Blends of polyamide-6 with acrylic core–shell impact modifiers

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Blends of polyamide-6 (PA6) and acrylic core–shell impact modifiers (CSIM) were made by an extruder process as well as a reactor process. On the extruder blends, the impact behaviour was studied as a function of temperature while changing the type of CSIM, the CSIM concentration (0–40%) and the blending conditions. Reactor blends were prepared from caprolactam/CSIM mixtures via a hydrolytic polymerization process initiated either with water or with aminocaproic acid. The aminocaproic acid-initiated process is faster. The influence of reaction conditions on the deagglomeration of the CSIM, the melt flow index and the impact behaviour of the blends were studied. The degree of grafting of PA6 on the CSIM and the melt rheological behaviour of some samples have been investigated. The CSIM agglomerates were found to be broken up in the caprolactam starting mixture and did not coalesce to bigger particles. With the reactor blend method, often highly viscous melts were obtained. This is probably due to the formation of a comb-like structure of CSIM chains dissolved in caprolactam to which PA6 chains had been grafted.

(Keywords: polyamide-6 blends; core–shell acrylic rubber; impact behaviour)

INTRODUCTION

Polyamides (PA) can be toughened by blending with rubber[1–3]. The notched Izod impact behaviour of these blends as a function of temperature shows two transitions as schematically presented in *Figure 1*. One is at the glass transition of the rubber, where the rubber becomes soft and can act as an impact modifier. The other is at the so-called brittle-to-tough transition temperature (T_{bt}). At this transition the fracture process changes from unstable to stable crack propagation. The parameters that affect this brittle-to-tough transition are the rubber concentration[3], the particle size[3,4], the type of rubber[5] and the molecular weight of the matrix material[6]. PA blends are usually made by reactive compounding. For this, rubbers are usually acid-modified to make grafting of PA chains onto the rubber particles possible. The surface grafts lower the interfacial tension, prevent coalescence and hence stabilize the dispersion. The rubber particle size changes with the blending conditions. For the impact behaviour, the optimal particle size for the PA systems is in the 0.2–0.3 μm range[4].

Instead of using a rubber that has to be broken up in the blending process, it is also possible to work with preshaped particles. These materials are supplied as watery emulsions or as precipitated agglomerates. To prevent the rubbery particles fusing together, they are given a hard shell. In the blending process these core–shell impact modifiers (CSIM) have only to be deagglomerated. Extrusion blends with CSIM give good impact behaviour[7,8]. The core–shell impact modifiers are frequently used in the toughening of polyesters.

The formation of toughened systems by a reactor process has been studied[9–12]. For optimum properties, the morphology of the reactor blends should be comparable to that of extrusion blends. The particle size of the rubber should be small and uniform and the rubber should remain rubbery. In a reactor no high shearing can be applied, and so in the reactor process a high-viscosity rubber cannot be broken up. To obtain a fine dispersion, other methods should be applied. The polymerization conditions limit the reactor blending process.

The synthesis of polyamide-6 (PA6) is usually hydrolytic, starting from caprolactam (CL) with water as initiator (few per cent). The slowest step in the reaction is the ring opening of CL with water to aminocaproic acid (ACA)[13]. At atmospheric pressure the reaction times at 260°C are in the order 16 h. The reaction times can be considerably shortened by increasing the water concentration during the ring-opening step. To do this the first step has to be carried out under pressure. If ACA is used as initiator (few per cent), the slow lactam ring-opening step can be avoided and the polymerization rates are much higher[13].

To obtain, with a reactor process, blends with a small particle size of the rubbery phase, a few approaches are possible. One can dissolve the rubber in the starting reaction mass and let it phase-separate out during the polymerization; one can temporarily lower the viscosity of the rubber; and one can add preshaped particles.

The solvent method approach was followed for ethylene–propylene monomer (EPM) rubbers[9,10]. D'Orazio

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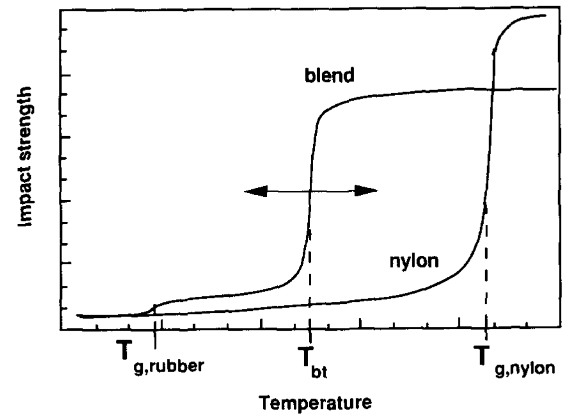

Figure 1 Schematic picture of impact behaviour of a polyamide and a polyamide blend

et al.[9] and Cimmino *et al.*[10] dissolved an EPM rubber in xylene and added this to a caprolactam–water mixture. Their polymerization was carried out at 260–270°C, for 4 h under vigorous stirring. Rubber particle sizes of 1–20 μm were obtained. The impact behaviour of these reactor blends was comparable to that of extrusion blends having the same rubber particle size.

With emulsion polymerization, emulsions of small rubbery particles in water can be obtained. The particles can be stabilized by giving them a hard shell, forming core–shell particles, e.g. acrylate rubber/PMMA (poly(methyl methacrylate)) and polybutadiene/SAN (styrene–acrylonitrile). These core–shell impact modifiers (CSIM) have a rubbery core and a hard shell, and are usually supplied as agglomerates. In a reactor blending process these agglomerates have to be broken up and dispersed. Udipi *et al.*[11,12] have shown that, without any specific interactions between CSIM and the reaction mass, this breaking up in the reactor is only partial. On subsequent injection moulding the dispersion is better. The dispersion could be improved by modifying the shell[11,12]. By starting from a latex of CSIM particles, an aggregate-free system was obtained[11].

The aim of this work is to study whether, with a reactor blending process, a good dispersion of the acrylic CSIM in a PA6 matrix can be obtained. The impact behaviour of these reactor bends will be evaluated and compared with that of extrusion blends.

EXPERIMENTAL

Materials

The suppliers of the materials were as follows: caprolactam (CL), DSM, Geleen, The Netherlands; aminocapronic acid (ACA), Merck, Darmstadt, Germany; PA6, K124, $\eta_{rel}=2.4$, and M258, $\eta_{rel}=5.8$ (both 1% solutions in 98% H_2SO_4), Akzo, Arnhem, The Netherlands; Paraloid EXL2300 acrylic CSIM (powder), and Paraloid EXL2386 acid-modified acrylic CSIM (powder), Rohm & Haas SA, France. All the materials were used as received.

Methods

Extrusion blending. PA6 and CSIM were blended in a co-rotating twin-screw extruder (Berstorff ZE 25, Hanover, Germany). The blending was carried out at standard conditions and at high-shear conditions. For the standard conditions the blending was at 100 rev min^{-1}, a throughput of 2 kg h^{-1} and with the temperature settings 280–280–280–280–290–290–290°C. For the high-shear conditions the compounding was at 400 rev min^{-1}, a throughput of 2 kg h^{-1} and with the temperature settings 240–240–240–240–250–250–250°C.

Injection moulding. Izod test bars ($10 \times 4 \times 80$ mm^3) of the dried polymers were injection moulded (Arburg Allrounder 221-55-250) with the temperature settings of 260–260–260–260–290°C and the mould at 90°C. The notched Izod strength was measured on test bars with a machined notch (ISO 180/1A) and determined after drying the samples (16 h in a vacuum oven at 110°C).

Melt flow index (MFI). The melt flow index (*MFI*) of the dried polymers was determined according to ASTM-D 1238-65T at 250°C.

Dynamic mechanical spectrometry (*d.m.s.*). With a 25/50 mm parallel-plate system, the rheological behaviour of the melt was studied with a Rheometrics RMS800 in the temperature range of 230–300°C.

Dynamic mechanical thermal analysis (*d.m.t.a.*). The torsional properties were studied with a Myrenne ATM3 (Germany) on dried test bars ($80 \times 10 \times 2$ mm^3) at 1 Hz with a heating rate of 2°C min^{-1}.

Scanning electron microscopy (*SEM*). The samples were cut with a LKB Nova cryomicrotome at −100°C. The rubber in the surface was extracted with boiling xylene (24 h). After drying, the sample was gold coated and studied with a SEM (JEOL JSM-35-CF).

Polymerizations

Water-initiated (*10% CSIM*). A 1 litre stirred autoclave (Juchheim, Germany) is charged with 360 g CL and 18 ml distilled water (5 wt%) warmed to 80°C. As soon as the CL has melted, 40 g of CSIM was added. After flushing with nitrogen the reactor is closed and a nitrogen starting pressure of 5 bar is imposed. The reaction mass is heated for 20 min at 200°C and 1 h at 270°C, during which the maximum pressure was held at 15 bar. Subsequently the pressure was reduced to atmospheric and held at that pressure for 5.5 h and 270°C. After the reaction mass was cooled, the sample was granulated. Free CL in the sample was extracted with boiling methanol (24 h).

Aminocapronic acid-initiated (*10% CSIM*). A 1 litre stirred autoclave (Juchheim, Germany) is charged with 326 g CL and 41.7 g aminocapronic acid (ACA) warmed to 80°C. As soon as the CL has melted, 40 g of CSIM was added. The reaction mass is heated for 1 h at 190°C and 5 h at 240°C at atmospheric pressure. After the reaction mass was cooled, the sample was granulated. Free CL in the sample was extracted with boiling methanol (24 h).

Adding CSIM to prepolymer. A 1 litre stirred autoclave (Juccheim, Germany) is charged with 360 g CL and 18 ml distilled water (5 wt%). After flushing with nitrogen the reactor is closed and a nitrogen starting pressure of 5 bar is imposed. The reaction mass is heated for 20 min at 200°C and 1 h at 270°C, during which the maximum pressure was held at 15 bar. Subsequently the pressure was reduced to atmospheric. At this point the prepolymer has η_{inh} of 1.3. To the stirred melt is added 40 g of CSIM and reacted for 4.5 h and 270°C at atmospheric pressure. After the reaction mass was cooled, the sample was granulated. Free CL in the sample was extracted with boiling methanol (24 h).

A prepolymer with η_{inh} of 1.6 was obtained by heating the CL–water reaction mass for 20 min at 200°C and 1 h at 270°C, during which the maximum pressure was held at 15 bar, and subsequently 1 h at 270°C at atmospheric pressure. After adding the CSIM the reaction at 270°C was continued for another 3.5 h.

Degree of grafting[14]. A sample, 5 g, is suspended in 100 ml 98% formic acid for 24 h. The suspension was centrifuged at 15 000 rev min^{-1} and the clear underlayer removed with a syringe. The remaining non-dissolved part is resuspended in formic acid. This procedure is repeated three times. The final residue is washed with water, dried and analysed by elemental analysis (the percentage of nitrogen (N%)). The PA content is calculated from N% using (N%/14) × 113.2 (mol wt PA repeat).

Stability of CSIM. A 1 litre stirred autoclave (Juccheim, Germany) is charged with 40 g CSIM and 18 ml distilled water. After flushing with nitrogen the reactor is closed and a nitrogen starting pressure of 5 bar is imposed. The reaction mass is heated for 5 h at 270°C, during which the maximum pressure was held at 15 bar. A film and a bar of this material were melt pressed. The hydrolysis of the acrylic ester was studied on a film with a Biorad FTIR, 16 scans for each spectrum. The bar was analysed with d.m.t.a.

RESULTS

Extrusion blends

PA6 and acrylic CSIMs were blended with a twin-screw extruder. Two types of impact modifiers were used, one with an acrylic ester shell (unmodified, EXL2300) and one with an acrylic shell with some free acid groups (modified, EXL2386). In the blending operation the CSIM agglomerates break up into primary particles. The particle size was found to be 0.32 μm for the EXL2300 and 0.30 μm for the EXL2386, both with a narrow size distribution. Changing the blending conditions to 'high-shear' conditions did not change the particle size. With CSIM only the agglomerates have to be broken up. The primary particles are not expected to be broken up and also coalescence is not expected to take place.

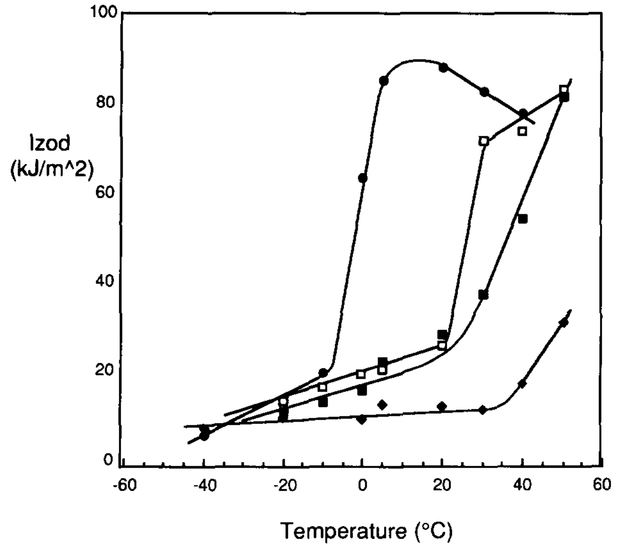

Figure 2 Impact behaviour of extrusion blends of PA2.4 and an unmodified CSIM (EXL2300). CSIM concentration (wt%): (◆) 10%; (□) 20%; (●) 30%; (■) 40%

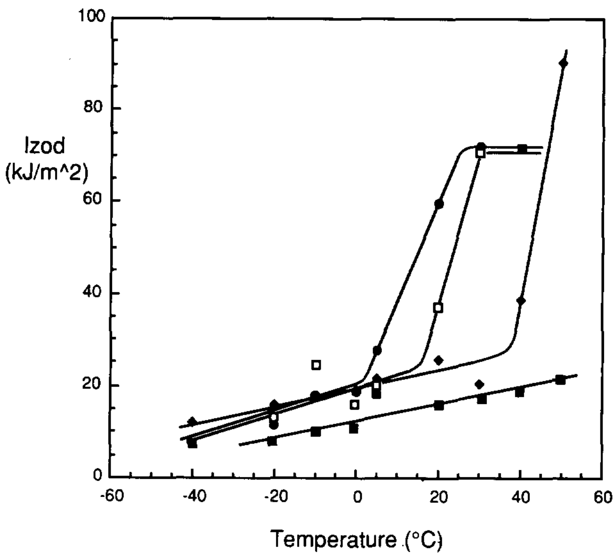

Figure 3 Impact behaviour of extrusion blends of PA2.4 and a modified CSIM (EXL2386). CSIM concentration (wt%): (◆) 10%; (□) 20%; (●) 30%; (■) 40%

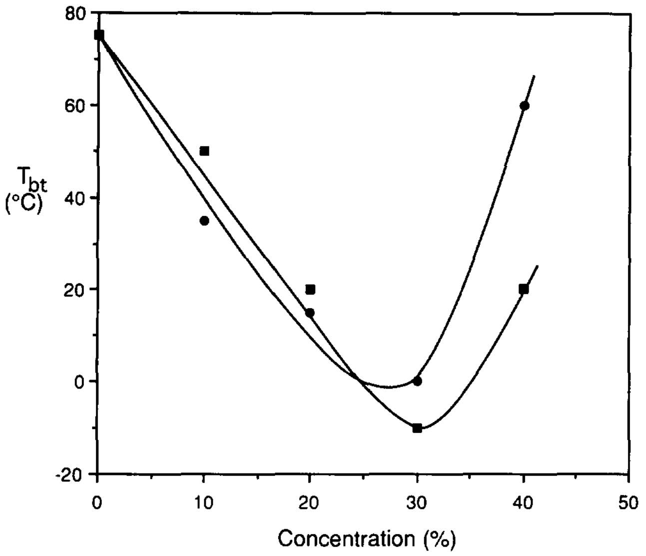

Figure 4 Brittle–tough transition temperature of the blends as a function of the CSIM concentration (wt%): (■) unmodified CSIM (EXL2300); (●) modified CSIM (EXL2386)

With these CSIMs, tough blends can be made (*Figures 2* and *3*). The impact levels in the brittle region can rise up to 20 kJ m^{-2} and in the tough region up to 70 kJ m^{-2}. These values are comparable to other PA–rubber blends. Most important in toughened blends is the shift in the brittle-to-tough transition. At a CSIM concentration up to 30% the brittle-to-tough transition temperature (T_{bt}) decreases linearly with concentration (*Figure 4*). Unexpected is the behaviour of the 40% blends,

Table 1 PA6/modified CSIM (EXL2386) blends (90/10)

No.	PA initial	Conditions (h/°C/bar)	PA η_{rel}	*MFI* blend (g/10 min)	Dispersion	Izod (kJ m^{-2})
1	Polymer, $\eta_{rel}=2.4$	Extruder, 6 min/260°C	2.4	–	No clusters	25.5
2	CL/H_2O	Reactor, 1/250/15 + 5.5/250/1	1.8	$\ll 1$	No clusters	7.0

Table 2 PA6/unmodified CSIM (EXL2300) blends (90/10)

No.	PA initial	Conditions (h/°C/bar)	PA η_{rel}	*MFI* blend (g/10 min)	Graft con. (%)	Dispersion	Izod (kJ m^{-2})
3	Polymer, $\eta_{rel}=2.4$	Extruder, 6 min/260°C	2.4	6.6	2.5	No clusters	10.5
4	Polymer, $\eta_{rel}=5.8$	Extruder, 6 min/260°C	5.8	–	–	No clusters	17.0
5	CL/H_2O	Reactor, 1/250/15 + 5.5/250/1	1.8	1	29.8	No clusters	8.5
6	CL/H_2O	Reactor, 1/250/15 + 5.5/250/N_2	2.4	$\ll 1$	40.8	No clusters	7.5
7	CL/H_2O	Reactor, 1/270/15 + 5.5/270/N_2	3.2	$\ll 1$	81.7	No clusters	11.0
8	Polymer, $\eta_{rel}=1.3$	Reactor, 4.5/270/N_2	3.2	0.3	–	Clusters	6.0
9	Polymer, $\eta_{rel}=1.6$	Reactor, 3.5/270/N_2	3.2	0.6	–	Clusters	5.5
10	CL/ACA	Reactor, 1/190/1 + 5/240/1	2.7	5.0	–	No clusters	12.5

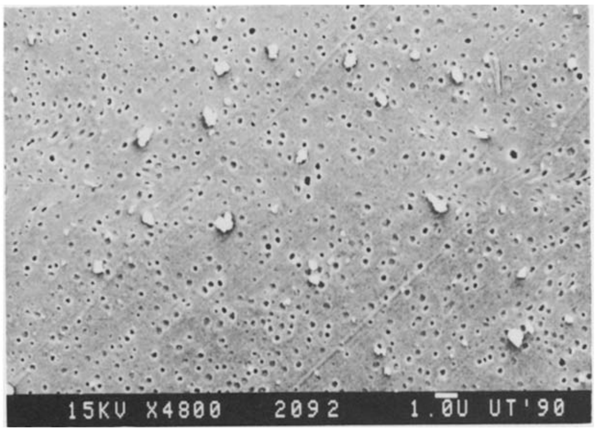

Figure 5 SEM analysis of sample 5, CSIM well dispersed

which have a very high T_{bt} again. In these 40% blends the CSIM have coagulated to >1 μm particles. This effect is to some extent already taking place in the 30% modified CSIM blend. The modified CSIM appears to be somewhat more effective at low concentrations.

Reactor blends

The CSIM seem to be interesting modifiers for reactor blends as they have a fine particle size and the CSIM agglomerates are easily broken up. The reactor blends were prepared in a stirred autoclave. In the first set of experiments (water-initiated) a calculated η_{rel} of the PA of 1.8 was obtained[13]. This is lower than the 2.4 used for extrusion blending (*Table 1*).

The 10% acid-modified CSIM, water-initiated polymerization. With 10% CSIM EXL2386 (acid-modified), extremely viscous blends were obtained (very low *MFI* values) (*Table 1*). SEM analysis showed that the CSIM agglomerates were broken up and evenly distributed. The impact strength was, however, low. Although the PA was short-chained (calculated η_{rel} of 1.8), the whole system seems to have gelled. For these reaction conditions, the acid-modified CSIM was too reactive and was not studied further.

The 10% unmodified CSIM, water-initiated polymerization. The reactor blend with 10% unmodified CSIM (EXL2300) was viscous but had not gelled (*Table 2*, No. 5). The CSIM agglomerates had been broken up and the particles were well dispersed (*Figure 5*). The notch impact strength was lower than that of the respective extrusion blends (Nos. 3 and 4). Changing the reaction conditions to obtain higher calculated PA molecular weights (*Table 2*, Nos. 6 and 7) decreased the *MFI* strongly and improved the impact strength. The molecular weight of the PA seems to be an important factor determining the impact strength (see also *Table 2*, Nos. 3 and 4).

The analysis of the degree of grafting of PA onto CSIM showed that extrusion blending leads to a low degree of grafting (*Table 2*, Nos. 3 and 4). Reactor blends (Nos. 5–7), however, display a much higher degree of grafting. The degree of grafting increased with the severity of the reaction conditions. With the high amount of grafting found for certain reactor blends it seems unlikely that this is only due to surface grafting reactions. In the reactions 5–7 the CSIM is added to the lactam, and as the lactam has a high solvation power it might have not only broken up the agglomerates but also dissolved some CSIM.

CSIM addition to prepolymer. Addition of the CSIM in a later stage of the polymerization reduces the solvation power. In the blends Nos. 8 and 9, the CSIM were added to prepolymers. This increased the *MFI* of the obtained blends but the CSIM agglomerates were now not broken up (*Figure 6*). The notched Izod impact strength was at a low level, which is not surprising. To obtain primary particles, it seems important to add the CSIM at the beginning of the reaction. To reduce the degree of grafting, the reaction conditions must be milder. Particularly, the initial stage of polymerization seems to be critical.

Table 3 PA6/unmodified CSIM (EXL2300) blends (80/20)

No.	PA initial	Conditions (h/°C/bar)	PA η_{rel}	*MFI* blend (g/10 min)	Dispersion	Izod (kJ m^{-2})
11	Polymer, $\eta_{rel}=2.4$	Extruder, 6 min/260°C	2.4	–	No clusters	22.0
12	CL/ACA	Reactor, 1/190+5/240	2.7	$\ll 1$	Some clusters	8.5
13	CL/ACA	Reactor, 1/190+1/240	1.6	0.8	Some clusters	3.0
14	CL/ACA	Reactor, 0.5/190+0.5/240/1	1.4	3.6	Some clusters	2.5

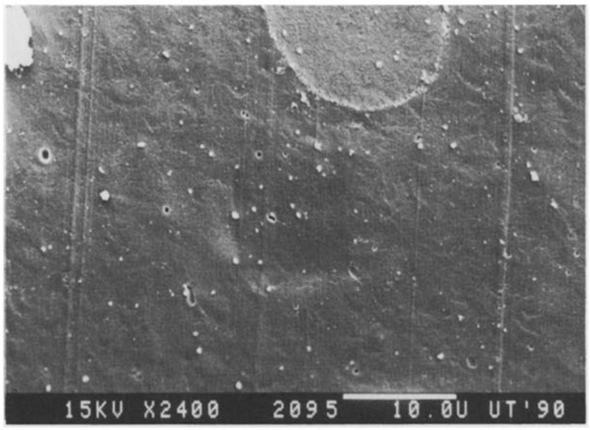

Figure 6 SEM analysis of sample 8, CSIM in clusters

Aminocapronic acid-initiated polymerization. The severity of the reaction conditions can be decreased considerably by initiating the reaction with ACA instead of water[13]. In this way the slow conversion of CL with water to ACA is left out and no autoclave step is needed. Reacting for 1 h at 190°C and 5 h at 240°C at atmospheric pressure gives a calculated η_{rel} of 2.7 (No. 10). The reactor blends with 10% EXL2300 under these conditions resulted in a *MFI* of 5 g/10 min. The CSIM particles were well dispersed. The notched Izod value was comparable to the extrusion blend (No. 3).

The 20% unmodified CSIM, ACA-initiated. Increasing the CSIM concentration to 20%, with the reaction conditions of No. 10, yielded a very low *MFI* (*Table 3*, No. 12). The impact strength was lower than that of the 10% reactor blend No. 10 or the 20% extrusion blend No. 11. By reducing the reaction time (Nos. 13 and 14) the *MFI* value could be increased. However, the impact strength was low, lower than for No. 12. For reactor blends with 20% CSIM, a combination of good dispersion, high *MFI* and high Izod value has not yet been obtained.

Reactor blend process

Addition of the CSIM to the CL instead of to the prepolymer or the polymer gave much lower *MFI* values. We observed also that adding the CSIM to the CL strongly increased the viscosity of the lactam mixture. So the acrylic partially dissolves in the lactam. This is in agreement with the findings of Udipi, who observed that the shell of an acrylic core–shell material dissolved in the lactam[11]. The lactam helps to deagglomerate the clusters but also dissolves some of the acrylic shell material. At these reaction conditions the amine end-group of the PA can react with the acrylic group of the dissolved acrylic. Each PA6 chain contains only one amine group and each acrylic polymer chain contains many acrylic groups. If several PA6 chains are grafted on the acrylic, comb-like structures are formed. It is expected that these comb-like structures give the reactor blends such high viscosities.

Stability of CSIM

Another question is whether the CSIM can withstand the reaction conditions without hydrolysis or thermal degradation. The CSIM (EXL2300) was kept for 5 h at 270°C and 15 bar steam pressure in an autoclave. A film and a bar of this material were melt pressed. The i.r. spectrum of the treated material had the same peak positions as the untreated material. The relative peak strength of the shoulder at 1692 cm^{-1} assigned to the free acid increased with the steam treatment (*Figure 7*).

The d.m.t.a. data showed that the G' modulus of the steam-treated CSIM, was over the temperature interval -100 to $+100$°C, somewhat lower (*Figure 8*). The T_g values at -42°C and 110°C had not shifted. The reaction conditions do not seem to have changed the rubbery character of the CSIM but the acid content is increased.

Rheological behaviour

The *MFI* data are low for the calculated η_{rel}. The viscoelastic behaviour of two samples (*Table 2*, Nos. 10 and 12) was studied in more detail with d.m.s. in the temperature region 230–300°C. For linear polymers the phase angle increases with decreasing frequency to a value of 90° (Newtonian). The phase angle as a function of frequency of sample 10 is given in *Figure 9*. This phase angle is, in the whole frequency and temperature region, clearly non-Newtonian. It is evident too that the material with increasing temperature becomes more elastic. It even seems that the material is crosslinking during the experiment.

The phase angle measurements of a 20% blend (sample 12) show an even stronger elastic effect (*Figure 10*). The upswing at 300°C and low frequencies suggests a disentanglement of the network and thus that a transient network was present. With these elastic effects it is not surprising that the *MFI* values are so low.

CONCLUSIONS

Acrylic core–shell impact modifiers can easily be deagglomerated by twin-screw extrusion blending. The observed particle sizes were independent of processing conditions. The notched impact behaviour is similar to that of other PA–rubber blends. The effect of toughening efficiency seems to be a shift in the brittle-to-tough transition temperature. With increasing

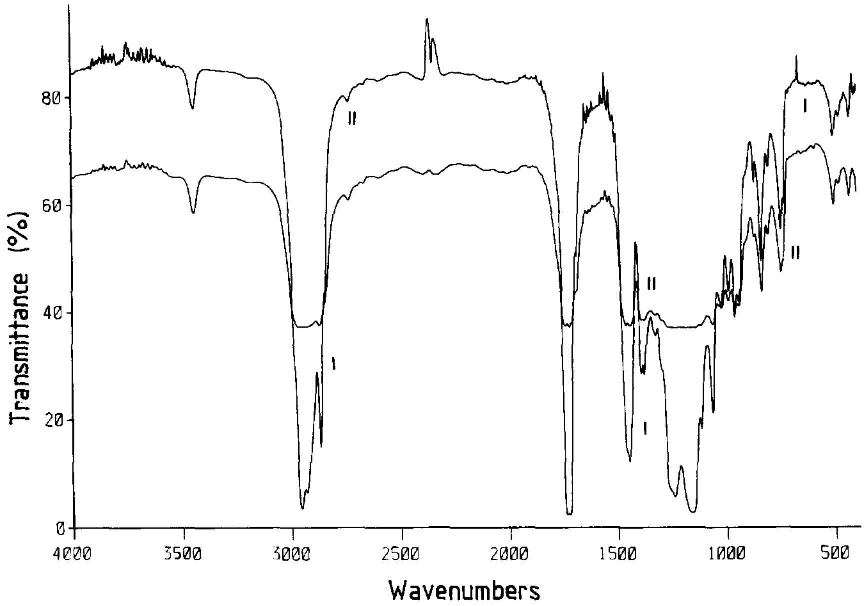

Figure 7 I.r. spectrum of EXL2300: (I) as obtained; (II) after steam treatment (5 h, 270°C)

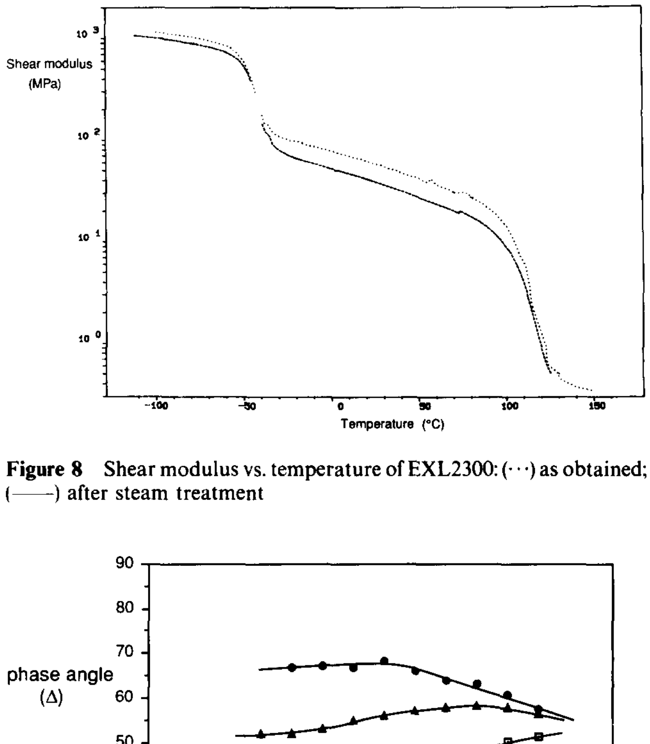

Figure 8 Shear modulus vs. temperature of EXL2300: (···) as obtained; (——) after steam treatment

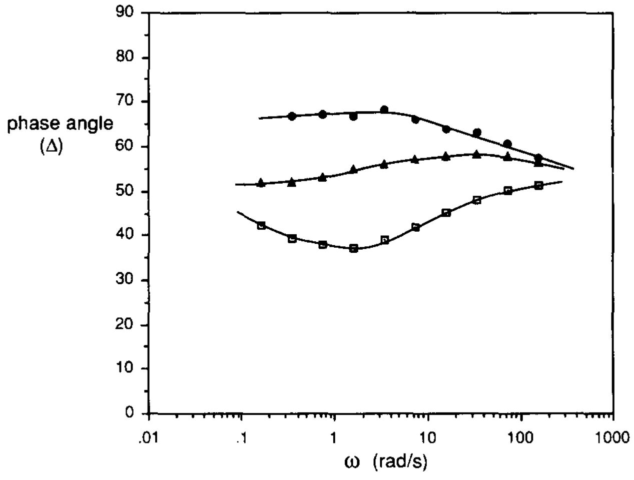

Figure 9 Melt rheological phase angle vs. frequency of blend No. 10: (●) 230°C; (▲) 260°C; (□) 300°C

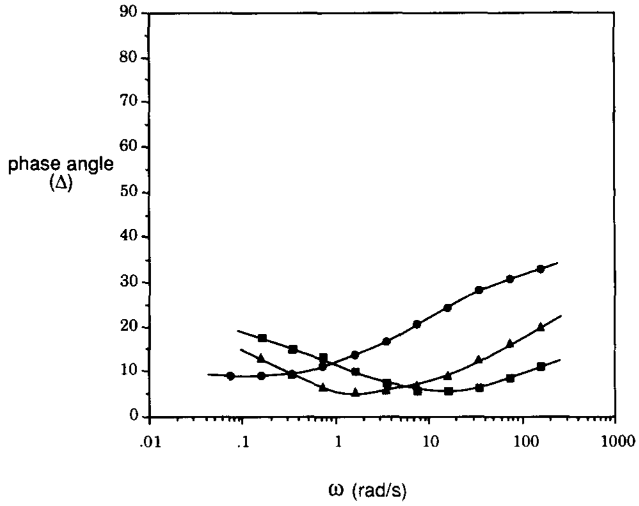

Figure 10 Melt rheological phase angle vs. frequency of blend No. 12: (●) 230°C; (▲) 260°C; (■) 300°C

CSIM concentration, this T_{bt} is decreased. The 40% blends coalesced. At low concentrations the modified CSIM seem to be slightly more effective. Some grafting of the PA on the unmodified CSIM particle takes place during extrusion compounding. CSIM particles seem to be ideal for reactor blends, as the preshaped particles have only to be dispersed.

For a good deagglomeration of CSIM in a PA6 reactor process, the material has to be added to the lactam. Adding the particles to the prepolymers did not give a good deagglomeration. The lactam is a strong solvent and it dissolves some of the CSIM. At a later stage in the PA polymerization a reaction between the acrylic or the hydrolysed acrylic and the PA6 growing chain is possible. Not only is the PA grafted on the particle surface, but probably also some grafted PA is grafted on dissolved acrylic chains forming comb-like structures in the matrix.

At severe reaction conditions, systems with a very low *MFI* were obtained. The polymer melt was clearly non-Newtonian and has a strong elastic component at low shear rates, suggesting that a transient network was formed. This is in agreement with the possible formation of comb-like structures in the system.

For a given length of the PA chain and having a deagglomerated CSIM system, the impact values of the reactor blends were comparable to those of extrusion blends. In future studies on reactor blends with these acrylic core–shell systems, one should avoid dissolving the acrylic CSIM but still break up the agglomerates.

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