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Manipulating morphology in thermoplastic protein/polyester blends for improved impact strength

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Abstract

Novatein thermoplastic protein was blended with 10 wt% poly(butylene adipate-co-terephthalate) (PBAT) compatibilized with Joncryl ADR-4368 and 2-methylimidazole (2MI). Morphology was tailored for favorable impact strength through changing viscosity ratio (λ) and interfacial tension (γ_{12}). For uncompatibilized blends, λ decreased and γ_{12} increased with increasing Novatein water content, whereas compatibilizers caused a decrease in both λ and γ_{12}. PBAT continuity was high when uncompatibilized, but dispersion improved with decreasing λ and increasing γ_{12}. The dispersed domain size decreased in all compatibilized blends; PBAT continuity was lowest in samples with the smallest λ. Compatibilized blends had higher impact strength than Novatein and uncompatibilized blends through improved interfacial adhesion, smaller domain size, and increased dispersion. By altering λ and γ_{12}, and with appropriate chemical interaction, a morphology can be created for improved impact strength. Increasing PBAT content showed further increases in impact strength; however, a cocontinuous morphology formed, demonstrating that composition can override the effect of λ and γ_{12}.

KEYWORDS
blends, impact resistance, morphology development, polyester, thermoplastic protein

1 | INTRODUCTION

Novatein thermoplastic protein is produced from bloodmeal, a waste product of the meat processing industry. It has low energy absorbing properties but can be improved to some extent through reactive polymer blending[1] or particulate reinforcement.[2]

Polymer blending is a solution for improving material properties; however, there is a fine balance between viscosity ratio, interfacial tension, and chemical reactivity to achieve the correct morphology. For binary blends of immiscible polymers, the breakup of the minor phase during processing is often governed by the ratio of shear stress to the interfacial stress, otherwise known as the capillary number (Ca).[3] Shear stress during processing is the driving force for the minor phase deformation, whereas interfacial tension resists the deformation. Hence, droplets will continue to break up during mixing as long as the shear stress is greater than the interfacial stress, a point which is quantified by the critical capillary number (Ca_{crit}).[4] In contrast, viscosity ratio (λ) governs the breakup time, which is why droplet formation is favoured when λ is lower and close to unity.[5] This situation becomes more complicated in ternary blends, and morphology is governed by the spreading coefficients and wettability of phases toward one another as shown in detail experimentally by Le Corroller and Favis.[6] Complex morphologies such as core-shell structures[7] and triple percolated (cocontinuous) phase structures[8] can be produced in ternary blends depending on the balance of all the aforementioned properties. It has also been stated that viscosity ratio plays less of a role in morphology development in ternary blends than interfacial tension.[9]

A large focus has been placed on the impact modification of biopolymers, such as polylactic acid (PLA), polyhydroxyalkanoates, and thermoplastic starch (TPS), due to their substandard energy absorbing properties, similar to Novatein.[10] For instance, the impact strength and other mechanical properties of PLA/polybutylene adipate-co-terephthalate (PBAT) blends were shown to increase drastically when compatibilized with functionalities such as epoxides[11] and anhydrides,[12] attributed to strong interfacial adhesion and formation of a dispersed droplet morphology. Other biopolymers have been shown to be effectively impact modified. For example, the impact strength and elongation of polyhydroxybutyrate-co-valerate (PHBV) could be enhanced by up to 120% when plasticized with epoxidized soybean oil.[13] Similarly, increased glycerol plasticizer content in TPS increased the impact resistance of TPS/polycaprolactone blends, albeit that the mechanism of modification is different to when relying on morphology.[14]

Polybutylene adipate-co-terephthalate is a synthetic rubbery biodegradable aliphatic-aromatic copolyester which has received considerable attention for its potential to modify the impact properties of polymers it is blended with.[15] For example, the inclusion of 20–30 wt% PBAT in a PLA matrix caused the impact strength to double compared to neat PLA, and triple when epoxy functionalized compatibilizer was added.[11,16,17] With good interfacial adhesion and dispersed droplet morphology, PBAT is a good candidate for impact modification in other biopolymer systems such as poly(trimethylene terephthalate).[18]

Novatein has previously been blended with biodegradable polyesters.[19–21] Blending with PBS, compatibilized with a dual system of poly-2-ethyl-2-oxazoline (PEOX), polymeric diphenyl methane diisocyanate (pMDI), brought about an increase in tensile energy-to-break,[19] while blends of Novatein and 10 wt% PBAT compatibilized with a GMA-modified styrene-acrylic copolymer (Joncryl) caused an increase in impact strength while tensile strength and elongation at break were maintained.[21] It was found that the Novatein/PBAT/Joncryl blend was the most promising, but improvements to mechanical properties were dependent on PBAT being present above a critical concentration, similar to particulate reinforced polymers. In a previous study,[2] using core-shell reinforced Novatein, the critical matrix ligament thickness was achieved at a particle content of 20 wt%, after which significant improvements were observed.

The previous study[21] examined compatibilization and compositional effects on morphology development in Novatein/PBAT blends. However, this investigation specifically examines the effect of changing viscosity ratio and interfacial tension on morphology development, while keeping the compatibilizer type and amount constant. The aim of this was to improve the energy absorbing properties of Novatein purely by tailoring the phase behavior of the minor component. This was carried out by altering the water content in Novatein (which is included as a processing aid with a plasticizing effect), which modifies both the viscosity and the interfacial tension.

2 | EXPERIMENTAL

2.1 | Materials

Novatein thermoplastic protein, comprising mainly of bloodmeal and a proprietary mixture of plasticizers and additives, was procured from Aduro Biopolymers LP, New Zealand. PBAT is an aliphatic-aromatic biodegradable polyester produced from 1,4-butanediol, adipic acid, and terephthalic acid. The grade used was BASF Ecoflex C1200 (MFI at 190°C, 2.16 kg = 2.7–4.9 g/10 min). Joncryl ADR-4368 is a multifunctional reactive coupling agent containing glycidyl methacrylate functionalities. Joncryl has an epoxy equivalent weight of 285 g/mol, molecular weight of 6,800 g/mol, and a functionality of 9.[22] Ecoflex and Joncryl were both sourced from Clariant, New Zealand. To catalyze epoxy ring opening, 2-methylimidazole (2MI) was acquired from Sigma-Aldrich, New Zealand.

2.2 | Processing

As received, Novatein granules (containing 36 $pph_{Bloodmeal}$ H_2O as a processing aid) was further hydrated over 7 days to produce Novatein containing 40, 60, and 80 $pph_{Bloodmeal}$ water to form Novatein 4020, 6020, and 8020, respectively. For compatibilized blends, the appropriate mass of 2-methylimidazole was dissolved in the water used for Novatein hydration, and upon the completion of rehydration, the Novatein/2MI granules were compounded with Joncryl in a LabTech corotating twin screw extruder (L/D 44:1) to form modified Novatein (m-4020, m-6020, m-8020). Previous studies determined that the optimal compatibilizer content for Joncryl/2MI systems was 70% of the PBAT phase but was limited to 5 wt% Joncryl and 2 wt% 2MI.

The relevant compositions of Novatein, m-Novatein, and PBAT (Table 1) were tumble mixed in ziplock bags prior to extrusion in the same corotating twin screw extruder. The extruder parameters were kept constant for processing modified Novatein and the subsequent blends. Temperature profile of the extruder was 70°C at the feed throat, 100–120°C along the main barrel section, increasing to 140°C at the die. Screw speed was 300 rpm.

A BOY 35A injection molding machine was used to produce test specimens. A barrel temperature profile of 100°C at the feed throat increasing to 150°C at the nozzle was used, and a temperature controlled mold was kept constant at 50°C. Conditioning of samples at 23°C and 50% RH for 7 days was carried out before testing.

TABLE 1 Blend compositions

Material/blend	Novatein (wt.%)	PBAT (wt.%)	Joncryl ADR-4368 (wt.%)	2-methylimidazole (wt.%)
4020	100	—	—	—
6020	100	—	—	—
8020	100	—	—	—
4020/PBAT-U	90	10	—	—
6020/PBAT-U	90	10	—	—
8020/PBAT-U	90	10	—	—
4020/PBAT-C	83	10	5	2
6020/PBAT-C	83	10	5	2
8020/PBAT-C	83	10	5	2
6020/PBAT30-C	63	30	5	2

2.3 | Analysis

Surface energy parameters of each material were determined using dynamic contact angle measurements of three solvents. Droplets of water, ethylene glycol (both polar), and diiodomethane (nonpolar) were placed onto a sample using an FTA1000B instrument (First Ten Angstroms, USA), and contact angle values were calculated from an average of six drops. The Young–Dupré equation[23] was used for surface energy calculations, and subsequently, the harmonic mean equation[24] was used to calculate blend interfacial tension.

Scanning electron microscopy was used to assess morphology. Impact fractured samples were mounted onto aluminum studs and placed into a Hitachi E-1030 ion sputter coater for platinum coating. The microscope used was a Hitachi S-4700 instrument, and the accelerating voltage used for imaging was 5 kV.

Dynamic mechanical analysis was carried out in single cantilever mode, from −80 to 150°C at a frequency of 1 Hz. A Perkin Elmer DMA 8000 instrument was used, and data were analyzed in Perkin Elmer's Pyris software. Injection molded impact bars were used for testing (thickness ~ 4 mm, width ~ 9 mm, free length ~ 13 mm) at a dynamic displacement of 0.05 mm. The conventional span-to-width ratio ~ 3.5 was not considered in this study for the convenience of using already prepared samples. This caused the storage modulus obtained to become closer to a shear modulus than a Young's modulus.

Viscosity ratio (λ) of blends was approximated as the ratio of the blend components complex viscosity (η*), from data obtained through unconditioned DMA testing of Novatein, modified Novatein and PBAT, with the same procedure described above. With the sample dimensions used, and by testing at a frequency of 1 Hz, complex modulus (E^*) approximates to complex shear modulus (G^*), from which η* (Equation 1) and λ (Equation 2) were calculated.

$$\eta^* = G/\omega \tag{1}$$

$$\lambda = \eta^*_{\mathrm{Novatein}}/\eta^*_{\mathrm{PBAT}} \tag{2}$$

Soxhlet extractions were conducted to remove PBAT from the blends using chloroform. Extractions were 18 hr long and performed in triplicate on samples (approximately 250 mg) sealed in 74-μm wire mesh. After the solvent extraction, samples were air-dried for 24 hr and oven-dried for a further 24 hr at 105°C. The final sample weight after extraction was corrected for the mass loss of pure Novatein and the mass fraction of Novatein in the blend (Equation 3); Novatein contains processing aids and plasticizers lost during drying and chloroform may also partially remove some additives in Novatein.

$$m_c = m_f + (m_i \times m_N) \times w_N \tag{3}$$

where m_c is corrected final sample mass, m_f is sample weight after extraction and drying, m_i is initial sample weight, m_N is the average percentage mass loss for pure Novatein after extraction and drying, and w_N is mass fraction of Novatein in the blend. Subsequently, mass loss (phase continuity) of PBAT in the blend could be calculated (Equation 4).

$$\text{Mass Loss} = (m_i - m_c)/m_i \times 100 \tag{4}$$

Moisture absorption of Novatein, PBAT, and blends was conducted on unconditioned, injection molded samples. These were submerged in a water bath (40°C) for 10 min. Before testing, and at each 1-min interval, samples were weighed and then placed back into the water bath. Testing was done in triplicate.

Injection molded samples were tensile tested using an Instron 33R4204 (ASTM D368) at a crosshead speed of 5 mm/min. A Ray-Ran Pendulum Impact System was used for Charpy impact testing, with a hammer weight of 0.952 kg and a speed of 2.9 m/s equating to an impact

TABLE 2 Surface energy parameters (mN/m), blend interfacial tension (mN/m), and viscosity ratio (Novatein/PBAT) for Novatein, modified Novatein, and PBAT

Material	γ^{TOT}	γ^{LW}	γ^{AB}	γ^{+}	γ^{-}	γ_{12}	λ
4020	37.81	30.99	6.81	0.39	30.62	3.93	1.44
6020	32.80	31.95	0.86	0.01	37.51	6.47	0.87
8020	30.59	30.42	0.18	0.00	26.05	8.78	0.58
m-4020	30.77	28.52	2.25	0.05	30.21	6.26	0.96
m-6020	36.33	35.09	1.24	0.02	37.07	4.56	0.79
m-8020	30.28	28.30	1.98	0.02	54.68	6.66	0.53
PBAT	53.46	48.19	5.27	1.05	6.64		—
Joncryl	50.74	48.30	2.43	0.27	5.50		—

energy of 4 J. Samples were tested in an edgewise orientation. For notched samples, an in-house built notch cutter was used (ISO 179).

3 | RESULTS AND DISCUSSION

3.1 | Surface energy, interfacial tension, and viscosity ratio

The harmonic mean equation was applied to calculate the blend interfacial tension (γ_{12}) using the measured solid surface energy of each blend component (Table 2). In blends containing reactive functionalities, the eventual composition of the interface is unknown, making the harmonic mean equation less accurate. However, it can be approximated as being inversely proportional to the interfacial thickness L (although it has been shown that $\gamma_{12} = 7.6L^{-0.86}$).[5]

For the unreactive systems, γ_{12} showed an increase in γ_{12} with increasing water content, brought about due to the decrease in polarity of Novatein. The dispersive component (γ^{LW}) for all Novatein formulations was relatively unaffected by changing water content or the inclusion of compatibilizer, meaning that the changes in interfacial tension are dictated by the polar component (γ^{AB}). It is known that the greater the polarity difference between blend components, the higher the interfacial tension will be.[5] Water, which is polar, interacts heavily with hydrophilic groups present along the protein backbone, which in turn causes aggregation of these groups. This exposes more apolar hydrophobic groups, leading to the decrease in polarity. This is supported by a decrease in both γ^{+} and γ^{-} signifying less electron acceptor/donor sites and less hydrogen bonding sites[25] due to the greater interaction of water with the protein.

The interfacial thickness of the compatibilized blends could not be measured, but based on using the harmonic mean equation it showed that γ_{12} fluctuated compared to uncompatibilized blends (Table 2); however, the exact composition of the interface is unknown. With m-4020, processing difficulties required high temperature and pressure for the material to be molded. This means that there are two possible reasons for the fluctuation; either the inclusion of Joncryl causes γ_{12} of all the blends to become similar (within reason) or the processing difficulties faced with m-4020 caused γ_{12} to be inaccurate. Furthermore, when incorporating compatibilizers into a blend, the interfacial tension is expected to drop, hence the latter situation is more likely. A decrease in γ_{12} tends to bring about a better dispersion of the minor phase, which occurs in this case, and is explained later.

The viscosity ratio decreased with increasing water content, as the increased water allowed for improved chain mobility, thereby producing a viscosity closer to PBAT. The values for λ are probably underestimated, as PBAT's viscosity drops more rapidly than Novatein's. Viscosity ratio was measured at 100°C and would be much higher at higher temperatures. However, the order of λ in the blends was 4020 > 6020 > 8020 and would remain in that order at higher temperature. What the results revealed was that blends with higher water content, that is 8020, will have a better dispersion of PBAT, and λ will likely be closer to unity.

The introduction of Joncryl/2MI compatibilizer reduced λ in all systems, likely due to the plasticization effect of the compatibilizer system. The most prominent change was seen in the m-4020 blend, whereas m-6020 and m-8020 systems only showed small decreases in λ, as these were already highly plasticized. These results suggest that the compatibilizer brings λ closer to unity during processing and would lead to a better dispersion of the minor phase.

3.2 | Morphology development

Scanning electron microscopy was used to assess the changes in morphology between Novatein, uncompatibilized, and compatibilized blends. It is known that Novatein fracture surfaces are featureless, with little plastic deformation. This observation is true regardless of water content (Figure 1). In contrast, the addition of 10 wt.% PBAT to Novatein brings about a heavily phase separated blend, with little to no interfacial interaction. With PBAT being hydrophobic and Novatein being hydrophilic, a lack of adhesion between phases is expected without compatibilizers present.

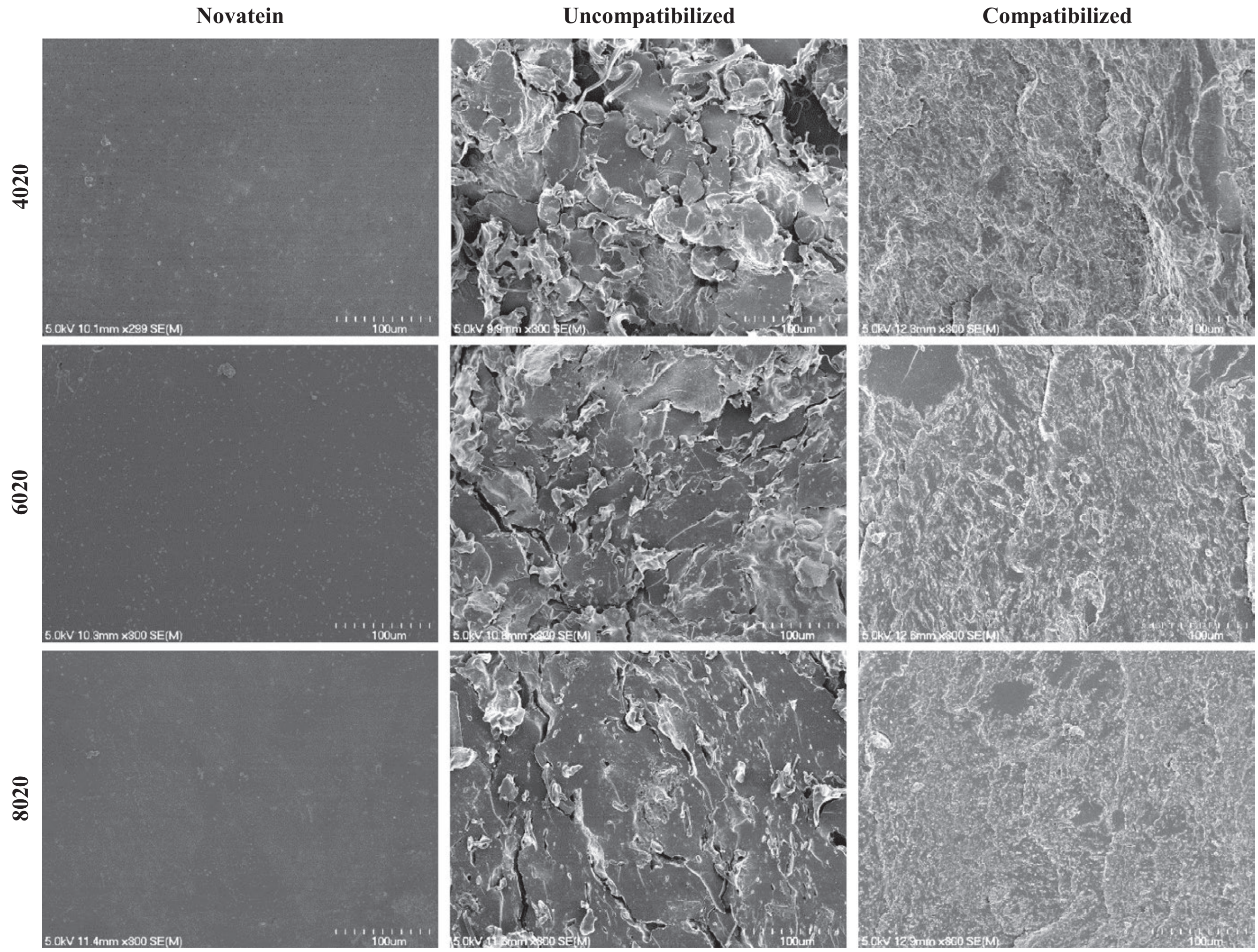

FIGURE 1 Scanning electron micrographs (×300 mag.) of notched impact fracture surfaces for Novatein, uncompatibilized, and compatibilized blends with varying water content

For uncompatibilized blends, the water content influenced the blend morphology strongly. In 4020/PBAT-U, and to some extent 6020/PBAT-U, PBAT encapsulated discrete regions of Novatein suggesting a percolated network of PBAT. It is known that the onset of percolation is less than 10 wt.% in Novatein when uncompatibilized.[21] On the other hand, PBAT appeared far better dispersed in 8020/PBAT-U; a result that was anticipated based on the high interfacial tension and lower viscosity ratio.

The inclusion of Joncryl and 2-methylimidazole changed the morphology of the blend drastically. The PBAT phase became better distributed and although there were some large domains of discrete Novatein (ranging up to 100 μm), the dispersion of PBAT was also greatly improved. On a macro-scale, it appeared that water content did not play a significant role in terms of the morphology developed during processing.

However, on a micro-scale, significant differences in morphology were present as water increased (Figure 2). At low water content, it was challenging to tell the two phases apart, although this is reminiscent of the Novatein/PBAT system presented previously.[21] For that system, it was established that a very fine cocontinuous network of PBAT had percolated throughout a Novatein matrix despite the appearance of a mostly homogeneous surface. In contrast, 6020/PBAT-C and 8020/PBAT-C showed discrete regions of PBAT dispersed through a Novatein matrix. These regions range from submicron to micron size. Some domains appeared to be connected to one another, suggesting that some percolation may have occurred in these samples, but on the whole a finely dispersed second phase was observed.

To further understand the morphology of the blends, soxhlet extraction was conducted with chloroform to remove any accessible PBAT while leaving the Novatein phase intact (Table 3). In the case of solvent extraction in polymer blends, the terms mass loss and continuity can often be used interchangeably. This is because with selective phase removal, the greater the mass that is lost directly correlates to the interconnectedness of the minor phase. With percolation often comes encapsulation of the major phase at some level, meaning it is feasible to lose greater mass than the wt% of the minor phase

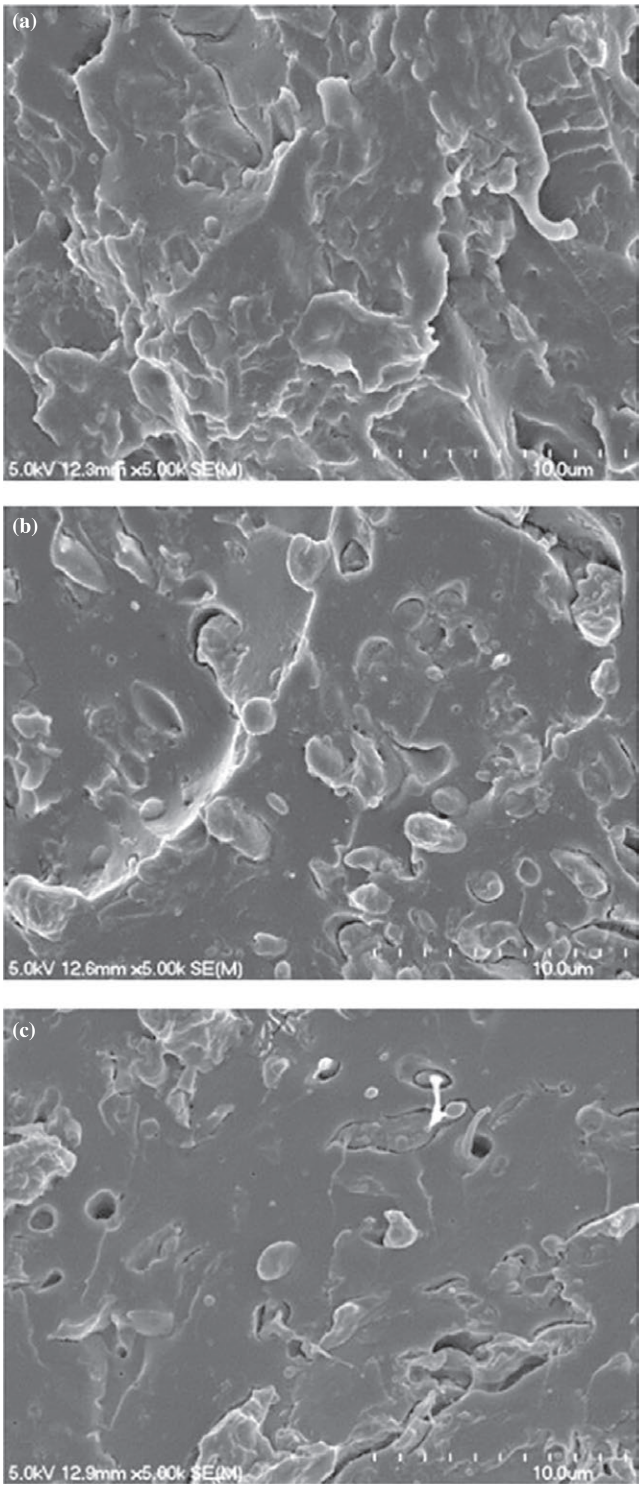

FIGURE 2 High magnification scanning electron micrographs (×5,000 mag.) of notched impact fracture surfaces. (a) 4020/PBAT-C; (b) 6020/PBAT-C; (c) 8020/PBAT-C

added, as the discrete particles of the major phase are also washed away.

In pure Novatein, mass loss increased with increasing water content, attributed to the greater starting amount of moisture that is lost in the drying phase after extraction. In

TABLE 3 Mass loss data from Novatein, uncompatibilized, and compatibilized blends after soxhlet extraction

Material/blend	Average mass loss (%)
4020	3.1 ± 0.3
4020/PBAT-U	27.9 ± 0.4
4020/PBAT-C	30.3 ± 1.3
6020	12.3 ± 0.2
6020/PBAT-U	25.1 ± 0.2
6020/PBAT-C	17.1 ± 0.2
8020	18.3 ± 0.5
8020/PBAT-U	23.4 ± 0.5
8020/PBAT-C	14.3 ± 1.0

uncompatibilized blends, mass loss increased dramatically compared with Novatein; however, the greatest mass loss (or PBAT continuity) was seen in 4020/PBAT-U, and the least in 8020/PBAT-U. This is in agreement with the SEM analysis, whereby it was determined that increasing water content caused the PBAT phase to become better dispersed, as a result of more favorable interfacial tension and viscosity ratio. However, a significant level of coalescence of the minor phase was present in all blends, despite the well-dispersed appearance in the SEM images. This highlights the need for multiple analysis techniques, as SEM only focusses on the sample in two dimensions.

With the inclusion of Joncryl/2MI, continuity of PBAT decreased greatly with increasing water content, supporting the theory that PBAT becomes much better dispersed. In 8020/PBAT-C, the mass loss dropped below that of pure Novatein, suggesting a substantial chemical change in the sample, attributed to the strong interfacial adhesion brought about by the Joncryl/2MI compatibilizer. In contrast though, the mass loss for 4020/PBAT-C showed a small increase. This tells us that although the PBAT appeared well dispersed on a macroscale, there was actually a substantial level of percolation of the PBAT phase throughout the Novatein matrix. At higher temperature, the increased λ of 4020/PBAT-C compared with 8020/PBAT-C facilitated coalescence, while the decrease in γ_{12} facilitated dispersion and a fine phase structure, hence the fine percolated phase structure of the lower water content sample.

The predicted morphology was confirmed through electron microscopy of the samples after soxhlet extraction. It was clear to see that the Novatein phase appeared less granular with increasing water content (Figure 3), highlighting the decreased percolation and better dispersion of PBAT. Similarly, the comparison of uncompatibilized blends with the relevant compatibilized samples showed that the minor phase became very finely dispersed with the inclusion of the compatibilizer (Figure 3). Phase size decreased from hundreds of microns

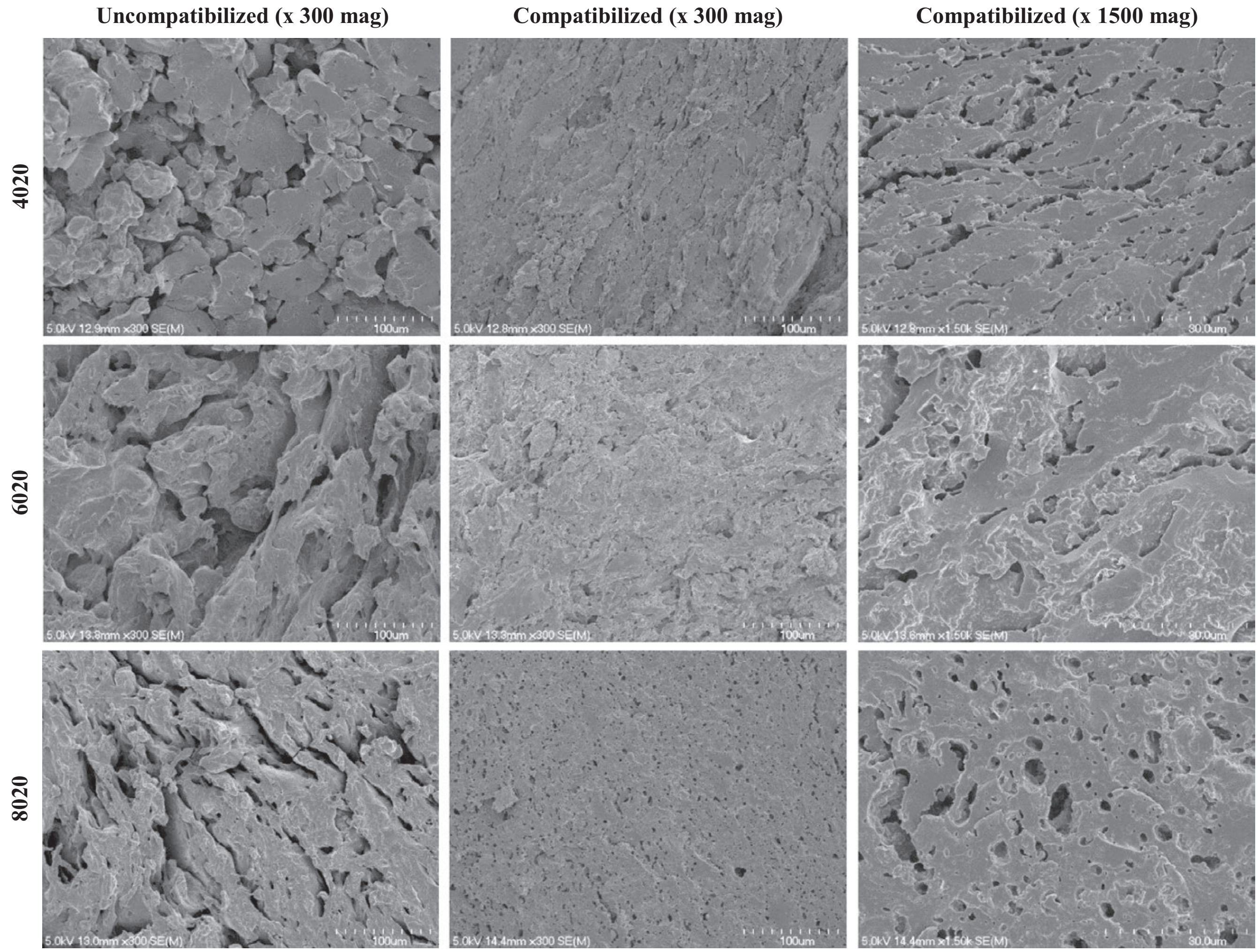

FIGURE 3 Scanning electron micrographs (×300 mag. and ×1,500 mag.) of the Novatein phase of uncompatibilized and compatibilized blends with varying water content, after soxhlet extraction of poly(butylene adipate-co-terephthalate)

in some cases, down to <5 μm; however, it appeared that the extracted domains in 8020/PBAT-C were more spherical than those in 6020/PBAT-C and 4020/PBAT-C, highlighting that viscosity ratio and interfacial tension are not completely overwhelmed by chemical interaction when forming morphologies in thermoplastic protein blends.

When looking more closely at the compatibilized samples, micro-domains remained after extraction (Figure 4), with some appearing as small as 500 nm in size. These domains were thought to be Joncryl, as PBAT would have been removed via the chloroform wash. These domains were found predominantly at what would have been the interface between Novatein and PBAT, although there was Joncryl seen in the Novatein phase as well, in both 6020/PBAT-C and 8020/PBAT-C. This suggests that a ternary blend had been produced, whereby the third component (Joncryl) compatibilizes the other two components.

Spreading coefficients can be calculated for ternary blends to predict the morphology based on the interfacial tension between blend components. Using the surface energy values for Novatein, PBAT, and Joncryl, and the method extensively described by Le Corroller and Favis,[6] the morphology predicted for Novatein/PBAT/Joncryl blends was as follows: in 4020/PBAT-C, the Joncryl phase would show complete wetting, locating exclusively in the PBAT phase, while in 6020/PBAT-C and 8020/PBAT-C, Joncryl would spread between the Novatein and PBAT phases evenly. In reality, Joncryl exhibits partial wetting, forming micro-domains whereby a line of contact is likely between all phases, due to the complex balance of viscosity ratio, interfacial tension, and the influence of chemical functionalities present on Joncryl. Polypropylene/polyethylene/polystyrene ternary blends fit the model exceptionally well[6]; however, the Novatein blends presented here did not appear to follow the same trend, suggesting that the influence of chemical functionality plays a significant role in morphology development, rather than just γ_{12} and λ.

Water absorption testing can also be used to establish morphology in the case of Novatein blends (Figure 5). Pure Novatein 4020 and 6020 both increased in mass ~16% after

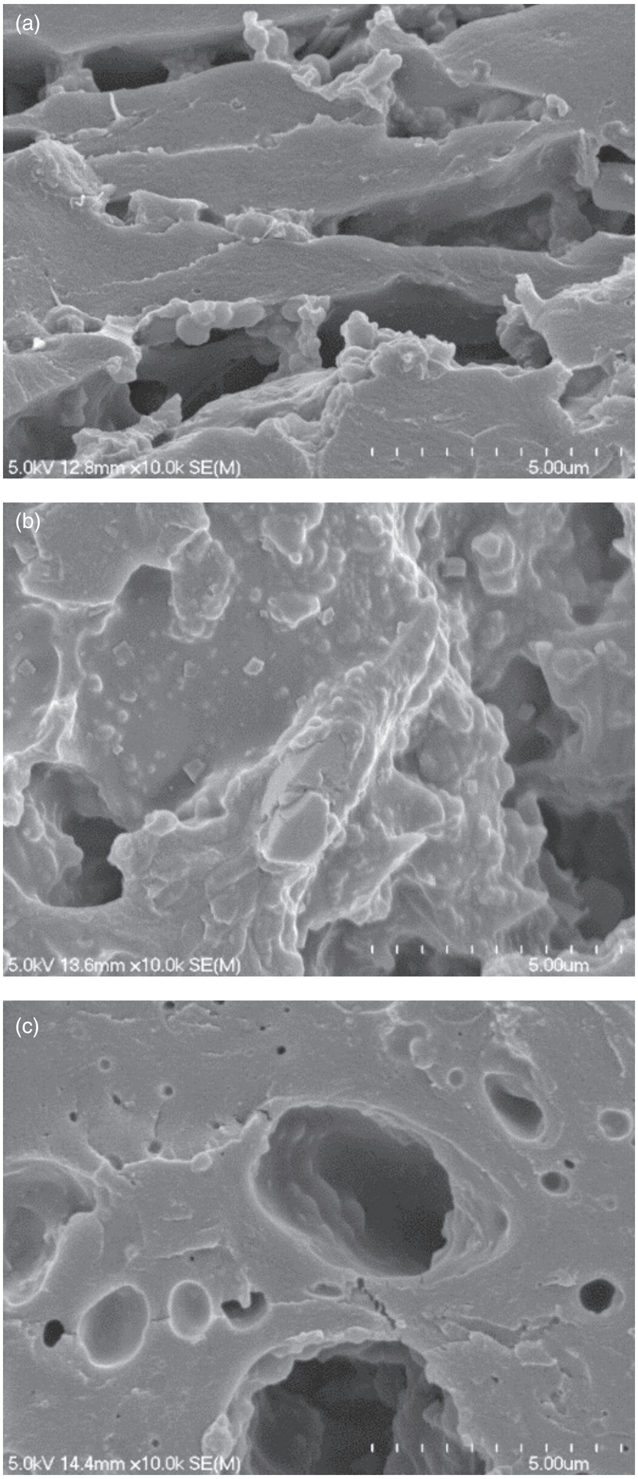

FIGURE 4 High magnification scanning electron micrographs (x 10000 mag.) of samples after soxhlet extraction. (a) 4020/PBAT-C; (b) 6020/PBAT-C; (c) 8020/PBAT-C

10 min in the water bath. This decreased to ~12% in Novatein 8020, attributed to the higher starting moisture content and increased hydrophobicity as described earlier. In comparison, PBAT's moisture absorption was negligible, with a mass increase of 0.3% after 10 min.

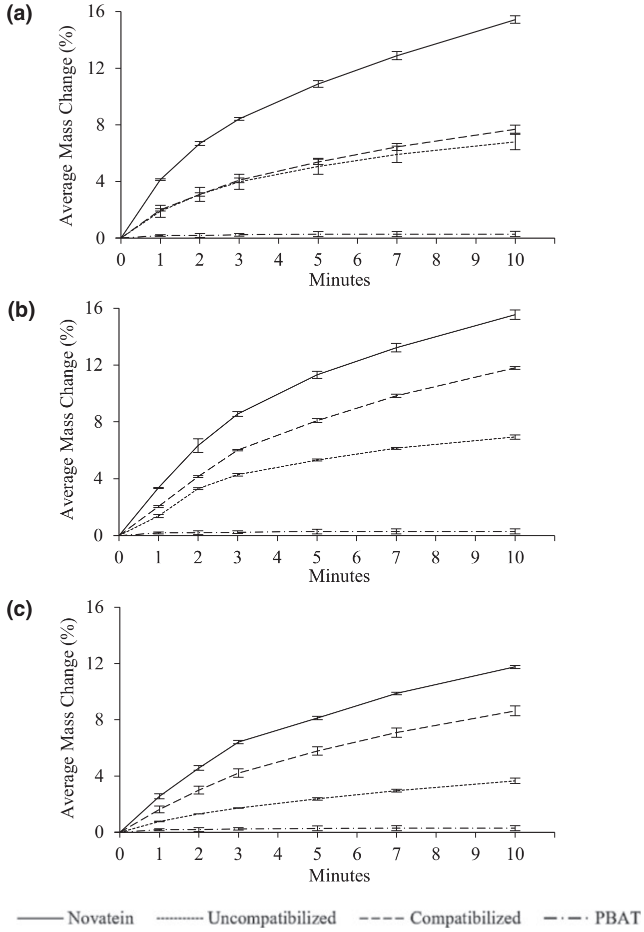

FIGURE 5 Moisture absorption data for (a) 4020 and blends; (b) 6020 and blends; (c) 8020 and blends

Interestingly, for all water contents, the compatibilized blends showed an increased change in mass compared to the uncompatibilized samples. The encapsulation of Novatein by PBAT in the uncompatibilized blends protected the protein phase, meaning less Novatein was available for the uptake of water. On the other hand, the greater dispersion of PBAT in compatibilized blends allowed Novatein to become more accessible to water, leading to greater moisture uptake. It should be noted that the mass change values for compatibilized blends were still far below pure Novatein, highlighting both the fact that there was some degree of percolation and protection from the PBAT phase and also that the chemical change in the blend at the interface between Novatein, Joncryl/2MI, and PBAT occurred at reactive functionalities that otherwise would have been involved in interactions with water.

Dynamic mechanical analysis, in particular storage modulus (E'), is helpful when determining morphology of blends. The modulus values will tend to mimic the matrix in a blend with a dispersed second phase; however, upon percolation of the minor phase, E' becomes an intermediate of the two. This is useful for determining whether the minor phase is

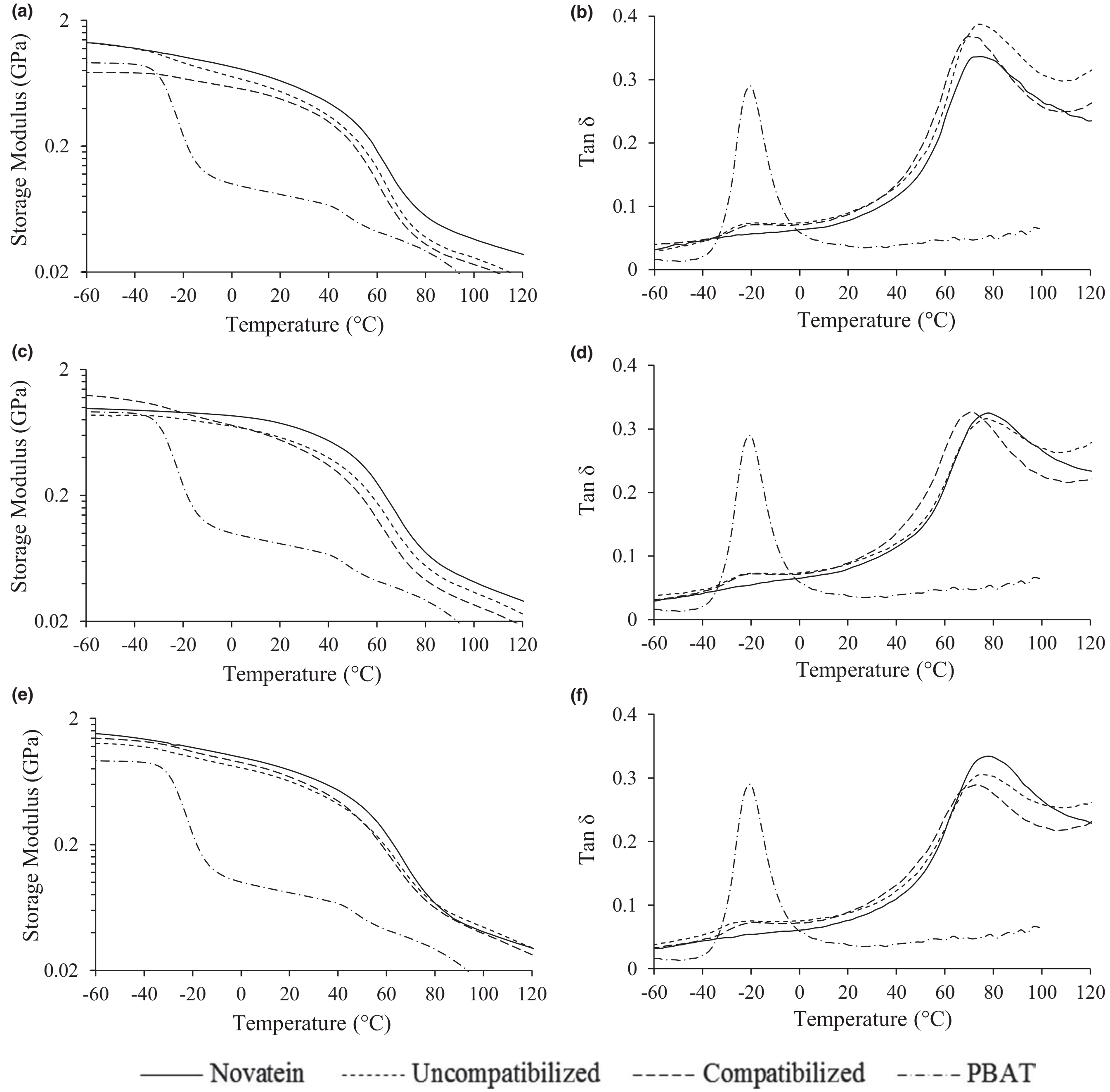

FIGURE 6 DMA plots for Novatein, poly(butylene adipate-co-terephthalate), and blends showing storage modulus (E') and tan δ of; (a and b) 4020; (c and d) 6020; (e and f) 8020

truly dispersed or whether a cocontinuous phase structure is formed.[26]

The E' plots for Novatein, PBAT, and blends (Figure 6) confirm the conclusion that with increasing water, a better dispersion of the minor phase was achieved. For 4020 and 6020 blends (Figure 6a,c), E' decreased compared to Novatein due to the effect of the onset of PBAT coalescence, whereas in comparison, the 8020 blends (Figure 6e) are very similar to the neat Novatein as the PBAT phase is well dispersed.

In the tan δ plots, PBAT showed a strong peak at −20°C, while Novatein had a major transition at ~80°C. Both of these peaks are attributed to the materials respective T_g's. With regard to all blends, the small PBAT T_g peak was visible at ~20°C and did not shift as a result of blending with Novatein or with the inclusion of Joncryl/2MI. Similarly, the Novatein T_g peak did not shift in the uncompatibilized blends, but the inclusion of compatibilizer caused a decrease in the Novatein T_g by 5–10°C. Also of interest was the decrease in magnitude of the Novatein peak in compatibilized blends with increasing water content attributed to increased energy absorption of the minor PBAT phase.

TABLE 4 Mechanical properties of Novatein, uncompatibilized, and compatibilized blends

Blend	Tensile strength (MPa)	Strain-at-break (%)	Secant modulus (MPa)	Energy-to-break (kPa)	Impact strength (kJ/m^2)	
					Notched	Unnotched
4020	15.1 ± 2.1	2.2 ± 0.6	948 ± 104	201.6 ± 92.4	0.56 ± 0.20	1.54 ± 0.49
4020/PBAT-U	5.2 ± 0.2	0.9 ± 0.1	765 ± 67	31.4 ± 4.3	1.07 ± 0.13	1.28 ± 0.15
4020/PBAT-C	8.8 ± 0.9	1.8 ± 1.2	709 ± 44	95.6 ± 27.4	1.07 ± 0.27	2.99 ± 0.48
6020	15.3 ± 1.5	14.1 ± 8.6	815 ± 115	1792.6 ± 1159.4	0.68 ± 0.27	1.71 ± 0.53
6020/PBAT-U	7.3 ± 0.4	2.2 ± 0.2	584 ± 34	109.1 ± 19.2	1.09 ± 0.18	1.30 ± 0.14
6020/PBAT-C	10.2 ± 0.6	3.9 ± 0.7	576 ± 68	265.5 ± 72.8	0.93 ± 0.19	3.84 ± 1.22
6020/PBAT30-C	9.9 ± 0.1	12.5 ± 1.1	391 ± 24	1031.9 ± 110.5	3.4 ± 0.3	15.6 ± 2.7
8020	15.0 ± 1.3	19.1 ± 15.2	791 ± 112	2386.3 ± 1996.4	0.82 ± 0.37	1.40 ± 0.34
8020/PBAT-U	8.3 ± 0.7	2.4 ± 0.4	612 ± 35	134.3 ± 34.8	1.02 ± 0.46	1.64 ± 0.40
8020/PBAT-C	9.0 ± 0.4	3.5 ± 0.8	577 ± 66	171.9 ± 77.6	0.99 ± 0.22	4.64 ± 1.64

3.3 | Mechanical properties

After conditioning to equilibrium moisture content, the tensile strength of Novatein was ~15 MPa regardless of water content (Table 4). However, with increasing water, strain-at-break increased drastically from ~2% in 4020 to ~20% in 8020, attributed to increased water before processing, which was found to have a significant effect on Novatein's mechanical properties after conditioning.[27] However, the deviation seen in strain-at-break for Novatein 6020 and 8020 was extremely large, and the calculated standard error for both groups (6.19 and 3.86 for 6020 and 8020, respectively) suggests that these mean values do not truly represent the sample group. Novatein has poor impact resistance, with notched impact strength falling between 0.5 and 1 kJ/m^2 for all Novatein formulations, while unnotched impact strength does not exceed 2 kJ/m^2.

The addition of PBAT to the blends caused a decrease in all tensile properties attributed to the poor interfacial adhesion between Novatein and PBAT. In contrast, there was an increase in notched impact strength and a maintenance of unnotched impact strength. It has been previously stated that a cocontinuous morphology is conducive to improved impact resistance, and in this case, it is likely that the PBAT phase was able to absorb much of the energy during fracture due to its continuous nature, despite the lack of adhesion between phases.

With the addition of Joncryl/2MI compatibilizer to the Novatein/PBAT system, there was increased tensile strength in all blends, but no significant change to strain-at-break, hence little change was seen in energy-to-break also. Secant modulus decreased slightly, potentially due to the low molecular weight of the Joncryl and 2MI (6,800 and 82 g/mol, respectively). Notched impact strength was maintained compared with uncompatibilized blends, while unnotched impact strength was doubled in 4020/PBAT-C and tripled in 8020/PBAT-C, with 6020/PBAT-C being intermediate of the two.

The mechanical properties presented from the compatibilized blends are underwhelming, considering that the morphology achieved appeared conducive to improved energy absorption. However, it is known that for Novatein reinforced with elastomeric core-shell particles, the critical reinforcement level needed for improvement in energy absorption was ~15–20 wt%,[2] while in reactive Novatein/polyethylene blends, this point was >20 wt% for some blends.[1] Furthermore, it has been shown that optimal properties of Novatein/polybutylene succinate (PBS) blends have a PBS content of >30 wt%.[19] This suggests that the 10 wt% PBAT included in blends in this study falls below the critical composition, hence a sample with 30 wt% PBAT (aiming to be above the composition threshold) was tested in Novatein 6020 as comparison.

3.4 | Effect of composition

Composition has a large influence on morphology development and subsequently mechanical properties; with increasing minor phase content, the likelihood of percolation is greater, hence a larger contribution of the minor phase is made to the material properties. Table 4 shows that 6020/PBAT30-C (30 wt% PBAT) showed substantial increases to both notched and unnotched impact strength compared with 6020/PBAT-C, as well as a maintenance of tensile strength and comparable strain-at-break to neat Novatein. There was also very little spread of values for 6020/PBAT30-C, as shown by the small standard deviations, suggesting good reproducibility. Of the 30 wt% PBAT samples, only the secant modulus was significantly less than the 10 wt% blend, but this is to be expected as neat PBAT has a much lower secant modulus (64 MPa) than Novatein. From this analysis, it was concluded that the critical composition was above 10 wt%

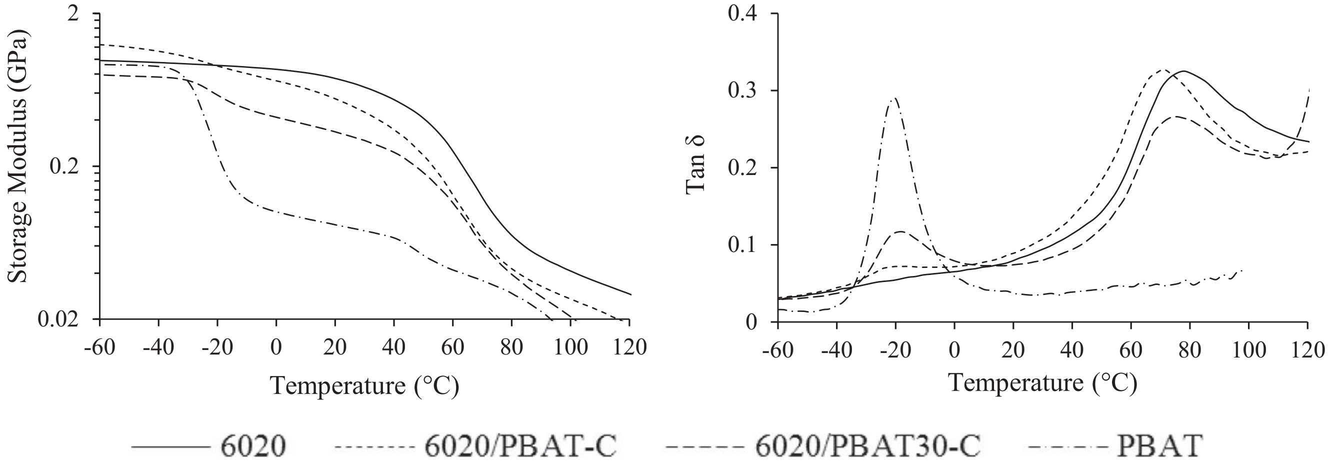

FIGURE 7 DMA plots for Novatein 6020, poly(butylene adipate-co-terephthalate), and 6020 blends showing storage modulus (E') and tan δ

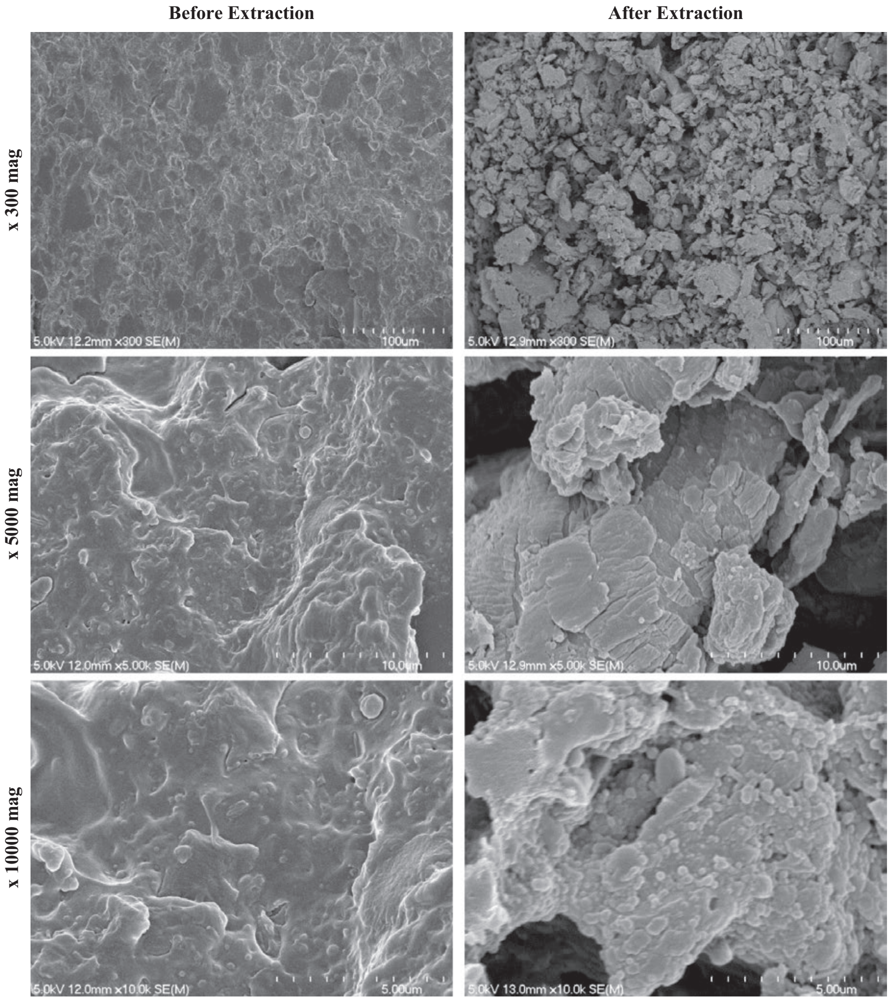

FIGURE 8 Scanning electron micrographs (×300 mag., ×5,000 mag., ×10,000 mag.) of 6020/PBAT30-C, before and after soxhlet extraction of PBAT

PBAT and that the 30 wt% sample was above this compositional threshold for improved energy absorption.

The comparison of DMA data for samples containing 10 and 30 wt% PBAT (Figure 7) shed light on the change in morphology with increasing minor phase. Storage modulus clearly showed a decrease in 6020/PBAT30-C, compared with the 10 wt% sample, highlighting the percolation of PBAT and the formation of a cocontinuous phase structure. Similarly, the increase in the PBAT peak in tan δ and corresponding decrease in magnitude of the Novatein T_g peak showed that the

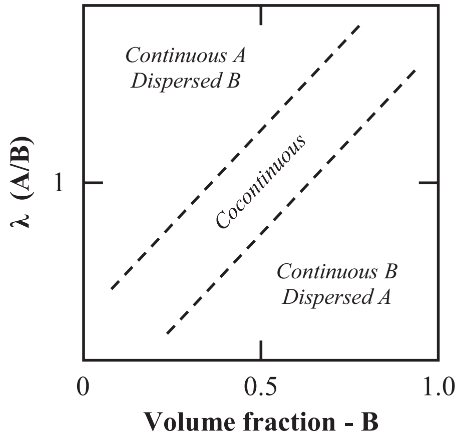

FIGURE 9 Relationship between composition and viscosity ratio with reference to morphology development[26]

PBAT phase had a bigger contribution in the absorption of energy. Similarly, the solvent extraction data of 6020/PBAT30-C showed a large increase in PBAT continuity compared to 6020/PBAT-C (10 wt% PBAT) (51.8 % and 17.1 % mass loss, respectively). This confirms the DMA findings that the PBAT phase is highly percolated throughout Novatein.

On a macro-scale, there appeared to be a homogeneous phase structure with high levels of plastic deformation as a result of the notched impact fracture (Figure 8), which brings about the improvement in impact strength. There were noticeable regions of Novatein, likely due to encapsulation by percolated PBAT. When magnified (Figure 8), it is apparent that there are phase separated micro-domains (some <0.5 μm in diameter). It is suggested that the micro-domains seen are Joncryl, as described previously, while the PBAT phase is highly continuous and cannot be distinguished from the Novatein phase. This is in agreement with the DMA and soxhlet analysis, which suggests a fully cocontinuous structure.

When examining 6020/PBAT30-C samples after soxhlet extraction, the cocontinuity becomes apparent. The mass loss was particularly high for the 30 wt% sample, losing ~52% mass, compared to ~17% mass for the corresponding 10 wt% sample. The macro-scale SEM image (Figure 8b) showed a somewhat granular structure to the Novatein phase after PBAT extraction. This may suggest that a phase inversion is likely to take place at compositions close to 30 wt% PBAT. Higher magnification images (Figure 8d,f) show that the Joncryl micro-domains seen in the notched impact fracture surface of the same sample are still present after extraction, again situating at what would be a three-way phase interface.

There is a well-known relationship between viscosity ratio and blend composition, whereby increasing minor phase content causes the onset of percolation before a phase inversion occurs (Figure 9).[26] The results from this study showed that composition had an overriding effect on morphology in Novatein/PBAT blends. The amount of PBAT was above the critical level for impact modification of Novatein and this was accompanied by a significant change in morphology. Both the Novatein phase and the PBAT phase were highly continuous, indicated by the high mass loss during soxhlet extraction, and the remaining Novatein phase being intact after extraction. It was concluded that the increase in PBAT wt% pushed the blend from being mostly dispersed PBAT in a Novatein matrix (albeit with some degree of interconnectedness) into the cocontinuous region displayed in Figure 9. This is in spite of the favorable viscosity ratio, interfacial tension, and chemical interaction demonstrated earlier.

The morphology developed in Novatein/PBAT blends can be tailored by altering viscosity ratio and interfacial tension through varying water content. The introduction of chemical functionalities in the form of Joncryl caused the influence of these parameters to become less, although not entirely unimportant. The development of phase structure in Novatein blends, at lower minor phase content, is a fine balance between viscosity ratio, interfacial tension, and chemical reactivity, and predictions must include all three parameters, although the latter appeared to play a greater role at lower minor phase content. As demonstrated here, however, composition can have an overriding effect of these parameters. Further study of this system must be concerned with establishing whether Novatein can be sufficiently impact modified, while the PBAT phase remains well dispersed, or if the onset of cocontinuity is the driving force behind high impact strength in Novatein blends.

4 | CONCLUSIONS

The morphology of Novatein/PBAT blends was successfully manipulated by altering interfacial tension (γ_{12}), viscosity ratio (λ), and chemical interaction, thereby producing an impact modified material. For uncompatibilized systems, increasing water content in Novatein caused an increase in γ_{12} and a decrease in λ, leading to better dispersion of PBAT. Coalescence was still high in all uncompatibilized blends, while the inclusion of Joncryl/2MI caused a decrease in both γ_{12} and λ which brought about a drastic reduction in phase size and coalescence of PBAT. This level of coalescence followed the same trend as uncompatibilized blends (4020 > 6020 > 8020); however, the relative change in continuity was much larger with Joncryl included. Moisture uptake of compatibilized samples was higher than uncompatibilized samples due to the protection that the continuous PBAT phase offered Novatein in the absence of Joncryl. DMA offered similar conclusions, whereby E' for the low water content blends tended more toward neat PBAT than compatibilized blends or higher water content blends, signifying greater continuity of the minor phase. The mechanical properties of compatibilized blends were far improved over those without Joncryl, attributed to the fine phase structure and good interfacial adhesion. Impact strength of compatibilized blends was greater than pure Novatein, regardless of water content, with unnotched impact strength increasing at least double, and threefold in the case of 8020/PBAT-C.

When PBAT content was increased to 30 wt%, it was highly continuous and indistinguishable from the Novatein phase. This was in agreement with the DMA and solvent extraction data, which suggested a fully cocontinuous structure. This blend (6020/PBAT30-C) showed substantial increases to both notched and unnotched impact strength compared with the 10 wt% blend, as well as a maintenance of tensile strength and strain-at-break. The amount of PBAT was above the critical level for impact modification of Novatein and this was accompanied by a significant change in morphology. It was concluded that the development of phase structure in Novatein blends, at low minor phase content, is a fine balance between viscosity ratio, interfacial tension, and chemical reactivity; however, composition can have an overriding effect.

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