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Morphology and mechanical behaviour of engineering soy plastics

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The morphology and mechanical behaviour of high protein content engineering soy plastics are investigated. These engineering soy plastics can possess significantly higher Young's moduli (4.4 GPa) than those of petrochemical engineering plastics, if the moisture content in the soy plastics is kept low ($<5\%$ by weight). The low moisture soy plastic is found to be tougher than diglycidyl ether of bisphenol-A epoxy resins ($0.96\,\mathrm{MPa\,m^{\frac{1}{2}}}$ vs $0.8\,\mathrm{MPa\,m^{\frac{1}{2}}}$). The observed high fracture toughness in the dry soy plastics is attributed to the formation of multiple line arrays of cavitated voids (croids) in the damage zone. The formation of croids may be associated with the presence of coagulated protein bodies ($<0.05\,\mu$m) in the soy plastics matrix. The ductility and dimensional stability of soy plastics is found to depend strongly on the moisture content or the level of plasticizer utilized in the matrix. The biodegradable soy plastics show good potential as an alternative for replacing petrochemical, nonbiodegradable, plastics for engineering applications. © 1997 Elsevier Science Ltd.

(Keywords: biodegradable; soy plastics; engineering application)

INTRODUCTION

The recycling of polymer (plastic) waste has been a high priority for all developed nations. Unfortunately, due to a lack of economic incentive and a feasible technology, there has been very little success in reducing plastic waste.

The recent environmental regulations, societal concerns, and growing environmental understanding throughout the world have triggered renewed efforts in industry to develop products and processes compatible with our environment[1]. These efforts include: (1) the utilization of annually renewable biodegradable resources to replace petroleum feedstocks; (2) the introduction of products and processes that are environmentally friendly; (3) the recycling of the waste stream; (4) the commercialization of biodegradable products and processes in applications that are economically sound. Compatibility of products and processes with the environment is also tied to the issue of waste management, i.e. disposing of waste in environmentally and ecologically sound practices.

Polymeric materials derived from agricultural feedstocks can play a major role in helping alleviate these environmental concerns. The processes, products, and technologies associated with the utilization of renewable resources are likely to be compatible with the environment, too. The waste stream generated from the manufacturing process can also be recycled or converted into biodegradable by-products. Minimal environmental pollution is thus expected.

On the other hand, petrochemical plastics are known to be strong, light-weight, inexpensive, easily processable and energy efficient. They have excellent water barrier properties, and are inert to biodegradation. It is these very qualities of strength and indestructibility that turns the synthetic plastics into nonbiodegradable solid waste. For instance, these lightweight and indestructible synthetic plastics have posed an alarming hazard to marine life in the ocean. The US Environmental Protection Agency (US EPA) estimates that 4205 metric tons of plastic waste are produced each year aboard government ships alone. Consequently, there is an urgent need to shift the paradigm, and reconsider how the plastics' raw materials should be prepared, manufactured, and utilized.

Thus, it is desirable to produce plastics that exhibit the attractive performance characteristics of petrochemical plastics, and which, at the end of their intended usage, can be disposed of in a manner such that they can be safely absorbed by the environment. Soy plastics, among the agricultural products, are considered to have high potential for engineering applications. The earliest documented uses of soy protein for nonfood plastics applications can be traced back to 50 years ago[2–4]. The Ford Motor Company was the first major company to attempt to utilize the blends of phenol-formaldehyde resin and soybean meal for automotive applications[5–7]. However, there has been no known commercial success in utilizing soy plastics for engineering structural applications.

Recently, many researchers have successfully

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demonstrated the potential uses of soy plastics to replace petrochemical plastics for commodity applications, such as food trays, spoons, and plastic bags[8–18]. These efforts have been shown to be functionally successful (i.e. the performance and processes associated with the soy plastics developed by these researchers are quite attractive), but they are still far from being considered commercially attractive, due to the higher raw material and process costs when compared to those of the petrochemical plastics equivalents, such as polyethylene and polypropylene. In order to make soy plastics immediately competitive with petrochemical plastics, it is possible to focus on the development of soy plastics for engineering structural applications where the overall cost of producing soy plastics may be competitive with their petrochemical plastic counterparts, such as polycarbonate and epoxy resins.

There are several types of soybean products that can potentially be utilized for engineering structural applications. Dehulled soybean, after solvent defatting and meal grinding, becomes a fat free, low fibre soy flour ($0.33/kg, 48.5% protein), which can be toasted to various degrees of protein solubility (measured via the nitrogen solubility index). The soy flour, after leaching out the water/alcohol-soluble sugars, is termed soy protein concentrate ($1.43/kg, 65+% protein). The soy protein concentrate, if it is further extracted by alkali and reprecipitated by acidification, becomes the purest commercially available soy protein isolate ($1.98/kg, 90+% protein). At this stage, it is uncertain what level of soy protein is needed for soy plastics to exhibit acceptable physical, mechanical, and rheological properties for engineering applications. It is also uncertain what form(s) soy protein needs to be in for preparing soy plastics. Water absorption problems have been experienced with soy protein plastics. However, both soy protein concentrates and soy protein isolates are available in isoelectric (water-insoluble) and neutralized (sodium salt) forms. The water-soluble form is suitable for food applications. The isoelectric form is more appropriate for engineering structural applications.

The present study focuses on investigations of the mechanical and fracture behaviour of soy isolate plastics in a dry form, in a moisturized form, and in a glycerol-plasticized form. The fracture process in soy plastics is studied in detail. The feasibility of using soy plastics for engineering structural applications is also discussed.

EXPERIMENTAL

Material and sample preparation

The soy plastic (SUPRO 760) utilized for the present study was obtained from Protein Technologies International, St Louis, MO. The plastic contains more than 87% by weight soy protein (dry basis) and *ca* 7% of water. The molecular weights of the soy plastics are about 320 000 daltons. Some soy plastics were plasticized with glycerol (25% by weight) before processing. The utilization of glycerol is both to improve the processability and to control moisture content in soy plastics.

The soy plastic, with and without the use of glycerol plasticizer, was compression moulded (Wabash compression-moulding machine, Wabash Metal Product Inc., Wabash, IN) at 150°C and 19.6 MPa for 6 min. Afterwards, the specimen was left in the mould to slowly cool to below 50°C before the specimens were removed. One set of soy plastic plaques was further dried in a vacuum oven overnight at 80°C before testing (with about 5% moisture content). Another set of soy plastic plaques was left in open air in the laboratory at 50% humidity, at 25°C, for 2 weeks before testing (approximately 10% moisture content). Plaques with dimensions of 10.16 cm × 15.24 cm × 0.635 cm (4″ × 6″ × 1/4″) and 10.16 cm × 15.24 cm × 0.3175 cm (4″ × 6″ × 1/8″) were moulded.

The 0.635 cm plaques were machined into bars with dimensions of 12.7 cm × 0.635 cm (5″ × 0.5″ × 0.25″) and dimensions of 6.35 cm × 1.27 cm × 0.635 cm (2.5″ × 0.5″ × 0.25″) for the double-notch four-point-bend (DN-4PB) experiment[19,20] and the single-edge-notch three-point-bend (SEN-3PB)[21,22] experiment, respectively. These DN-4PB and SEN-3PB bars were notched with a milling tool (250 μm tip radius), followed by razor blade tapping to wedge open a sharp crack with a parabolic crack front. The ratio between the final crack length (a) and the specimen width (W) was held in the range between 0.4 and 0.6. The 0.3175 cm plaques were machined according to the ASTM D-638 Type I specimens requirement for tensile tests and bars with dimensions of 6.35 cm × 1.27 cm × 0.635 cm for dynamic mechanical spectroscopy (DMS) study.

Dynamic mechanical spectroscopy

To determine whether or not the modulus of soy plastics is a strong function of temperature, and to obtain a general idea of the damping behaviour of soy plastics, DMS (Rheometrics RMS-805) of soy plastics under a torsional mode was investigated. A constant strain amplitude of 0.05% and a fixed frequency of 1 Hz were used. The sample was analysed at temperatures ranging from −150°C to 200°C, with 5°C steps. The storage modulus (G') vs temperature and the $\tan\delta$ vs temperature curves were plotted. For comparison purposes, DMS of commercially available epoxy resin and polycarbonate samples were also obtained.

Tensile test

The 0.318 cm thick ASTM D-638 Type I tensile bars were tested at 25°C at crosshead speeds of 0.05″ min^{-1} and 0.5″ min^{-1} for the neat and glycerol-plasticized soy plastics, respectively. An extensometer (MTS, Model 632.11b-20) was utilized to measure the instantaneous true strain of the sample. Care was taken to ensure alignment of the tensile bar with the testing fixture.

Fracture toughness measurements

A Sintech-2 screw-driven mechanical testing machine was used to conduct both the SEN-3PB and the DN-4PB experiments, at a crosshead speed of 0.508 mm min^{-1} (0.02″ min^{-1}). The SEN-3PB method was utilized for fracture toughness measurement, i.e. plane strain critical stress intensity factor (K_{IC}), following the procedures described in the literature[21,22]. The critical strain energy release rate (G_{IC}) is calculated based on:

$$G_{IC} = \frac{K_{IC}^2(1-\nu^2)}{E}$$

where E is Young's modulus and ν is Poisson's ratio. When the DN-4PB experiment was performed, care was taken to ensure that the upper contact loading points were touching the specimen simultaneously.

Microscopy investigation

The damage zone around the survived (the crack that grows subcritically) DN-4PB crack was cut along the thickness direction (i.e. the crack propagation direction) into two halves, using a diamond saw. The plane strain core region of these two pieces was prepared for reflected optical microscopy (ROM) and transmission electron microscopy (TEM) investigations, respectively. In the ROM experiment, the plane strain core region was polished following the procedure described by Sue *et al.*[23]. The polished surface of the damage zone was then studied using an Olympus Vanox-S microscope, under both bright field and cross-polarization conditions.

For TEM investigations, the core region of the damage zone was carefully trimmed to an appropriate size, i.e. an area of *ca* 3 mm × 3 mm, and embedded in D.E.R. 331 (diglycidil ether of bisphenol A) epoxy resin/diethylene triamine (12/1 ratio by weight). It was cured at 38°C for 16 h. The cured block was then further trimmed to a size of *ca* 0.3 mm × 0.3 mm with the crack tip in the damage zone roughly at the center of the trimmed surface. A diamond knife was then used to face off the trimmed block. Afterwards, ultra-thin sections, ranging from 60 to 80 nm, were obtained using a Reichert-Jung Ultracut E microtome with a diamond knife. The thin sections were placed on 200-mesh formvar-coated copper grids and examined using a JEOL 2000FX ATEM operated at an accelerating voltage of 100 kV for TEM observation.

RESULTS AND DISCUSSION

To demonstrate the feasibility of soy plastics for engineering applications, the dynamic mechanical behaviour, Young's modulus, and fracture toughness of soy plastics were measured and compared to those of the commonly utilized petrochemical engineering plastics, such as polycarbonate and epoxy. The fracture mechanisms in soy plastics were also investigated.

Dynamic mechanical spectroscopy

The dynamic mechanical spectra of soy plastics in a dry form, in a moisturized form, and in a glycerol-plasticized form are shown in *Figures 1* and *2*. For comparison purposes, the dynamic mechanical spectra of polycarbonate and epoxy are also plotted in *Figures 1* and *2*.

It is evident that dry soy plastic exhibits significantly higher storage moduli across the entire temperature range probed (−150°C to 170°C) than those of either polycarbonate or epoxy. This is indicative of the high performance nature of soy plastics. However, when the soy plastics are exposed to a humid environment (*Figure 1*), an order of magnitude drop in Young's modulus is observed at room temperature. This suggests that the presence of moisture in soy plastics may deteriorate the properties of soy plastics significantly. Therefore, it is critical that the level of moisture content in soy plastics be controlled for any engineering applications.

Glycerol has been utilized as a processing aid and as a plasticizer for soy plastics[8]. It is quite clear that the presence of glycerol tends to lower the G' of the soy plastics significantly, except in the extremely low temperature regime (*Figure 1*). This means that, depending on the application, appropriate amounts of glycerol-like plasticizers can be incorporated to improve the processability, and to control the rigidity of the soy plastics. In the extremely low temperature regime, the glycerol has an anti-plasticization effect to stiffen the soy plastic at temperatures below the freezing temperature (*ca* −80°C) of glycerol. This implies that the use of plasticizers may not only help widen the processing

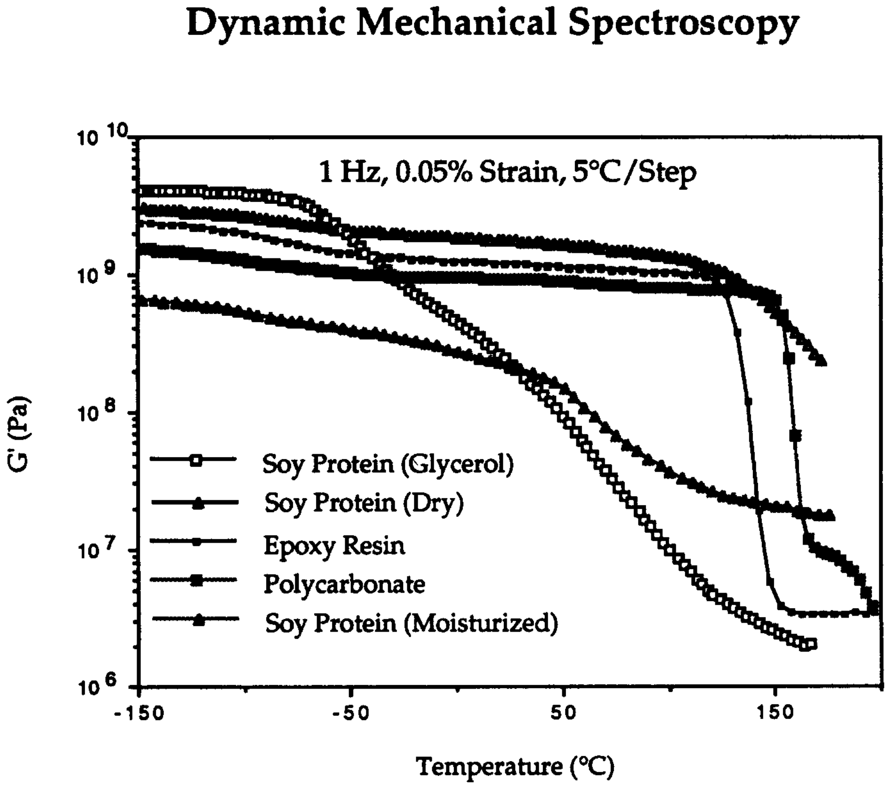

Figure 1 DMS (G' vs temperature) of polycarbonate, epoxy, and various forms of soy plastics

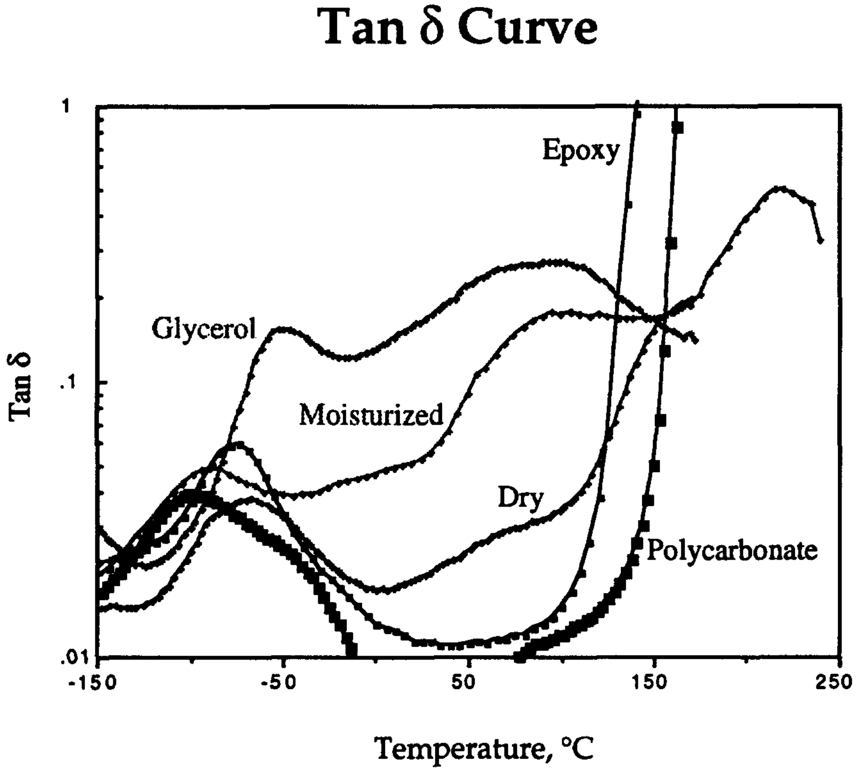

Figure 2 DMS (tan δ vs temperature) of polycarbonate, epoxy, and various forms of soy plastics

Table 1 Typical physical and mechanical properties of soy isolate plastics

	G' at 25°C (GPa)	Young's modulus (GPa)	T_g (°C)	K_{IC} (MPa m$^{0.5}$)
Soy (dry)	1.76	4.40	150	0.96 ± 0.14
Soy (moisturized)	0.22	0.53	150	–[a]
Soy (glycerol)	0.21	0.52	−50	–
Epoxy	1.20	3.00	145	0.80 ± 0.05
Polycarbonate	0.93	2.10	155	2.00 ± 0.20

[a] Too tough for valid linear elastic fracture mechanics measurements

window, but also increase the modulus if the application is cryogenic in nature, e.g. for space station and cryogenic refrigeration container applications.

The soy plastic was found to become thermally unstable after the temperature reached above 165°C (*Figure 1*). Unfortunately, the soy plastic appears to have a glass transition temperature (T_g) of about 165°C. As a result, it becomes uncertain whether or not the soy plastic sample is crosslinked, i.e. no rubbery plateau modulus is detected in soy plastics.

The tan δ vs temperature curve can usually be utilized to reveal information concerning molecular and/or segmental scale motions in polymers. The tan δ curves of the soy plastics, in three different forms, show that significant energy dissipation motion(s) are present (*Figure 2*). This suggests that soy plastics may be either ductile or toughenable. This aspect will be addressed in a separate paper.

Modulus measurements

In order to determine whether or not the Young's modulus of the dry soy plastic is indeed much higher than that of the epoxy and polycarbonate, ASTM-D638 Type I tests were conducted. The Young's moduli of the soy plastics in various forms as well as the Young's moduli of epoxy and polycarbonate are listed in *Table 1*. For convenience, the T_g and the storage modulus (G' at 25°C) are also shown in *Table 1*.

The dry soy plastic has a Young's modulus of 4.4 GPa at 25°C. That is about 25–50% higher than that of the commonly utilized petrochemical engineering plastics. This broadens the amount of plasticizers that can be utilized in soy plastics to improve ductility and processability, while still maintaining a rigidity comparable to that of an engineering plastic.

Fracture toughness measurements

The fracture toughness of dry soy plastics is slightly better than that of epoxy resins, and is comparable to those of polystyrene and poly(methyl methacrylate)[24]. It is quite surprising to find that the dry soy plastic exhibits such a high fracture toughness. When the soy plastic is exposed to humidity, or contains plasticizers such as glycerol, the crack will no longer grow upon SEN-3PB testing. This indicates that the fracture toughness of soy plastics may be easily improved. This conjecture is also

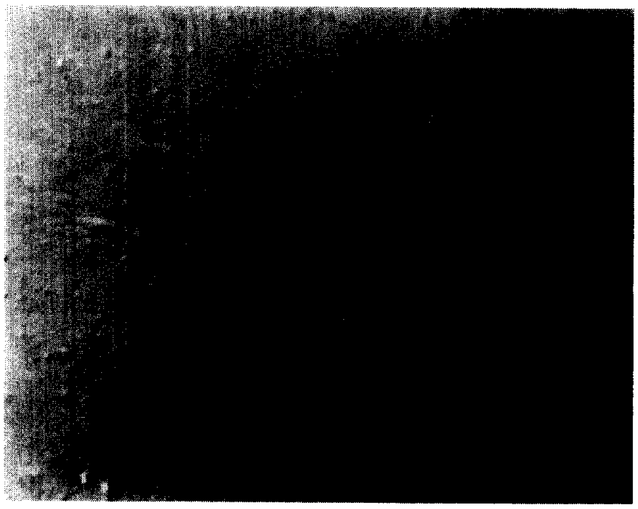

Figure 3 ROM taken at the DN-4PB damage zone of dry soy plastic

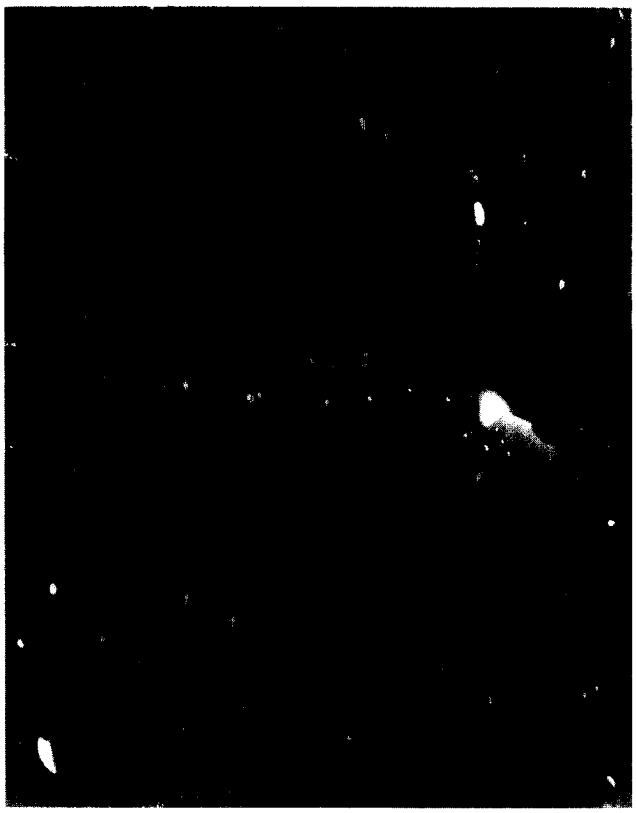

Figure 4 TEM taken at the DN-4PB damage zone of dry soy plastic

supported by the high tan δ curve of soy plastics via DMS measurement (*Figure 2*). The feasibility of using soy plastics for engineering applications is high.

Fracture mechanisms and morphology investigations

The soy plastics investigated here exhibit reasonably good fracture toughness values. In order to find out the cause(s) for such fracture behaviour, the ROM and TEM investigations were conducted.

The ROM observation indicates that multiple cracking occurs around the subcritcally propagated DN-4PB crack tip (*Figure 3*). No signs of plastic deformation are observed. The toughening may be coming from the multiple cracking mechanisms. For the multiple cracking mechanism to take place, it usually involves either the presence of a defect (second phase particles), or the crack growing dynamically. Since the testing is conducted at a slow rate, it is likely that the soy plastic is multi-phase in nature. To investigate how the multiple crack is evolved, and to find out the morphological characteristics of soy plastics, TEM observation was conducted.

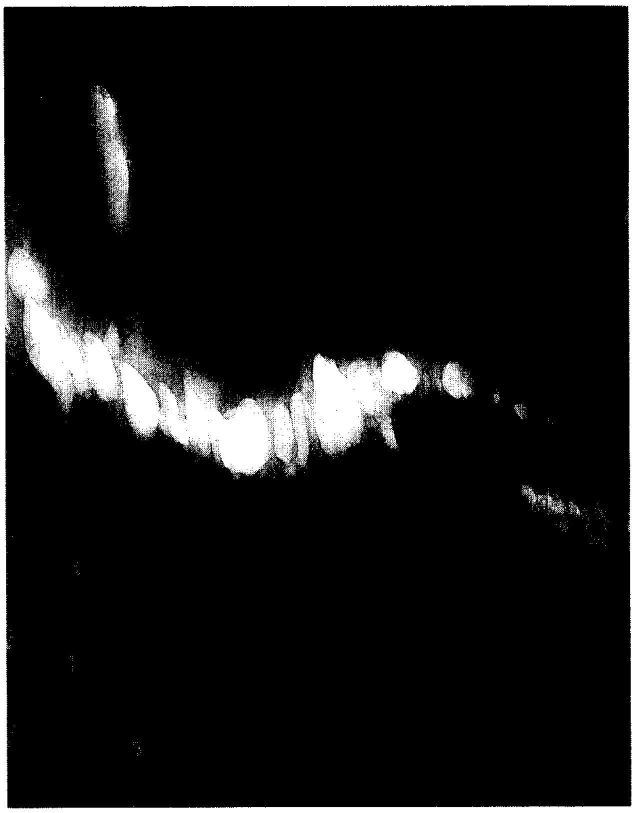

Figure 5 TEM taken, at higher magnification than *Figure 4*, at the DN-4PB damage zone of dry soy plastic

TEM investigation of the DN-4PB crack tip indicates that the observed 'multiple cracking' phenomenon, in fact, results from the formation of line-arrays of voids (*Figures 4* and *5*). The voids appear to be initiated from the sub-micrometer domains (see arrows in *Figure 5*). These line arrays of voids were also observed in a series of core-shell rubber-toughened epoxy systems[25]. They are called 'croids' (i.e. the crack-like voiding pattern). The size of the void is significantly larger than that of the sub-micrometre domains. This finding suggests that the soy plastic must have undergone a large scale, localized, dilatational plastic deformation, present around the voids. This may be the main source of toughening for soy plastics. Although it is still unclear what composition and physical nature the domain exhibits, it is possible that the micro-domains are formed due to the coagulation of protein bodies[26,27]. If the toughness of the soy plastics is to be further improved, it is imperative that the unknown micro-domain be carefully analysed.

The above studies indicate that high protein content soy plastics have a tremendous potential to become a new kind of engineering plastic which are biodegradable. However, it is also apparent that, as indicated in *Table 1* and *Figure 1*, if soy plastics are exposed to moisture, their physical and mechanical properties may begin to deteriorate. Their dimensional stability will worsen. Furthermore, the moisturized soy plastics are more prone to micro-organism attacks. These factors, if not prevented or carefully managed, may harm the chances of using soy plastic for engineering applications.

CONCLUSION

The morphology and fracture behaviour of soy plastics with high soy protein content were investigated. It was found that the soy plastics may exhibit high modulus, high toughness, and good processability, if the appropriate amount of plasticizer or moisture is present in the matrix. The fracture mechanism in dry soy plastic is mainly the formation of croids in the crack tip damage zone. No signs of shear plastic deformation were observed. The formation of croids appears to be associated with the presence of sub-micrometre domains. The physical nature and composition of the sub-micron domains is still unclear. The feasibility of utilizing soy plastics to replace petrochemical plastics for engineering applications is high.

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