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Melt compounding of rigid PVC formulations with hydrotalcites

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Hydrotalcites, compounds of magnesium–aluminium–hydroxycarbonate, are promoted as environmentally safe materials for costabilisation of PVC products. Commercial grades of hydrotalcites have been added to rigid PVC formulations, containing a range of different stabiliser types, to evaluate their contribution to heat stability and their effect on mechanical properties. Hydrotalcites are confirmed to be effective costabilisers for rigid PVC: static thermal stability (through oven testing) and dynamic thermal stability (via torque rheometry) of PVC compounds are modified by their presence. The extent of change is determined by the primary stabiliser type and the grade of the hydrotalcite. Detailed analysis of mechanical properties has been carried out on compression moulded samples and on extruded compounds. With the former, no significant change in tensile or impact performance was observed, for hydrotalcite levels up to 5 phr. Charpy impact data on extruded PVC have shown significant increase in performance of compounds containing an acrylate modifier when hydrotalcites are used.

Introduction and objectives

Over recent years attention has been paid to the use of synthetic hydrotalcites as stabilisers for PVC. Hydrotalcites are forms of hydrated magnesium–aluminium–hydroxycarbonates: a typical formula is $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. The structure consists of layers of magnesium hydroxide and aluminium hydroxide with anionic interlayers comprising the carbonates and the bound water. The carbonate can be substituted with other anions, such as sulphates and nitrates, to form other hydrotalcite like layered double hydroxides (LDHs). It is the capacity of hydrotalcites for anionic exchange that makes the materials highly suited to the task of stabilising PVC. Papers on the use of hydrotalcites alone, and in combination with CaZn, lead and tin stabilisers are now reviewed.

van der Ven et al.[1] evaluated the stability of PVC with a range of hydrotalcite like materials of the general formula of $Mg_3ZnAl_2(OH)_{12}.A.nH_2O$ with different anions (A). They concluded that the stabilisation offered by hydrotalcites relates to the capacity of the materials to react with HCl formed during the degradation of PVC through a two step process: first, the interlayer anions react with HCl and second, the hydroxide layers are lost as these react with HCl to form metal chlorides.

Lin et al.[2] drew the same conclusion as van der Ven et al.,[1] regarding the mechanism of stabilisation of PVC, after testing compression moulded composites of calcium stearate/zinc stearate stabilised PVC–P with

nanoparticles of hydrotalcite like Mg–Al–CO_3 LDHs. They also reported that materials with a Mg/Al ratio of 2 gave maximum enhancement of thermal stability and the optimum addition level appeared to be 2 phr. In a subsequent paper by Lin et al.[3] modification of a Mg–Zn–Al–CO_3 hydrotalcite by reaction with maleic acid produced a Mg–Zn–Al–maleate LDH with increased spacing between the hydroxide layers. PVC–P composites containing this intercalated structure also had greatly improved stability but to a much lesser extent than the Mg–Al–CO_3 LDH.

The stabilisation of PVC by lead stearate in combination with hydrotalcite (Alcamizer 1) has been studied by Kalouskova et al.[4] A range of PVC foils produced at 180°C were assessed by colour change at 180°C (oven test). As expected increasing the lead stearate content to 3 phr progressively improved the thermal stability of the PVC, while, a stabiliser combination of 0·75 phr of the stearate plus 2 phr of the Alcamizer (i.e. a costabiliser system) performed even better. However, perhaps the most interesting result was the colour change comparison of the PVC without any stabiliser (initially red) and the PVC with 2 phr of the hydrotalcite (initially clear/pink). The former darkened to reddish/black over 65 min, while the latter did the same over 70 min, via a pink to orange to red sequence. This evidence showed the hydrotalcite only acts as a HCl acceptor and does not prevent (dis)colouration of the polymer.

Stabilisation of PVC by untreated and surface treated hydrotalcites in combination with organotin and lead stabilisers has also been reported. Evidence gathered from thermogravimetric analysis and ultraviolet spectra, but primarily from Congo red tests,[5,6] showed the stability of PVC was substantially improved by a

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combination of titanate treated hydrotalcite and tin stabiliser. It appeared that the optimum addition level for the hydrotalcite was 5% by weight. Injection moulding was used to produce notched Izod and tensile test pieces from compounds of PVC plus hydrotalcite.[6] Izod impact strength, tensile strength and elongation at break all declined as the hydrotalcite content was increased to 10%.

In some cases in the literature, researchers have used hydrotalcites synthesised in their own laboratories. However, for the work presented here, two commercial grades of hydrotalcites have been obtained: Alcamizer P93 from Kisuma Chemicals[7] and Sorbacid 911 from Sud-Chemie.[8] The materials are promoted as environmentally safe costabilisers for PVC, which contribute to excellent thermal stability, have excellent dispersability and are well suited to transparent applications.

In this study, hydrotalcites have been processed via two routes after dry blending of rigid PVC formulations: mill mixing followed by compression moulding and by extrusion. In both cases processing conditions have been employed with the objective of generating products with levels of gelation associated with good mechanical strength. (Rather than minimise thermal history that might exaggerate thermal stability.) As the commercial grades are considered to be ultrafine, majority of particles smaller than 1 μm, effective dispersion of the particles ought to produce good mechanical strength in tandem with the anticipated enhancement of both dynamic and thermal stability.

Experimental

Materials and processing conditions

Hydrotalcites

Table 1 gives details of the two grades of hydrotalcite used in this work.

Sample preparation by compressing moulding

The hydrotalcites were added to PVC formulations containing tin and CaZn stabilisers, and an organic based stabiliser (OBS). The formulations (Table 2) were blended at 3500 rev min^{-1} (to a discharge temperature of 120°C) using a Henschel FML 10 laboratory scale high speed mixer. Dry blends were mixed further on a two roll mill at 155°C for tin stabilised and hydrotalcite

only formulations and at 165°C for CaZn and OBS formulations. Compression moulded sheets, of nominally 1 or 1·5 mm thickness, were produced from the milled sheets at 195°C.

Preparation of extrudates

The core content of all formulations comprised PVC (INEOS ChlorVinyls K68), stabiliser (Chemson PWX15840), processing aid (Rohm and Haas Paraloid K120N) and titanium dioxide (Kronos 2220). An impact modifier (Rohm and Haas KM 355) and the hydrotalcites were added to the 'core' formulation as listed in Table 3, where each formulation has been assigned an identifier. All formulations were dry blended as stated earlier. Blends were processed using a Krauss Maffei KMD 2–25KK laboratory twin screw extruder fitted with a slot die (dimensions of the slot were 30 × 5 mm). The screw speed and screw temperature were respectively 20 rev min^{-1} and 165°C and the following temperature profile was employed:

Barrel zone 1	Barrel zone 2	Adaptor	Die
180°C	190°C	190°C	200°C

Thermal stability and characterisation

Dry blends

The dynamic stability of dry blends was evaluated using a Haake Rheocord 90. The chamber was set at 190°C, the rotor speed was 60 rev min^{-1} and the batch weight 60 g. After loading the chamber, the torque versus time curve initially shows two peaks: the first for compaction of the blend and the second when the blend has gelled. After this, the torque falls and levels out to a steady value. The subsequent increase in torque arises due to degradation of the melt. In this study, three values were derived from the torque–time curves: the time to the gelation peak, the equilibrium torque and the 'stability time': the interval between the time to the gelation peak and the onset of degradation.

Products

Thermal stability of products was assessed quantitatively from colour changes arising from oven heating of products at 190°C over a range of regular time intervals. Gelation was determined using a TA Instruments 2010

Table 1 Properties of hydrotalcites[7–10]

Grade	Alcamizer P93	Sorbacid 911
Supplier	Kisuma Chemicals	Sud-Chemie
Appearance	White powder	White powder
Chemical nature	Hydrated magnesium zinc aluminium hydroxycarbonate	Hydrated magnesium aluminium hydroxycarbonate
Particles >5 μm	None	None
Particles <1 μm	82%	>50%
Average particle size, μm	0·7	Not specified

Table 2 PVC formulations for compression moulding

Component	Supplier/grade	phr	phr	phr	phr
PVC resin	INEOS ChlorVinyls EVIPOL SH6830	100·0	100·0	100·0	100·0
Hydrotalcites	As Table 1	5	0–10	0–5	0–5
CaZn stabiliser	Chemson PWX15840 (one pack)		4·5		
OBS	Chemson PWX15861			4	
Tin stabiliser	Akcros BTS71				2

differential scanning calorimeter, where samples of 15 mg were heated from ambient temperature to 240°C under a controlled rate of 20°C min^{-1}. Reflectance mode X-ray diffraction patterns, over the range of $2\theta=5$ to 50°, were obtained using a Bruker D8 X-ray diffractometer with a Cu K_α source. Images of sections through samples were taken with a JEOL 2000FX TEM at 200 kV.

Mechanical properties

Tensile testing

For both compression moulded and extruded products a template was used to cut dumbbell shaped tensile testpieces with overall dimensions of $100 \times 12\cdot5$ mm with a waisted section of 30 mm gauge length by 4·4 mm width. Tests were carried out at 10 mm min^{-1} on a Hounsfield tensometer fitted with 1 kN load cell for moulded samples and 10 kN for extruded products. For a given product at least six samples were tested.

Impact testing of mouldings

A Rosand instrumented falling weight impact tester was used to test the compression mouldings. A 10 mm diameter hemispherical tipped striker attached to a 10 kg mass was dropped from a height of 1 m giving an impact velocity of 4·4 m s^{-1} and impact energy of 98 J. From the load deflection curve, three properties were derived: peak force, peak energy and failure energy (peak energy plus energy required for striker to completely penetrate the sample). Six samples of a given product were tested.

Impact testing of extrudates

For extruded products, Charpy samples (type A with notch tip radius of 0·25 mm) were prepared in accordance with BS ENO 179-1:2001. These were tested using a RAY-RAN universal pendulum impact tester fitted with a standard hammer that struck samples at

3·8 m s^{-1} with an energy of 7·5 J. For each extrudate batches of 10 or 15 samples were prepared.

Results and discussion

In the data tables of mechanical properties presented in this section, calculated average values are given with standard deviations in brackets. Also, the results on OBS formulations in Tables 4–6 and in Fig. 1 were drawn from work by Algahtani.[11] Measurements obtained by differential scanning calorimetry (DSC) will not be included in the results here. However, a number of comments on the data are included. Differential scanning calorimetry showed that the level of gelation in compression moulded samples was good with the enthalpy of the melt endotherm being consistent across the range of stabiliser types: typically 4–5 J g^{-1}. It also confirmed that the actual compression moulding temperature was close to 195°C. Differential scanning calorimetry analysis of the extrudates was also reasonably consistent (melt enthalpies of 3·5–4·5 J g^{-1}) and showed the processing temperature to be ~194–196°C. The derivation of enthalpy associated with melt endotherm and processing temperature from DSC curves is well established.[12–14]
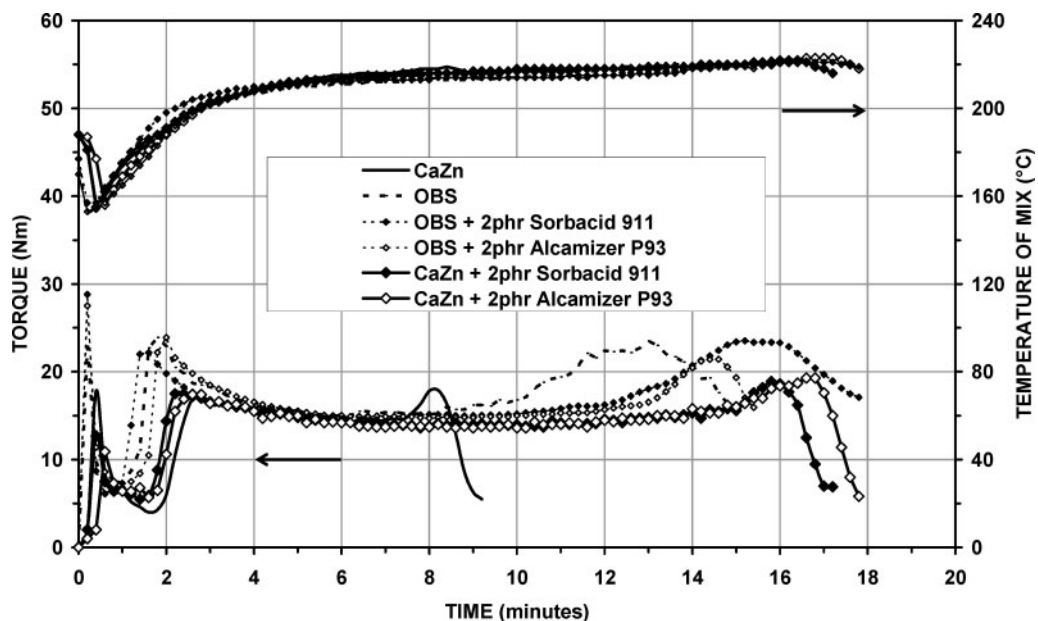
At this point it is appropriate to make some observations upon the two formulations of PVC plus 5 phr of each hydrotalcite. When the hydrotalcite only blends were milled the banded sheet initially appeared to be clear. However, as milling continued the sheet turned pink, which darkened to red by the end of the mill mixing regime. Compression moulding of the milled products generated sheets that were very dark red in colour. This sequence of colour changes can be seen to some extent, and almost identically, in the respective thermal stability charts of Lin *et al.*[3] and of Kalouskova.[4] Colour change is one of the most

Table 3 Formulations for extrusion

	phr	phr	phr	phr	phr	phr	phr	phr	phr	phr
PVC resin	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0
CaZn stabiliser	4·5	4·5	4·5	4·5	4·5	4·5	4·5	4·5	4·5	4·5
Processing aid	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Titanium dioxide	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0	4·0
Impact modifier		7·0	7·0	7·0	7·0		4·0	7·0	7·0	7·0
Alcamizer P93			2·0	5·0	10·0	5·0	5·0			
Sorbacid 911								2·0	5·0	10·0
IDENTIFIER	CORE	REF	2A/7M	5A/7M	10A/7M	5A/0M	5A/4M	2S/7M	5S/7M	10S/7M

Table 4 Torque rheometry data for 'compression moulding' formulations

Hydrotalcite, phr	Time to gelation peak, min	Equilibrium torque, Nm	Stability time, min	Time to gelation peak, min	Equilibrium torque, Nm	Stability time, min
	Alcamizer P93			Sorbacid 911		
5	2·2	18·5	3·7	2·2	18·7	3·6
	Tin+Alcamizer P93			Tin+Sorbacid 911		
0	1·0	13·7	6·6	1·0	13·7	6·6
5	1·6	16·5	3·8	1·2	15·5	7·3
	CaZn+Alcamizer P93			CaZn+Sorbacid 911		
0	2·8	15·1	4·6	2·8	15·1	4·6
2	2·8	14·2	10·5	2·2	14·4	12·6
5	1·8	14·1	13·0	1·6	14·1	13·2
	OBS+Alcamizer P93			OBS+Sorbacid 911		
0	1·8	15·4	8·1	1·8	15·4	8·1
2	2·0	14·9	11·2	1·5	15·1	10·7
5	1·8	15·2	11·5	2·0	15·5	11·2

1 Effect on dynamic stability of adding 2 phr of hydrotalcite

apparent indicators of degradation of PVC and the sequence is often seen as yellow to reddish brown and ultimately to black. In some studies this progression in colour has been attributed to the formation of strongly coloured carbonium salts.[15] However, it is more commonly attributed to the conjugated double bonds that arise from dehydrochlorination, where polyene

sequences of just seven conjugated double bonds can cause PVC to change colour, and sequences of up to 30 have been found in the course of the process.[15] Thus, it appears in the presence of hydrotalcites only, particular polyene sequences are generated during degradation that give rise to the observed colour changes. It should also be noted that the extent of degradation to cause colour

Table 5 Tensile properties of compression mouldings

Hydrotalcite, phr	Yield strength, MPa	Strength at break, MPa	Elongation at break, %	Yield strength, MPa	Strength at break, MPa	Elongation at break, %
	Alcamizer P93			Sorbacid 911		
5	51·6 (0·2)	52·0 (1·5)	154·0 (14·0)	51·8 (0·5)	51·0 (1·7)	149·3 (10·1)
	Tin + Alcamizer P93			Tin + Sorbacid 911		
0	58·1 (1·9)	53·3 (5·0)	163·0 (15·5)	58·1 (1·9)	53·3 (5·0)	163·0 (15·5)
5	56·5 (1·7)	54·8 (4·9)	178·7 (19·9)	56·6 (2·0)	53·2 (3·5)	165·8 (21·8)
	CaZn + Alcamizer P93			CaZn + Sorbacid 911		
0	52·5 (1·0)	51·9 (3·0)	152·6 (13·6)	52·5 (1·0)	51·9 (3·0)	152·6 (13·6)
2	52·5 (1·0)	53·7 (4·9)	153·8 (27·3)	50·1 (1·1)	50·0 (2·5)	143·0 (9·0)
5	49·1 (1·3)	50·1 (3·4)	154·9 (16·3)	48·7 (1·7)	50·3 (3·4)	154·8 (14·9)
10	47·0 (0·8)	51·1 (1·2)	175·0 (5·6)	46·5 (0·8)	48·7 (3·0)	156·4 (21·2)
	OBS + Alcamizer P93			OBS + Sorbacid 911		
0	51·1 (3·2)	53·0 (5·3)	170·0 (19·7)	51·1 (3·2)	53·0 (5·3)	170·0 (19·7)
2	50·5 (1·3)	55·7 (2·1)	181·0 (10·7)	51·0 (1·0)	53·3 (3·0)	164·7 (13·0)
5	48·8 (0·4)	54·6 (2·4)	183·3 (11·3)	48·8 (0·6)	46·4 (7·4)	124·0 (53·3)

Table 6 Instrumented falling weight impact tester data for compression moulded samples*

Hydrotalcite, phr	Peak force, N mm^{-1}	Peak energy, J mm^{-1}	Failure energy, J mm^{-1}	Peak force, Nm m^{-1}	Peak energy, J mm^{-1}	Failure energy, J mm^{-1}
	Tin + Alcamizer P93			Tin + Sorbacid 911		
0	D 1363 (39)	7·19 (0·53)	11·80 (0·49)	D 1363 (39)	7·19 (0·53)	11·80 (0·49)
5	D 1363 (27)	7·28 (0·32)	12·03 (0·40)	D 1366 (16)	7·40 (0·15)	12·14 (0·13)
	CaZn + Alcamizer P93			CaZn + Sorbacid 911		
0	D 1363 (32)	6·98 (0·30)	11·30 (0·32)	D 1363 (32)	6·98 (0·30)	11·30 (0·32)
5	M 1321 (24)	6·70 (0·72)	10·41 (0·93)	M 1318 (21)	6·98 (0·53)	10·73 (0·83)
10	B 1254 (183)	6·20 (1·72)	9·31 (2·20)	B 1292 (33)	6·57 (0·96)	9·82 (1·00)
	OBS + Alcamizer P93			OBS + Sorbacid 911		
0	D 1430 (25)	7·40 (0·17)	11·50 (0·21)	D 1430 (25)	7·40 (0·17)	11·50 (0·21)
2	D 1446 (44)	7·30 (0·81)	11·00 (0·61)	D 1432 (18)	7·40 (0·28)	11·10 (0·28)
5	D 1403 (33)	7·40 (0·18)	10·70 (0·18)	M 1428 (37)	7·30 (0·59)	10·60 (0·52)

*Letters in peak force boxes denote mode of failure: D – all failures were ductile (sample punctured), B – all failures were brittle (sample shattered) and M – mixture of D and B.

2   Oven stability chart for PVC formulations

change is very low: a loss of mass of just 0·1% from PVC, by dehydrochlorination, is enough.[16]

Torque rheometry and dynamic stability

In Table 4 hydrotalcites, in combination with the tin stabiliser, appear to have a mixed effect: stability time is significantly reduced with Alcamizer, but improved with Sorbacid. In fact, the stability time for tin with Alcamizer is little different from the Alcamizer only formulation. This might be related to the increased torque on adding the Alcamizer to the tin stabilised formulation, however, adding Sorbacid to the tin stabilised formulation also increases torque but still improved stability time. For the CaZn stabiliser, adding 2 phr of hydrotalcite greatly increases stability time, which is further increased at 5 phr of the additive. Similar trends, but less pronounced, are found on adding hydrotalcite to the OBS formulation.

Figure 1 shows the effect of adding 2 phr of hydrotalcite to CaZn and OBS formulations. The curves illustrate how hydrotalcites do not significantly affect equilibrium torque or change the temperature reached by the mix.

Thermal (oven) stability

An oven stability chart is shown in Fig. 2 for sets of samples cut from compression mouldings of three formulations: tin stabilised and similar tin stabilised plus 5 phr Alcamizer or Sorbacid. The chart shows that in terms of stability the formulations can be ranked: tin+Sorbacid > tin only > tin+Alcamizer. This is in complete agreement with the torque rheometer data. Another significant feature is the sequence of colours observed. For tin only the sequence is clear to yellow to black. With the hydrotalcites this sequence is punctuated by the appearance of orange and dark red coloured samples, at 30 and 40 min respectively with the Alcamizer, and by orange coloured samples at 50 min with the Sorbacid.

Oven stability tests for hydrotalcites in combination with the CaZn stabiliser and the OBS also agreed with the dynamic stability results. In both cases, the time at which the samples ultimately went black was substantially delayed by adding hydrotalcites. In terms of time to initial colour change the OBS only formulation changed well before the formulations of OBS with hydrotalcites. However, with CaZn, the first formulations to show colour change were those with 5 phr hydrotalcite, while the three formulations of CaZn alone, and of CaZn with 2 phr of the hydrotalcites all seemingly began to discolour at about the same time. Figure 2 illustrates this for 2 and 5 phr additions of Alcamizer. Thus, 2 phr of hydrotalcite in combination with CaZn offers both greatly improved dynamic stability and oven stability, but increasing the additive level to 5 phr, has additional benefit in terms of dynamic stability but seemingly reduces oven stability. Evaluation of the oven aged samples of CaZn and of CaZn plus 5 phr hydrotalcite by Raman spectroscopy confirmed that unsaturation of PVC chains increased in the presence of hydrotalcite.[17]

3 Notched Charpy sample with two examples of breaks and 'non-breaks'

Mechanical properties of compression moulded samples

Tensile properties

Table 5 shows that very good tensile properties are obtained for all formulations tested, even the highly discoloured red compression mouldings of PVC plus hydrotalcite alone. From the table it is clear that adding hydrotalcites reduces yield strength, but not greatly: at 5 phr it is down by 2·6% with tin, by ~7% with CaZn and by 4·5% with OBS. Also, Alcamizer appears to have no detrimental effect upon properties at break, while 5 phr of Sorbacid does significantly lower the break values when combined with OBS. A slight reduction of yield strength, if accompanied by increased elongation or ductility, is a desirable response that may have potential for impact modification and/or toughness enhancement.

Impact properties

These are presented in Table 6 for various formulations. The results correlate with the tensile properties, in that very good impact properties (especially those of peak force and peak energy) are seen across the table. It appears that adding 5 phr of hydrotalcite has little effect on values of peak force and peak energy but does reduce failure energy where sample batches displayed a mix of ductile and brittle failures (denoted by 'M' in Table 6). For OBS in particular, with 5 phr Alcamizer, impact properties are very good, as all samples failed in a ductile manner, whereas with 5 phr Sorbacid, a mix of ductile and brittle failures occurred, which resulted in a reduction in failure energy, which correlates with the relative low tensile properties at break seen in Table 5.

Overall, adding hydrotalcites up to 5 phr does not appear to have any detrimental effect on the mechanical performance of compression moulded PVC. The evidence for CaZn plus 10 phr of hydrotalcite is that this level of addition is too high as some significant loss of both tensile strength and impact strength occurs.

Mechanical properties of extrudates

Properties of the extrudates are given in Table 7. For ease of comparison, the data have been divided into three sets and the results for two formulations, 'REF' (no hydrotalcite and 7 phr impact modifier) and '5A/7M' (5 phr Alcamizer and 7 phr impact modifier) appear twice. Table 7 shows that tensile properties are consistently good for all formulations, while notched Charpy impact strengths show substantial variations.

Tensile properties

Sets 1 and 3 show that adding hydrotalcite up to 10 phr has little influence on yield strength, while properties at break show some slight variations, but with no real pattern. In Set 2, it is very apparent that an initial addition of Alcamizer at 5 phr, followed by increasing the impact modifier content, reduces yield strength, and it is only with the '5A/7M' formulation that strength at break is affected.

Notched Charpy impact strength

Figure 3 illustrates the appearance of samples after impact testing and in Table 7 the number of breaks and

Table 7 Tensile properties and notched Charpy impact strength of extrudates

Identifier	Tensile			Notched Charpy impact		
	Yield strength, MPa	Strength at break, MPa	Elongation at break, %	No. of breaks	No.of non-breaks	'Energy absorbed', kJ m^{-2}
Set 1						
REF	43·8 (0·5)	42·3 (4·0)	112·3 (32·1)	13	1	38·7 (27·8)
2A/7M	44·0 (1·4)	48·6 (2·9)	159·3 (19·7)	2	12	124·2 (27·4)
5A/7M	43·9 (0·6)	43·0 (4·1)	139·5 (26·2)	0	15	139·2 (9·7)
10A/7M	44·1 (2·1)	45·1 (3·3)	137·8 (10·9)	0	15	125·7 (16·0)
Set 2						
CORE	51·3 (0·7)	52·8 (3·6)	129·5 (18·1)	10	0	7·7 (2·7)
5A/0M	49·9 (0·4)	51·9 (3·4)	139·1 (21·1)	10	0	13·7 (4·2)
5A/4M	46·4 (0·6)	53·0 (3·2)	165·8 (13·9)	10	0	42·6 (25·0)
5A/7M	43·9 (0·6)	43·0 (4·1)	139·5 (26·2)	0	15	139·2 (9·7)
Set 3						
REF	43·8 (0·5)	42·3 (4·0)	112·3 (32·1)	13	1	38·7 (27·8)
2S/7M	44·0 (0·6)	41·3 (4·8)	86·3 (35·9)	3	7	63·3 (48·4)
5S/7M	43·1 (0·8)	45·2 (5·6)	130·5 (42·6)	0	10	146·5 (10·0)
10S/7M	41·2 (0·7)	40·3 (3·6)	104·5 (31·6)	0	10	122·0 (13·1)
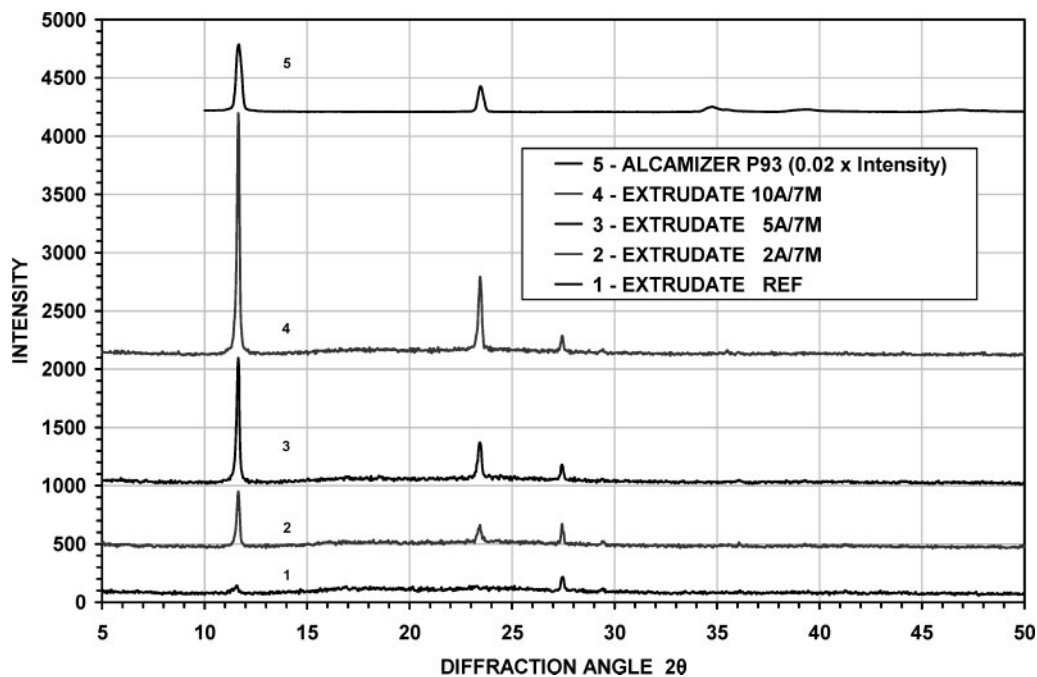
4 X-ray diffraction patterns for extrudates with different additions of Alcamizer

non-breaks is shown for each formulation. To compare impact strength, average values of 'energy absorbed' have been calculated for each formulation, whether the formulation gave 100% breaks, 100% non-breaks or a mixture of the two types of failure mode. Sets 1 and 3 show substantial increases in impact strength on adding 2 and 5 phr of hydrotalcite. A further increase to 10 phr of hydrotalcite reduces the enhancement in impact performance. In Set 2, adding 5 phr of Alcamizer only to the core formulation does improve impact strength, however, only to a level that can be considered insignificant when compared to the reference formulation (Set 1). The introduction of impact modifier in Set 2 at 4 phr gives an impact strength comparable to the reference formulation and at 7 phr a substantial increase in impact strength is found.

Overall, very good tensile properties are found with all extrudates. In terms of impact performance, adding hydrotalcites in combination with an impact modifier can greatly improve notched impact strength. It would appear that this benefit can be accrued with 2 phr of Alcamizer and maybe 3 phr of Sorbacid.

Characterisation of extrudates

X-ray diffraction patterns are shown in Fig. 4. The top pattern[5] is that of Alcamizer alone, with its intensity scaled down considerably, to enable this pattern to be compared with those from extrudates.[1–4] In the figure it is very evident that as the Alcamizer content of extrudate is increased, the main reflections of the hydrotalcite, at $2\theta = 11\cdot65$ and $23\cdot42°$, increase accordingly. There are two other points to note. First, the lowest pattern,[1] the reference formulation with no added hydrotalcite, has a small peak at $2\theta = 11\cdot65°$ showing that some form of hydrotalcite is one of the components of the CaZn stabiliser one pack. Second, the reflection close to $2\theta = 27\cdot5°$ arises from the titanium dioxide.

Transmission electron microscopy images, obtained from sections through the same set of extrudates displayed in Fig. 4, are shown in Fig. 5 (where the hydrotalcite particles have an elongated shape and titanium dioxide particles appear more circular as in the REF image in Fig. 5). The images confirm that the hydrotalcite, especially the fine particles, are well dispersed. It is this feature that produces the significant enhancement in impact strength.

Conclusion

Hydrotalcites are very effective costabilisers for PVC. The evidence presented here, on compression moulded samples, suggest that in combination with CaZn and
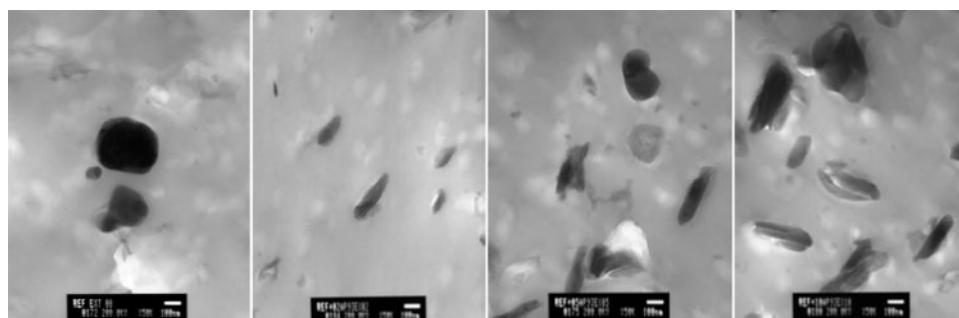
5 Transmission electron microscopy images of extrudates with different additions of Alcamizer: white bars equal 100 nm (from left to right: REF, 2A/7M, 5A/7M and 10A/7M)

OBS, as primary stabilisers, additive levels ~ 2 phr would be optimal. This level of addition has no detrimental effect upon mechanical performance. It is clear that in CaZn stabilised extrusion formulations, hydrotalcites (at 2–3 phr) act as reinforcing particles, as long as an impact modifier is present.

To follow on from these findings, research objectives are to:

(i) reevaluate the tin stabiliser but with hydrotalcites at 1 and 2 phr

(ii) assess the performance of extrudates costabilised with OBS and hydrotalcites (1, 2 and 5 phr)

(iii) further investigate the early stages of degradation of PVC formulations containing hydrotalcite by Raman spectroscopy.

It is also recognised that potential exists to further exploit the enhanced stability and mechanical properties offered by hydrotalcites by reducing particle size. Work on the synthesis of such hydrotalcites is currently in progress at IPTME.

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