4 RESULTS AND DISCUSSION

The raw data are given in Appendix C as the average values measured together with the standard deviations. Owing to the nature of the materials studied here, the precision of the data is low. For clarity of data trends, the standard deviations are not indicated in the figures presented.

4.1 Thermoplastic Starch

4.1.1 Extrusion

The TPS extrudate obtained using the Berstorff twin-screw extruder was hard, brittle and glassy, even for formulations with a plasticiser content of up to 25%, with barrel temperatures at 100 °C throughout all barrel zones. Different temperature settings were also evaluated along the entire profile. At temperatures higher than 100 °C, the resulting extrudate was light brown in colour and smelled slightly burnt (like caramel). Adding additional water to the mixture yielded a foamed, brittle material. These observations indicate degradation of the starch owing to the high shear generated in the twin-screw machine. Since extrudate with good mechanical properties could not be obtained, the Berstorff twin-screw extruder was not used for the preparation of thermoplastic starch and its blends. Instead, the Rapra single-screw extruder was used throughout this work for the preparation of thermoplastic starch and its blends.

Table 5 provides an overview of the processing window for TPS compounded in the Rapra extruder. Four types of behaviour were observed. At very low water and glycerol contents, the powders were too dry and the material simply degraded in the extruder. At slightly higher water and plasticiser contents, gelation did occur but the resulting melt was too viscous and rapidly caused blocking of the die. At very high levels of water and glycerol, the feed was too wet to be fed into the extruder. It was therefore concluded that suitable, well-gelatinised extrudates were only possible for formulations containing 20 or 25% water, or 15% or less glycerol. However, the mixture containing 15% water and 15% glycerol also performed well.

Note that Figure 8 (Section 2.8) indicates that increasing glycerol content simultaneously decreases the melting point and the degradation temperature of thermoplastic starch. However, the melting point decreases more rapidly with increasing glycerol content and therefore the net effect is an increase in the processing temperature window [Liu *et al.*, 2001].

Table 8: Processing window of the HiMaize^{TM} TPS formulations using the Rapra single-screw extruder

		Water content [% mass]						
		0	**5**	**10**	**15**	**20**	**25**	**30**
Plasticiser content [% mass]	0	Burnt	Burnt	Blocked	Blocked	√	√	Wet
	5	Burnt	Burnt	Blocked	Blocked	√	√	Wet
	10	Burnt	Burnt	Blocked	Blocked	√	√	Wet
	15	Burnt	Blocked	Blocked	√	√	√	Wet
	20	Blocked	Blocked	Blocked	Wet	Wet	Wet	Wet
	25	Blocked	Blocked	Blocked	Wet	Wet	Wet	Wet
	30	Blocked	Blocked	Blocked	Wet	Wet	Wet	Wet

4.1.2 Evaluation of plasticisers

Urea was not found to be a good plasticiser during this study, although it is mentioned as a plasticiser in the literature [Shogren *et al.*, 1992]. Its solubility parameter is not very high and its hydrogen-bonding capability falls well within the range of that of the other plasticisers. The main problem with urea is that its thermal degradation starts just above the melting point (ca. 140 °C). Therefore there is no temperature range in which the urea forms a thermally stable liquid. During extrusion, the extruder blocked at the die zone with the evolution of gas in the extruder, which led to "spluttering" and "shooting" of material from the extruder die. When heated to high temperatures, the urea cross-linked with the starch and this caused the blockage of the extruder. It was not possible to obtain sTable Cxtrusion conditions.

It has been reported that the addition of mineral acids reduces cross-linking [Khalil *et al.*, 2002]. For this reason phosphoric acid was added to some samples during extrusion. Although it did make the extrusion process more stable, the product obtained was brown and had a "burnt" smell. The extrudate was weak and broke easily. The extrusion process was also a health hazard due to the emission of ammonia and carbon dioxide. When the extrusion temperatures were lowered to below 120 °C, the extrusion process became stable, but the product obtained was not gelatinised sufficiently and was thus quite weak.

Initial extrusion and moulding trials revealed that the TPS compounds were very difficult to process. Difficulties were encountered with feeding the dry blends into the compounding extruder. The addition of precipitated silica produced a free-flowing starch blend which fed without blocking the extruder. It was mixed into the starch/water/plasticiser mixtures just before compounding at levels of 2 to 3%. This yielded a free-flowing mixture for extrusion, preventing lump formation and bridging in the throat of the extruder.

It was found that the TPS produced inside the processing window determined above was almost impossible to mould owing to the very high melt viscosity. Therefore, the addition of lubricants was investigated. The addition of more than ca. 2% epoxidised soya bean oil, stearic acid, magnesium and calcium stearates or glycerol monostearate (GMS) significantly retarded or even prevented gelatinisation of granular starches in the extruder. This was apparent from the poor dispersion of these additives in the final extrudates and this affected the material properties adversely. These additives form thin lubricating layers around the starch granules which may also have retarded the absorption of the water required for gelatinisation. The addition of many of these additives also caused problems with the feeding of material into the single-screw extruder.

Stearyl alcohol added at levels between 1 and 1,5% was found to be the best lubricant, based on visual observations of the flow behaviour during compounding and injection moulding. The addition of 2,5% precipitated silica was necessary to facilitate feeding of the dry blends into the compounding extruder. After considerable trial and effort, the best feeding and processing performance was achieved with the formulation given in Table 9. This was chosen as the base TPS formulation used in this study.

Table 9: Thermoplastic starch base formulation

Constituent	Mass %
HiMaize^{TM}	67,5
Glycerol	15
Water	15
Stearyl alcohol	1,5
Precipitated silica	2,5

Extrusion to produce thermoplastic starch aims to gelatinise the starch with the minimum deterioration in the molar mass. For this reason, shear was applied gradually in the presence of water and plasticisers to protect the starch from degradation. The extrusion temperatures at the die zone were kept at a 100 ºC to prevent foaming.

4.1.3 Effect of starch source on the mechanical properties

The effect of starch type was evaluated using the TPS base formulation given in Table 6. The effect of ageing on the tensile properties is presented in Figures 14 and 15.

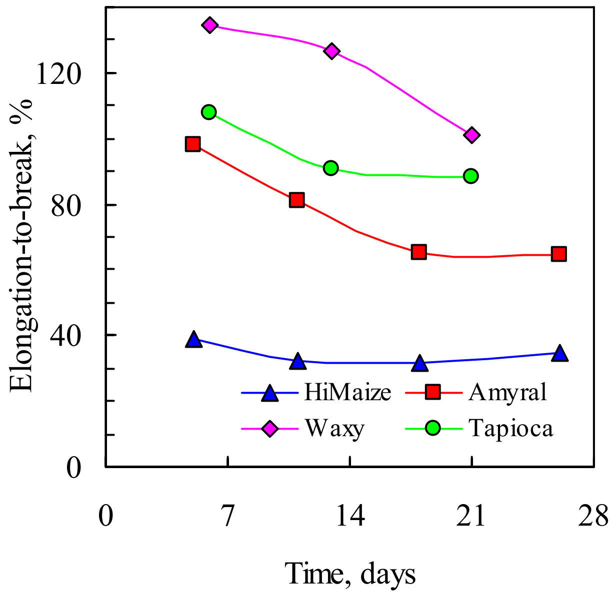

Figure 14: Effect of ageing at 30°C and 60% RH on the elongation-at-break

The TPS compounds based on waxy maize and tapioca starch showed very high shrinkage (> 20%) on ageing. This resulted in gross deformation of the tensile test pieces. The TPS based on high-amylose maize starch shrank by less than 5%. The linear amylose molecules easily pack closer together, resulting in stronger interactions and hence a higher degree of crystallinity. They also have a lower molar mass and consequently the melt is less viscous. This makes it possible to achieve more complete denaturing of the starch granules. Conversely, these materials, in the liquid state, are also able to crystallise more rapidly to form entangled structures based on crystallites connected by tie molecules. In the high-amylopectin samples, the molar mass is much higher and the molecules are highly branched. The melt viscosity is also much higher, implying that the chain-diffusion coefficients are also much lower. The processing time was apparently too short to allow full chain relaxation and crystallisation during the forming process. Note that the Tg for these samples with a water content of ca. 15% in the moulded state is below 5 ºC (Van Soest *et al.*, 1996b). The ageing therefore took place at 30 ºC, i.e. above the Tg. This explains the extensive retrogradation and gross deformation (over several days of ageing) of the samples containing high levels of amylopectin.

The mechanical properties of the TPS materials reflect their multi-phase morphology. They form a complex network of completely plasticised starch, recrystallised starch, partially destructurised granular starch and intact granular starch (Van Soest *et al.*, 1996b). Obviously, the extent of this morphology development depends on the molecular nature of the starch and the formulation's composition. However, the processing parameters, including the shear rates applied and their duration, have a very significant effect as well. It is clear that the processing freedom available in this project was very limited and it is therefore likely that the properties that were measured are not the ultimate values that could be achieved in the ideal case. In fact, the results may be counter-intuitive as the "best" morphological development was clearly not achievable with the available processing procedures.

The elongation-to-break decreased with a decrease in the amylopectin content. Van Soest *et al.* (1996b) explained that this phenomenon can be attributed to the difference in molecular mass of amylose and amylopectin. The latter has a much higher molar mass and therefore the chains are more entangled in the amorphous network. The samples with a high amylopectin content can be stretched much further before complete chain disentanglement occurs. For TPS from HiMaize, there is a slight decrease in elongation-to-break for the first ten days and thereafter it remains almost constant. A slight decrease in elongation-to-break is also observed with ageing time for the high-amylopectin starches, which is attributed to retrogradation, i.e. a considerable change in physical properties on ageing.

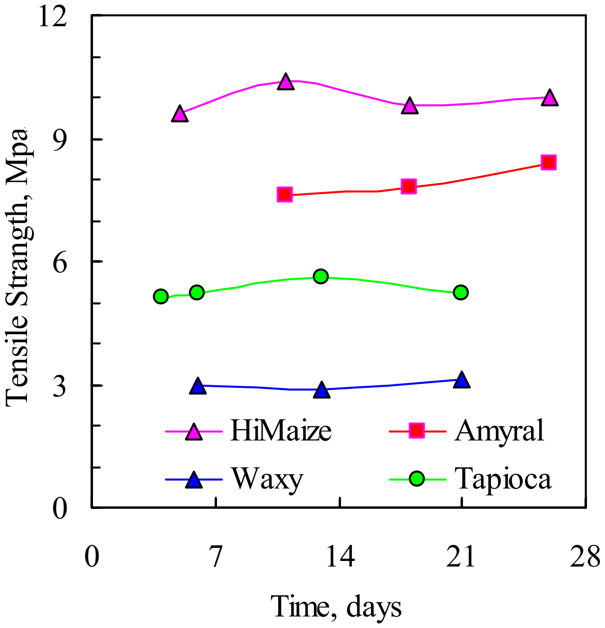

Figure 15: **Effect of ageing at 30°C and 60% RH on TPS tensile strength**

The tensile strength remained approximately constant for all starch types, but decreased with an increase in amylopectin. Van Soest & Borger [1996] explained this in terms of the differences in structure of amylose and amylopectin, as explained above. The difference in mechanical properties reflects the effects of the differences in starch morphologies resulting from the inherent structure of the starch and the degree of processing applied. Of the starches tested, the high-amylose starch yielded the best tensile properties and was least prone to ageing [Van Soest & Vliegenhart, 1997]. Based on the evaluations performed on the various grades of maize starch with varying amylose:amylopectin ratios, HiMaize$^{\mathrm{TM}}$ showed the best retention of tensile properties with ageing time [Sita *et al.*, 2003]. This is in agreement with the work done by Van Soest & Borger [1996].

The effect of plasticiser content on normal maize starch was determined using the same base formulation. Only the relative proportions of water and glycerol were varied. The results are presented in Figures 16 and 17. Elongation-at-break decreased with ageing time, while tensile strength increased. This is due to the decrease in the number of chains in the amorphous state and the shortening of tie molecules between crystallites over time. The time-dependent behaviour is affected by plasticiser content. The rate of recrystallisation is determined by the amount of glycerol in the materials. Crystallisation rate increases with an increase in both water and glycerol content [Van Soest & Knooren, 1997].

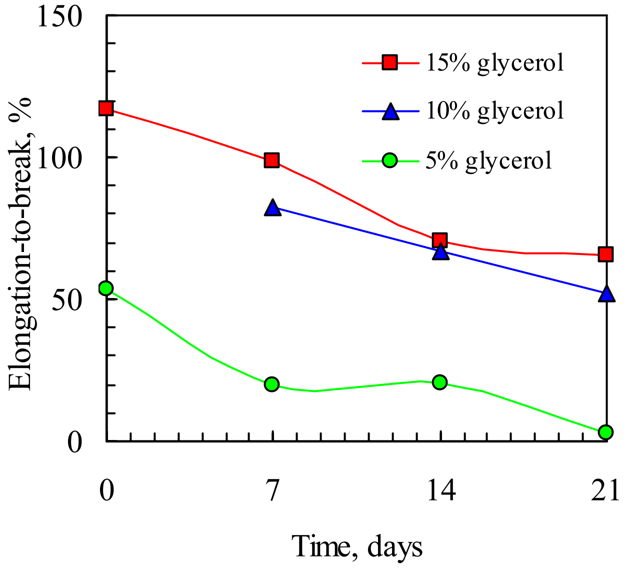

Figure 16: **Effect of glycerol content on the breaking strain of normal maize-based TPS aged at 23 °C and 44% RH**

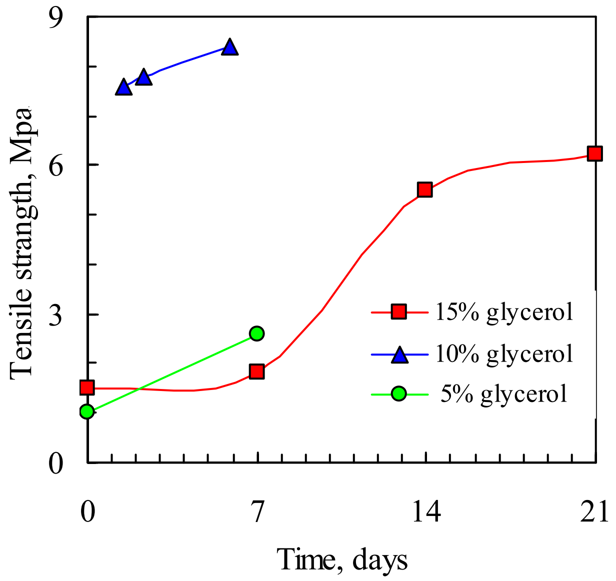

Figure 17: **Effect of glycerol content on the tensile strength of normal maize-based TPS aged at 23 °C and 44% RH**

4.1.4 Effect of filler

The addition of fillers (anhydride gypsum, mica, vermiculite, silica and talc) to granular starch yielded mixtures that were very viscous, as indicated by the very high torque required for them to be compounded. This is caused in part by (a) the effect that fillers have in increasing the effective viscosity of a suspension, and (b) the reduction in water and in the availability of plasticiser for gelatinisation owing to occlusion inside agglomerates of filler particles. This led to slow gelatinisation, forming a thermoplastic starch that was only slightly plasticised, resulting in high viscosities. For this reason, high torque was required to mix the starch with the filler. Only formulations containing less than 8% filler could be extruded.

In an attempt to overcome this problem, thermoplastic starch was initially prepared and compounded with the filler in a second step. This did not work well with the equipment used in this study. Pre-mixing of thermoplastic starch pellets with powder fillers did not lead to the formation of homogenous mixtures due to the differences in particle size and density of the two components. Secondly, the single-screw extruder used in this work is not really suitable for compounding fillers into polymer melts and therefore samples with poor dispersion of the filler in the polymer were produced.

The results of the extrusion trials done using the Berstorff twin-screw extruder and the Rapra single-screw extruder illustrate that the conversion of granular starch into thermoplastic starch requires the gradual application of shear in the presence of high levels of plasticiser. Excessive shear is harmful to the starch and results in breakage of the polymer chains (reduction in the average molar mass), ultimately leading to brittle materials. Every extruder is unique and therefore the processing parameters, barrel temperatures, screw speeds, etc. should be set up by systematic experimentation.

All TPS compounds showed poor processability during injection moulding, especially the sprue part. This was improved by adding stearyl alcohol at ca. 1,5% as an external lubricant and mould-release agent. Nevertheless, for some compositions it was also necessary to use a mould-release agent during injection moulding. Commercial “Spray-and-Cook” was found to be adequate for this purpose. The processing window for injection moulding was found to be relatively small and had to be determined by trial and error for each composition.

Good mechanical properties were achieved only by using high-amylose starch. Starch high in amylopectin was very difficult to process and showed extensive retrogradation, with samples even cracking spontaneously during ageing. Increasing the glycerol content increased the elongation-to-break but reduced the tensile strength of the TPS compounds.

4.2 TPS-PVB blends

The extrusion temperatures for TPS–PVB blends are presented in Table 10. The extrusion parameters were highly influenced by the composition of the formulation. Higher temperatures were necessary for formulations with high TPS contents.

Table 10: Extrusion parameters TPS-PVB blends

Polymer Blend	**Barrel Temperature, ºC**			
	Feeding zone	**Compression zone**	**Metering zone**	**Die**
100% TPS	120	150	150	100
92% TPS	120	155	150	95
78%TPS	120	150	145	94
50% TPS	120	135	130	80
22% TPS	120	140	135	85
8% TPS	120	140	135	85
0% TPS	100	115	115	70

Injection moulding was again a difficult process: Very high injection pressures were required for blends with high starch contents. As with extrusion, the injection-moulding processing parameters were influenced by the formulation of the blend. For each formulation the optimum settings were those that allowed 100% filling of the mould without warpage and flashing. The injection-moulding parameters are given in Table 11. Sticking in the sprue bush was a problem, despite the inclusion of stearyl alcohol in the formulation. "Spray & Cook" had to be sprayed into the mould after every shot.

Table 11: Injection-moulding parameters for TPS-PVB blends

Polymer Blend	Barrel Temperature, °C	Injection Pressure, bar
100% TPS	140; 145; 145; 150	70
92% TPS	125; 130; 130; 140	85
78%TPS	125; 130; 130; 140	105
50% TPS	125; 130; 130; 140	95
22% TPS	125; 130; 130; 140	105
8% TPS	125; 130; 130; 140	110
0% TPS	125; 130; 130; 140	110

The moisture content of the single components and the blends increased during equilibration at 30 ºC and 60% RH. For the TPS it was 2,4% and 3,6% after 14 and 30 days respectively. By comparison, the moisture content of the recycled PVB after 30 days was 1,3%, whereas for the blends with 22, 50 and 78% TPS it was ca. 1,8%.

Figure 18 shows the effect of ageing at 30 °C and a humidity of 60% RH on the tensile properties of the TPS-PVB blends. For the neat PVB, the tensile strength and the Young's modulus decrease on ageing owing to the increasing moisture content. Clearly, water also plasticises PVB, lowering its glass transition temperature and its tensile properties. The modulus of the plasticised PVB is rubber-like and decreases from ca. 5 MPa to 1 MPa on ageing (Figure 18).

The tensile strength and modulus of the TPS increased with ageing. However, the neat TPS compound shows a strong decrease in elongation-to-break (ε_B) with time. This correlates with an increasing brittleness of these samples and is attributed to the retrogradation of the starch compound [Kim *et al.*, 1997], as also explained above.

With blends, the modulus increases by two orders of magnitude, in a nearly log-linear manner, as the TPS content is increased to 100%. The ε_B of PVB and the blends rich in PVB are not much affected by ageing (Figure 18). The blends with 22% or less of PVB have an ε_B of less than 40%, i.e. similar to that of the starch-based TPS. The ε_B exceeds 200% for blends containing 50% or more of PVB. This suggests that the properties of the continuous phase approach PVB behaviour down to 50% PVB. In general, the tensile strength of the blends that contain 50% or more TPS is lower than expected from the linear blending rule. However, the 22% TPS compound shows significantly higher values.

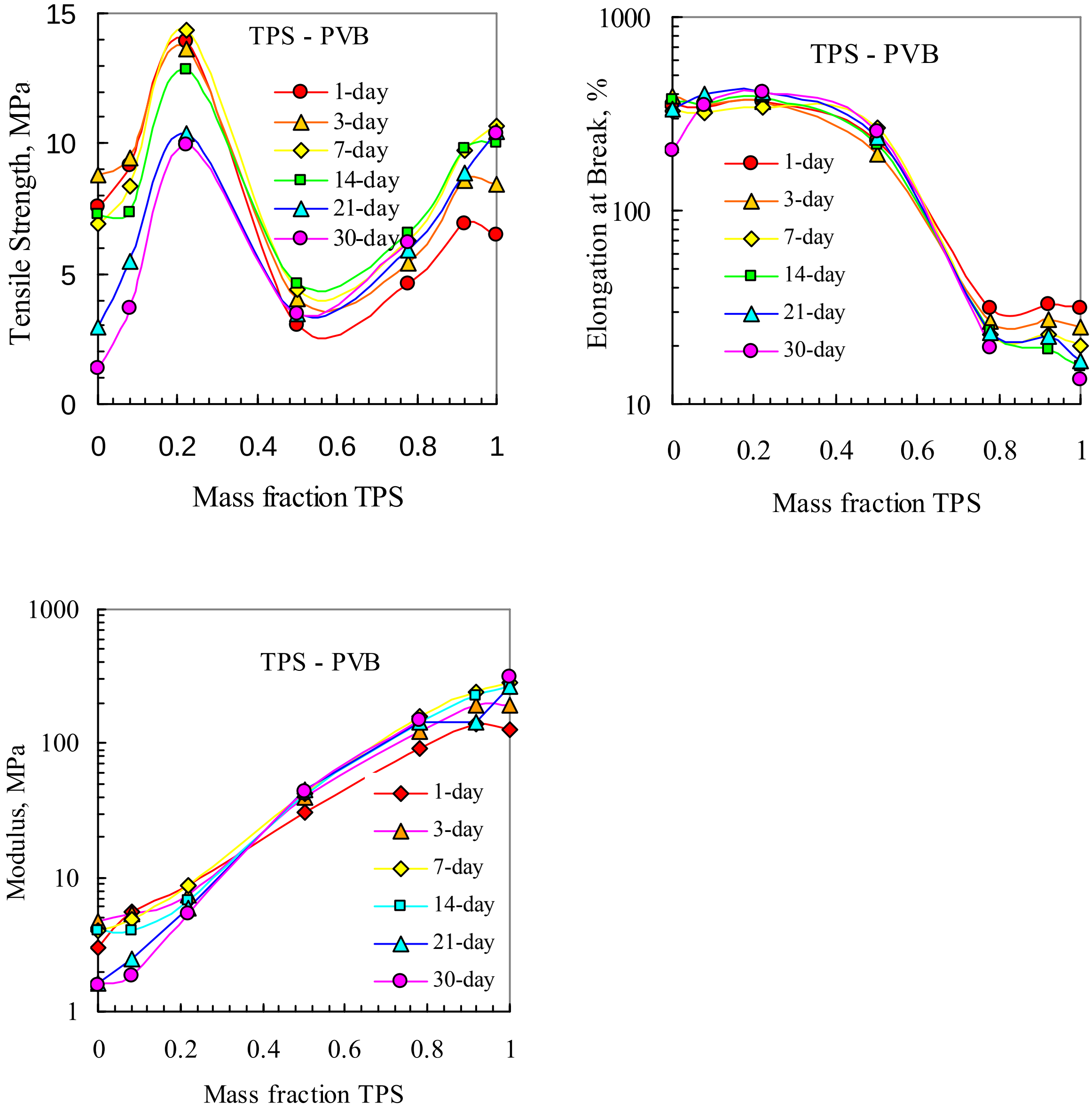

Figure 18: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-PVB blends

Although the compound containing 22% TPS also showed property losses on ageing, it had the best water resistance: Figure 19 shows that it was the only composition tested that retained a significant portion of its tensile strength in the water-soak tests. Noteworthy is the complete loss of mechanical properties for the blends with high starch contents in which the starch forms the continuous phase.

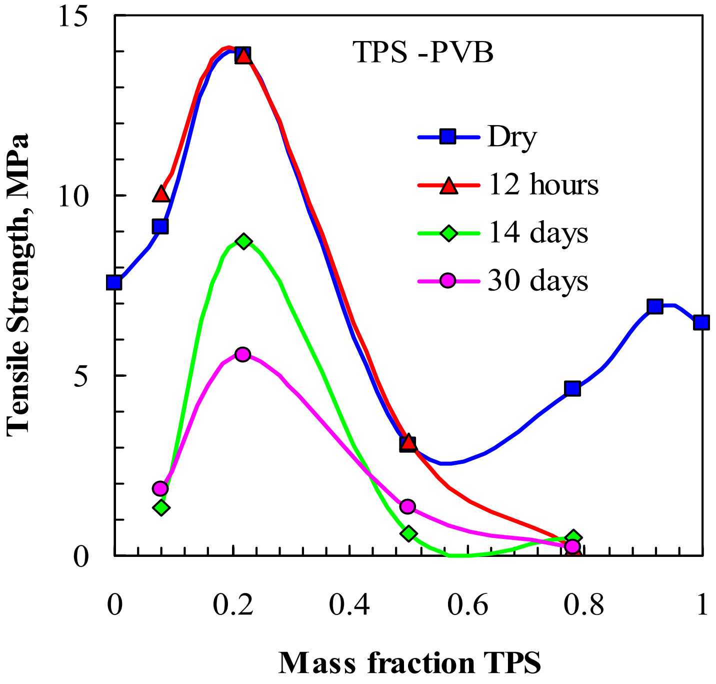

Figure 19: Effect of water soak on the tensile strength of TPS-PVB blends

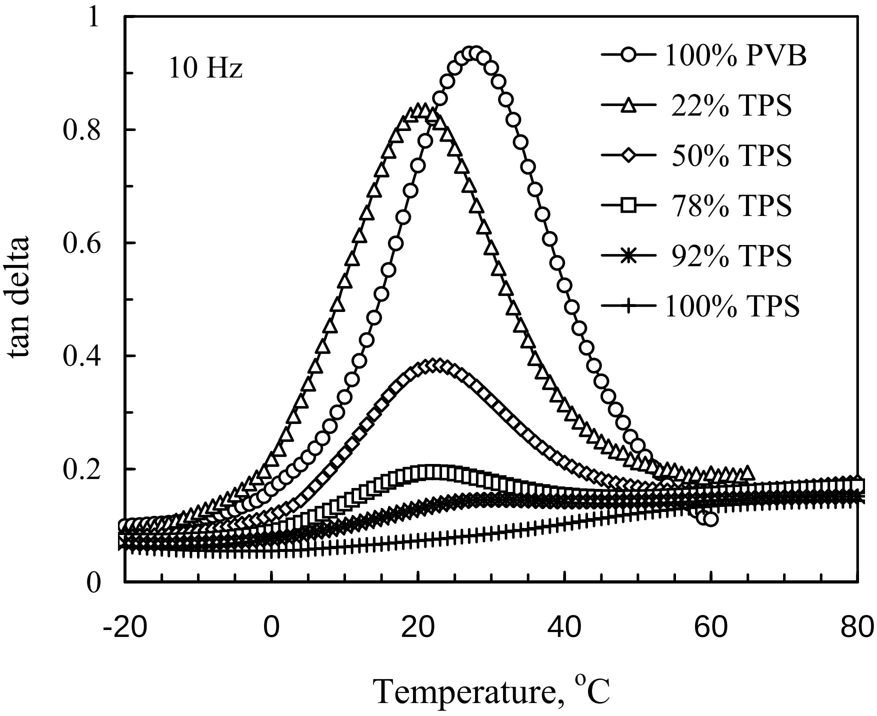

Figure 20: Tan δ (loss factor) at 10 Hz for TPS-PVB blends aged at 30 °C and 60% RH for at least 30 days

Figure 20 shows the tan δ results obtained in the –20 to 80°C temperature window. PVB shows a strong loss peak at 28 °C. TPS shows a weak loss peak below –45 °C and a broad, but weak loss feature, with two peaks at higher temperatures in the DMA (not shown in Figure 20). The two high-temperature peaks are located at 94 °C and 126 °C respectively. Forssell *et al.* [1997] also observed low- and high-temperature loss peaks using differential scanning calorimetry (DSC) and dynamic thermal analysis (DMA) of barley starch-glycerol-water mixtures. They attributed this to phase-separation in the TPS. The system is composed of starch-rich and starch-poor regions with different glass transition temperatures (Tg's) corresponding to these two phases.

Figure 20 reveals that the addition of TPS shifts the tan δ peak temperature to a location that is about 5-7 °C lower than that for the neat PVB. This could indicate a degree of compatibility between the starch and PVB. However, it is more likely that the observed lowering of the Tg is the result of the PVB phase scavenging the glycerol plasticiser from the TPS. This loss peak does not shift with changing blend composition and decreases in intensity as the TPS content is increased. These observations are consistent with a two-phase nature for the TPS-PVB blends.

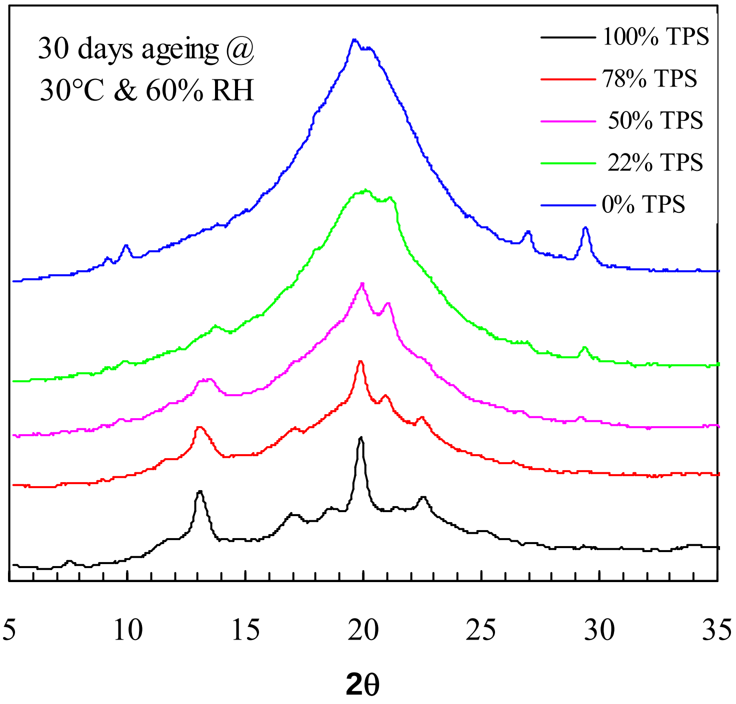

Figure 21: **XRD spectra of TPS-PVB blends aged for 30 days at 30 °C and 60% RH**

XRD spectra of the PVB showed only a broad amorphous peak located at ca. 2θ = 20°. The XRD spectrum of TPS features two strong, sharp peaks at 2θ = 13° and 20° and also some other minor peaks. These peaks do not change much in intensity during ageing. The blend with 78% TPS shows three peaks at 2θ = 13°, 20° and 21° respectively. With ageing the first two peaks increase, whereas the third decreases in relative intensity up to the 21-day point. This indicates that the presence of PVB inhibits the crystallisation of the starch. The blend with 22% TPS still shows the lower-angle starch peak, but it is now located at 2θ ≈ 13,5°. It is likely that most of the retrogradation of the TPS observable by XRD had already occurred before the XRD spectra were obtained: It was unfortunately not possible to get immediate access to the XRD machine after the moulded samples had been prepared.

The XRD spectra are in agreement with the observations of Van Soest & Borger [1996]. The observed crystalline structure is called the V_h type and is process-induced. It results from the rapid recrystallisation of amylose in glycerol-containing TPS. The absence of B-type crystallinity shows that the granular structure of native starch was completely broken down during compounding [Van Soest & Borger, 1996]. These peaks do not change much in intensity during ageing. The blend containing 78% TPS shows exactly the same three peaks at 2θ = 13°, 20° and 21° as the pure TPS. For the blends containing 50% TPS, the peak at 2θ = 13° broadens, while the other two decrease in intensity. For blends containing 78% PVB and more, there is a very broad peak at 2θ = 20° and the other two disappear completely. This indicates that the presence of PVB inhibits the recrystallisation of the starch.

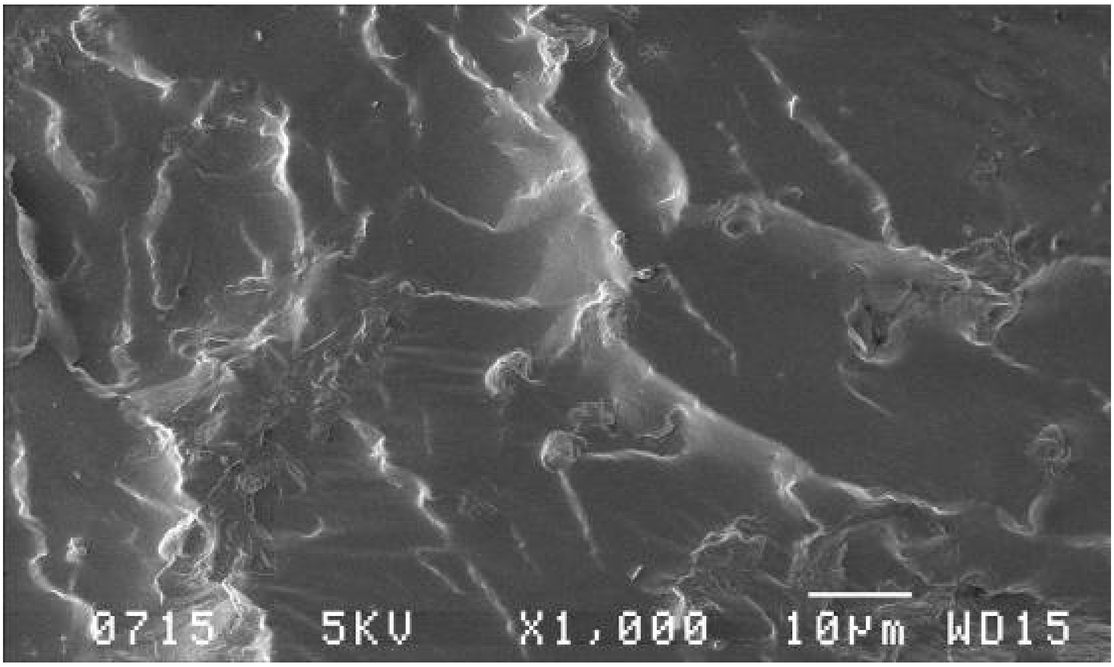

Figure 22: Scanning electron micrograph of a fracture surface of the blend containing 22% TPS

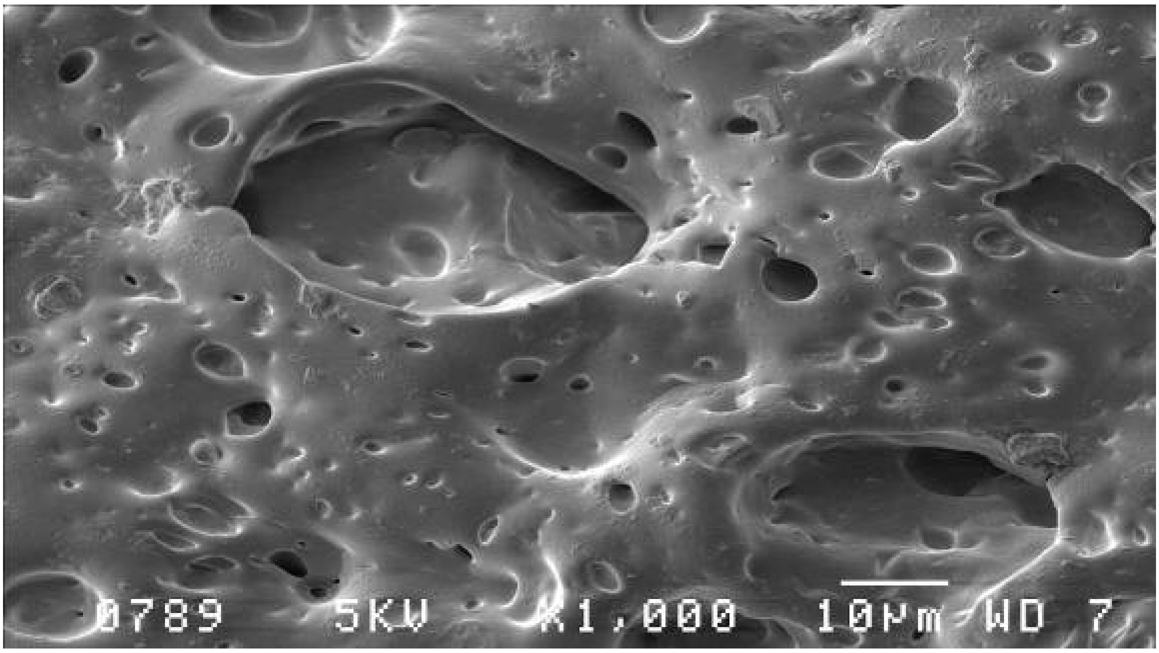

Figure 23: Scanning electron micrograph of an enzyme-eroded fracture surface of the blend containing 22% TPS

SEM studies confirmed the two-phase structure of the TPS-PVB blends. Figures 22 and 23 show fracture surfaces for the 22% TPS blend, before and after enzyme erosion. On exposure to the enzyme, the rough fracture surface develops widely distributed cavities, with sizes ranging from ca. 1–50 µm. This suggests that the cavities result from a loss of the starch phase. The image for the 50% TPS blend appears similar, except that the cavities are more irregular in shape. As the starch content decreases, the number of cavities observed on the enzyme-eroded fracture surfaces decreases as well.

The SEM, TMA and water-resistance data all confirmed the two-phase nature of the TPS-PVB blends. This is not surprising as most polymer pairs are thermodynamically immiscible [Paul & Newman, 1978]. Phase separation leads to the creation of internal interfaces. If these have a high interfacial tension, the adhesion between the two phases will be poor. The end-result will be poor stress transfer between phases and a loss in mechanical properties [Paul & Newman, 1978]. The blends rich in PVB show improved mechanical properties, especially the compound with 22% TPS. This indicates that there is a measure of mechanical compatibility among the blends. However, similar improvement in mechanical properties was obtained merely by using gypsum as filler. Thus it is likely that, at low starch loadings, the high-stiffness starch domains simply act as dispersed particles of reinforcing filler. The high elongation-to-break values are consistent with the PVB forming the continuous phase up to 50% TPS. The lower-than-expected tensile strength of this blend can be attributed to its coarse-phase domain structure.

4.3 PVB-polyamide blends

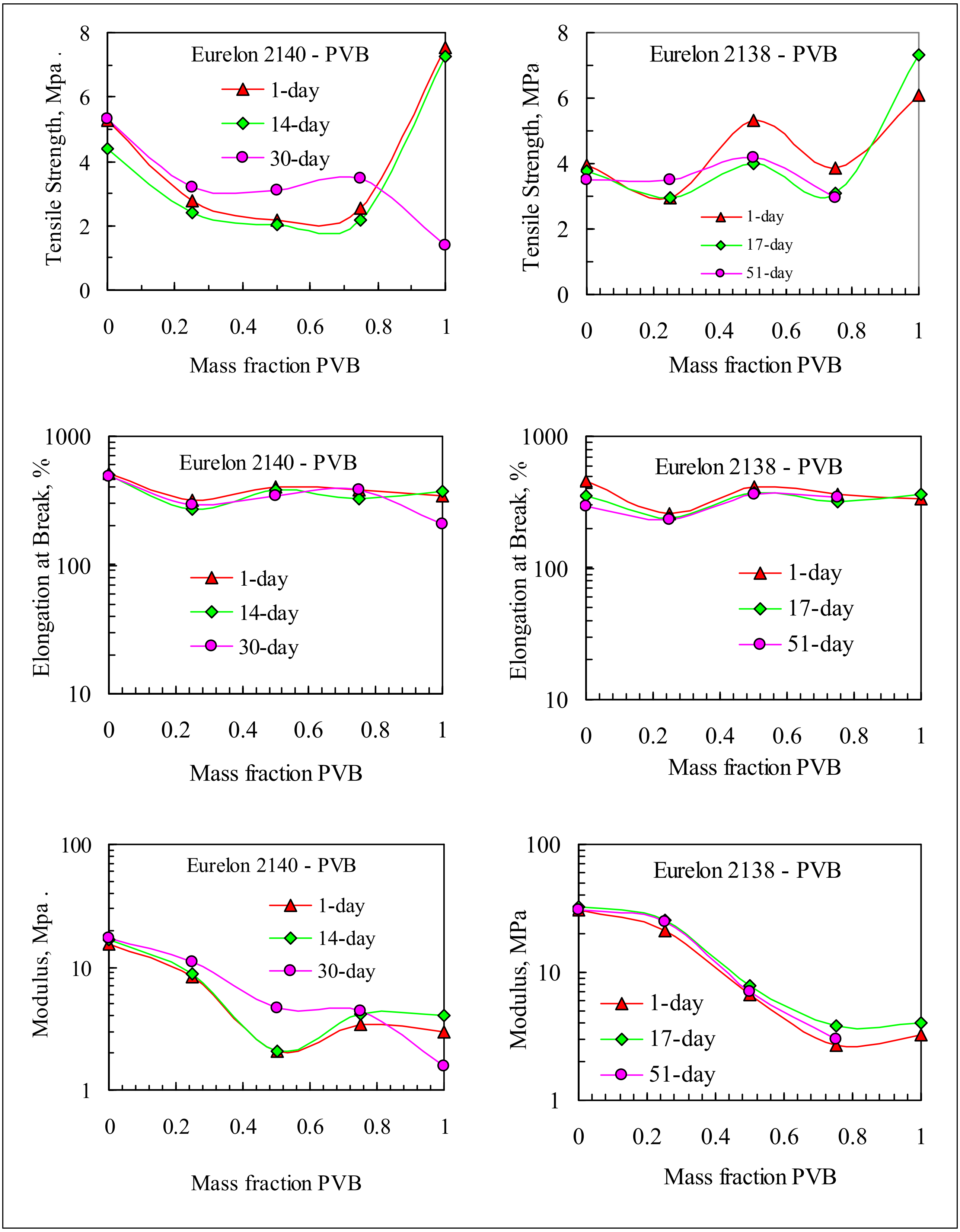

Figure 24: Effect of ageing at 30 °C and 60% RH on the mechanical properties of PVB-Euremelt blends

The mechanical properties of the Euremelt-PVB binary system are presented in Figure 24. There is scatter in the data for the effect of ageing on tensile strength for both polyamides. An initial decrease in the tensile strength is observed for the first 14 days, followed by an increase from 14 days to 30 days for both Euremelts. The modulus decreases with an increase in PVB content for both Euremelts. This is because PVB has a much lower T_g than both the Euremelts and is therefore more flexible than both the Euremelts at storage temperatures. There is no significant change in the elongation-to-break for blends containing both polyamides. This shows that the mechanical properties of these blends are not affected by ageing as are the blends containing TPS.

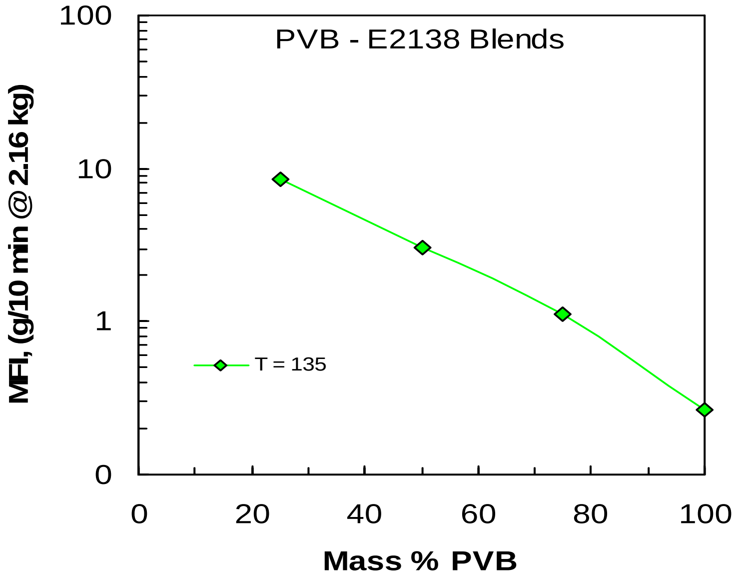

Figure 25: Effect of composition on the melt flow index (MFI) of a PVB-Euremelt blend

The melt flow index (MFI) results for the PVB-E2138 blends are presented in Figure 25. The MFI decreases with an increase in PVB content. This is because PVB behaves more like a rubber and hence is highly viscous. From the results of these experiments it was anticipated that blending PVB with polyamides would give blends with lower viscosities, which would be processable at lower temperatures and torques during extrusion, as well as allowing the injection-moulding temperatures and injection pressures to be lowered during extrusion when they were blended with TPS.

4.4 TPS-polyamide blends

The extrusion temperatures are presented in Table 12. The extrusion parameters were highly influenced by the composition of the formulation. Higher temperatures were observed for TPS-Euremelt blends with high TPS content. The reason for the lower processing temperature for blends with high Euremelt content is that the melting temperature of the Euremelts is ca. 50 ºC. As a result, the extrusion parameters of the latter blends were below 100 ºC, which is lower than the glass transition temperature of TPS. In these blends the TPS acted as a filler embedded in the polyamide matrix.

Table 12: Extrusion parameters for TPS-E2140 blends

	Barrel Temperature, ºC			
Polymer Blend	**Feeding zone**	**Compression zone**	**Metering zone**	**Die zone**
100% TPS	120	150	150	100
92% TPS	110	140	140	100
78%TPS	110	120	120	75
50% TPS	110	120	120	75
22% TPS	80	90	90	50
8% TPS	80	90	90	50
0% TPS	65	70	70	50

Injection moulding was a difficult process. Sticking in the sprue bush was a problem, despite the inclusion of stearyl alcohol in the formulation. “Spray and Cook” had to be sprayed into the mould after every shot. The injection pressures were lower than those of the TPS-PVB blends. As with extrusion, the injection-moulding processing parameters were influenced by the formulation of the blend. For each formulation the optimum settings were those that enabled the mould to be filled 100% without warpage and flashing. The injection-moulding parameters for the TPS-Euremelt blends are given in Table 13.

Table 13: Injection moulding parameters for TPS-Euremelt [E2140 and E2138] blends

Polymer Blend	Barrel Temperature, °C	Injection Pressure, bar
100% TPS	140; 145; 145; 150	80 (all compositions)
92% TPS	140; 140; 140; 130	
78%TPS	140; 140; 140; 130	
50% TPS	100; 105; 110; 100	
22% TPS	90; 90; 90; 90	
8% TPS	90; 90; 90; 90	
0% TPS	90; 90; 90; 90	

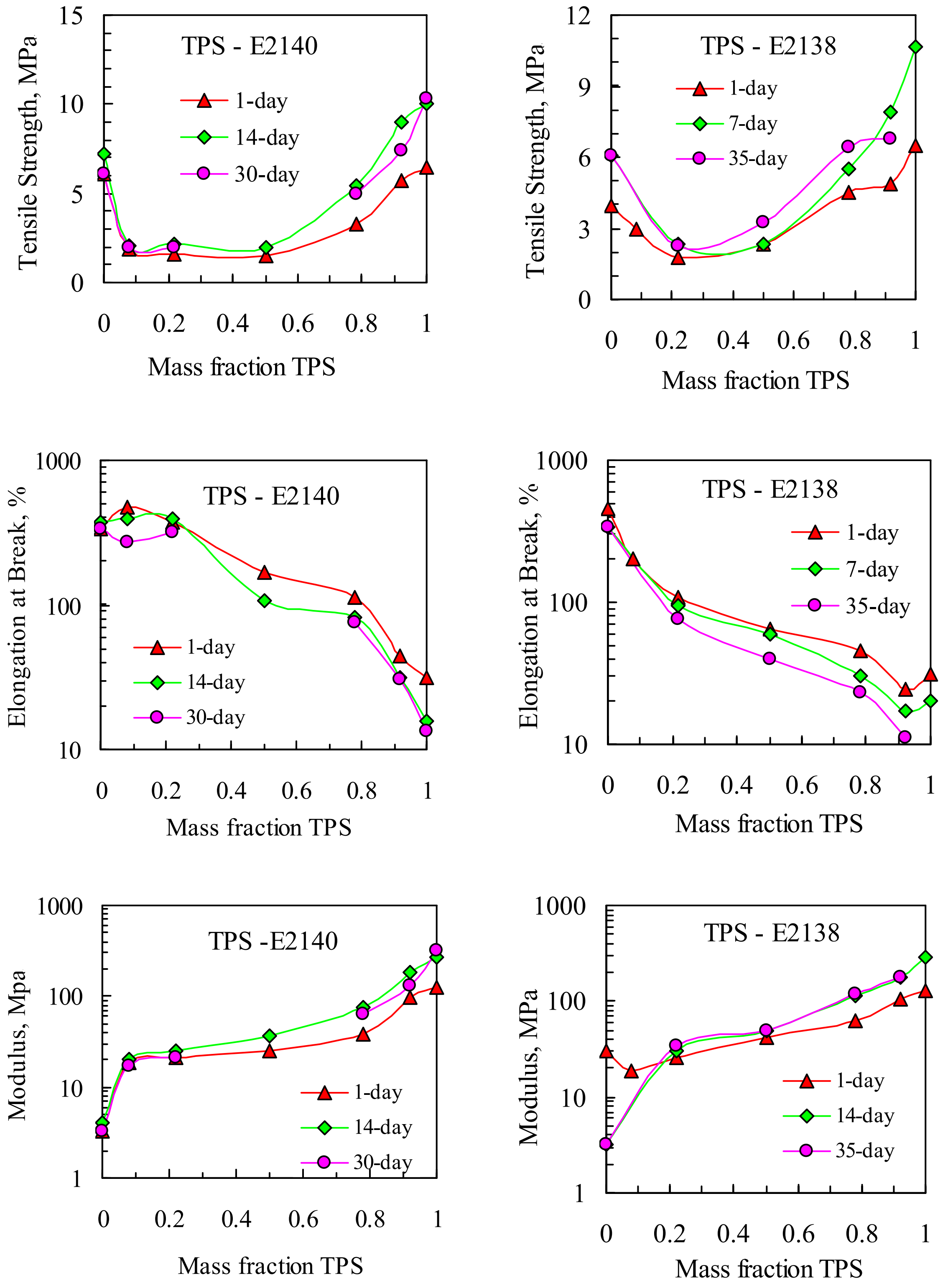

Figure 26: Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-polyamide blends

The mechanical properties for the TPS-polyamide binary system are illustrated in Figure 26.

For blends containing more than 22% polyamide, there is a general increase in tensile strength and the Young's modulus increases with an increase in ageing time, while the elongation-to-break decreases. This is true for blends of both Eurelon 2140 and Eurelon 2138 and is due to retrogradation. Retrogradation is the change in properties of thermoplastic starch-based materials with time, in this case caused by the recrystallisation of amylose and amylopectin during ageing. Materials with a high TPS content are very brittle, while materials with a high polyamide content are tough and strong for both the E2140 and E2138 blends. For blends containing E2140, the numerical values for the tensile properties after 14 days of ageing are very close, in some instances equal, to the values after 30 days of ageing. This means that the degree of recrystallisation is very low between 14 and 30 days of ageing.

There is a general decrease in tensile strength for blends containing up to 78% polyamide. This is because the melting temperature for TPS is ≈ 144 °C and these blends were processed well below this temperature (refer to Table 12). The starch granules did not melt-mix with the polyamides at these concentrations and therefore acted like flaws. This resulted in the decrease in tensile strength compared with the pure components. This phenomenon is, however, not very visible on the SEM micrograph for the blends containing 92% Euremelts as presented in Figures 27 and 28.

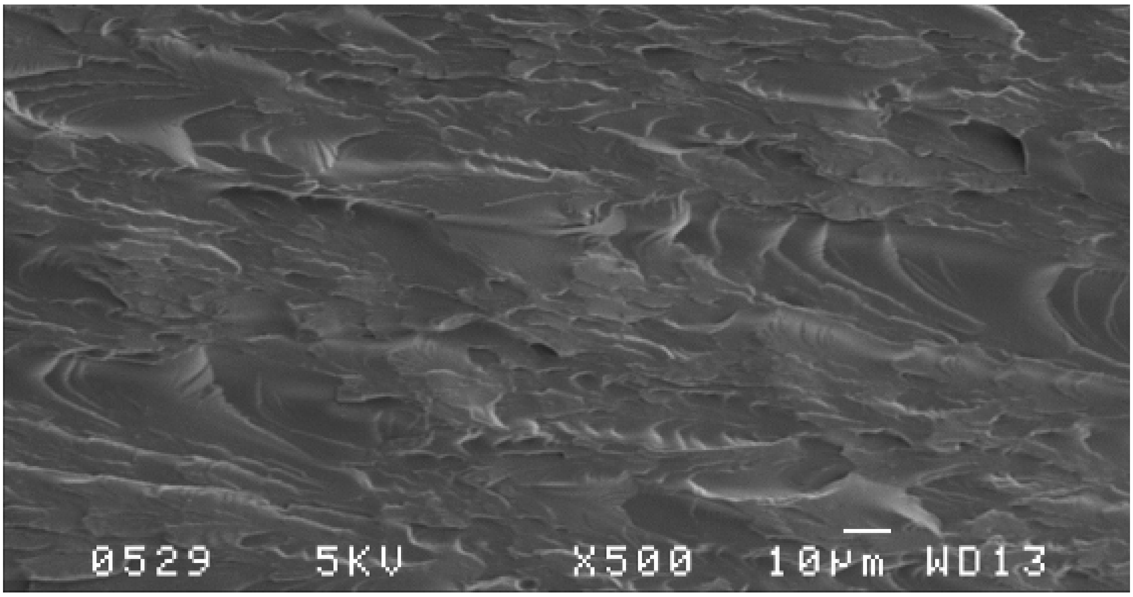

Figure 27: Scanning electron micrograph of a fracture surface of the blend containing 92% E2138

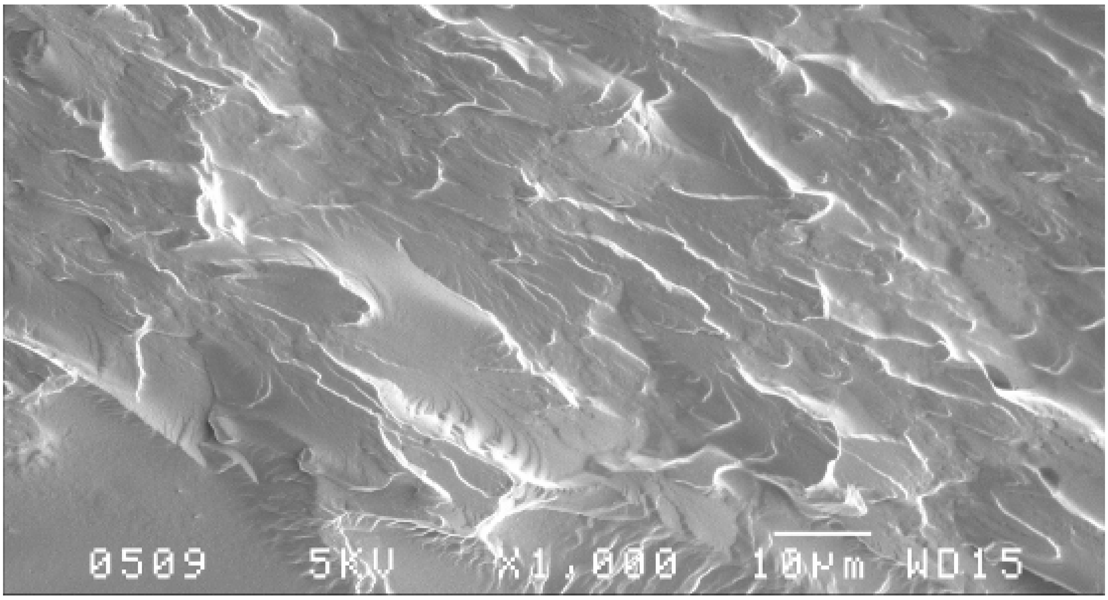

Figure 28: **Scanning electron micrograph of a fracture surface of the blend containing 92% E2140**

More information can be interpreted from Figures 29 and 30, which show optical micrographs of the blends containing 92% E2138 and E2140. In these micrographs the starch behaves as a particulate filler in a continuous phase of both polyamides. The dark particles in the micrographs are chunks of TPS that were broken down by shear forces during extrusion. These particles act like flaws in the polyamide, resulting in a decrease in tensile strength.

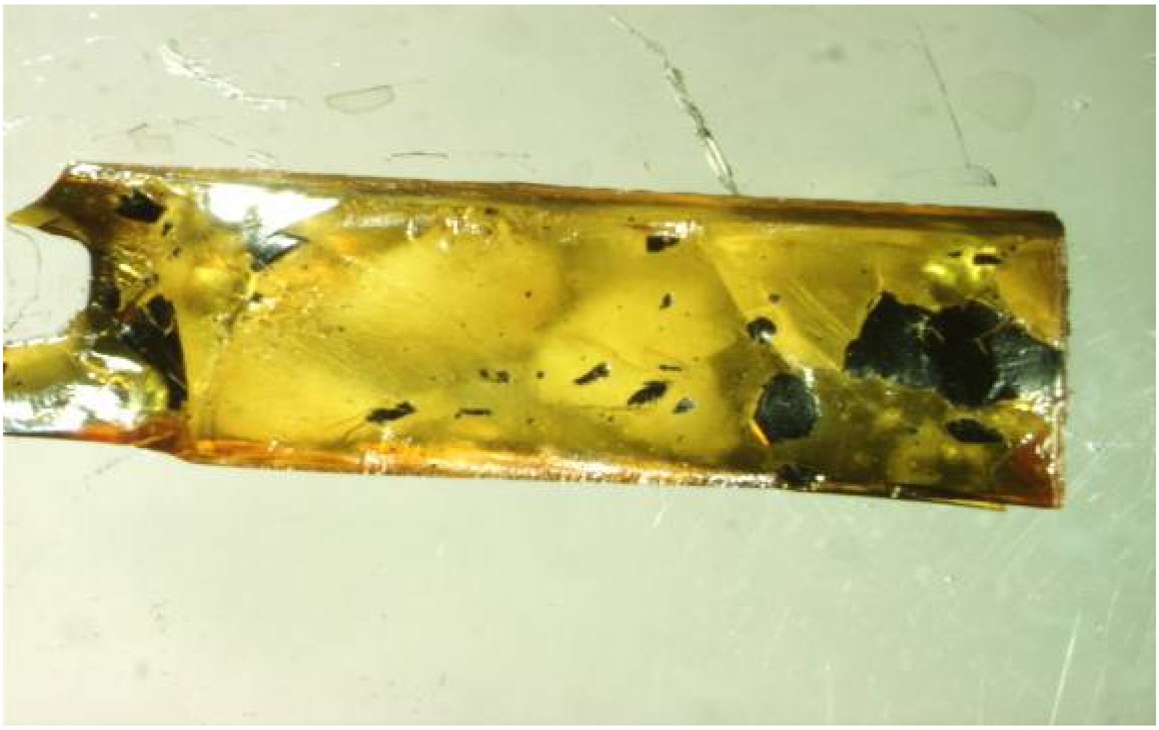

Figure29: **Optical micrograph of a fracture surface of the blend containing 92% E2138**

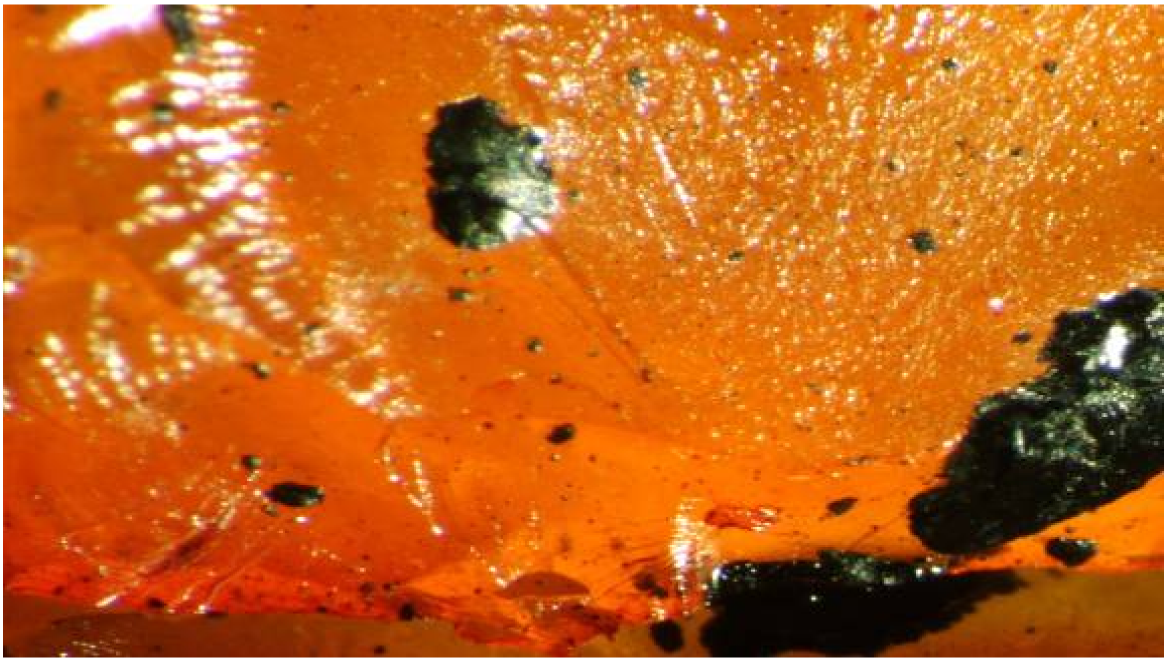

Figure 30: **Optical micrograph of a fracture surface of the blend containing 92% E2140**

Figure 31 illustrates the effect of water soak on the mechanical properties of the TPS-Euremelt 2140 blends. The blend containing 50% E2140 shows the best water resistance. These values decrease with ageing time. Blends containing more than 50% polyamide lasted for the first seven days, while pure TPS did not last even for a day.

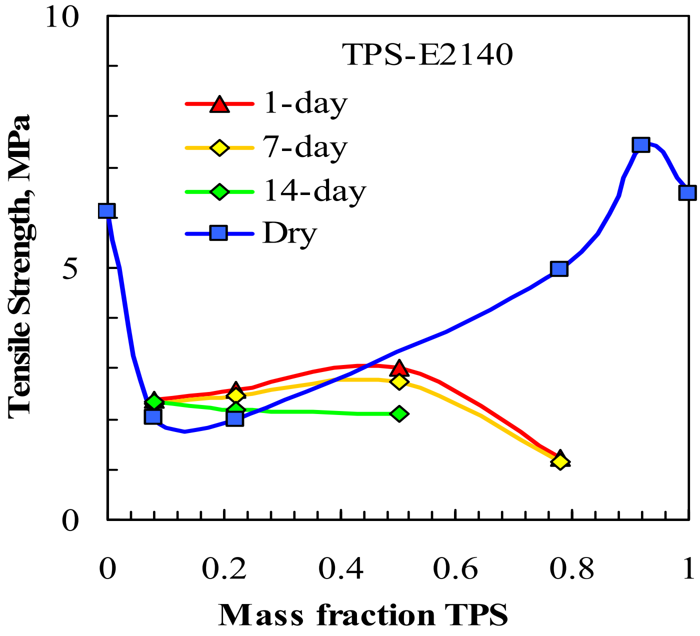

Figure 31: Effect of water soak on the tensile strength of TPS-E2140 blends

All the X-ray diffraction micrographs for TPS-Euremelt blends are contained in Appendix A. The micrographs for the pure compounds and all the formulations after 30 days of ageing are presented in Figure 32. For both the pure polyamides there is a broad peak at 2θ = 20°, showing that they are both amorphous polymers. Blends containing 50% and more of TPS have two sharp peaks: a higher-intensity one at 2θ = 20° and a smaller one at 2θ = 13.5°. With decreasing TPS content, the intensity of both peaks decreases. For blends containing 92% polyamide, a small bump can be seen at 2θ = 13.5° and a broad peak at 2θ = 20°.

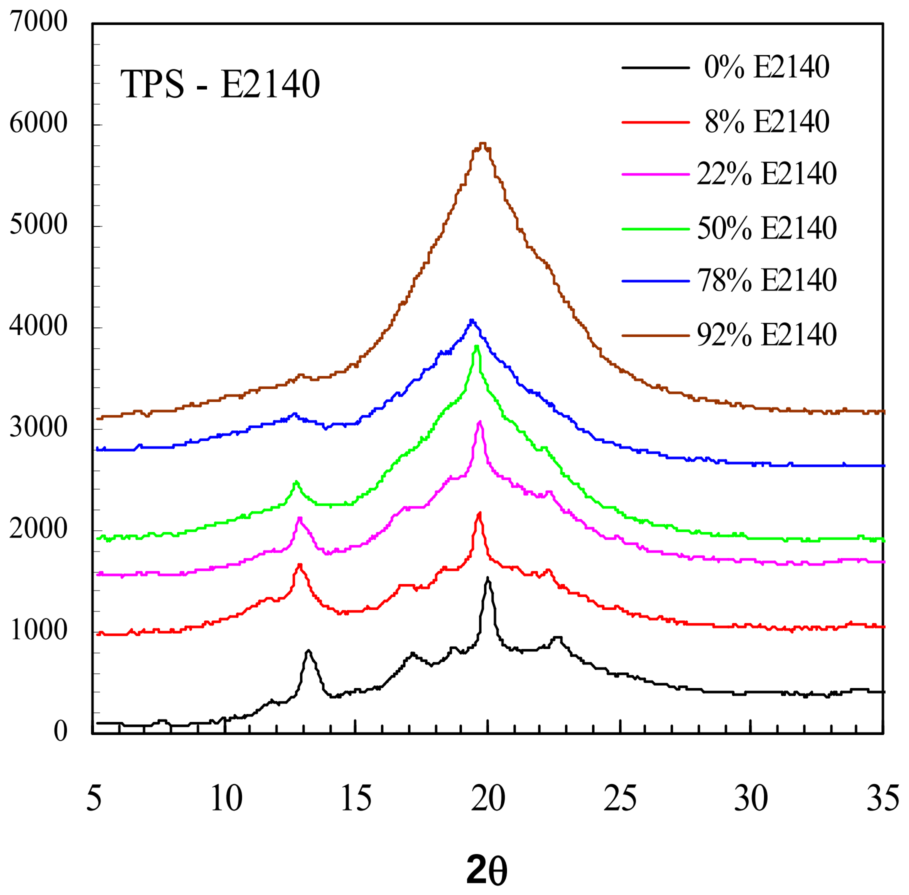

Figure 32: **XRD spectra of TPS-E2140 blends aged for 30 days at 30 °C and 60% RH**

The effect of ageing at 30 ºC and 60% RH on the mechanical properties of the TPS-EMS blends is different from that observed for the Euremelt hot-melt-adhesive polyamides. These trends are illustrated in Figure 33. Tensile strength and elongation-to-break decrease with an increase in TPS content, while the Young's modulus remains unchanged. There are no significant changes in the mechanical properties with ageing. TPS is compatible with EMS and results in single-phased blends. The fact that there are no changes in the mechanical properties with ageing shows that EMS effectively retards retrogradation of thermoplastic starch [Beuhler *et al*., 1994].

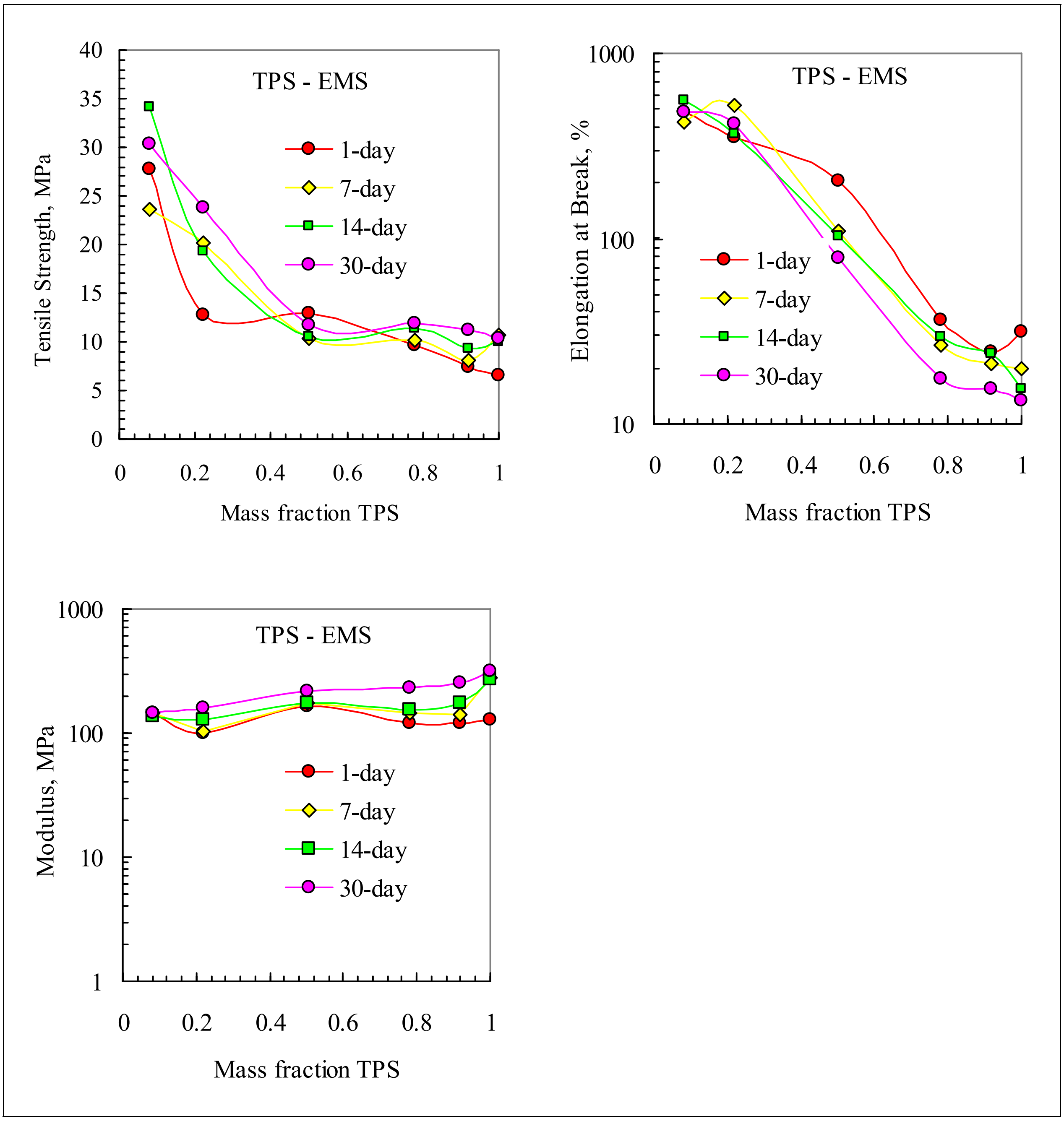

Figure 33: **Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-EMS polyamide blends**

4.5 TPS–PVB-polyamide systems

The processing parameters of TPS-PVB-polyamide blends are given in Table 14. The extrusion parameters of these blends are lower than those of TPS-PVB blends and slightly above those of TPS-E2140 blends. This is in agreement with the MFI results for the PVB-polyamide blends discussed in Section 4.3. With an increase in the PVB content, the MFI decreased. This suggests that blending PVB with E2140 results in blends with lower viscosities and hence the decrease in the processing temperatures required for the TPS-PVB-E2140 blends.

Table 14: Extrusion parameters for TPS-PVB-E2140 blends

Polymer Blend	Barrel Temperature, °C Feeding zone	Compression zone	Metering zone	Die zone
TPS 6	115	120	120	70
Eu 10	115	120	120	70
Eu 12	115	120	120	70
Eu 11	115	120	120	70
Eu 9	115	120	120	70

The injection-moulding parameters for the TPS-PVB-E2140 blends are given in Table 15. The injection-moulding temperatures decrease with a decrease in TPS content in the formulation.

Table 15: Injection moulding parameters for TPS-PVB-E2140 blends

Polymer Blend	Blend Composition, mass % TPS	PVB	E2140	Barrel Temperature, °C	Injection Pressure, bar
TPS 6	100	0	0	140; 145; 145; 150	70
Eu 10	66.8	16.6	16.6	135; 120; 120, 110	80
Eu 12	33.3	33.3	33.3	105; 115; 110, 100	80
Eu 11	16.6	16.6	66.8	105; 115; 110;100	80
Eu 9	16.5	66.8	16.6	110; 115; 110; 100	80

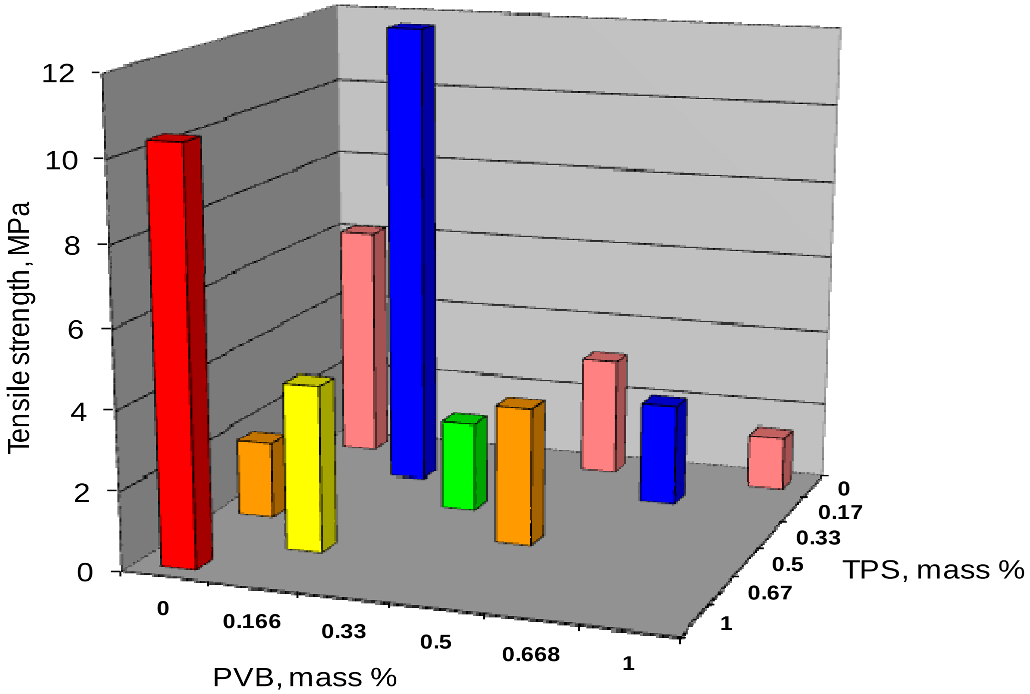

Figure 34: Effect of ageing at 30 ºC and 60% RH on the tensile stress of TPS-PVB–polyamide (E2140)

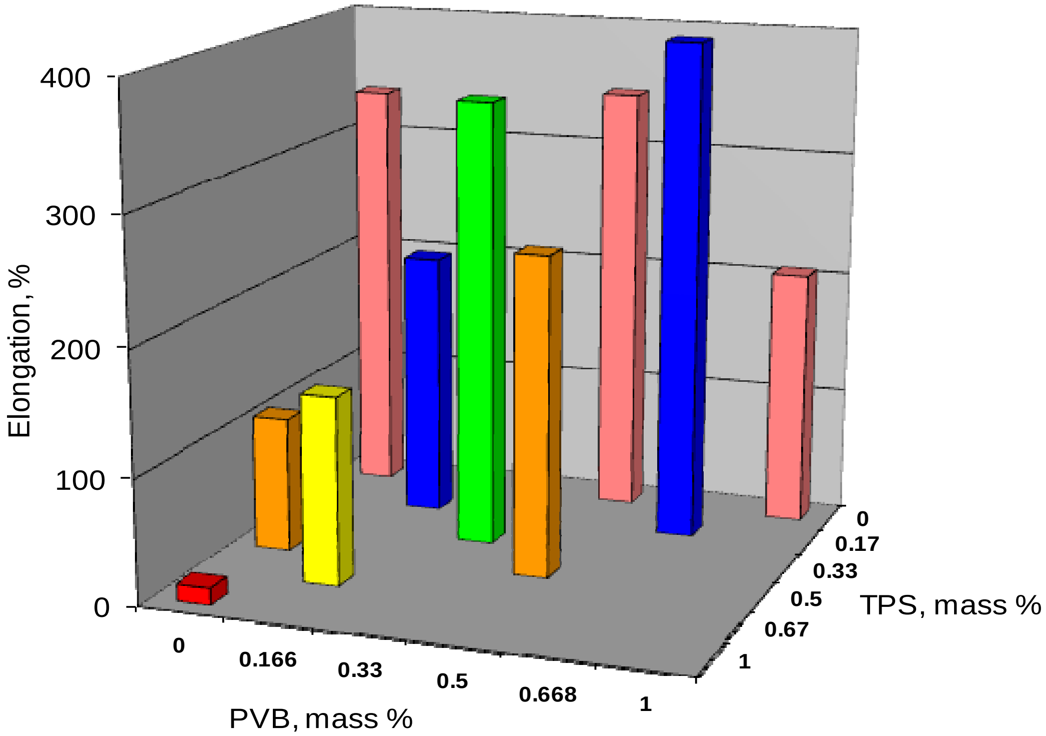

Figure 35: Effect of ageing at 30 ºC and 60% RH on the elongation-to-break of TPS-PVB–polyamide (E2140)

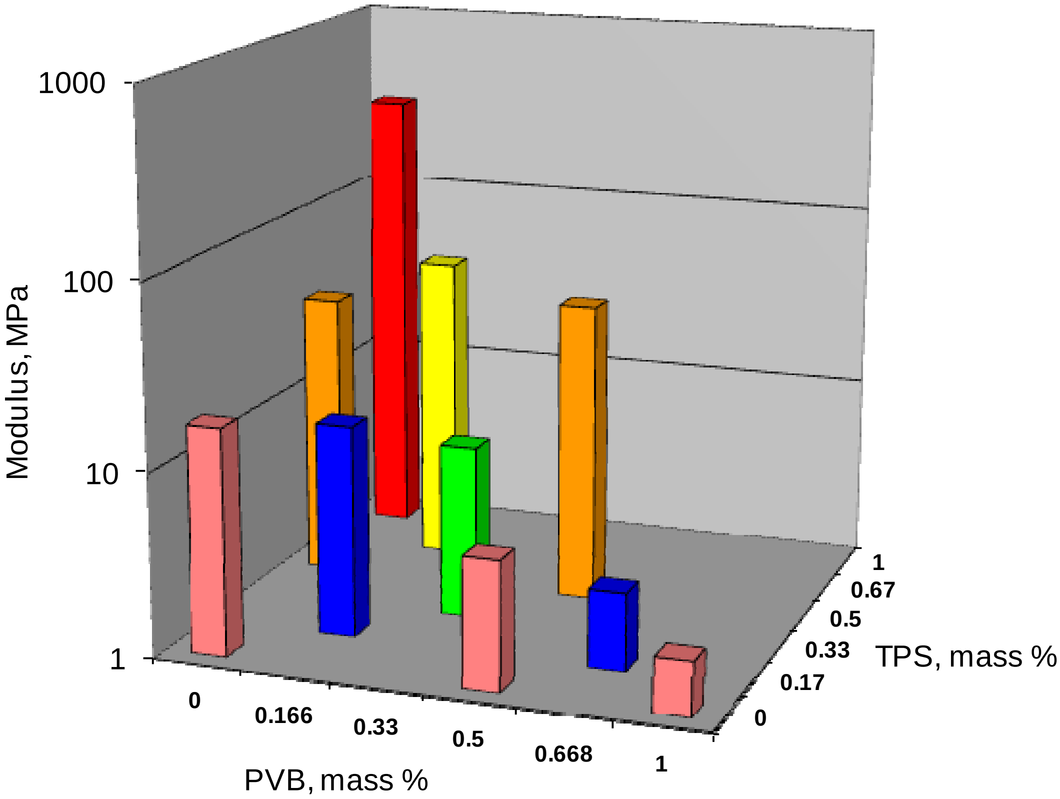

Figure 36: **Effect of ageing at 30 ºC and 60% RH on the modulus of TPS-PVB–polyamide (E2140)**

The effect of ageing on the mechanical properties of TPS-PVB-polyamide (E2140) blends is presented in Figures 34 to 36. Tensile strength and modulus increase with an increase in TPS content, while elongation-to-break decreases. This is due to retrogradation. A slight increase was observed for the tensile strength and modulus over the first 14 days and thereafter no further changes in mechanical properties were observed. However, the ageing process was only monitored for a period of 30 days and further changes may be possible after longer periods of ageing.

4.6 TPS–PVB-anhydride systems

In order to incorporate more than 8% filler content into TPS-PVB blends, PVB was pre-compounded with PVB. This is because of (a) the effect that fillers have in increasing the effective viscosity of a suspension, and (b) the reduction in water and in the availability of plasticiser for gelatinisation owing to occlusion inside agglomerates of filler particles. This led to slow gelatinisation, forming a thermoplastic starch that was only slightly plasticised, resulting in high viscosities. High torque was therefore required to mix it with the filler. Only formulations containing less than 8% filler could be extruded with TPS.

The anhydride ("dead burned" calcium sulphate) was used as a filler for PVB. A 50%-filled (by mass) PVB compound was first prepared using the twin-screw extruder. Thereafter, this compound was melt-mixed with TPS by extrusion using the single-screw extruder, resulting in TPS-PVB-anhydride polymer blends. Up to 25% anhydride compound could be melt-mixed with TPS. The extrusion parameters for the TPS-PVB-anhydride blends are given in Table 16 and the injection-moulding parameters in Table 17.

Table 16: Extrusion parameters for TPS-PVB-anhydride blends

Polymer Blend	Barrel Temperature, °C			
	Feeding zone	Compression zone	Metering zone	Die
TPS 9	120	150	148	100
TPS 10	120	150	145	90
TPS 11	110	135	130	80
TPS 12	120	150	150	90
TPS 13	120	150	150	100

Table 17: Injection moulding parameters for TPS-PVB-anhydride blends

Polymer Blend	Blend Composition, mass %			Barrel Temperature, °C	Injection Pressure, bar
	TPS	PVB	Anhydride		
TPS 10	78	11	11	150; 140; 135; 130	70
TPS 9	50	25	25		82
TPS 12	39	38	25		82
TPS 11	25	50	25		82
TPS 13	11	64	25		105

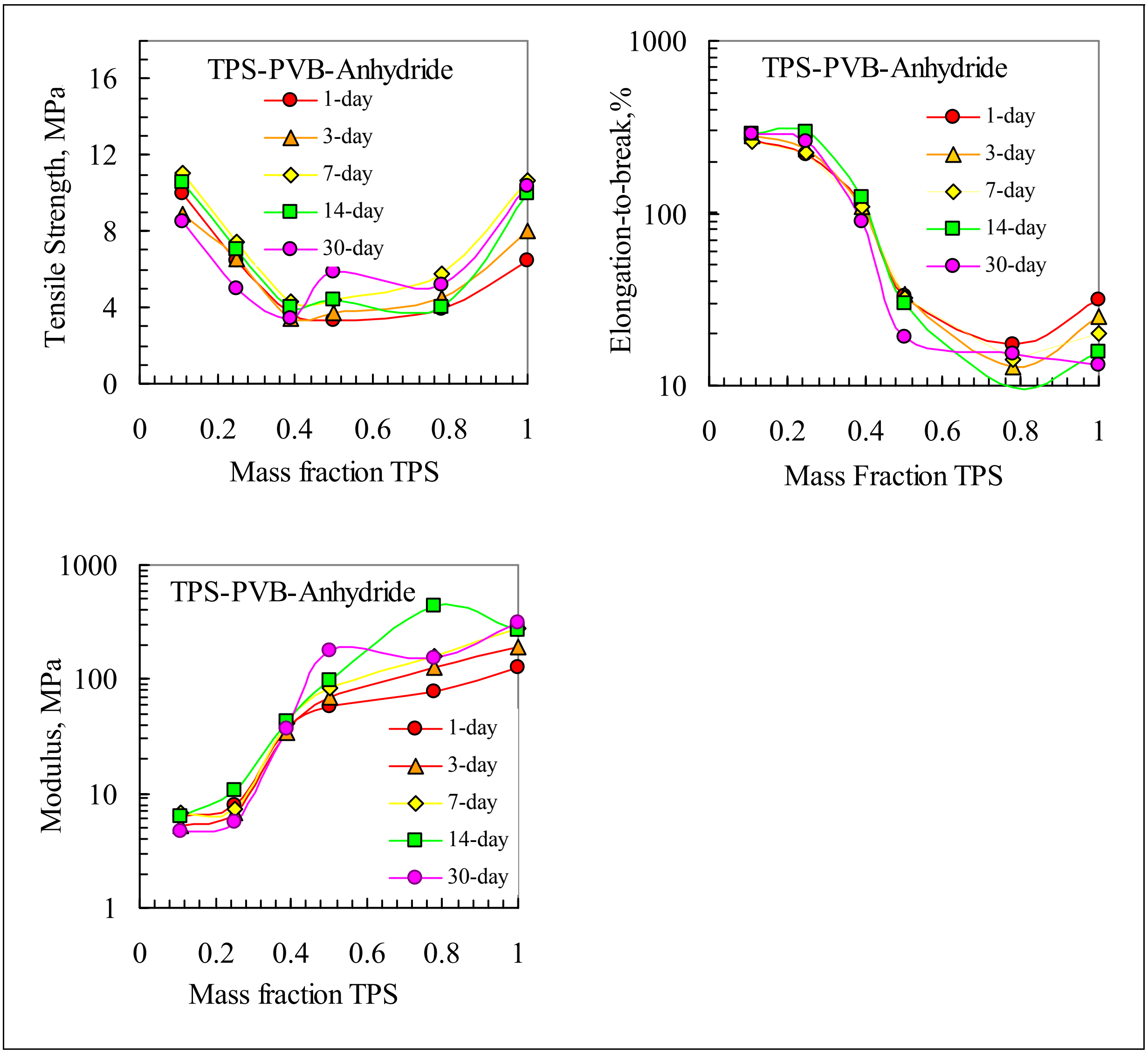

Figure 37: **Effect of ageing at 30 °C and 60% RH on the mechanical properties of TPS-PVB–anhydride blends**

The effect of ageing on the mechanical properties of TPS-PVB-anhydride blends is presented in Figure 37. There is a decrease in elongation-to-break with an increase in TPS content, while the modulus increases. There is a general decrease in the tensile strength for blends containing 25% by mass of anhydride, and a slight increase is noted for the blend containing 78% TPS and equal amounts of PVB and anhydride This trend is independent of the anhydride content since its concentration is kept constant at 25% by mass. This phenomenon cannot be explained by retrogradation. It is more likely that the TPS acts as a filler in this blend, hence the observed decrease in elongation-to-break and the increase in the modulus.