HGCA

RESEARCH & DEVELOPMENT

PROJECT REPORT No. OS35

A FEASIBILITY STUDY INTO THE FORMULATION AND MANUFACTURE OF RAPESEED MEAL BIOCOMPOSITES

OCTOBER 1998

Price £2.00

PROJECT REPORT No. OS35

A FEASIBILITY STUDY INTO THE FORMULATION AND MANUFACTURE OF RAPESEED MEAL BIOCOMPOSITES

by

Yvonne Chui & Peter Hornsby

Wolfson Centre for Materials Processing, Brunel University,
Uxbridge, Middx UB8 3PH

This is the final report of a three month project which started in November 1997. The work was funded by a grant of £10,735 from the Home-Grown Cereals Authority (HGCA Project no OS10/1/97).

Summary

This report summarises the findings from a three-month feasibility study concerned with the formulation and potential use of rapeseed meal in biocomposite manufacture. A primary objective was to establish the effectiveness of rapeseed meal as a matrix or binder phase and in particular, as an alternative to soyabean, which is currently exploited for this purpose in the United States.

The strategy used to chemically modify and formulate rapeseed meal composites is discussed, and includes use of various additives of naturally occurring and synthetic origin. Mechanical properties of mouldings produced from these formulations are presented, which under optimum circumstances compare favourably or outperform reported results for commercially available composite board structures.

Twin-screw extrusion and injection moulding technologies, more commonly used for processing of polymers, have been employed, which could facilitate industrial production of rapeseed-containing materials, or be applied to specific application areas. Perceived benefits of rapeseed meal materials are identified, forming a basis for future development and subsequent commercial exploitation in collaboration with industrial partners.

1. Introduction

Soyabean that contains only 20% oil has very high protein content in the residue after oil extraction. Besides serving as a source of oil and protein supplement for livestock, soyabean extract has also been used as binder and adhesive. Phenix Biocomposites Inc. in the USA, have developed formulation and processing know-how for the preparation of composite materials, which can be formed into board or shaped products with a stone-like appearance [1, 2]. Components in the formulation include a legume-based thermosetting resin derived from soyabean, which has adhesive binding qualities, in combination with cellulosic material obtained, for example, from waste newspaper.

Similarly in the UK, rapeseed is currently grown, principally as a source of oil, with the residue after oil extraction, used as an animal feed. However, rapeseed and soyabean are generally similar in structure both chemically and physically. Primarily they are both rich in oil, protein and carbohydrate content. In the process of oil extraction, soyabean gives yields of about 20% of oil and 80% of useful high-protein meal (Table 1). In the case of rapeseed, the oil content is about 30% higher than that of the soyabean. The rapeseed meal is, however, lower in protein but richer in fibre and carbohydrate contents, which could potentially be useful in the manufacture of bio-composite materials.

Table 1 Chemical composition of rapeseed and soyabean.

	Seed		Dry Seed Meal		
	Oil %	Meal %	Protein %	Carbohydrate %	Crude fibre %
Rapeseed	58	40	36	37	11
Soyabean	20	78	48	29	7

Other substances present include ash, moisture and residual oil.

This three-month feasibility study was instigated to determine the viability of using rapeseed meal for this purpose and in particular, to establish the nature of necessary formulation and processing developments required in order to make it effective. Specific objectives of this investigation were:

- To consider the potential of rapeseed meal as a binder or matrix phase in bio-composite fabrication through preliminary experimentation.
- To establish general formulation and processing requirements for possible commercial development.
- To identify potential markets for such materials with a view to future exploitation through further collaborative work with selected industrial partners.

2. Experimental procedure

2.1 Characterisation of materials

Rapeseed meal, supplied by Cargill Plc. and Croda Chemicals, was initially characterised using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) prior to use for composite preparation.

TGA was used to determine the moisture content of the materials together with their thermal sensitivity, which was considered important in processing operations undertaken at elevated temperatures. DSC was also applied to identify physical and chemical changes occurring in selected chemically modified biocomposite formulations.

2.2 Formulation and preparation methodology

The potential of these materials for use in biocomposite manufacture was primarily based on measurement of the mechanical properties of moulded specimens. To this end, a variety of formulation and process variants were explored, involving chemical pre-treatments (using acids and alkalis) and inclusion of various reactive chemical binders of natural and synthetic origin. More specifically the properties of the following compositions were evaluated:

- unmodified rapeseed meal for use as a control
- chemically pre-treated rapeseed meal to induce hydrolysis
- rapeseed meal formulations modified by inclusion of (a) long chain, flexible thermoplastic reactants, (b) short chain reactants and (c) functionalised thermosetting polymeric additives. These additives were included as a minority component in the formulation.

2.3 Sample preparation

2.3.1 Solution mixing

Mixtures of rapeseed meal and liquid chemical modifiers were prepared in a heated flask fitted with an electric stirrer. For trials with larger quantities of material, a high-speed mixer with integrated temperature control was used.

2.3.2 Extrusion pulping

Some compositions were also prepared using an extrusion pulping technique involving a co-rotating twin-screw extruder (Fig. 1). This facility has a high mixing capability and in addition applies controlled shear to the material thereby influencing the size and structure of the rapeseed meal composite. Its use could ultimately form the basis of a production facility for treatment or preparation of rapeseed meal composites.

Preliminary work was also undertaken with this technology to establish whether rapeseed meal could be used as a low cost filler for plastics. In this connection polyethylene composites containing 30% by weight of rapeseed meal were melt compounded at 180°C, then successfully injection moulded into test samples without evidence of filler degradation.

2.3.3 Compression moulding

The different rapeseed meal compositions were pressed into square plaques (100x100x6 mm). PTFE spray was used to facilitate mould release. Mouldings were prepared in a pre-heated press under varying processing conditions differing in time, mould temperature and applied pressure.

2.4 Mechanical testing

Compressed rapeseed meal mouldings were machined into standard test bars (10x6x100mm) for mechanical testing. In order to determine flexural modulus and strength a three point bending test was adopted, in accordance to BS2782: Part 3: Method 335A. In this test, the specimen is freely supported as a beam and centrally deflected at a rate of 2mm/min until failure occurs. During this procedure the force applied and the deflection of the specimen is measured and recorded as stress and strain values. Flexural modulus is calculated as the ratio of stress to corresponding strain values within the linear region of the stress/strain relationship. Flexural strength is identified from the failure point of the stress/strain curve.

Charpy impact strength of the various systems was determined in accordance to BS2782: Part 3: Method 359. Un-notched test specimens were supported as a horizontal beam, with a span of 62mm, then fractured using a 2-Joule pendulum. Impact strength is expressed in kilojoules of impact energy absorbed in breaking the specimen per square metre of the cross-sectional area of the specimen (kJ/m^2).

All mechanical tests were undertaken at 23°C and approximately 50% relative humidity. In each case mechanical test results were obtained from an average of 5 independent determinations.

3. Results and Discussion

3.1 Characterisation of rapeseed meal

3.1.1 Determination of moisture content of rapeseed meal by TGA

The moisture content of rapeseed in equilibrium with atmospheric moisture generally ranges from 9 to 12%. It is important to maintain a consistent moisture in the raw material from batch to batch, since it was found that the water content in the rapeseed meal can significantly affect their binding properties and the wet strength of the pressure-formed products.

TGA is a useful technique for distinguishing between freely and tightly bond water and in addition provides information on thermal stability. Fig.2 shows a typical TGA thermogram of unmodified rapeseed meal, which reveals its moisture content and onset degradation temperature at around 200°C.

3.1.2 Monitoring of chemical reactions in rapeseed composites using DSC

DSC provides complementary information concerning energy changes associated with moisture content and thermally induced degradation processes. However, in addition, the time, temperature and kinetics of any crosslinking reactions can also be determined through DSC analysis. The example in Fig.3, shows an exothermic energy change occurring from rapeseed meal hydrolysis and an endothermic energy change associated with water and volatile removal.

3.2 Mechanical properties

3.2.1 Unmodified rapeseed meal

The mechanical properties of various rapeseed meal systems produced are summarised in Figs. 4 to 9. When unmodified rapeseed meal containing about 10% moisture was compressed at low temperature, a moulding with relatively poor mechanical properties was produced (Fig.4). However, it was apparent that some adhesion had taken place between the rapeseed meal particles, which is attributed to hydrogen bonding between protein and cellulosic chains.

Experimentation revealed that further significant improvement in mechanical strength, stiffness and toughness could be achieved by varying water content, applied pressure and in particular, moulding temperature, as shown in Fig. 4.

3.2.2 Chemically treated rapeseed meal

The strong inter-molecular hydrogen bonding existing in the unmodified rapeseed meal inhibits the availability of potentially reactive and polar groups present in the protein and cellulosic constituents, which might facilitate binding in the preparation of biocomposites. An acid and alkaline hydrolysis treatment is required to break internal bonds and uncoil the polar chains. By adopting this approach, compressed rapeseed meal mouldings were produced which demonstrated markedly enhanced mechanical properties relative to unmodified rapeseed meal (Fig. 5).

Since the hydrolysed rapeseed meal exhibited sticky, glue-like properties, particularly at elevated temperatures, composites containing wheat straw were also prepared using the modified rapeseed meal as a binder. Although the approach showed some potential, the composite was mechanically weak and further work is required to optimise the formulation and preparation conditions.

3.2.3 Long chain thermoplastic chemical reactants

Rapeseed meal formulations containing various long chain reactive modifiers were prepared with the intention of promoting crosslinking between reactive sites on the protein and cellulosic structures. Mechanical properties obtained from these systems (Fig. 6) demonstrate a noticeable all round improvement relative to unmodified rapeseed meal mouldings, but give similar values to the best chemically hydrolysed materials, shown in Fig. 5.

3.2.4 Short chain reactive chemical reactants

More reactive chemical modifiers, with greater functionality but shorter chains, were also employed as binding agents for rapeseed meal. The significantly enhanced modulus and flexural stress values obtained using these additives (Fig. 7), demonstrates their high chemical affinity towards functional groups on the rapeseed meal.

It is interesting to note that these compositions exhibit higher strength and stiffness than longer chain reactive modifiers (see Fig. 6), yet their toughness is, in general, much lower. This suggests that the chemical reactivity and the molecular weight of the modifying additive may both be important criteria for achieving optimum properties.

3.2.5 Polymeric thermosetting binder systems

Extending the understanding gained from previous experiments, compositions were prepared and moulded using chemically modified rapeseed meal in combination with high molecular weight multifunctional adhesive derivatives. In most instances this approach proved to be highly effective giving substantial improvements to the bending strength and modulus of the rapeseed meal mouldings (Fig. 8).

3.2.6 Comparison with alternative biocomposite materials

Drawing on available data obtained for various commercial or development biocomposite materials, it can seen that the optimum rapeseed meal formulation produced in this study compares very favourably with these alternative systems, in terms of flexural strength and modulus properties (Fig. 9). It is important to note, however, that unlike the rapeseed meal composition, the other materials were believed to comprise a high proportion if not totally of fibrous matter, together with binding agent.

4. Conclusions

The binding properties of rapeseed meal, derived as a by-product after oil extraction, have been explored, with a view to its potential use in biocomposite manufacture. Mouldings of rapeseed meal were produced and their strength, stiffness and toughness measured to evaluate their possible industrial application.

Simply compressing rapeseed meal at elevated temperature yielded stable and mechanically sound mouldings, although the properties were strongly influenced by water content and processing conditions. Enhanced mechanical performance was achieved by first hydrolysing the rapeseed meal under acidic or alkaline conditions, enabling greater interaction between inherently reactive groups present within the rapeseed meal structure.

However, the results presented show the greatest improvement when rapeseed meal is formulated with various synthetic and naturally occurring binders. These were chosen in order to react with amine and carboxylic functional groups in the rapeseed meal and provide a chemically crosslinked structure. They act, therefore, as a secondary adhesive phase to augment the natural binding tendencies of the rapeseed meal.

Using this approach, the mechanical properties achieved were greatly superior to those obtained for compressed unmodified rapeseed meal, and in the optimum case, outperformed many commercial fibre board systems. The rapeseed meal mouldings produced in this study possessed properties that matched published results for analogous soyabean composites, even though these contained an added cellulosic reinforcement.

In addition to establishing basic formulation and processing requirements to yield rapeseed meal mouldings with favourable mechanical properties, the work has highlighted the potential of alternative technologies more commonly employed for polymer processing, which might aid subsequent commercialisation. These include the use of twin-screw extrusion as a combined pulping and additive binding technology and injection moulding of polymer melts containing rapeseed meal as a modifying filler.

To compete successfully with alternative materials in the industrial market place, rapeseed meal composites need to offer cost advantages and/or functional benefits in terms of their available properties and special characteristics. These include:

- Tailor-made rapeseed meal mouldings and biocomposite structures with defined mechanical properties, which compare favourably with alternative natural fibre materials
- Totally biodegradable compositions, produced using naturally-occurring binders
- Water resistant formulations made with synthetic binding aids of polymer origin
- Highly glossy surfaces achievable on mouldings due to the presence of residual rapeseed oil.
- Beneficial qualities of rapeseed meal as a natural fertiliser and animal feed.

- The availability of chemically reactive functional groups enabling its use, for example, as a reactive filler for polymers.
- Potentially exploitable adhesive qualities after chemical modification.

5. Future work

This feasibility study has provided a good basis for further development and industrial application of products based on rapeseed meal composites. Within the programme, a number of possible application areas have been identified within different market sectors. Discussions have been held with potential industrial partners with a view to collaboration in a future more extensive research and development programme. This would consider not only the scientific and technological requirements for the economic preparation of rapeseed meal products with added value, but also the market acceptance of such materials.

6. References

1. Phenix Biocomposites Inc., 'Biocomposite material and method of making', US **Patent 5593625**, (1997).

2. Phenix Biocomposites Inc., 'Board stock and method of manufacture from recycled paper', US **Patent 5611882**, (1997).

Fig.1 Co-rotating intermeshing twin-screw extruder (only one screw shown).

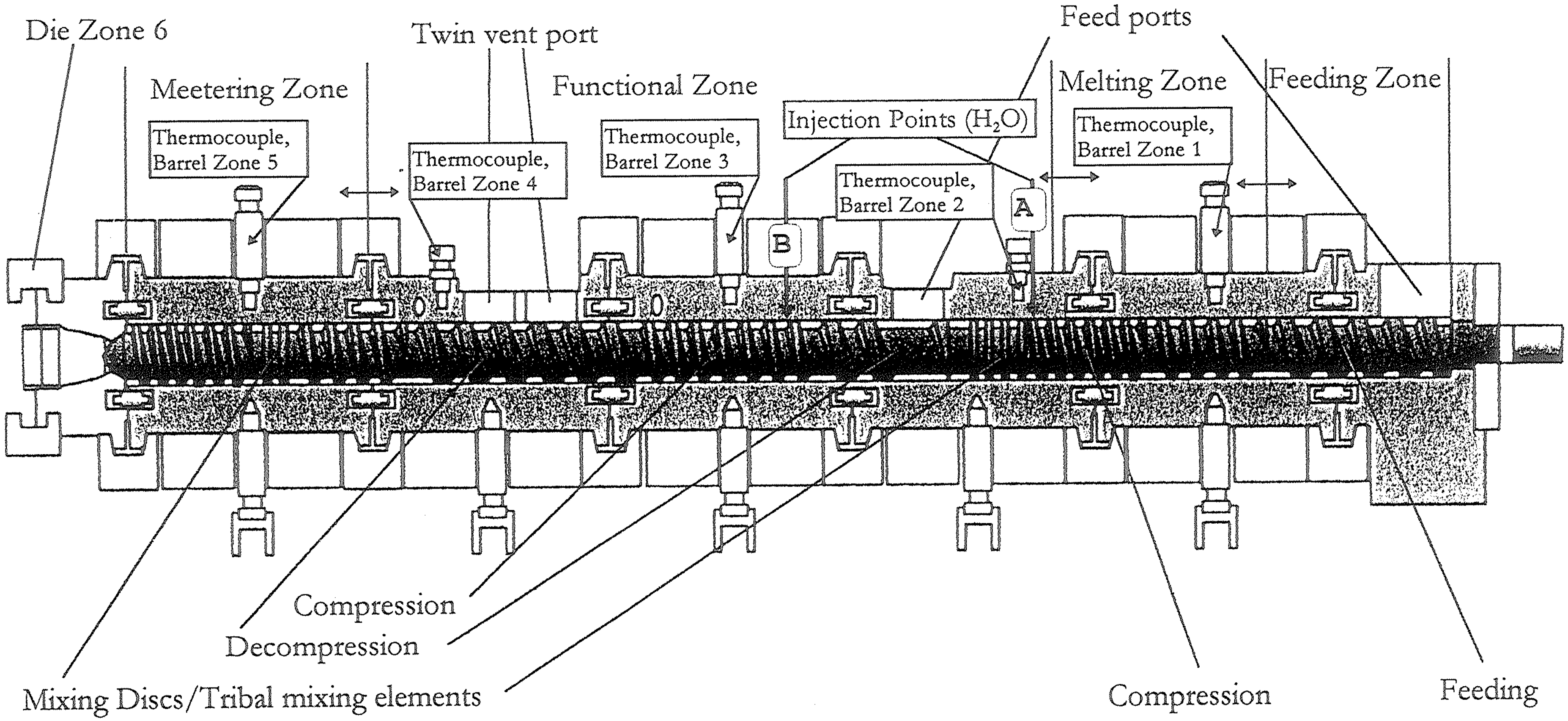


Fig. 2 Typical TGA thermogram of unmodified rapeseed meal for determination of moisture content and degradation temperature.

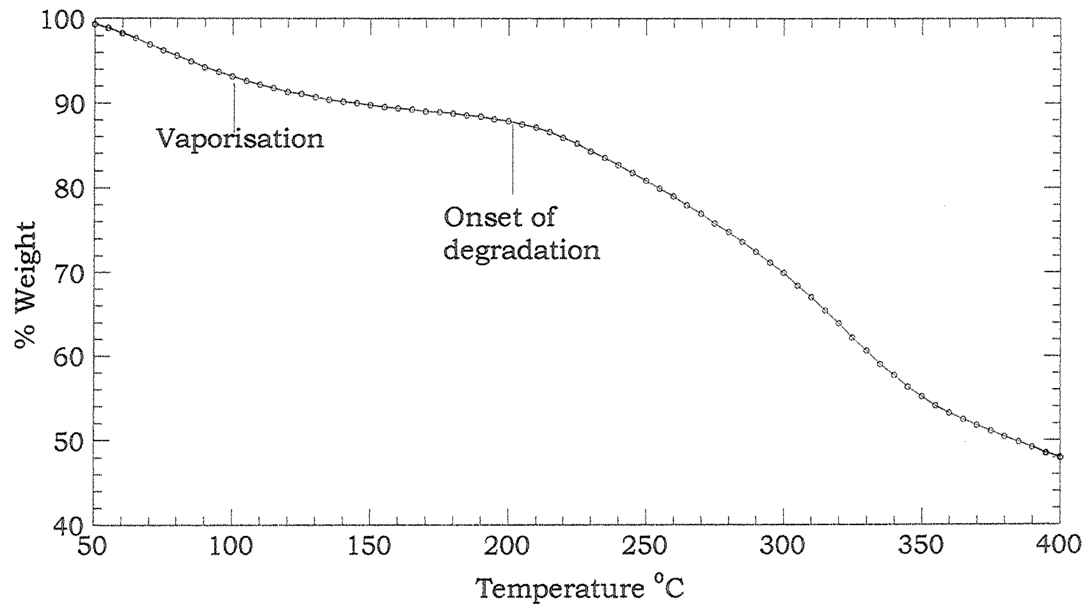


Fig. 3 DSC thermograms of various rapeseed meal systems.

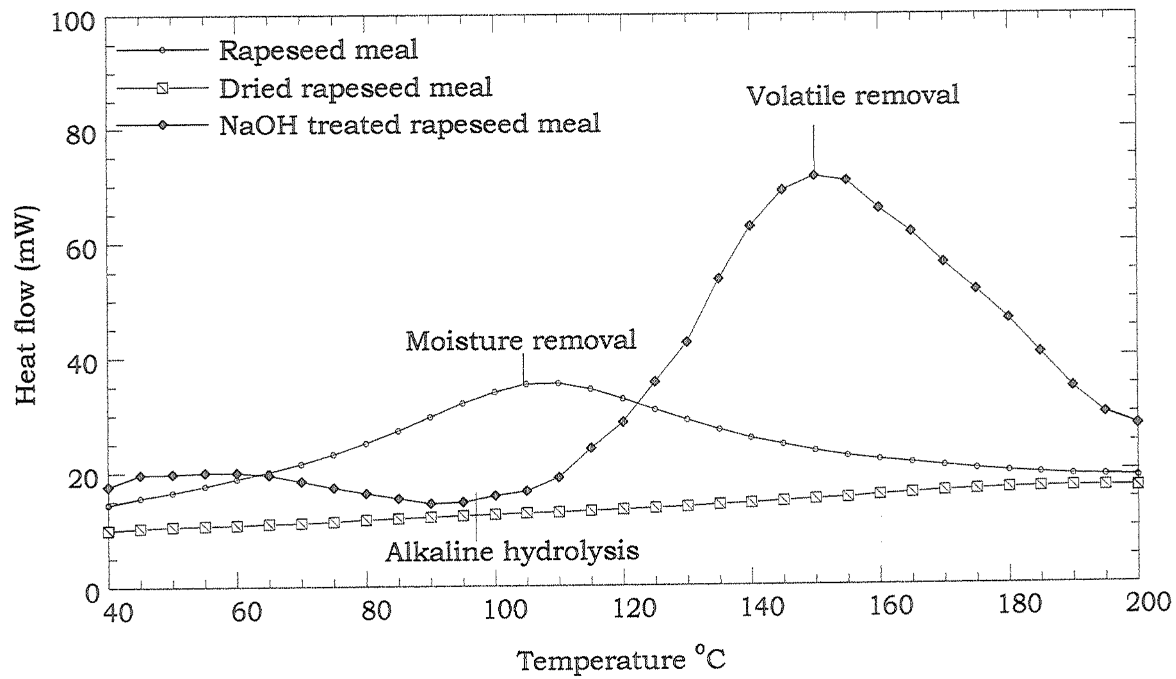


Fig. 4 Mechanical properties of unmodified rapeseed meal compressed at various temperatures.

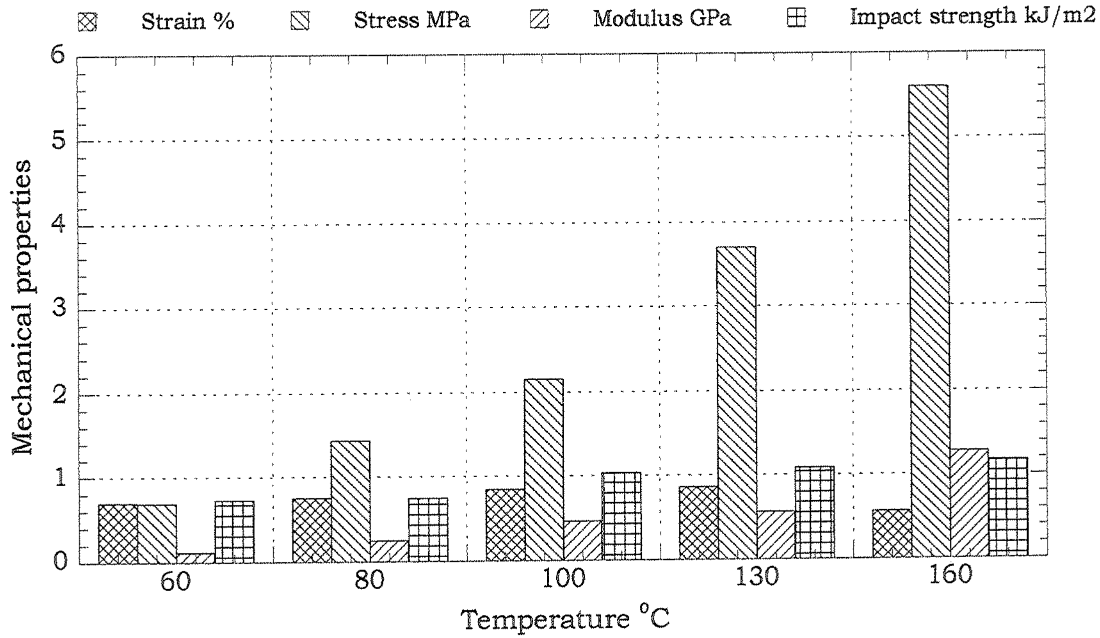


Fig. 5 Mechanical properties of various chemically treated rapeseed meal systems.

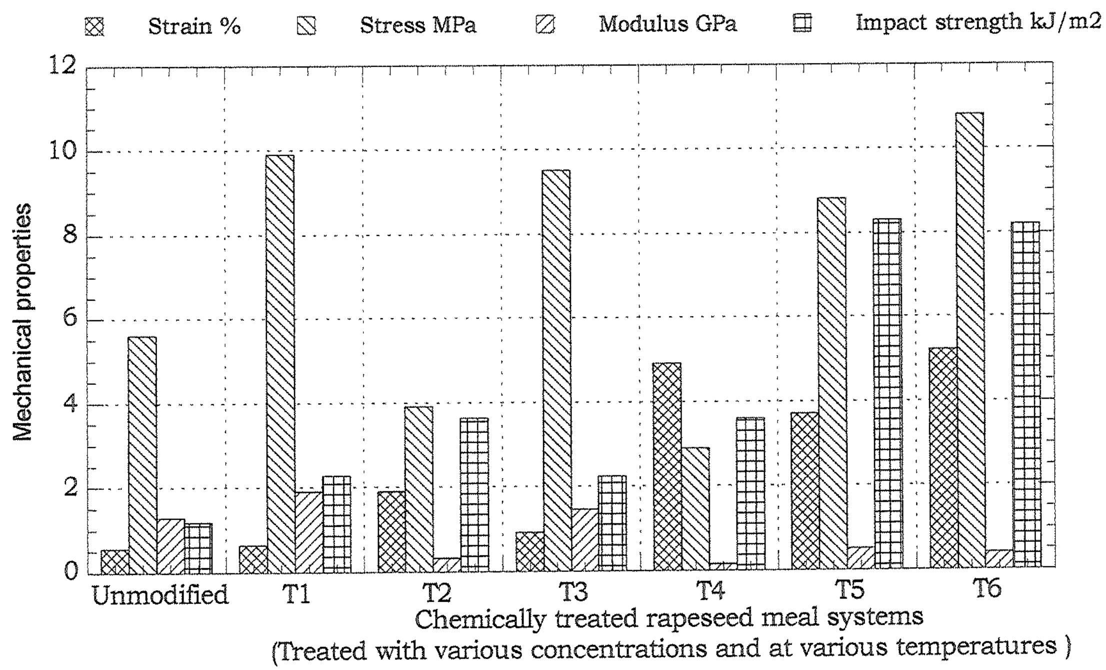


Fig. 6 Mechanical properties of various rapeseed meal/long chain adhesive systems.

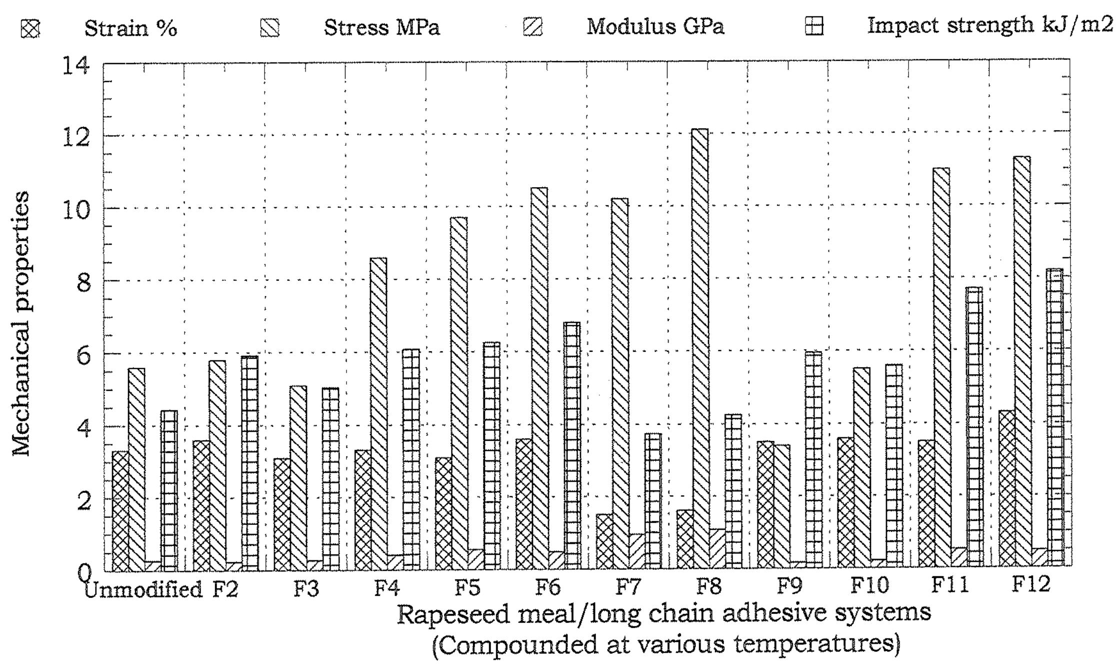


Fig. 7 Mechanical properties of various rapeseed meal/short chain adhesive systems.

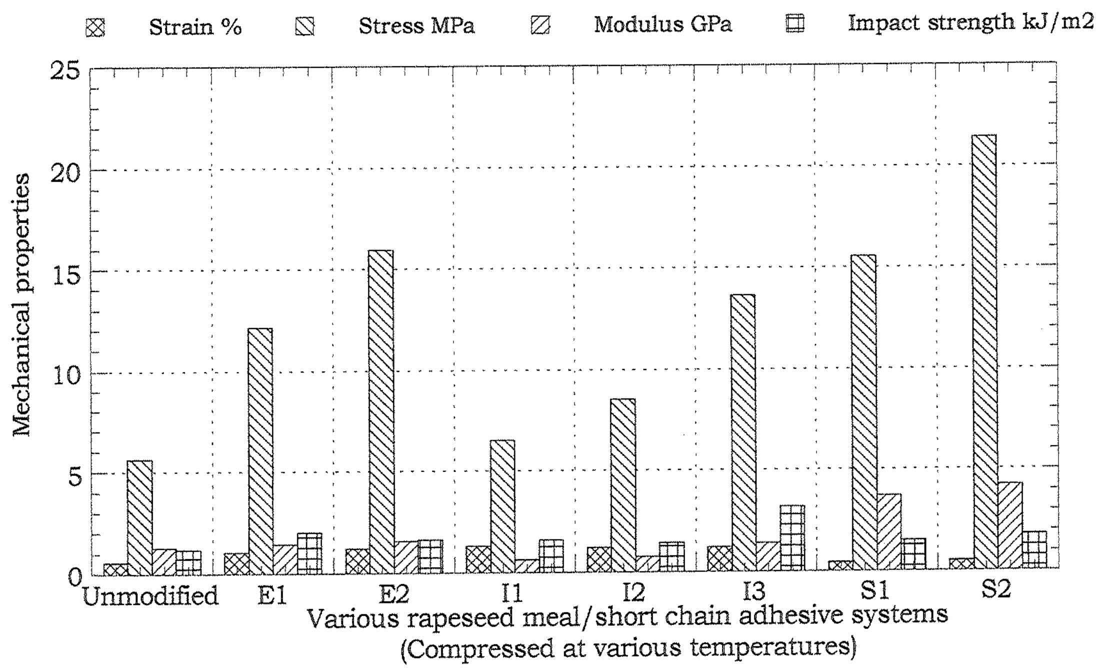


Fig. 8 Mechanical properties of various rapeseed meal/polymeric adhesive systems.

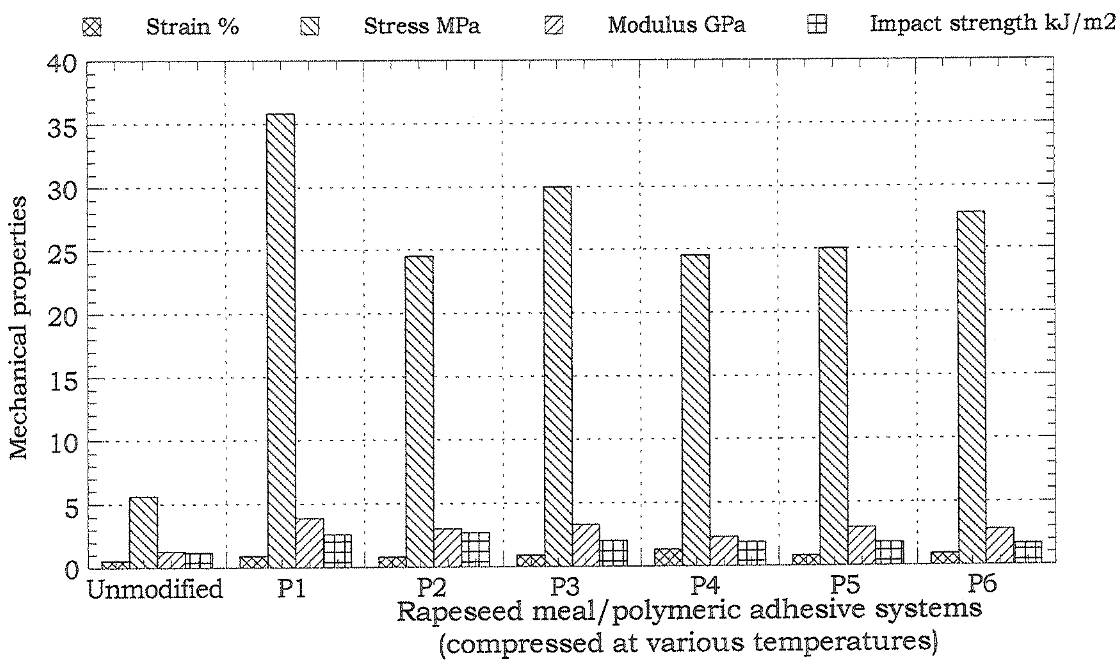
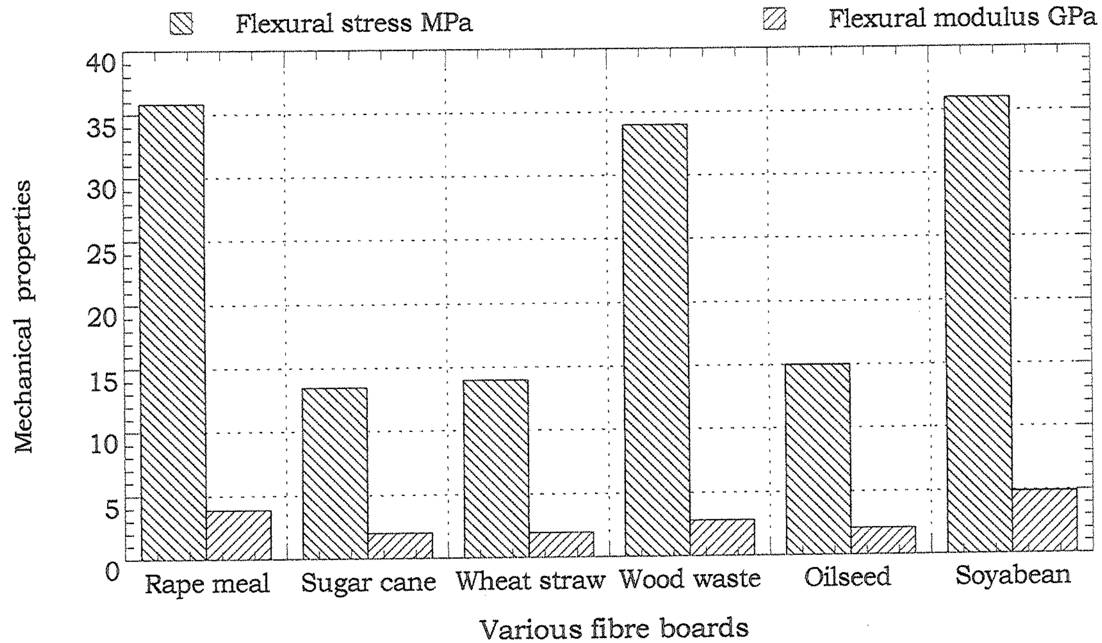


Fig. 9. Mechanical properties of various fibre board systems.



The Home-Grown Cereals Authority is a public body set up by the Cereals Marketing Act 1965. A number of important amendments to the Act were made by the Agriculture Act 1986 and the Cereals Marketing Act (Application to Oilseeds) Order 1989. The Act, as amended, defines the Authority's functions, constitution and the specific functions which it may undertake for the purpose of improving the production and marketing of home-grown cereals and oilseeds. In 1990 the HGCA Oilseeds Levy Scheme was introduced to fund research and development.

As well as sponsoring research and development in relation to both cereals and oilseeds, the Authority's other functions are:-

- providing a market information service for cereals and oilseeds;
- developing UK cereals exporting capabilities;
- promoting increased consumption of cereal based products in the home market and overseas.

The Authority is funded principally by levies paid by growers of cereals and oilseeds and by cereal dealers and processors.

The Authority administers its R&D function with the assistance of two Advisory Committees, one dealing with cereals and the other with oilseeds R&D. Cereals growers, dealers and processors all contribute in differing proportions to the funding of cereals R&D and all these sectors are represented, therefore, on the R&D Advisory Committee for Cereals. The R&D Advisory Committee for Oilseeds represents the interests of oilseed growers who are the sole funders of oilseeds R&D.

Details of subject areas of interest to both committees are published in strategy documents. Reports of all funded R&D are also published and promoted within the industry.

Further copies of this document may be obtained from:

Home-Grown Cereals Authority

Caledonia House, 223 Pentonville Road, London N1 9NG

Tel: 0171 520 3920 Fax: 0171 520 3931

For price, including postage and packing within the UK, see title page.