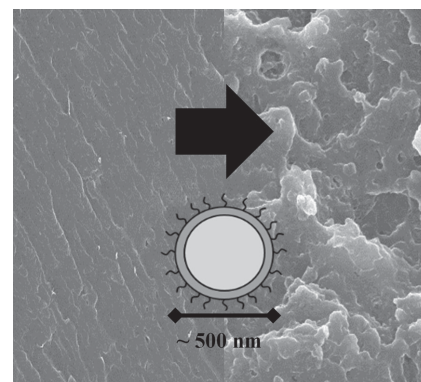


Impact Modification and Fracture Mechanisms of Core–Shell Particle Reinforced Thermoplastic Protein

Matthew J. Smith,* Casparus J. R. Verbeek

Mechanical properties and fracture mechanisms of Novatein thermoplastic protein and blends with core–shell particles (CSPs) have been examined. Novatein is brittle with low impact strength and energy-to-break. Epoxy-modified CSPs increase notched and unnotched impact strength, tensile strain-at-break, and energy-to-break, while tensile strength and modulus decrease as CSP content increases. T_g increases slightly with increasing CSP content attributed to physical crosslinking. Changes to mechanical properties are related to the critical matrix ligament thickness and rate of loading. Novatein control samples display brittle fracture characterized by large-scale crazing. At high CSP content a large plastic zone and a slow crack propagation zone in unnotched and tensile samples are observed suggesting increased energy absorption. Notched impact samples reach critical craze stresses easily regardless of CSP content reducing impact strength. It is concluded that the impact strength of thermoplastic protein can be modified in a similar manner to traditional thermoplastics.



1. Introduction

Proteins are naturally occurring biopolymers and offer a green alternative to some petrochemical thermoplastics. Many protein resources are noncompetitive with food streams, are waste or by-products of other processes, and are biodegradable when in thermoplastic form. For example, proteins such as wheat, soy, peanut, meat and bone meal and fish meal have all been precursors for thermoplastic material.^[1–6] Another example is bloodmeal, a by-product of the meat processing industry which has a very high protein content (≈ 90 wt%) making it suitable

for thermoplastic processing.^[7] This material, known as Novatein thermoplastic protein, has a tensile strength (9.6 MPa) and modulus (534 MPa) comparable to low density polyethylene (LDPE) but a much lower impact strength (0.9 kJ m^{-2}) and strain- and energy-to-break (12% and 0.8 MPa).^[8] Novatein is mostly used in the meat industry during animal slaughtering for devices preventing meat contamination. The nature of Novatein causes it to become brittle after production due to the evaporation of water, which is used as a plasticizer during processing.

Impact modification of polymers can be achieved in a number of ways. Rigid particles, such as nanoscale CaCO_3 , have been shown to effectively toughen and modify impact strength of semi-crystalline polymers. Hard particles act as stress concentration points in the matrix and are only deemed effective if cavitation and debonding of the particle is possible allowing matrix yielding. However, these particles can greatly increase the modulus of

M. J. Smith, Prof. C. J. R. Verbeek
University of Waikato
Private Bag 3105, Hamilton 3240, New Zealand
E-mail: matthewjsmith90@gmail.com

the composite for only a small relative change in impact strength and toughness.^[9]

Second phase rubber toughening is another prevalent technique used in engineering plastics. The idea of using a dispersed phase to improve the impact strength of both thermoplastics and thermosetting resins is common practice.^[10] Core–shell particles (CSPs) can be used to offer improved interaction at the interface between the elastomeric and matrix phases of immiscible blends. CSPs have a core formed typically of an elastomeric polymer, covered by a shell of a different, more rigid polymer. These particles can be synthesized through emulsion polymerization to have shells that are specifically miscible with the intended matrix, or they can be functionalized with chemical groups that can react with the matrix polymer. Reactive groups present on the shell of the particle also aid dispersion during melt blending, as reactive compatibilizers act as emulsifying agents preventing coalescence.^[11] Both examples here suggest that the interfacial adhesion between matrix and modifier is extremely important.

Brittle failure is often characterized by extensive crazing of the matrix, whereas the primary mechanism seen in ductile failure is plastic shear yielding. Shear yielding in polymers is desirable as it is more efficient at dissipating energy than crazing.^[12] The inclusion of rubbery particles typically aids this transition from crazing to shear yielding. Wu^[13] stated that the critical parameter for promoting impact strength or toughness with rubber particles was the surface-to-surface interparticle distance (matrix ligament thickness, τ) rather than particle size or volume fraction alone. However, τ is dependent on particle size and volume fraction (Equation 1). For a given particle diameter, D , and volume fraction, ϕ_r , τ can be calculated using Equation (1)^[13]

$$\tau = D \left[\left(\pi / (6\phi_r) \right)^{1/3} - 1 \right] \quad (1)$$

At a critical ligament thickness, τ_c , a brittle to ductile transition has been observed. For rubber-toughened nylon 6,6 this was 0.3 μm .^[13] This theory has since been extended to show that the percolation of “stress spheres” surrounding particles, and therefore the stress state of the ligaments, is the governing factor.^[14] It was established that below a certain thickness these ligaments could undergo shear yielding as a result of the transition from plane strain to plane stress, thereby dissipating energy more efficiently.^[15] However, there is still some disagreement as particle size and composition, along with the inherent ductility of the matrix, influence the brittle to ductile transition.^[10,16]

Cho et al.^[17] showed that CSPs in polycarbonate increased the size of the plastic deformation zone at the

tip of the notch in impact testing. An increase in the size of the plastic zone decreases the mean stresses at the crack tip and also ensures that craze initiation stresses are not reached in the matrix. Large amounts of energy are therefore absorbed at the crack tip before catastrophic failure. Furthermore, cavitation of particles also offers additional impact resistance as debonding of particles relieves triaxial stresses within the matrix. The disappearance of triaxial stress causes a matrix to behave as if under plane-stress conditions, similar to decreasing the ligament thickness, allowing shear yielding of the matrix.^[18] The subsequent void formation acts as a further stress concentration point, however as voids are unable to bear a load, they will only offer limited toughness modification.^[10]

The modulus of the particle is important for toughening polymers. A low modulus core will allow for more efficient stress transfer and deform more. High modulus cores tend to have low strength, causing a decrease in overall composite strength.^[19] For example, Schneider et al. showed that a prevulcanized (higher modulus) natural rubber (NR) core in a poly(methyl methacrylate) (PMMA)/NR CSP was less effective at toughening polystyrene than a lower modulus noncrosslinked NR core.^[12] Similarly the inherent ductility of the matrix will affect the influence that rubbery inclusions will have on the material. If a matrix is more prone to shear yielding and cold drawing it is able to be toughened much more greatly than a brittle polymer.^[20]

Julien et al.^[21] postulated that there was a number of transitions of crack growth during fracture; from fully stable to partially stable and finally fully unstable. It was observed that as loading rate increased during the compact tension testing of PMMA, the crack growth mechanism changed from partially stable at low rates to fully unstable at fast rates. The introduction of rubber particles into the PMMA matrix stabilized crack growth at lower testing rates due to cavitation and shear yielding of the matrix thereby inducing a larger plastic zone at the crack tip. This was evident through an increase in K_{IC} fracture toughness over that of neat PMMA. However at high testing speeds, a decrease in K_{IC} was observed due to the time dependent nature of polymer chain relaxation.

Many bioderived thermoplastics have undesirable mechanical properties. They are typically brittle, with low elongation, energy-to-break and impact resistance. However, the addition of plasticizers, second polymer components, and reinforcing agents such as particles and fibers can have a desirable effect on energy absorbing properties.^[22]

In this study, CSPs consisting of an elastomeric butyl acrylate and 2-ethylhexyl acrylate core and a poly(methyl methacrylate) shell were used to modify the impact strength of Novatein thermoplastic protein. Novatein is

a newly developed material and its fracture mechanism, with and without modification, was also assessed using epoxy functionalized and regular CSPs.

2. Experimental Section

2.1. Materials

Pre-extruded injection molding grade of Novatein IR3020 was acquired from Aduro Biopolymers (Hamilton, NZ) in powder form. Two grades of core-shell impact modifiers (CSPs), DOW Paraloid EXL 2390 and EXL 2314, were acquired from Plastral (Auckland, NZ) in powder form. Both grades had a crosslinked elastomeric core consisting of butyl acrylate and 2-ethylhexyl acrylate, and a rigid PMMA shell. The EXL 2314 grade was modified with a glycidyl methacrylate (GMA) functionality on the PMMA shell while EXL 2390 had no functionality. Individual CSPs had been measured as ≈ 500 nm in diameter using scanning electron microscopy (SEM).

2.2. Sample Preparation

Initial blends included 10 and 20 parts of either EXL 2390 (2390-10 and 2390-20) or EXL 2314 (2314-10 and 2314-20) per hundred parts Novatein (pph_{NTP}). After these scoping trials, blends containing different amounts of just EXL 2314 were produced up to 30 pph_{NTP}, with the number of the blend name denoting the amount of CSPs in pph_{NTP} (2314-5, 2314-10, 2314-15, 2314-20, 2314-30).

Pre-extruded Novatein powder was tumble mixed with one of the Paraloid impact modifiers in a zip lock bag before extrusion. Blends were prepared by melt blending in a LabTech corotating twin screw extruder (L/D 44:1) with a screw speed of 200 rpm. Temperature profile increased over 11 barrel heating sections, from 70 °C at the feed throat to 100 °C along the main barrel, and increasing to 120 °C at the die. Blends were granulated using a triblade granulator with a 4 mm plate (Castin Machinery, NZ).

Tensile bars (ASTM D368) and impact bars (ISO 179) were produced in a BOY 35A injection molding machine, with a temperature profile of 100, 135, 150, 150, 150 °C from feed to nozzle. Mold temperature was kept constant at 50 °C. Notches for notched impact samples were cut according to ISO 179 using an automated notch cutter. All test pieces were conditioned at 50% relative humidity and 23 °C for 7 d before testing.

2.3. Analysis

Tensile testing was conducted according to ASTM D638 on an Instron model 33R4204 tensile testing rig. A crosshead speed of 10 mm min⁻¹ was used with an extensometer with a 50 mm gauge length. Notched and unnotched Charpy impact testing was conducted on a Ray-Ran Pendulum Impact System. A hammer weighing 0.457 kg with a test speed of 2.9 m s⁻¹ was used for all tests, equating to a pendulum energy of 2 J. Notched and unnotched testing was conducted in an edgewise orientation.

Dynamic mechanical analysis (DMA) was conducted on sections of impact bar (thickness of ≈ 4 mm and width of ≈ 9.5 mm)

using a Perkin Elmer DMA8000 instrument. Scans were run in triplicate using a single cantilever configuration at 1 Hz from -100 to 180 °C. A free length of ≈ 13 mm was used at a dynamic displacement of 0.05 mm. Data collected were analyzed using Perkin Elmer's Pyris software.

Morphology of Novatein and blends containing CSPs was assessed using fractured ends of tested samples mounted on aluminum studs. The samples were then sputter coated with platinum using a Hitachi E-1030 ion sputter coater. SEM was carried out using a Hitachi S-4700. An accelerating voltage of 3 or 20 kV was applied, however, this did not affect resulting images. Optical images were obtained at a magnification of either $\times 16$ or $\times 40$ using a Nikon Digital Sight DS-U1 camera mounted on a Wild Heerbrugg M3B optical microscope, using similar fractured surfaces.

3. Results and Discussion

3.1. Effect of Surface Modification

Tensile data for surface modified and unmodified blends (Figure 1) showed a decrease in tensile strength and modulus with increasing CSP content. The decrease in strength and modulus in rubber-modified polymers is typically accompanied by an increase in elongation due to increased plastic yielding (covered in later sections). This was evident in the blends containing epoxy modified CSPs (2314-10 and 2314-20) whereby a significant increase in strain-at-break was seen. However, the blends containing unmodified CSPs actually showed a decrease in strain-at-break, as well as a far greater decrease in tensile strength than EXL 2314 blends.

In the case of 2314-10 and 2314-20, the increase in strain-at-break far outweighed the decrease in tensile strength bringing about a large increase in energy-to-break (up to 4.59 MPa compared to 0.22 MPa for Novatein). In contrast, the blends with unmodified particles displayed a decrease in energy-to-break. It was apparent from notched Charpy impact testing that unmodified

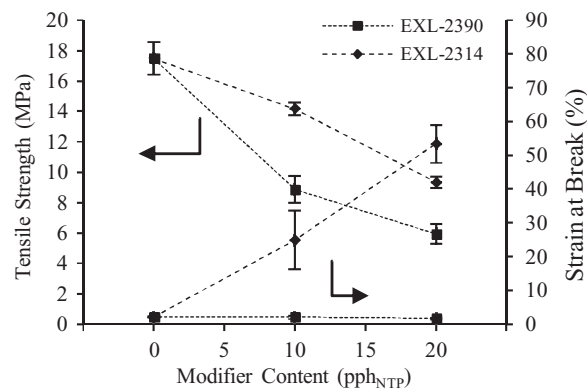
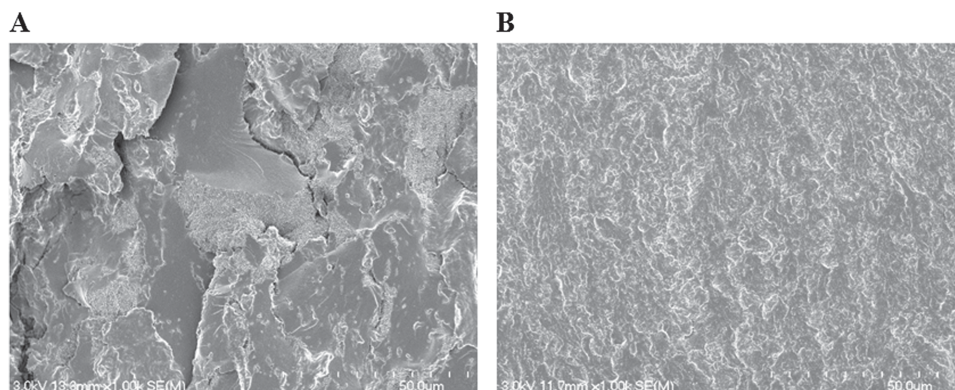


Figure 1. Selected mechanical properties of blends containing modified and unmodified core-shell impact modifiers.



■ Figure 2. Impact fracture surface of A) 2390–20; B) 2314–20.

CSPs were far less efficient at improving impact strength than the epoxy modified CSPs. The inclusion of 20 pph_{NTP} EXL 2390 caused a reduction in impact strength compared to that of Novatein (0.75 kJ m⁻² compared to 0.9 kJ m⁻², respectively). In contrast, the notched impact strength for 2314–20 (≈2.5 kJ m⁻²) was much larger than the Novatein control.

The fracture surface of 2390–20 shows that while unmodified CSPs were agglomerated, these agglomerations were well distributed throughout the sample. In contrast the 2314–20 fracture surface revealed good distribution of CSPs through the sample, as well as good dispersion of individual particles. Agglomeration resulted in no toughening effect, as large cracks can readily propagate through the material with little resistance. Furthermore, the large crazes present in 2390–20 do not appear to terminate in the rubbery CSPs, as is the case in 2314–20 (Figure 2). The fracture surfaces suggest that interfacial adhesion is good in both cases. There appears to be little debonding and cavitation of CSPs, therefore the toughening mechanism seen in the epoxy modified particle blends is not only as a result of the increased adhesion, but as a function of better dispersion and the increased level of crazing of the matrix (Figure 2B).

In contrast to these results, Li et al.^[23] found that the inclusion of Paraloid EXL 2330 (unmodified CSP similar in composition to Paraloid EXL 2390) in polylactic acid (PLA) produced a greater increase in impact strength than blends containing the epoxy functionalized CSPs used in this study. The difference in impact strength was attributed to the presence of the GMA functionality causing a change in rubber particle size, quality of dispersion and adhesion to the matrix, however no concrete evidence was given. There was a similar decrease in tensile strength and modulus between the two PLA blends, however, strain-at-break was higher in the modified particle blend. It is likely that the reactive functionality, while acting like a crosslinking point which potentially decreases chain mobility, may also have increased interfacial adhesion.

Therefore, at a high rate of loading (impact testing) the CSPs will be less likely to cavitate and behave in a more brittle fashion, similar to thermosetting resins. In contrast, under a low rate of loading (tensile testing), despite the physical crosslinking caused by the reactive functionality, cavitation of particles and yielding of the matrix is more likely, due to the time dependent nature of chain relaxation and fracture. This induces shear yielding due to the transition from plane strain to plane stress.

3.2. Effect of Composition

Due to the superior mechanical properties of blends containing Paraloid EXL 2314, the effect of composition was restricted to blends containing these CSPs only. Higher CSP content resulted in higher impact resistance (Figure 3A,B), regardless of whether a sample was notched or unnotched. In notched samples very little change in impact strength was seen up to 10 pph_{NTP} however an increase was seen after this. By including 30 pph_{NTP} CSPs, the notched impact strength of increased by ≈300%. In contrast, the unnotched impact strength of pure Novatein was approximately doubled with the inclusion of 10–15 pph_{NTP} CSPs, and increased by an order of magnitude after 20 pph_{NTP} CSPs.

The absolute values of the unnotched samples are far higher than those of the notched samples, but this is to be expected due to the high level of stress concentration and pre-existing defects at the notch tip. Also, the relative changes in impact strength are far greater in unnotched testing. This observation suggests that Novatein and blends containing the CSPs are sensitive to the effect of the notch. It must be noted that the standard deviation in the impact results is large, particularly at high loading. Even with a larger sample size (15–20 specimens), a large variation was observed, however the standard error of the mean was decreased greatly. A Student's *T*-test showed that for both notched and unnotched conditions there were significant differences (*p* value < 0.05) between the control (pure Novatein) and all sample

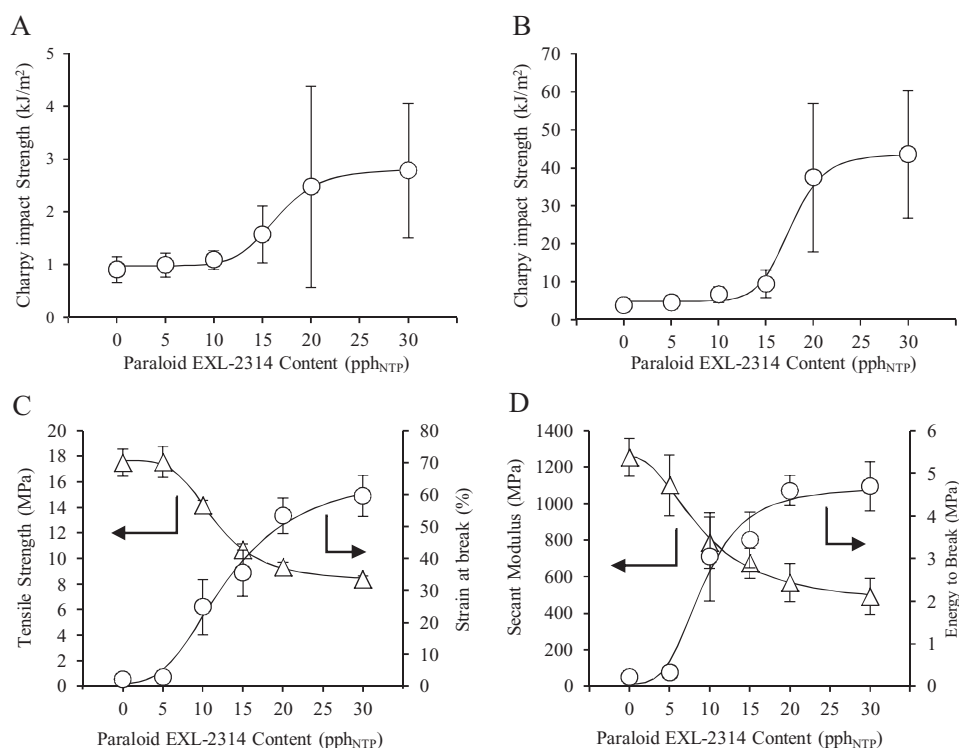


Figure 3. Mechanical properties of Novatein as a function of modifier content A) notched impact strength; B) unnotched impact strength; C) tensile strength and strain-at-break; D) secant modulus and energy-to-break.

groups, except 2314–5 which could be expected due to the negligible effect of the CSPs at this low inclusion level. In the notched samples, there are no significant differences between sample groups until an inclusion of over 10 pph_{NTP}, which corresponds well to the brittle to ductile transition observed in the mechanical data. Furthermore, there was no significant difference between sample groups at the higher CSP content (i.e., between 2314–20 and 2314–30 values). The mechanical data presented suggest that the values reach a plateau between 20 and 30 pph_{NTP} CSPs. This can be considered a positive result in terms of potential upscaling for commercial applications, as an increase of expensive CSPs above 20 pph_{NTP} will not be required. The inclusion of particles can cause “crack bowing,” whereby microscopic crazes and cracks change direction depending on the positioning of the particles.^[24] By increasing the distance that the crack travels and thus the surface area over which the impact energy is calculated, a difference in impact energy can be seen from sample to sample, hence the large variation at high CSP content. This mechanism is not present at all, or negligible, in low CSP content samples and therefore little variation is seen. This mechanism has not been explored in this manuscript and can be the subject of further investigation.

For some unnotched 2314–20 and 2314–30 samples, the sample did not break during impact testing, but

instead stopped the hammer fully. The recorded values for these samples was taken as the maximum energy that the hammer can fully exert on the sample ($\approx 50 \text{ kJ m}^{-2}$). These values were included in the calculations for the averages in Figure 3B.

The matrix ligament thickness for toughening the protein matrix can be determined from Equation (1). In theory according to Wu, to reach τ_c ($0.3 \mu\text{m}$),^[13] ≈ 10 pph_{NTP} CSPs are required. However, for Novatein, even at a ligament thickness of less than $0.3 \mu\text{m}$ (15 pph_{NTP}), no increase in impact strength was observed. The main toughening effect was seen above 17 pph_{NTP} and would give a matrix ligament thickness of $21 \mu\text{m}$ (based on inflection point, Figure 3A,B). This would suggest that ligament thickness is not the only variable that affects toughness and impact resistance.

Tensile testing results supplement the impact testing data and support the theory that energy absorption of the material increases as ligament thickness decreases. However, this increase in energy absorption occurs at much lower CSP content (the inflection point is seen at ≈ 10 pph_{NTP}) (Figure 3C,D). This brittle to ductile transition is also evident from the tensile stress–strain curves as there are clear yield points in blends with greater than 5 pph_{NTP} CSPs (Figure S1, Supporting Information). This difference in inflection point between tensile results and impact results is due to rate of loading and will be

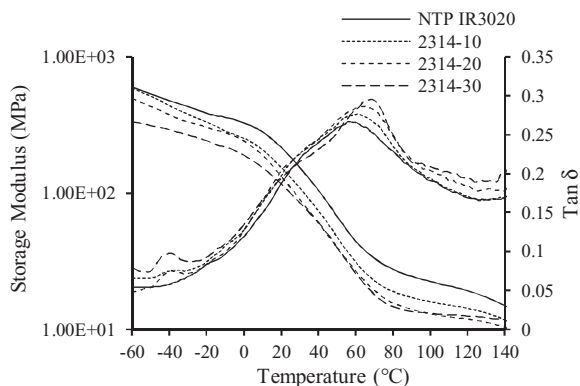


Figure 4. Dynamic mechanical analysis of impact modified Novatein.

addressed later. It must also be noted that strain softening occurs in the blend containing 10 pph_{NTP} CSPs. This is consistent with rubber toughened epoxies that show strain softening as a result of low T_g inclusions.^[18]

A brittle to ductile transition with increasing CSP content is often observed for rubber-toughened polymers. At this transition, strain-at-break and energy-to-break drastically increase, while modulus and tensile strength significant decrease. The properties of the inclusion often dictate the properties of the overall material in particulate reinforced composites.^[19] The same behavior was observed for Novatein reinforced with CSPs.

3.3. Thermal Analysis

DMA revealed a decrease in relative storage modulus over the entire temperature range with increasing CSP content. This is to be expected with rubber modified polymers,^[19] where the contribution of the rubbery core is to lower the blend's average modulus.

The $\tan \delta$ plots (Figure 4) show a clear T_g at ≈ -40 °C attributed to the rubbery core of the CSP. The magnitude of this peak increases with an increase in CSP content. In a similar fashion, the magnitude of the large $\tan \delta$ peak at ≈ 60 °C increases in magnitude with increasing CSPs. This can be attributed to the increased damping ability of the blends as a result of the rubbery inclusions that has a much lower T_g than the matrix. It is well documented that β -transitions seen in $\tan \delta$ below the T_g of a material can be related to its impact resistance.^[25] In this case, it appears that the β -transition of Novatein is masked by the CSP T_g and therefore this relationship cannot be confirmed. It is interesting to note that the magnitude of the $\tan \delta$ peak at the matrix T_g (60 °C) also increases in magnitude with increasing CSP content. However, the relationship between increasing α -transition peak magnitude and impact strength at higher CSP content cannot be confirmed and may be the subject of further investigation.

There is a clear increase in the T_g of the Novatein matrix (taken to be the large peak in $\tan \delta$ at ≈ 60 °C) with increasing CSP content. This could be attributed to the chemical reaction or interaction between the epoxy groups on the PMMA shell and reactive amino acids along the protein chain. Usually, in rubber modified thermoplastics, an increase in T_g would not be expected, however with strong interactions, the “crosslinking” effect of the nanoparticles has a similar effect to increasing crosslink density or chain entanglement.^[25]

Memon^[26] suggested that CSPs in the matrix covers a much greater fraction of the blend than just the volume fraction of the inclusion. The interaction between the matrix and the functional groups (on the surface of the particles) forms an interphase, effectively increasing the particle volume fraction. In highly filled blends, the large effective volumes of the particles overlap, thereby forming a network structure of particles. It was shown through low-frequency plate–plate rheometry of polycarbonate and CSPs that almost 100% of the matrix was interacting with the shell of the inclusions at 20% modifier content, decreasing as a function of decreasing modifier content.^[26] The shift in T_g seen in for Novatein could be due to this large effective area of the epoxy functionalized CSPs and the subsequent network structure formed. This in turn is likely to cause decreased chain mobility in the protein matrix which will require more energy for the onset of chain movement.

3.4. Fracture Behavior

As with the mechanical properties, the mechanism of fracture changes as the level of reinforcement changes (Figure 5). However, while there were differences as a result of filler loading, there were also differences in failure mechanisms as a result of the rate of loading, i.e., impact testing versus tensile testing.

3.4.1. Impact Testing

As interparticle distance decreases, thin matrix ligaments are more prone to plastic yielding. This is particularly evident when comparing a pure Novatein impact-fracture surface with a sample containing 30 pph_{NTP} CSPs (Figure 6). The impact fracture surface of the Novatein sample is characterized by a number of large, uninterrupted crazes running parallel with the direction of impact. In contrast, at high particle content there is a much greater level of crazing, which is interrupted by the rubbery CSPs. The CSPs act as both nucleation and termination sites for the microscopic crazes. The blends containing up to 15 pph_{NTP} CSPs exhibit similar behavior to Novatein, with uninterrupted crazing dominating despite the inclusion of CSPs. However, above this point, blends behave in a similar fashion

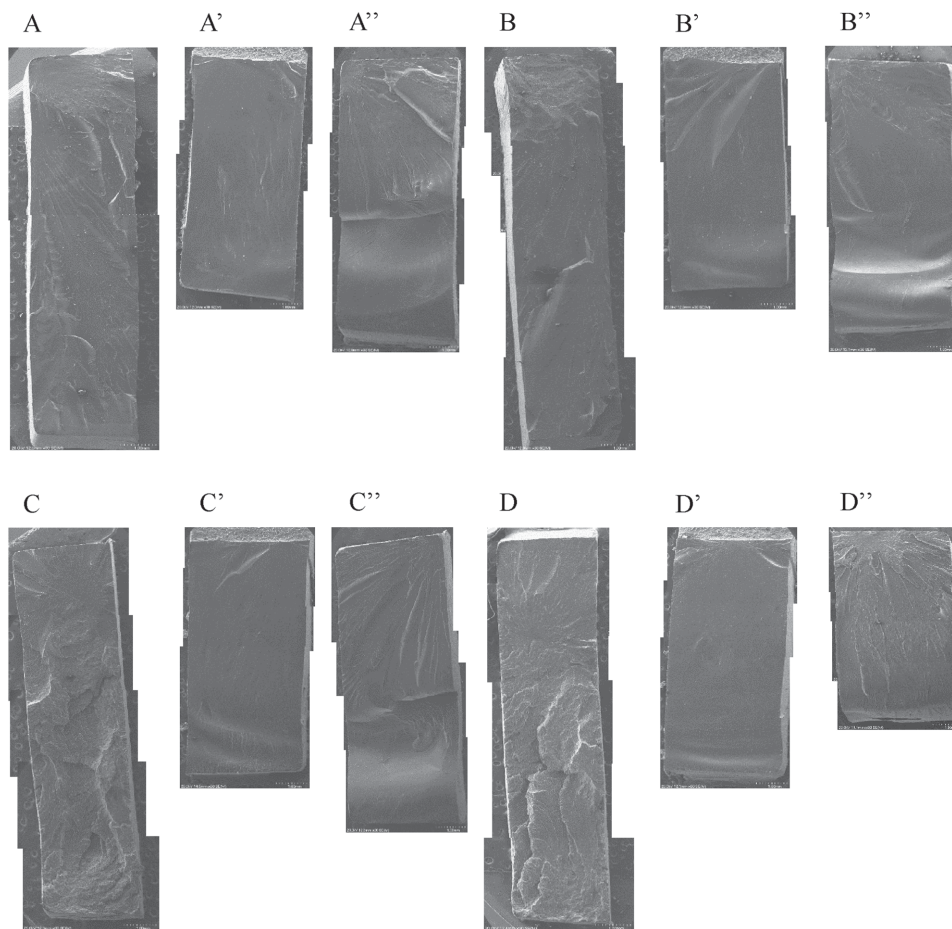


Figure 5. Tensile, notched, and unnotched fracture surfaces, respectively of A,A',A'') Novatein; B,B',B'') 2314-5; C,C',C'') 2314-15; D,D',D'') 2314-30.

to 2314-30. This is to be expected however, by examining the impact testing results (Figure 3A,B). Those blends below the inflection point behave in a brittle manner, as Novatein, while those above the inflection point begin to behave in a ductile fashion.

Notched and unnotched impact tests were considered to evaluate the effect of severe stress concentration on the

fracture behavior of Novatein. The plastic zone is the area of plastic deformation where fracture initiates and from where cracks propagate (Figure 7). If sufficient stress is reached in this area, crazes will begin to propagate slowly in a radial fashion. The size of this slow propagation region is dependent on the critical craze stress and matrix yield stress. Once the critical craze stress is reached,

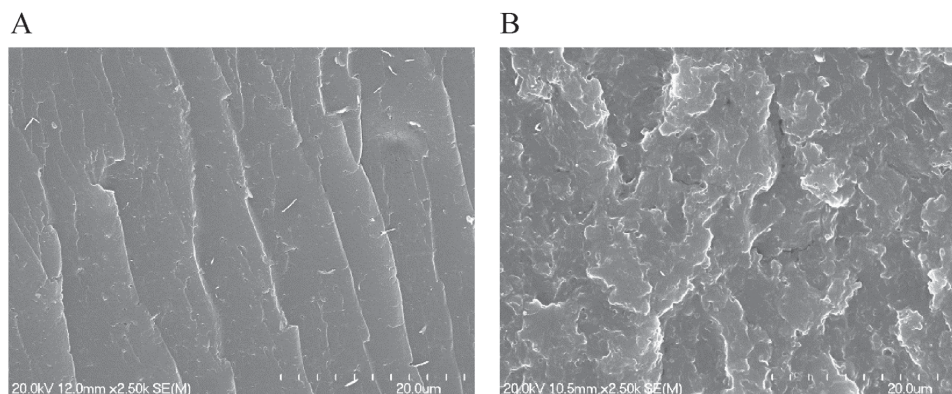


Figure 6. Unnotched impact fracture surfaces of A) Novatein; B) 2314-30.

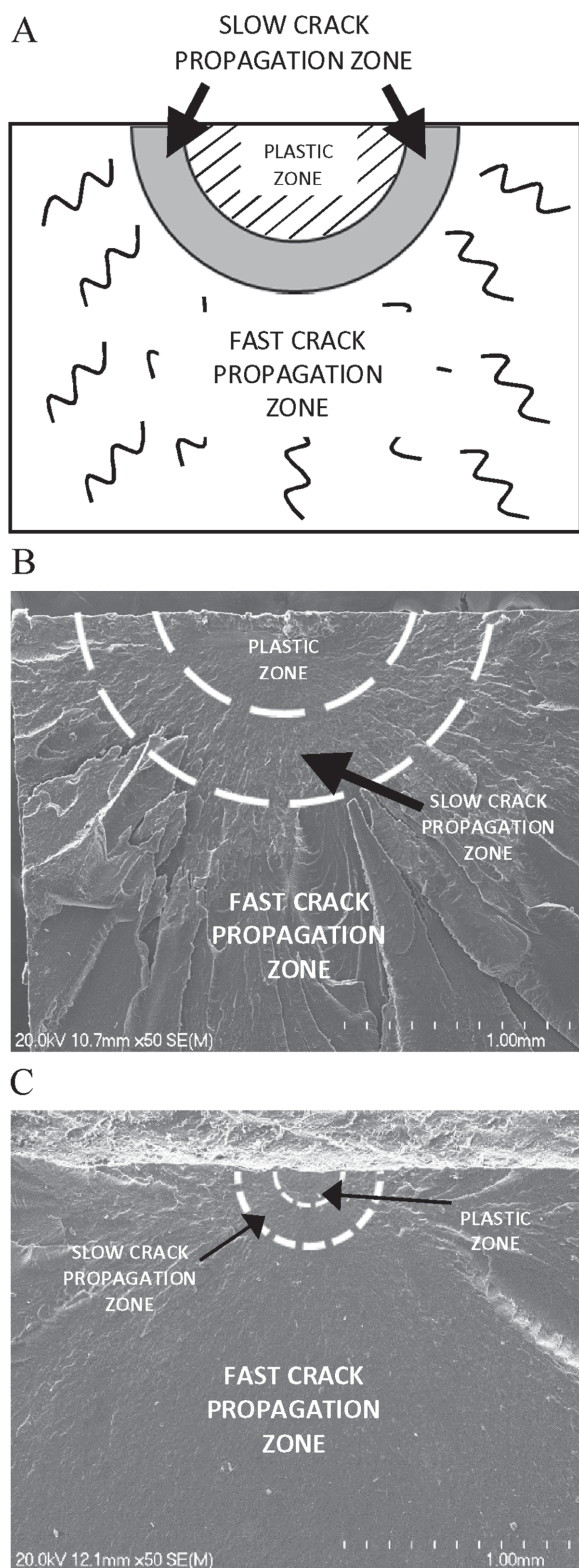


Figure 7. Identified regions during crack propagation and fracture: A) schematic diagram; B) example of regions in unnotched 2314–30; C) example of regions in notched 2314–30.

catastrophic crazing will occur and the material will fail. For unnotched samples, the absence of the intentional stress concentration (i.e., the v-notch) allows for increased plastic flow and yielding, therefore the increase in impact resistance as a function of composition was far greater for unnotched samples.

The increased impact strength with increased CSP content was attributed to more effective dissipation of energy in the plastic zone, a greater level of slow crack propagation and more chaotic crazing (random termination and nucleation of microscopic crazes, e.g., Figure 6B). Due to the dispersed nature and good adhesion to the matrix there is effective stress transfer, and although the rate of loading may be too high for sufficient chain realignment and yielding, the matrix ligaments in the plastic zone are more prone to plastic deformation as a result of plane stress conditions.

The introduction of CSPs causes both stress concentrations to form in the matrix and also the transition from plane strain to plane stress of matrix ligaments that are thinner than τ_c . With a decrease in ligament thickness, stress concentrations around particles may overlap, and the rate of chain relaxation is accelerated in the overlapping region and shear bands may form in these regions. This is highly dependent on strain rate and in the past this phenomenon has been labeled “strain-accelerated relaxation.”^[18] This supplements the argument that the transition from plane strain to plane stress allows thin ligaments of the matrix to yield. When the matrix polymer is said to be under plane strain it is constrained under triaxial stresses and unable to elongate in one plane, therefore strain in that plane is equal to zero. As the ligament thickness decrease, a transition to plane stress is seen and the material can freely elongate as the triaxial stresses have been relieved, causing stress in the plane of elongation to equal zero. Therefore, the thin matrix ligaments, now in plane stress, can yield plastically,^[13,27] forming the plastic zone.

Cho et al.^[17] states that the total energy absorbed during deformation and fracture is comprised of energy from yielding plus the energy from crazing. However, as crazing is a feature of brittle fracture and typically absorbs very little energy, the total energy absorbed is said to be approximately the energy absorbed during yielding. The size of the plastic zone can therefore be related to the total energy absorbed during fracture. The plastic deformation zone will be small, or not present at all, if the critical craze initiation stress is below the yield stress of the material. The tensile yield stress for Novatein is at the break point (≈ 18 MPa) which decreases to ≈ 8 MPa when using 30 pph_{NTP} CSPs. When examining the tensile stress–strain curves of all blends (Figure S1, Supporting Information) it can be assumed that the critical craze

stress in Novatein must fall between 18 and 14.5 MPa, as significant yielding occurs in 2314–10 suggesting that the critical craze stress is not immediately met. It must be noted that these values are for tensile testing and not impact testing, and the variation of rate of loading will affect this.

The large stress concentration in notched samples means that the critical craze stress is reached very easily and only limited yielding can occur. In this case, the material showed highly brittle fracture through large-scale crazing, thereby absorbing very little energy in contrast to unnotched samples with less stress concentration. The slow crack propagation zone is also much larger than in the notched blends, further increasing energy absorption (Figure S2, Supporting Information). The influence of the particles is seen further away from the plastic zone, whereby those with high loading are more prone to cold drawing and yielding.

This can be detected by a change in color of the material as seen under the optical microscope (for color figure the reader is directed to the Supporting Information, Figure S3). In a gray-scale image however, this change in the material can be seen by producing a binary copy (Figure 8). The areas of high deformation (and which are orange in Figure S3, Supporting Information) are seen as dark regions while the bulk matrix appears white. This change of color in the physical sample is brought about by the refraction of light in the cold drawn material and it is clear that there is a separation between the dark sections of the matrix and the orange filament-type structures (Figure S3C, Supporting Information).

It is evident in the optical microscopy images of notched impact samples (Figure S3D,E, Supporting Information) that the main mechanism of fracture is large-scale crazing. There is very little of the orange colored drawn material as seen in the equivalent unnotched samples. However, it is clear that there is some level of yielding and drawing at the edge of the sample, with

crazing dominating through the center of the sample. This edge yielding is likely due to plane stress conditions that exist at the edge of the sample and ductile elongation appears to dominate. In contrast, the constraint of the material in the center of the sample it is likely to bring about plane strain, making it unlikely to yield and hence brittle crazing dominates.

This edge yielding is much more prevalent in the sample with high CSP content (Figure S3E, Supporting Information) due to the decreased ligament thickness, but was not observed along the whole length of the fracture surface. The energy of the hammer remains unchanged throughout the impact, but the cross sectional area (which is able to absorb this energy) decreases as the cracks propagate. Therefore, at some distance from the notch, the critical craze stress will be reached and large-scale crazing will become the main fracture mechanism, rather than mixed mode yielding and crazing.

3.4.2. Tensile Testing

The brittle to ductile transition seen in the tensile mechanical properties (Figure S1, Supporting Information) is supported through observations in the blend fracture surfaces. Novatein exhibited highly brittle crazing throughout the sample, similar to what was seen in the impact fracture surface. It does display low levels of shear banding, however large-scale yielding is not seen (which is also evident from a low strain-at-break). The same behavior is seen at low filler content (2314–5); both exhibit a plastic zone (top section of Figure 5A,B), but these are small and it is clear that crazing dominates the fracture. Even though Novatein and 2314–5 exhibit plastic zones, this is the only area of significant deformation which accounts for the low strain-at-break during tensile testing (Figure 5A,B). At high particle content ductile fracture and large-scale yielding dominate, but this is to be expected after analyzing the tensile data.

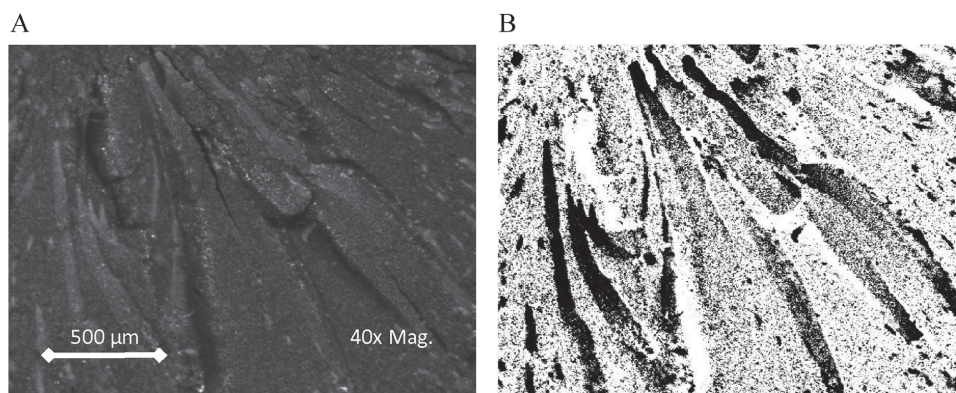


Figure 8. A) Optical microscope image of unnotched impact fracture surface from 2314–30. B) Binary representation of image in panel (A) highlighting regions of high deformation.

Using tensile testing or impact testing, a different τ_c was observed. For tensile data, 10 pph_{NTP} CSPs was identified as the minimum CSP level to bring about a brittle to ductile transition, while this was 15 pph_{NTP} for impact strength; the difference being rate of loading. The very low rate of loading in the tensile tests allowed for reorientation of protein chains along the axis of the applied force, allowing the thin matrix ligaments to yield excessively (at 15 pph_{NTP} CSPs or more). Also, the point at which significant yielding occurred (brittle to ductile transition) was almost identical to the value that Wu stated to be the critical ligament thickness (0.3 μm for nylon yielding in

a nylon/rubber blend).^[13] In this study it was shown that yielding of the Novatein matrix (and thus the ligaments) occurred at a calculated ligament thickness of 0.33 μm .

From previous literature^[21] it is possible to establish how stable crack propagation is during fracture in Novatein. During impact testing, pure Novatein and low CSP content blends show fully unstable crack growth, meaning that crazing is dominant, concurrent with other results. The introduction of elastomeric particles into the matrix (higher CSP content) stabilizes crack growth somewhat and induces cavitation and shear yielding of the matrix thereby inducing a larger plastic zone and more

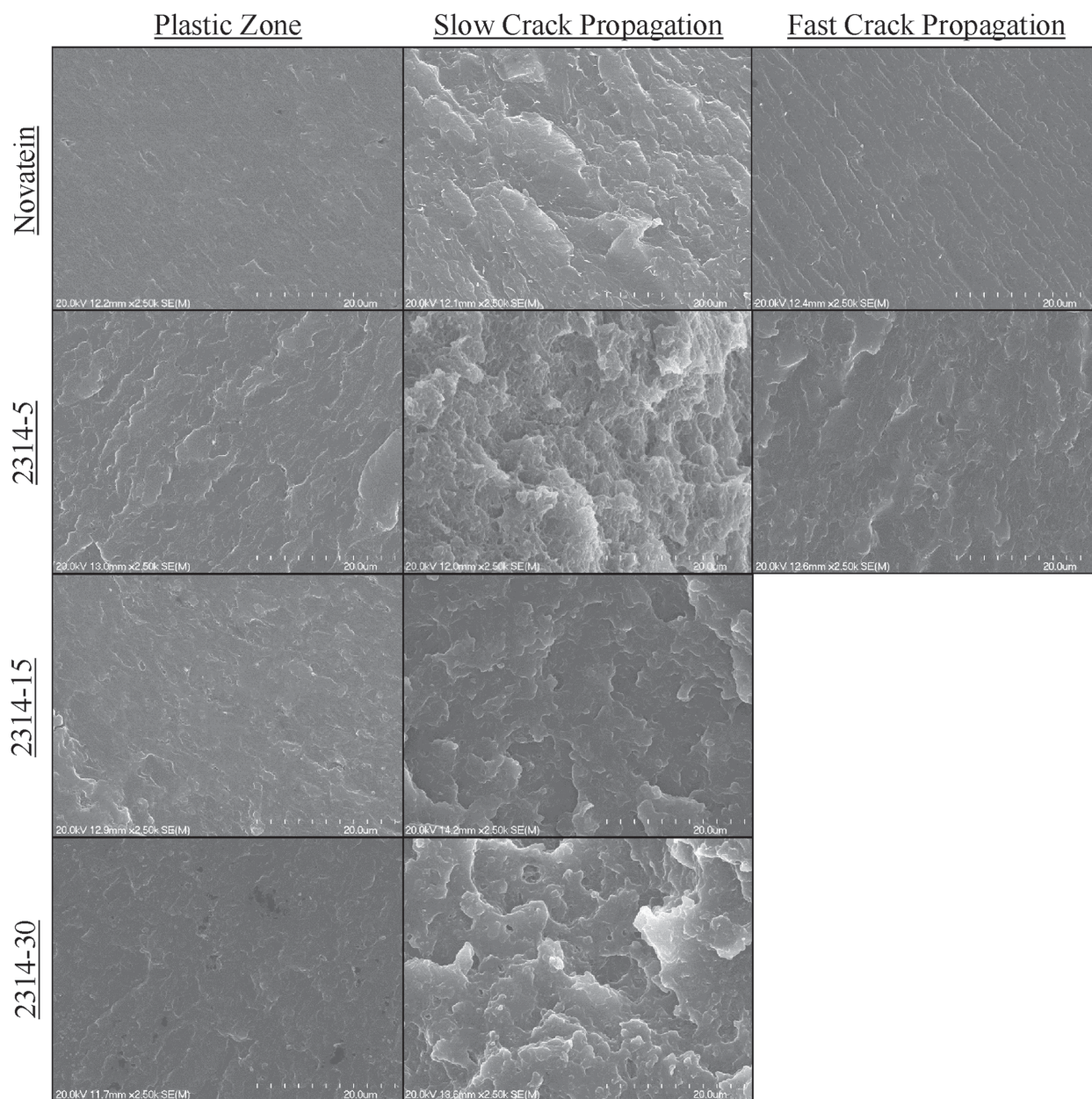


Figure 9. Microscopic features of plastic zone, slow crack propagation, and fast crack propagation regions in selected tensile fracture samples.

effective dissipation of energy. In contrast, tensile testing appears to bring about partially stable crack growth in Novatein and 2315–5, while the increase in CSP content causes the fracture to become fully stable, as there does not appear to be large-scale brittle fracture. This means that the critical craze stress is not reached and yielding as a result of thin matrix ligaments and cavitation dominates.

3.4.3. Microscopic Features of the Plastic, Slow, and Fast Propagation Zones

It is apparent that the plastic zone for Novatein and low CSP content samples were very similar, while intermediate and high CSP content samples also had a similar plastic zone, again pronouncing the brittle-to-ductile transition (Figure 9). The inclusion of CSPs for all samples brought about an increase of interrupted crazing, however this appears to become more pronounced at higher CSP content. The level of crazing in the slow crack propagation region appears to increase over that of the plastic zone, although this is to be expected as fracture progresses. Compared to Novatein, the high CSP content blend displayed large-scale plastic deformation and yielding, with no transition from ductile to brittle fracture. In the fast crack propagation region of Novatein and 2314–5, crazes appear large and uninterrupted as described previously, leading to a low level of energy absorption during tensile fracture.

Cavitation is also present in all samples containing CSPs, however it had a greater influence in samples that also showed significant yielding. At high magnification, the cavitation of CSPs is clearly visible (Figure 10) and when compared to a region of fast fracture it is evident that far more plastic deformation occurs, thereby facilitating energy absorption.

It has been argued that cavitation and debonding of particles is the main mechanism of toughening in thermosetting resins rather than a decrease of ligament thickness.^[18] However, both features relieve triaxial stresses

in the matrix and allow plastic yielding of ligaments. It must be noted that in a ductile matrix that is able to yield without cavitation, the debonding of particles will offer additional toughening, although the void formed as a result of this is not load bearing and the additional influence will not be drastic.

4. Conclusions

The mechanical properties and fracture mechanisms of Novatein thermoplastic protein were heavily influenced by the introduction of CSPs. Epoxy modified CSPs were better dispersed than unmodified CSPs and brought about better mechanical properties. The introduction of CSP's at a content of greater than ≈ 15 pph_{NTP} significantly increased the impact strength in both notched and unnotched samples. A CSP content of ≈ 10 pph_{NTP} caused a decrease in tensile strength and modulus, while strain-at-break and energy-to-break drastically increased. DMA revealed that both the peak in $\tan \delta$ associated with the T_g of the CSP rubber core, and the magnitude of the $\tan \delta$ peak associated with Novatein increased in magnitude with increasing CSP content. However, for Novatein it did shift to higher temperatures, attributed to the large effective area of the epoxy functionalized particles and resulting physical crosslinking, thereby causing decreased chain mobility in the protein matrix.

Novatein control samples in both tensile and impact testing showed highly brittle fracture, dominated by large-scale crazing with very little yielding. The high impact strength with increased CSPs was attributed to more effective energy dissipation in the plastic zone, a greater level of slow crack propagation and more chaotic crazing. Unnotched impact samples had a larger plastic zone than notched samples, yet the slow propagation zone size did not appear to change significantly as the CSP content varied. Plastic zones for unnotched and tensile samples were very similar for the Novatein

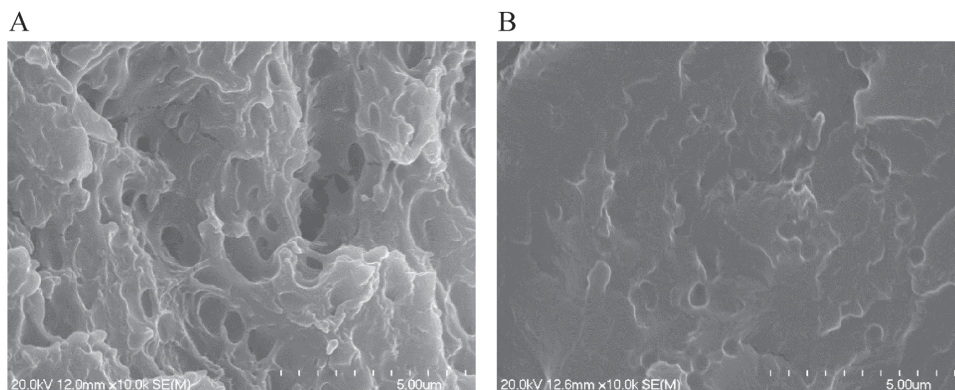


Figure 10. A) Cavitation in the plastic zone of 2314–5; B) fast crack propagation of 2314–5.

control. The intermediate and high CSP content blends, while appearing similar to each other, had plastic zones very different to Novatein due to the effect of the CSPs. There was variation in the plastic zones of the unnotched impact and tensile samples of the low CSP content blend attributed to rate of loading.

The large stress concentration in notched impact samples meant that the critical craze stress is easily reached and only limited yielding occurred. In this case, all blends showed highly brittle fracture through large-scale crazing, thereby absorbing very little energy in contrast to unnotched samples. Similarly, the Novatein control and low CSP content samples exhibited brittle behavior during tensile testing, while a CSP content of greater than 10 pph_{NTP} brought about large-scale yielding, cavitation, and little evidence of fast propagation, particularly at high CSP content. The introduction of CSPs caused stress concentrations to form in the matrix and also led to the transition from plane strain to plane stress of thin matrix ligaments that are thinner than τ_c , causing significant yielding.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This research was funded under the Extrusion Plus Project, SCION, New Zealand.

Received: January 26, 2016; Revised: March 14, 2016;
Published online: May 4, 2016; DOI: 10.1002/mame.201600043

Keywords: biopolymers; core–shell polymers; fracture mechanisms; impact resistance; thermoplastic protein

- [1] L. Chen, N. Reddy, X. Wu, Y. Yang, *Ind. Crops Prod.* **2012**, *35*, 1.
- [2] B. Cuq, N. Gontard, S. Guilbert, *Polymer* **1997**, *38*, 16.
- [3] D. Graiver, L. H. Waikul, C. Berger, R. Narayan, *J. Appl. Polym. Sci.* **2004**, *92*, 5.
- [4] S. Lukubira, A. A. Ogale, *J. Appl. Polym. Sci.* **2013**, *130*, 1.
- [5] N. Reddy, L. Chen, Y. Yang, *Ind. Crops Prod.* **2013**, *43*, 159.
- [6] J. Svenson, A. S. Walallavita, C. J. R. Verbeek, *Waste Biomass Valorization* **2013**, *4*, 1.
- [7] C. J. R. Verbeek, L. E. van den Berg, *J. Polym. Environ.* **2011**, *19*, 1.
- [8] C. J. R. Verbeek, L. E. van den Berg, *Macromol. Mater. Eng.* **2011**, *296*, 6.
- [9] B. Cotterell, J. Y. H. Chia, K. Hbaieb, *Eng. Fract. Mech.* **2007**, *74*, 7.
- [10] W. G. Perkins, *Polym. Eng. Sci.* **1999**, *39*, 12.
- [11] S. Bruce Brown, in *Polymer Blends Handbook* (Eds: L. A. Utracki, C. A. Wilkie), Springer, Dordrecht, The Netherlands **2014**, pp. 517–675.
- [12] M. Schneider, T. Pith, M. Lambra, *J. Mater. Sci.* **1997**, *32*, 23.
- [13] S. Wu, *J. Appl. Polym. Sci.* **1988**, *35*, 2.
- [14] J. Z. Liang, R. K. Y. Li, *J. Appl. Polym. Sci.* **2000**, *77*, 2.
- [15] A. Margolina, S. Wu, *Polymer* **1988**, *29*, 12.
- [16] R. Bagheri, R. A. Pearson, *Polymer* **2000**, *41*, 1.
- [17] K. Cho, J. H. Yang, B. Kang, C. E. Park, *J. Appl. Polym. Sci.* **2003**, *89*, 11.
- [18] A. F. Yee, R. A. Pearson, *J. Mater. Sci.* **1986**, *21*, 7.
- [19] S. Shi, E. Liu, T. Tan, H. Shi, T. Jiang, Y. Yang, S. Luan, J. Yin, Y.-W. Mai, R. K. Y. Li, *RSC Adv.* **2013**, *3*, 21563.
- [20] R. A. Pearson, A. F. Yee, *J. Mater. Sci.* **1989**, *24*, 7.
- [21] O. Julien, P. Béguelin, L. Monnerie, H. H. Kausch, in *Toughened Plastics II* (Eds: C. K. Riew, A. J. Kinloch), American Chemical Society, Washington, DC, USA **1996**, pp. 233–249.
- [22] B. Imre, B. Pukánszky, *Eur. Polym. J.* **2013**, *49*, 6.
- [23] T. Li, L. Turng, S. Gong, K. Erlacher, *Polym. Eng. Sci.* **2006**, *46*, 10.
- [24] R. J. Zhou, T. Burkhart, *J. Mater. Sci.* **2010**, *45*, 11.
- [25] K. P. Menard, *Dynamic Mechanical Analysis: A Practical Introduction*, 2nd ed., CRC Press, Florida, USA **2008**.
- [26] N. A. Memon, *J. Polym. Sci. Polym. Phys.* **1998**, *36*, 7.
- [27] D. Roylance, *Mechanics of Materials*, John Wiley & Sons, New York, USA, **1996**, p. 258.