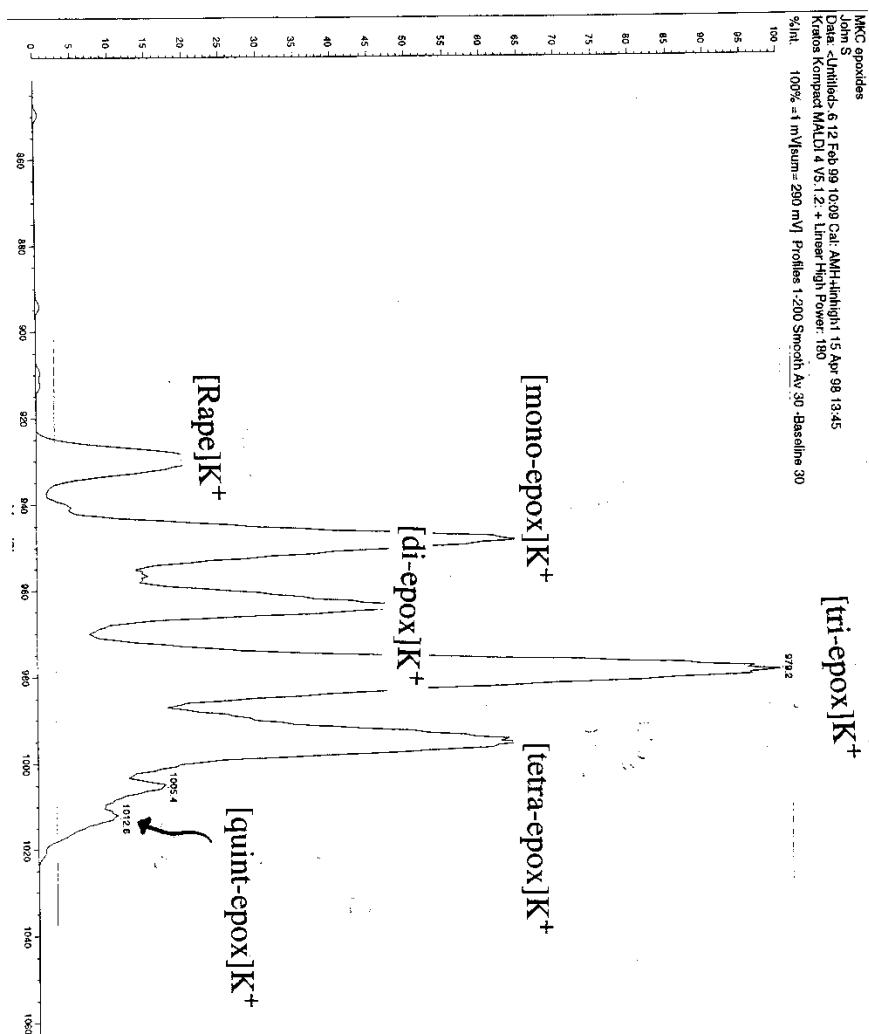


Fig., B

MALDI spectra of hydroxylated rapeseed

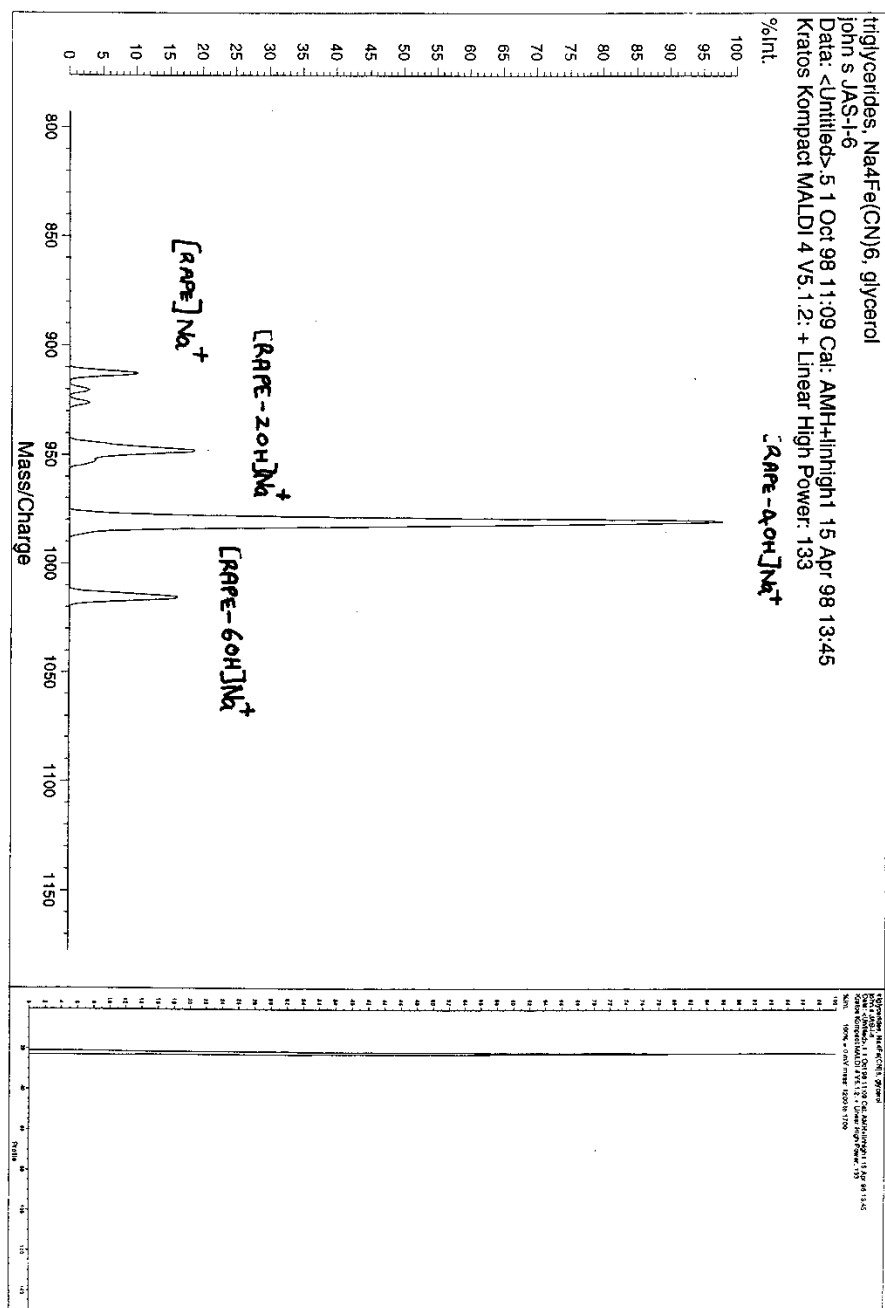


Fig. C

FTICR of ring opened rapeseed clearly showing monomer and dimer formation due to intramolecular ring opening

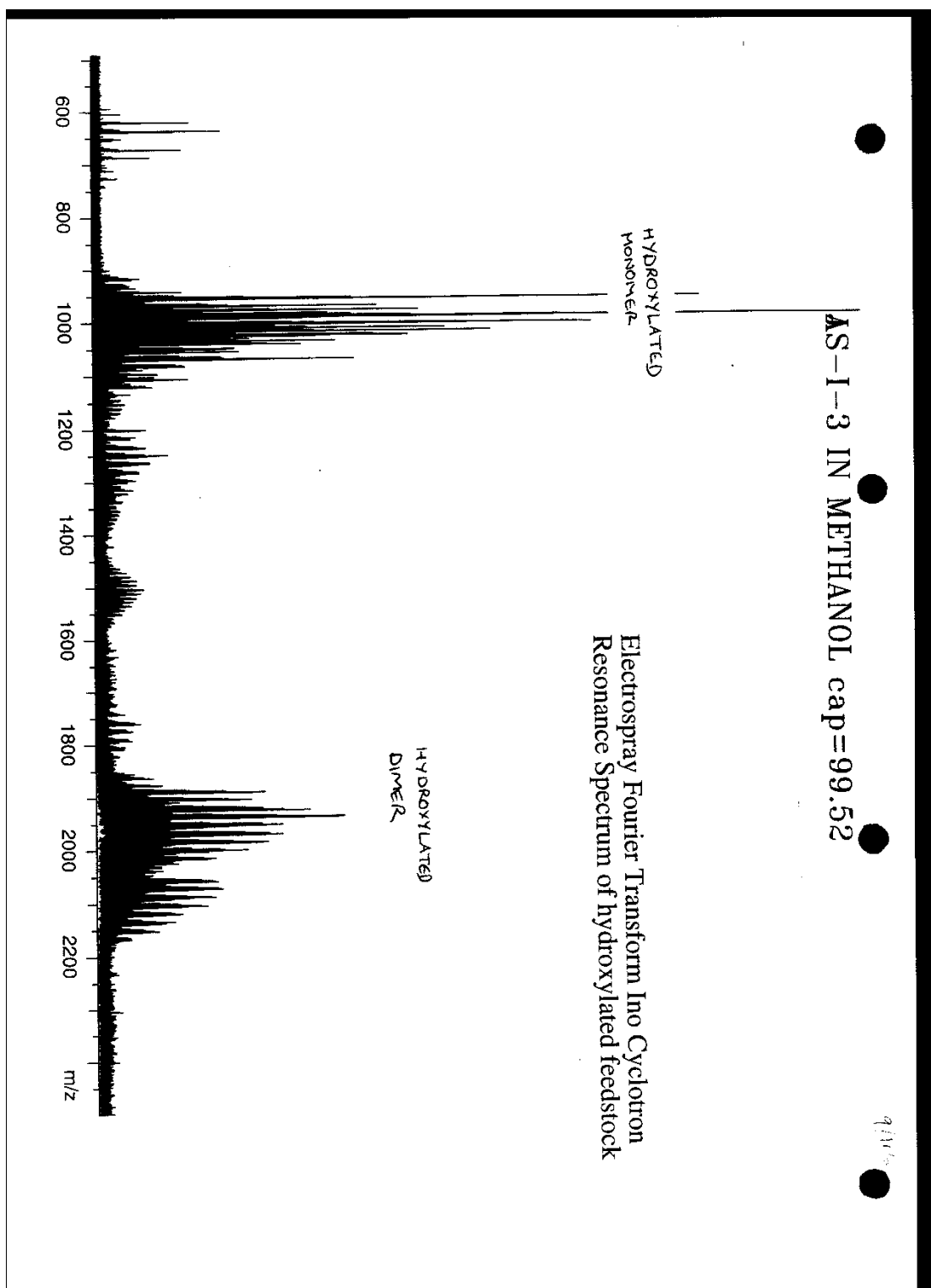


Fig. D

GPC of high hydroxylated monomer showing oligomers

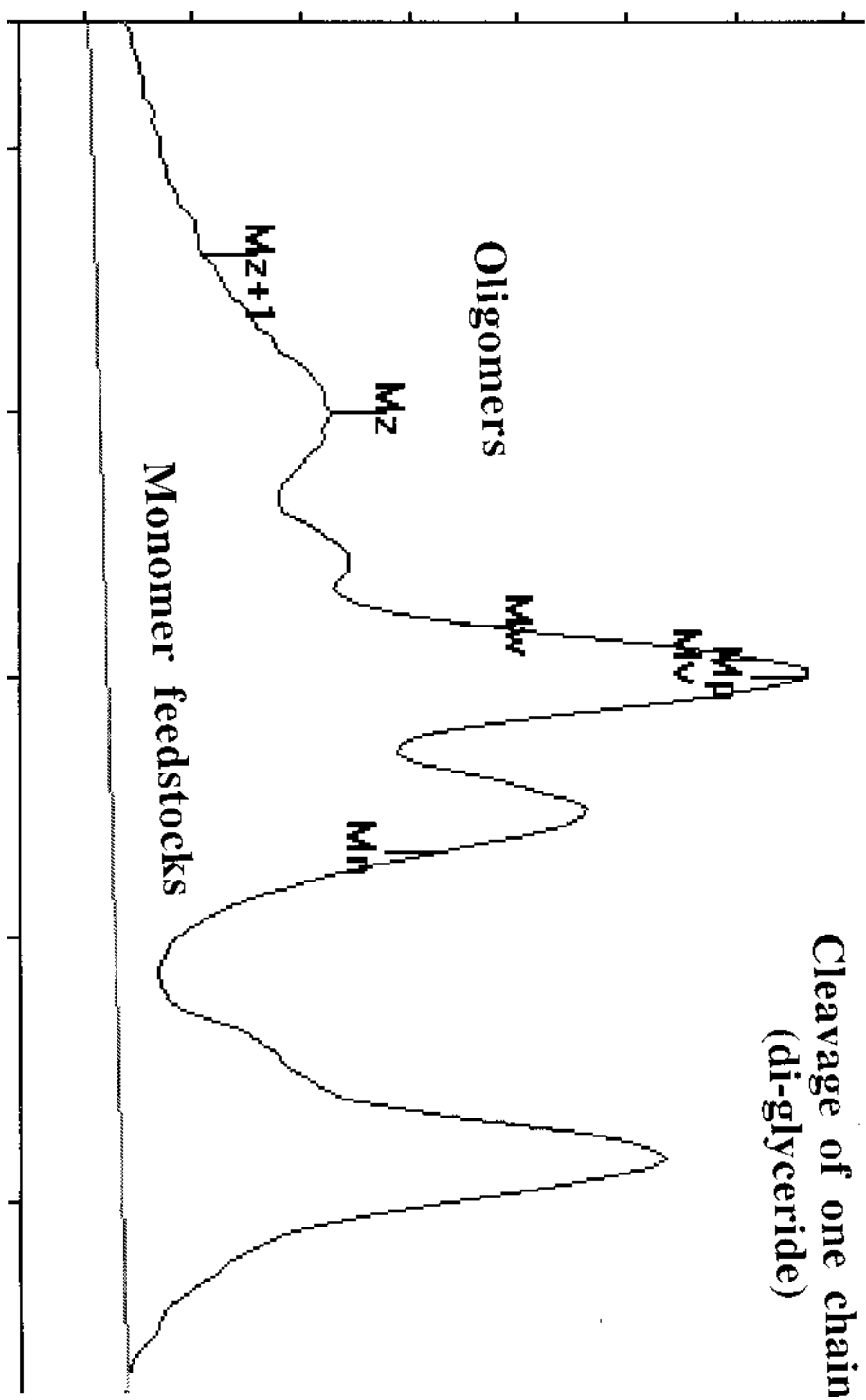


Fig E and F
Analysis of polymers prepared from castor oil and high hydroxylated euphorbia oil.

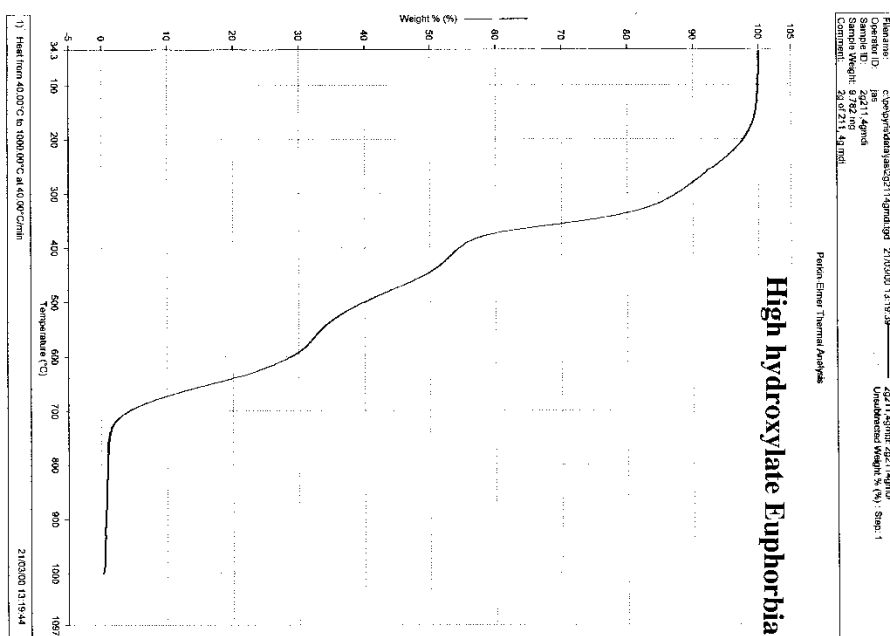
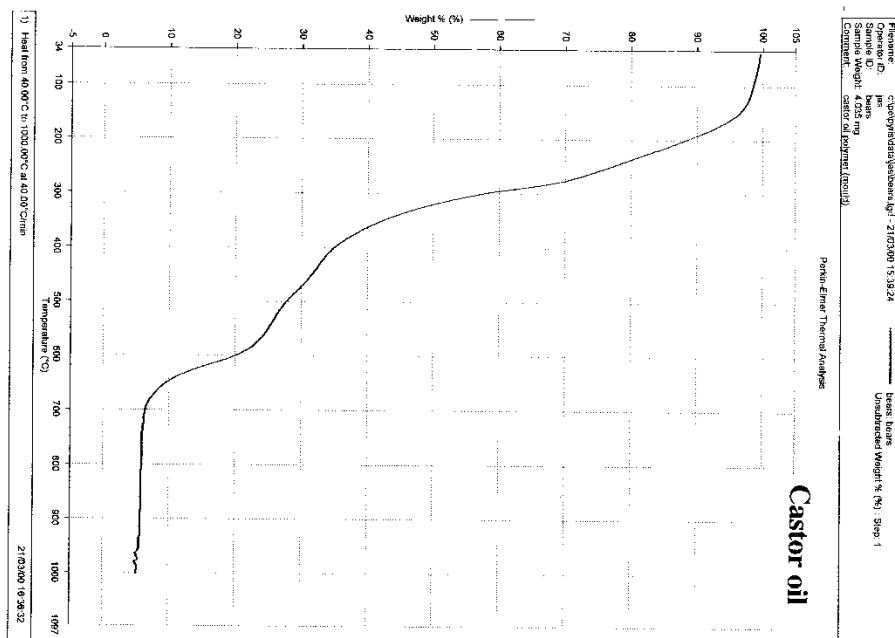


Fig G and Fig H

Fig. G MALDI for Euphorbia (C18 = saturated chain or unsaturated schain), V = Vernolic acid

Fig. H MALDI for epoxidised euphorbia

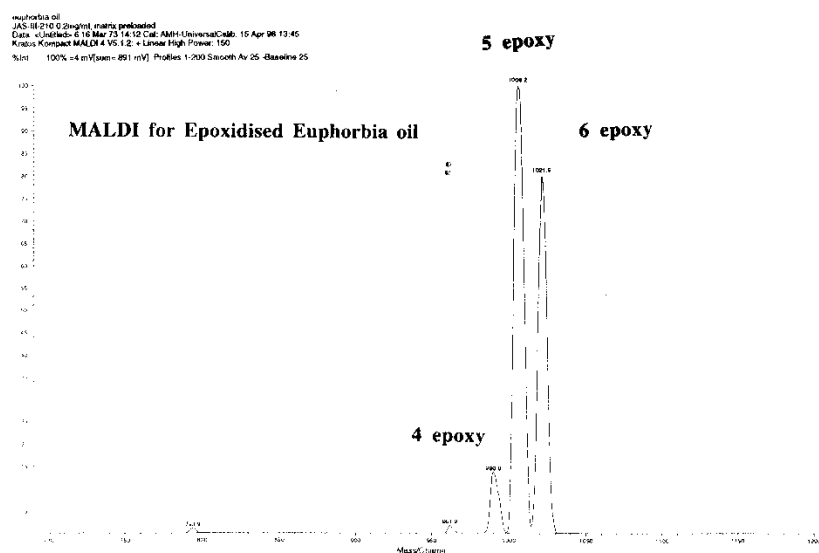
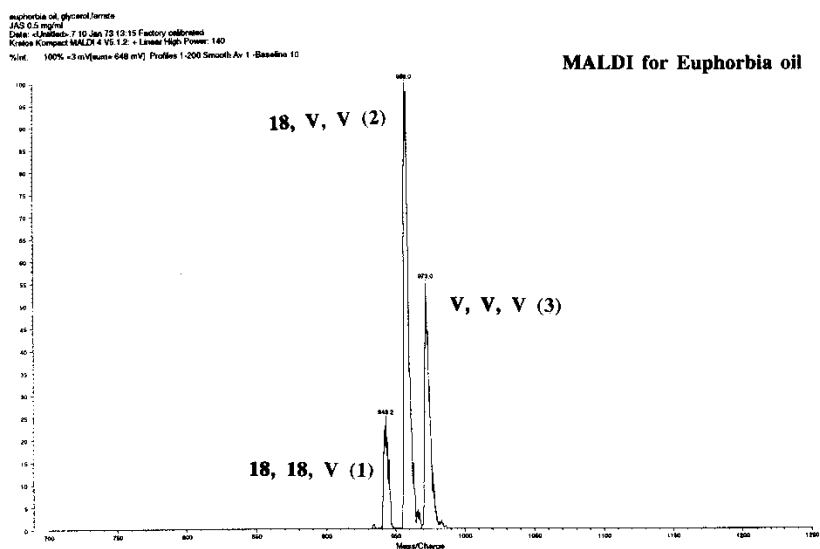
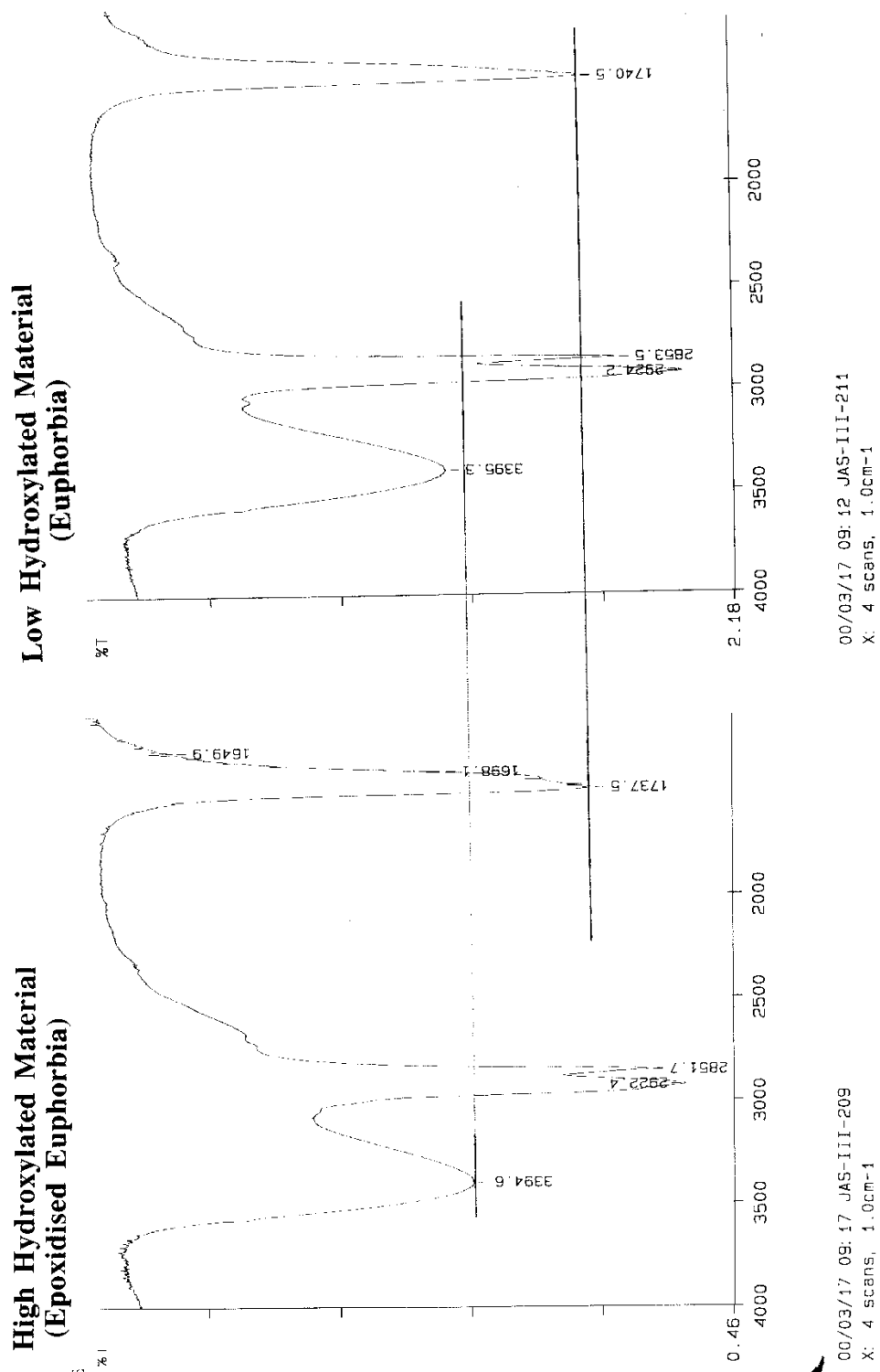


Fig. I.

IR of high and low hydroxylated euphorbia. Great OH content can be clearly observed in the high euphorbia.



APPENDIX B

Feature Article in peer reviewed Journal

Lipid Technology, 2000, 12, 129-132

November 2000

Lipid Technology

FEATURE

New chemical feedstocks from unsaturated oils

John A. Sherringham, Andrew J. Clark and Brian R.T. Keene

Unsaturated oils, such as rapeseed oil, linseed oil and soybean oil, can be used to generate polyols and polyepoxides, which can replace petrochemical derived chemical feedstocks used in the polymer industry. Treatment of the oils with Venturello's catalyst and hydrogen peroxide gives epoxides, which can then be ring-opened to form polyols. The polyols generated can be used in the manufacture of polyurethanes and polyesters, and the epoxides used for making epoxy resins. Alternatively, euphorbia oil, which already contains epoxides, could be used for making epoxy resins or could be ring-opened to give polyols, but use would be limited by the lack of control over the degree of epoxidation/hydroxylation.

Introduction

The use of non-renewable fossil fuels for chemical feedstocks causes large environmental problems for the polymer industry. Renewable vegetable oils, such as rapeseed and linseed oils, offer a non-toxic, non-polluting, biodegradable alternative, with attendant manufacturing benefits for the chemical industry.

Polyurethanes are used globally on a scale of around 7 million tonnes a year and this is rising at a rate of about 1 million tonnes a year. When no longer required, the products are typically dumped in landfill sites. We wish to combine the use of vegetable oils with polyurethane production to make biodegradable polyurethanes, polyesters and epoxy resins from renewable resources.

Typically, however, the unsaturated vegetable oils do not possess the epoxides necessary for the production of epoxy resins (vernolic acid is an exception). Nor do they possess the hydroxyl groups necessary for the production of polyurethanes and polyesters (ricinoleic acid, a constituent of castor oil is an exception and castor oil is already used for making polyurethanes [1]). In order not to compromise the environment-friendly nature of the use of vegetable oils, methods of epoxidizing or hydroxylating unsaturated triacylglycerols are required

which have minimal environmental impact.

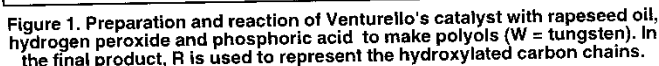
The only process currently used industrially for the epoxidation of unsaturated oils uses performic acid generated in place from hydrogen peroxide and formic acid. This is currently used on the tonne scale for the production of epoxidized soybean oil. However, there are several other methods for the generation of epoxides from unsaturated fatty compounds. These include the use of dioxiranes, hydrogen peroxide/methyl trioxorhenium and hydrogen peroxide/ peroxyphosphotungstenates (2). Typically, these processes are performed in an organic solvent, which would need to be disposed of or recycled in some fashion, with a corresponding increase in the cost of the process.

Epoxides and polyols from vegetable oils

Venturello's catalyst, $Q_3PO_4[W(O)(O_2)_2]_4$ (where Q is a phase transfer catalyst, typically based on a quaternary nitrogen) (3), can be used in conjunction with hydrogen peroxide to effect conversion of an unsaturated oil to the corresponding epoxide. The reaction can be accomplished without the use of a solvent. This is because the active form of the catalyst is able to dissolve both in the aqueous phase and in the fatty acid phase of the reaction mixture, as long as the reaction mixture is properly emulsified.

This catalyst can be prepared from tungsten powder, hydrogen peroxide and phosphoric acid, followed by addition of a phase transfer catalyst such as Adogen 464 [methyltrialkyl (C_8-C_{10}) ammonium chloride]. The catalyst can be extracted into an organic solvent such as dichloromethane and stored until needed, but typically it is added directly to the reaction. Reaction times vary from around an hour at 100°C, to a few days at room temperature, with reasonably clean reactions. The catalyst can be recovered at the end of the reaction and recycled, thus avoiding further contaminating waste.

To produce polyols from polyeponoxides, a second reaction is necessary. This is the acid-catalysed ring opening of the epoxides. Fairly harsh conditions are required of 50% phosphoric acid (by weight with respect to the natural oil), 100°C and vigorous stirring. This transformation can be accomplished relatively easily in organic solvents mixed with water (for example tetrahydrofuran-water), with a much lower reaction temperature and acid concentration. There are problems in recovering the desired polyols from the solvent and in disposal of the acidic waste; in contrast, the aqueous phosphoric acid-catalysed process allows the product to be easily separated from the acidic phase, which is reusable (as is the Venturello's catalyst).



wheels/tyres, packaging, textiles and fibres. The three major groupings of polyurethanes are:

- flexible polyurethanes;
- coatings, adhesives and sealants (CAS); and
- rigid polyurethanes.

Within rigid and flexible polyurethanes, there are two further subdivisions—foams and solid polyurethanes. About 44% of the demand for polyurethanes in 1996 was for flexible polyurethanes, 28% was for CAS, and 28% for rigid polyurethanes (4).

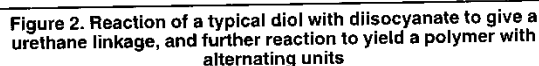
Polyurethanes can be used for a wide variety of applications. These include construction, transportation, tanks and pipes, bedding, furniture, carpets, appliances, electronics,

The reaction of a diol with a diisocyanate in the presence of a catalyst to give a urethane linkage is shown in **Figure 2** (amines are commonly used as catalysts for this reaction, as are tin compounds such as dibutyltin dilaurate). Further reaction gives a polymer with alternating units. If the alcohol unit has more than two hydroxyl groups, then cross-linking will occur and the polymer will have extra rigidity. The most

commonly used isocyanates are toluene diisocyanate (TDI) (34%), methylene di-*p*-phenyl diisocyanate (MDI) (9%) also shown in **Figure 3** and a polymeric form of MDI (53%) (4).

For their manufacture, different types of polyurethanes require polyols with different degrees of hydroxylation and different chain lengths. For a given polyol-isocyanate system, the higher the OH content of the polyol, the greater the degree of cross-linking and hence the more rigid the polyurethane. Also, the shorter the diol component, the more rigid the polyurethane formed. Conversely, the longer the diol component, the more flexible the polyurethane formed. The importance to the preparation of polyurethanes from naturally occurring hydroxylated vegetable oils (such as castor oil) is that the type of crop plant chosen to provide the oil fixes the chain length and degree of hydroxylation.

In order to generate polyurethanes with given characteristics, control of the derivatization process is needed. The whole spectrum of hydroxyl



content from 0% to the maximum theoretically possible should be obtainable if the hydroxylated vegetable oil is provided by reaction of an unsaturated oil with suitable hydroxylating reagents (because the reaction can be stopped at any point throughout its course). This increases the number of different polyurethanes that can be obtained from a given vegetable oil, and hence increases the chance that a given vegetable oil crop will be able to provide suitable chemical feedstocks.

An alternative way of controlling the hydroxyl content is to fully epoxidize, but only partially ring-open the epoxides. This would give a chemical feedstock that was a hybrid material, part poly-epoxide, part polyol.

In the course of our research with the Venturello's catalyst and phosphoric acid system, we have found that there is also the possibility of polymerization occurring. In addition to the expected ring-opening reaction with water, the intermolecular reaction shown in **Figure 4** can occur, leading to dimers, trimers etc. This reaction seems to produce the same profile of polymeric products over a fairly wide range of acid concentrations and reaction temperatures. Long reaction times or very high concentrations of acid do however result in cleavage of one or more of the fatty acid chains attached to the central glycerol, with the end result being complete hydrolysis of the triacylglycerol. While changing the acid concentration does not seem to be particularly effective in generating different precursors, it does show that the process is a robust one with a high degree of reproducibility.

Examples of polyurethanes produced from rapeseed oil derivatized in this way include an elastomer manufactured from material with low hydroxyl

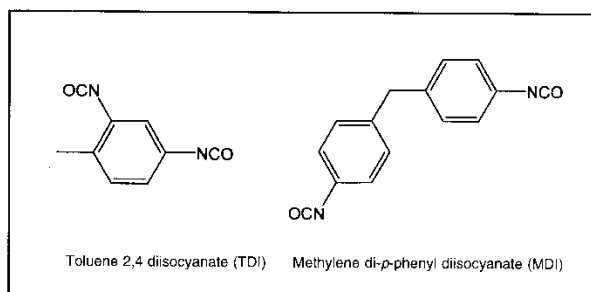


Figure 3. Typical diisocyanates used by the polyurethane industry.

content, a rigid foam from fully epoxidized/ring-opened material, and rigid polyurethanes also from high hydroxyl content material. Thus we need to find ways of controlling the degree of epoxidation in a reproducible way. The use of lower reaction temperatures causes the rate of epoxidation to be much slower. Thus it is easier to assay the reaction and stop it at the desired degree of epoxidation. Step-wise addition of hydrogen peroxide can also prevent over-epoxidation occurring.

In order to analyse the reaction mixture we used nuclear magnetic resonance (NMR) and matrix-assisted laser desorption-ionization-time of flight (MALDI-TOF) spectrometry. The MALDI-TOF spectrum of fully epoxidized conventional linseed oil is shown in **Figure 5**. The composition of the linseed oil used determines which epoxidized species are present in the product. An estimated composition distribution of linseed oil and epoxidized linseed oil is also shown in **Figure 5**. Note that all the major mass peaks in the spectrum correspond to expected products of the epoxidation reaction. This method of analysis has proved less successful for hydroxylated materials, but the reactions that produce these materials are typically run to complete loss of epoxide, as determined from NMR studies.

Use of alternative oils

A naturally-occurring epoxidized triacylglycerol such as euphorbia oil could be used as an alternative to rapeseed oil. Euphorbia oil contains vernolic acid, a C_{18} fatty acid with a 9,10 double bond and a 12,13 epoxide. It has the advantage of being already epoxidized — the only step needed would be to ring-open the epoxides to give polyols.

However, the degree of epoxidation is fixed unless the crop were to be genetically-modified, and there is

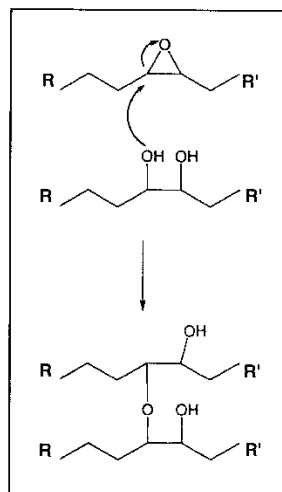


Figure 4. Dimerization of oleate in a vegetable oil through its epoxide and diol.

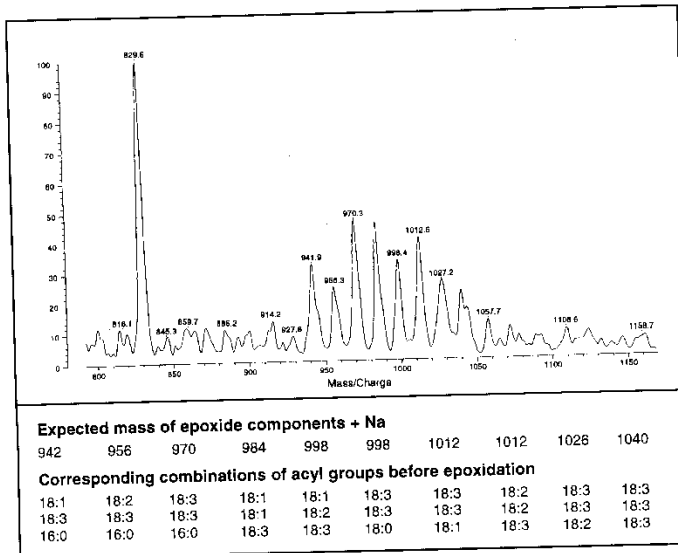


Figure 5. The spectrum of fully epoxidized conventional linseed oil determined using matrix-assisted laser desorption-ionization-time of flight (MALDI-TOF) spectrometry, and a table of the expected major mass peaks of the epoxide products.

Table 1. Fatty acid compositions of rapeseed oil and euphorbia oil (% of total).

Fatty acid	Euphorbia	Rapeseed
16:0	5	4
18:0	2	2
18:1	24	60
18:2	12	20
18:3	1	8
Vernolic acid	55	0

considerable public resistance against genetically-modified plants. The vernolic acid content is approximately 55% (Table 1), and this will result in around 10% of the material not being able to react with isocyanates. This material would not take part in the formation of polyurethanes, but would exude from the polymer formulation when the polymer was cured.

This is a problem that can occur with all low-hydroxyl-content vegetable oils that have been prepared by stopping the

epoxidation reaction early. The oil could still be used in a similar way to other unsaturated oils — treatment of euphorbia oil with the Venturello's catalyst system described earlier would epoxidize the double bonds in the molecule. Treatment with phosphoric acid would then yield hydroxylated material, but with the added bonus that less peroxide would be required to generate a given level of epoxidation.

Conclusions

A process for converting unsaturated vegetable oils into hydroxylated materials suitable for the preparation of polyurethanes has been developed. This process does not require chemicals that are particularly hazardous,

flammable or volatile, and produces material at a cost that is estimated to be comparable to castor oil. It is unlikely to be used as a castor oil replacement, because the cost per tonne does not significantly undercut castor oil, extra formulation work would need to be done, and investment in new equipment would be required.

On the positive side, a great deal of control over the hydroxyl content is possible, hence the number of possible uses is broadened with respect to castor oil and therefore it would be used for new rather than existing applications.

Difficulties arise if a vegetable oil with a low hydroxyl content is prepared, as in some

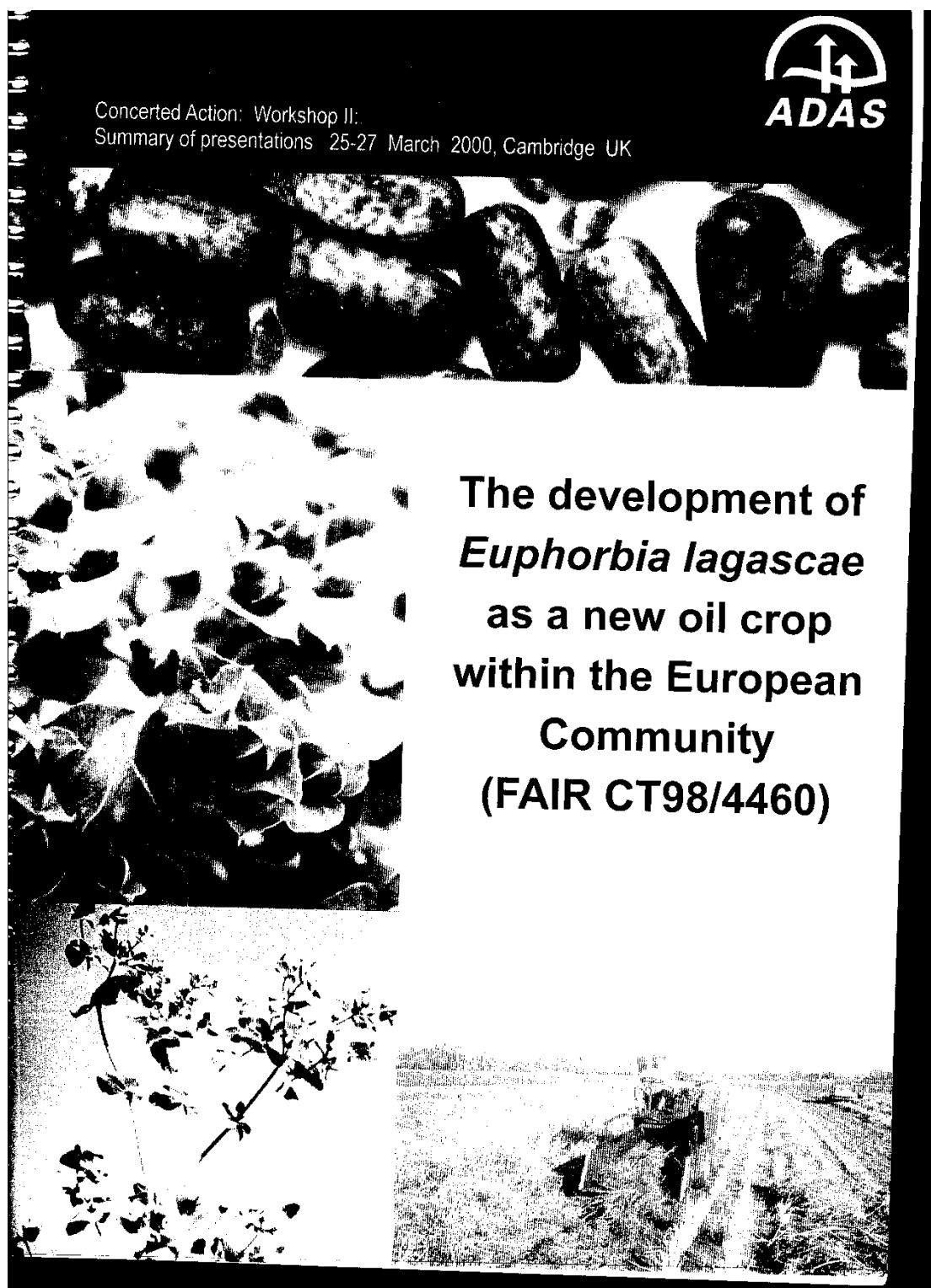
formulations there may be a problem with exudate from the polymers. This exudate may prove useful in the preparation of 'drawn' polyurethanes, as long it does not make up a significant proportion of the mass of the polymer.

References

1. Das, S.K. and Lenka, S. (1999) *Polymer Plastics Technology and Engineering*, 38, 149-153.
2. Biermann, U. *et al.* (2000) *Angew. Chem. Int. Ed.*, 39, 2206-2224.
3. Venturello, C. *et al.* (1983) *J. Org. Chem.*, 48, 3831-3833.
4. Alliance for the Polyurethanes Industry, web site: <http://www.polyurethane.org/>

J.A. Sherrington and A.J. Clark are in the Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK; tel: +44-24-7652-3242; fax +44-24-7652-4112; e-mail A.J.Clark@warwick.ac.uk. All correspondence should be addressed to Andrew J. Clark. We regret to inform readers that Brian R.T. Keene, an independent consultant, has died since this paper was accepted for publication.

Appendix C
Invited contribution to the Concerted Action Workshop on the Development of
***Euphorbia lagascae* as a new crop**



First page of slides containing summary

The development of *Euphorbia lagascae* as a new oil crop within the European Community (FAIR-CT98/4460).
Proceedings of Workshop II, March 2000

SESSION II ECONOMICS, MARKETS, OIL UTILISATION AND COMPETITOR PRODUCTS.

III. Characterisation and preliminary experiments on chemical manipulation of Euphorbia oil towards polymer feedstocks

Dr. Andrew Clarke
Dept of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

Summary

Feasibility studies on chemical manipulation of Euphorbia oil towards feedstocks for the polymer industry have been undertaken. Both Euphorbia oil and chemically modified epoxidised Euphorbia oil have been ring opened to give polyhydroxylated materials containing different levels of hydroxylation respectively. The Euphorbia, epoxidised Euphorbia, low hydroxylated and high hydroxylated monomer feedstocks have been characterised by ^1H and ^{13}C NMR, IR, and MALDI-TOF-MS. Analysis indicates that epoxidation using peroxyphosphotungstate and hydrogen peroxide in water, furnish high levels of epoxides resembling epoxidised soybean oil. Interestingly, the epoxide profile is different to that of other oils such as epoxidised rapeseed oil indicating that Euphorbia may be able to be used for the synthesis of different polymeric materials to those obtained from rapeseed. Potential applications involve polyurethane, polyester and epoxyresin formulations. The application of chemically modified Euphorbia to the synthesis of some polyurethane materials has been undertaken and will be described.

FEEDSTOCKS FOR THE POLYMER INDUSTRY

Poly(urethanes)
*Flexible and rigid foams,
elastomers, extrusions,*

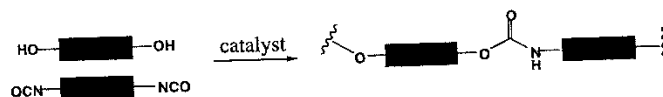
Hydroxylated monomers
Coatings, adhesives.

Poly(esters), unsaturated poly(esters)
*Flooring, auto body repair,
boat hulls*

Epoxidised monomers
Epoxy resins
*Protective coatings,
adhesives, flooring,
plasticizers, foams*

HYDROXYLATED MONOMERS

POLY(URETHANES)



Invited contribution to Oilseed Rape Pipeline Seminar



OILSEED RAPE PIPELINE SEMINAR

8th June 1999
Manchester Conference Centre, UMIST, UK

Alternative Crops Technology Interaction Network
- *working with industry for a sustainable future*

Pira House, Randalls Road, Leatherhead, Surrey, KT22 7RU, UK
Telephone + 44 (0) 1372 802054 Facsimile: + 44 (0) 1372 802245
E-mail info@actin.co.uk : Website: www.actin.co.uk

Contents showing presentation by myself and an industrial collaborator Barrie Colvin who unveiled a new packaging/insulation foam with excellent fire retardation and insulation properties made from our feedstocks

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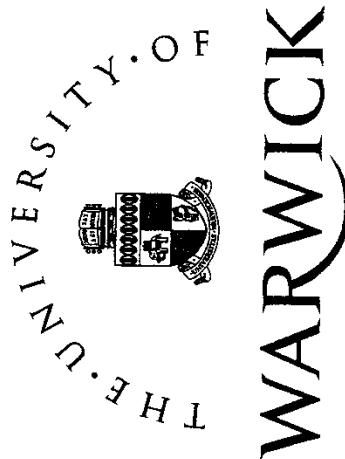
- *Bruker UK Ltd*
- *Cargill Refined Oils*
- *Lipid Technology*
- *Springdale Crop Synergies Ltd*

Oilseed Rape Pipeline Seminar – 8th June 1999 Manchester Conference Centre, UMIST, UK
Organised by ACTIN (Alternative Crops Technology Interaction Network)

RAPESEED OIL AS A CHEMICAL FEEDSTOCK

Dr. Andrew Clark

Chemistry Department



Funded by the Home-Grown Cereal Authority