Evolution of Chemistry, Morphology and Rheology of Various Polymer Systems along a Twin-Screw Extruder

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Plasticating extrusion is probably the most important single operation in polymer processing. Extruders are a fundamental part of any extrusion (e.g., for producing pipes, profiles, blown and flat film, mono and multi-filaments, coated wire) and compounding line (e.g., for the incorporation of additives in general, polymer modification and polymer blending), and are also used in blow molding and injection molding machines, although in modified form.

Intermeshing twin-screw extruders have found special application niches where their characteristics are used with greater advantage. Counter-rotating machines are nowadays the standard choice for extruding PVC dry blends, given their positive pumping characteristics, narrow residence time distribution and relatively low viscous dissipation as compared to conduction heat transfer (Rauwendaal, 1990). The relatively gentle thermo-mechanical environment that is created by a proper screw design and an adequate definition of the mechanical gaps, together with the inherent low screw speeds, is well suited to the limited thermal stability and the high viscosity levels of unplasticized PVC compounds (Covas et al, 1988). The co-rotating solution is often used for compounding operations, mainly because its distributive and dispersive mixing capabilities are quite good and, like the residence time distribution, can be controlled by exploring the geometrical flexibility (modular construction) of the equipment and the range of processing conditions than can be selected (Todd, 1998). Co-rotating extruders are used in important applications such as the compounding of filled polymer systems and masterbatches, the homogenization of polymer melts, the modification of polymers and the preparation of incompatible polymer blends (Xanthos, 1992; Todd, 1998). Very often, the last two operations involve, apart from polymer processing, chemical reactions. Classical examples are the peroxide-induced degradation of polypropylene to prepare grades with controlled rheology, and the grafting of maleic anhydride onto polyolefins to improve their compatibility with other polymers, respectively. A variety of other reactions/applications could also be cited (Xanthos, 1992, Utracki, 1994).

The input of thermal energy and mechanical stresses to the polymer system upon flow in the extruder, which are determined by the geometry of the equipment and by the operating conditions, will cause

Intermeshing twin-screw extruders have been recently identified as useful in special application niches such as the extrusion of PVC dry blends (counter-rotating machines) and compounding operations (co-rotating machines). Thus, it is of interest to study the mechanical and/or chemical effects that occur along the screw axis of the extruders, since they will dictate the characteristics and performance of the final material. This work aims at illustrating the usefulness of a simple experimental tool recently developed for the study of the physical, chemical and morphological evolution along the extruder of polymer based systems, data being presented and discussed for a number of composites and blends.

Les extrudeuses bi-vis engrenées ont aujourd'hui trouvé des niches d'application propres, telles que l'extrusion des mélanges secs de PVC (machines contre-rotatives) et les opérations de compoundage (machines co-rotatives). Ainsi, il est intéressant d'étudier les effets mécaniques et/ou chimiques qui surviennent le long de l'axe des vis des extrudeuses, puisque ceux-ci dicteront les caractéristiques et la performance du matériel final. Ce travail vise à illustrer l'utilité d'un outil expérimental simple développé récemment pour l'étude de l'évolution physique, chimique et morphologiques le long de l'extrudeuse pour des systèmes polymériques, des données étant présentées et examinées pour plusieurs composites et mélanges.

Keywords: twin-screw extrusion, process monitoring, composites, polymer blends, reactive extrusion.

mechanical, chemical, or mechano-chemical effects along the screw axis that will dictate the characteristics, and therefore the performance, of the final material. For example, in the case of the incorporation of high aspect ratio fillers (such as glass or graphite), the fiber bundles must be broken apart and subsequently distributed and wetted to the polymer.

The final fiber length and length distribution will depend on the configuration of the various mixing sections and on the operating conditions (Todd, 1998). Processing of PVC requires that a minimum gelation level must be generated if an optimized product performance is to be achieved, i.e., processing of PVC must involve the progressive destruction of the initial granular hierarchy and structural order and the development of a network of molecular entanglements and of some remaining supermolecular entities (Covas et al., 1988). The rate and intensity of this process determines the success of the entire operation. Chemical reactions can simply occur by the conjugation of high temperatures and the presence of oxygen. If these reactions are uncontrolled, the polymers processed will probably exhibit inferior properties due to the so-called degradation. However, mechano-chemical effects can be used to change the chemical structure of a polymer in a controlled manner. For example, it was demonstrated that maleic modified rubber undergoes chemical reactions during melt blending with polyamide, PA, the rubber's anhydride groups reacting with the polyamide's amine end groups to produce PA grafts on the rubber. Eventually, a very fine and stable dispersion of the rubber phase is obtained, improving dramatically the impact behavior of the PA (Borggreve and Gaymans, 1989). It has been shown that there is a strong interrelationship between chemical conversion and morphology development, both being affected by the geometry of the equipment and the operating conditions selected (Machado et al., 1999a).

Therefore, it may be important to monitor the evolution of the characteristics of a particular polymer system along the extruder axis in order to better apprehend the physical and chemical phenomena involved. The authors have been using for some time sample-collecting devices that can be inserted between barrel segments of a twin-screw extruder (or, alternatively, a series of devices can replace one barrel segment of the machine), in order to remove and collect quickly relevant samples of material from inside it without affecting the local steady-state flow characteristics. This enables the subsequent off-line monitoring of the rheology, morphology and/or chemical evolution of the polymer system along the screw axis (recently, a complementary concept of on-line capillary rheometry has been presented and explored: Covas et al., 2000; Maia et al., 2002). The system allows sample collection to be carried out anywhere along the machine, as long as positive pressure develops.

The present work aims at illustrating the usefulness of this simple experimental tool for the study of the evolution along the extruder of polymer-based systems. This will be illustrated by presenting and discussing data for thermoplastic/ carbon fiber composites, microfibrillar reinforced composites, thermoplastic/LCP blends, polyamide/rubber blends and PVC dry blends.

Sample Collecting Device

The sample-collecting device used in this work is shown in Figure 1. Is has been described and validated elsewhere, namely by comparing the characteristics of the samples made available with those from other well-established sample collecting techniques (Machado et al., 1999b). The three illustrations of the figure refer to important stages of the sampling routine. The figure on top shows the device positioned to collect a polymer sample from the extruder. A lateral hole in the barrel enables pressure flow towards the cavity machined in a rotating

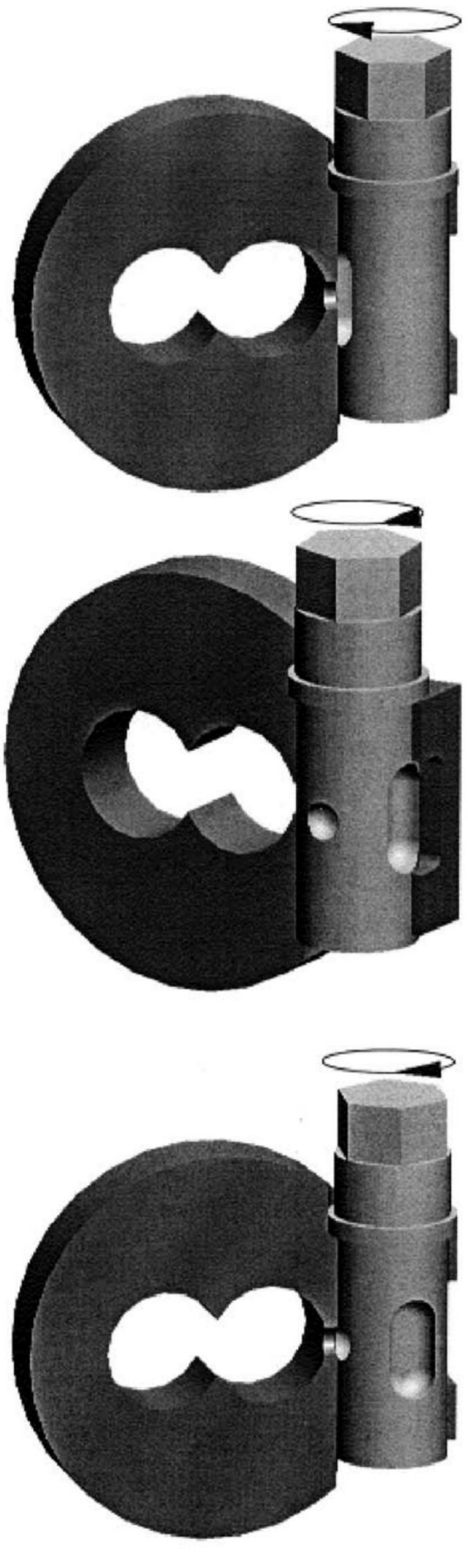

Figure 1. Sample collecting device. See text for the operating sequence. cylinder, which is rapidly filled with the material diverted. Upon rotation of 180°, it is possible to access the sample (middle figure). When the extruder is operating normally and the cavity is not exposed, polymer material can accumulate in the hole of the lateral barrel. Therefore, in order to collect a portion of fresh material from inside the extruder, it is possible to expose first to the incoming flow a second smaller cavity in the rotating cylinder (bottom figure), which will retain the material with higher residence time. Then, upon a further rotation of the cylinder, the bigger cavity is exposed. Collecting ca. 1 to 2 g of polymer (two sizes of devices were developed in order to vary the axial distance between two consecutive collecting ports) takes typically less than 3 s.

Thermoplastic/Carbon Fiber Composites

Carbon fibers are widely used as reinforcements in several high technology applications due to their mechanical, thermal and electrical properties. Short carbon fiber/thermoplastic composites can be manufactured using single or twin-screw extrusion. The critical point of the process is the progressive breakage of the fibers caused by the high mechanical efforts promoted by the local flow conditions, that, if not controlled, compromises their reinforcement capabilities. This effect is particularly severe upon melting of the thermoplastic matrix (Ramani et al., 1995; Dospisil et al., 1994). Therefore, it is important to correlate the length of carbon fibers with the thermo-mechanical stresses developed during compounding. This section aims at estimating fiber length reduction along one mixing section of an intermeshing co-rotating twin-screw extruder by making use of the sampling devices described above, which provide material for off-line measurements.

Experimental

The polypropylene, PP-carbon fiber composite consists of a Montell PP grade (Moplen F30F, MFI = 14) and 12%w/w fibers supplied by Kureha Chemicals GMBH (Kcreca chop C-106T). These are ex-PAN with a nominal length of 6 mm, and L/D above 330 (data from the manufacturer). Due to practical difficulties in feeding the fibers in a controlled manner directly into the extruder, plaques of composite were previously compression molded and milled. This preliminary operation reduced the fiber's initial length to 2.83 ± 1.33 mm.

Compounding was performed in a Leistritz LSM 30.34 modular intermeshing co-rotating twin-screw extruder. The screws were fitted with a first mixing block in the downstream direction made up of eleven kneading discs staggered at 90° (shown in Figure 2), thus assuring melting and homogenization. The extruder was operated with a feed rate of 2.3 kg/h, barrel/die set temperature of 210°C, and screw rotational speed of 100 rpm. Samples were collected at the beginning (location I) and end (location II) of the kneading block (see Figure 2). The fibers (ca. 500 in each sample) were measured using an optical microscope coupled to a Leica Quantimet 550 image analyzer.

Results and Discussion

As mentioned above, the preliminary incorporation of the fibers into the PP matrix by compression molding reduced their average length from 6 mm to ca. 2.8 mm . Compounding in the twin-screw extruder continued this process, as expected. The average length of the samples collected at the beginning and end of the first mixing zone were measured as 1.50 ± 0.84 mm and 0.90 ± 0.33 mm, respectively. This corresponds to a progressive reduction of ca. 40% in each stage (hopper-location I and location I-location II), and to a total reduction of 68%, when the initial length before extrusion is considered. The polypropylene was already molten at location 1 . The stresses causing this change were also responsible for the significant fiber breakage in the first stage.

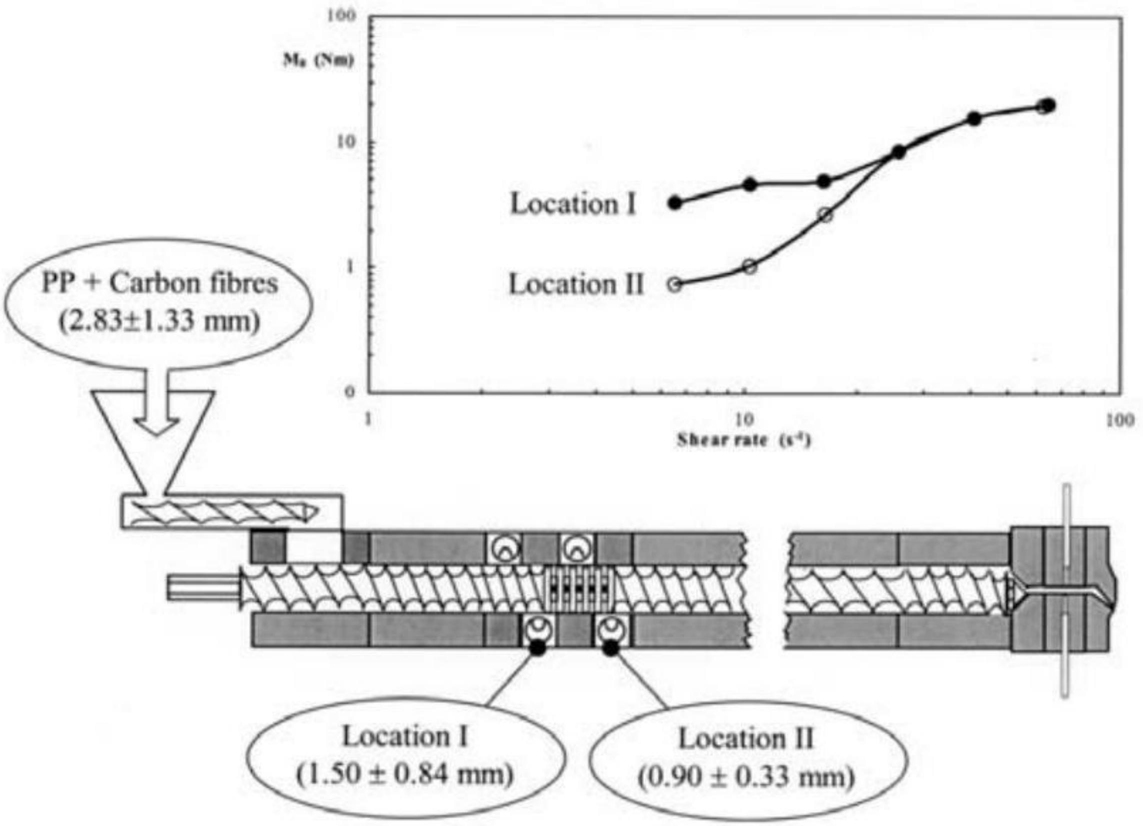

Figure 2. Extruder layout, location of the collecting devices (valves), average fiber lengths and torque corresponding to entry effects.

Off-line fiber measurement is a time-consuming task, totally unsatisfactory for practical process monitoring purposes. However, fiber length can be correlated with the rheological behavior of the composite, which is easier to monitor on-line, using e.g. the on-line capillary rheometry technique developed by the authors and described and validated elsewhere (Covas et al., 2000).

The on-line experiments carried out at $210^{\circ}\mathrm{C}$ using two dies of 1 mm diameter and L/D of 4 and 8 , showed that extensiondominated flows are much more sensitive to fiber length variation than shear-dominated flows. Similar to available convergent flow analyses (Cogswell, 1972; Binding, 1988), the extensional behavior of a melt can be related to the entry pressure drop in the rheometer (or, in this particular case, to the required torque,

M_0). The torque corresponding to entry effects is shown in Figure 2. As can be seen, a pronounced decrease in the entry torque from 3.0 to 0.7 Nm occurred along the kneading block, when a shear rate of approximately 6 s^{-1} is considered.

Conclusions

This section discussed two possibilities of monitoring the evolution of fiber length along a twin-screw extruder: i) direct off-line measurements on samples collected by the sampling devices; ii) correlation of on-line rheological measurements with the average fiber length. The results confirmed that fiber length degradation does indeed occur in the mixing block, and allowed a direct quantification of the effect to be performed.

Microfibrillar Reinforced Composites

Microfibrillar reinforced composites are produced from thermoplastics blends, the microfibrils being created by orienting and annealing the blend below the melting temperature of its higher melting temperature component (see, e.g., Fakirov et al., 2000). The mechanical properties of these composites are, in terms of tensile strength and tensile modulus, typically 30% to 50% higher than the values calculated from the mixing rule (calculated with the properties of the individual components). These blends have been prepared under laboratorial conditions, for example by blending the polymers in a single screw extruder, quenching in a water bath and drawing in a tensile

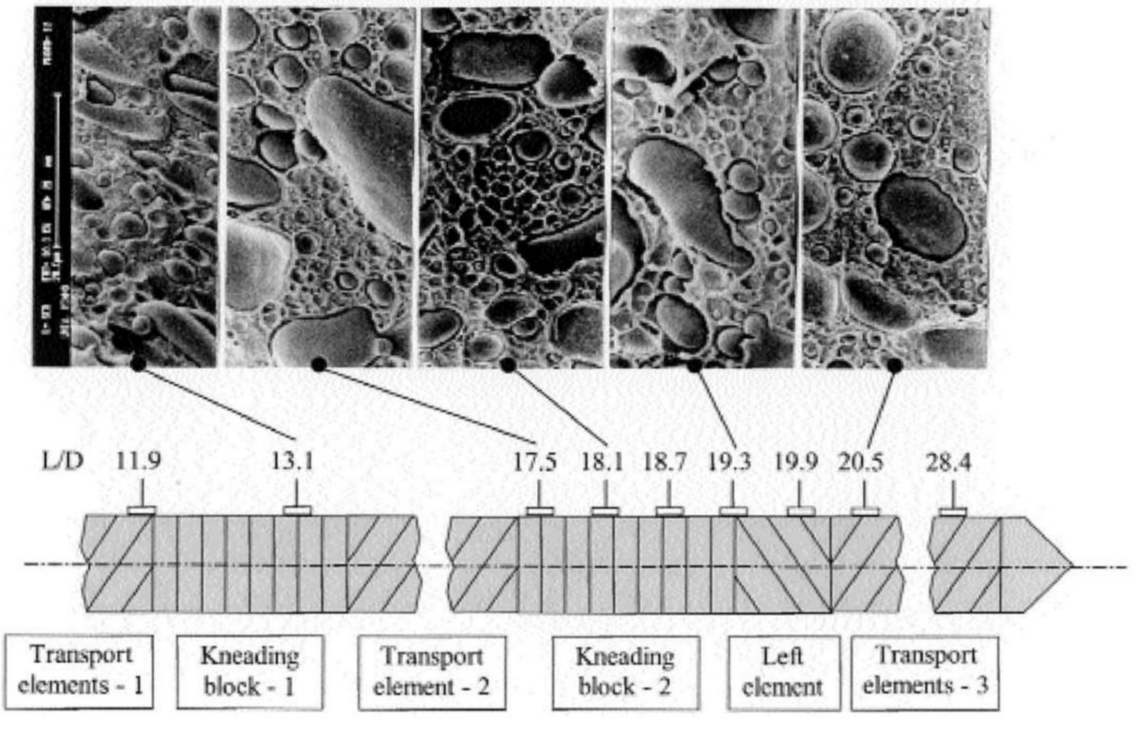

Figure 3. Extruder layout, location of the collecting devices (valves) and SEM micrographs of the morphology of the blend along the first and second kneading blocks.

testing machine (Evstatiev et al., 2000), but recently they were produced under conditions where scale-up to an industrial process can be foreseen (Covas et al., 2001).

The performance of this type of composites should depend on the degree of the distributive and dispersive mixing achieved during the extrusion step. The former guarantees the uniform presence of microfibrils in the composite. The drawability of the blend, i.e., its ability to form fibrils, should depend on the average particle size of the dispersed phase and on the viscoelastic character of the blend. Therefore, it is essential to monitor the evolution of the blend morphology along the extruder axis in order to improve its reinforcing capabilities. This section will report the off-line morphological and rheological characterization of samples of a thermoplastic blend, suitable to withstand the high draw-ratios required for the formation of microfibrils, sample collection having been performed by resorting to the sampling devices.

Experimental

A 70/30 weight ratio blend of a high density polyethylene, HDPE, Type HE8342, from Borealis and of a poly(ethylene terephthalate), PET, Type D-405, from Trevira Fibras, S.A., with a melting range of $221^\circ\mathrm{C}$ to $242^\circ\mathrm{C}$, as determined by Differential Scanning Calorimetry (DSC), was prepared in a single stage operation. Blending, quenching and drawing were performed sequentially in the same extrusion line. Blending was carried out in the Leistritz extruder using the screw schematized in Figure 3. The location of the various sampling devices is also shown in the figure. The extruder was operated at a feed rate of $2\ \mathrm{kg/h}$, the barrel set temperatures increasing from $220^\circ\mathrm{C}$ to $240^\circ\mathrm{C}$ towards the die, and the screws rotating at 100 rpm . After emerging from the die, the extrudate was cooled down while drawn with a draw-ratio of 2:1. Microfibrils were formed during a second drawing step using a hot water bath (set at $94^\circ\mathrm{C}$) and a drawratio of 4:1 (for details, see Covas et al., 2001).

The morphology of the blend was observed under a Leica S360 scanning electron microscope (SEM). The (oscillatory) rheological characterization was carried out in a Reologica StressTech HR rotational rheometer, using 25 mm diameter parallel plates and a 1.1 mm gap. Frequency sweeps (from 4×10^{-3} to 40 Hz) were performed at $240^\circ\mathrm{C}$. Sample preparation of the samples for these measurements involved the compression molding of the nut-shaped samples collected.

Results and Discussion

Figure 3 also shows the morphological evolution of the blend, as assessed by SEM. Apparently, there exists a bimodal distribution of the PET particles, since it is possible to observe particles with approximately 1 to $2\mu\mathrm{m}$ diameter and others 30 to $40\mu\mathrm{m}$

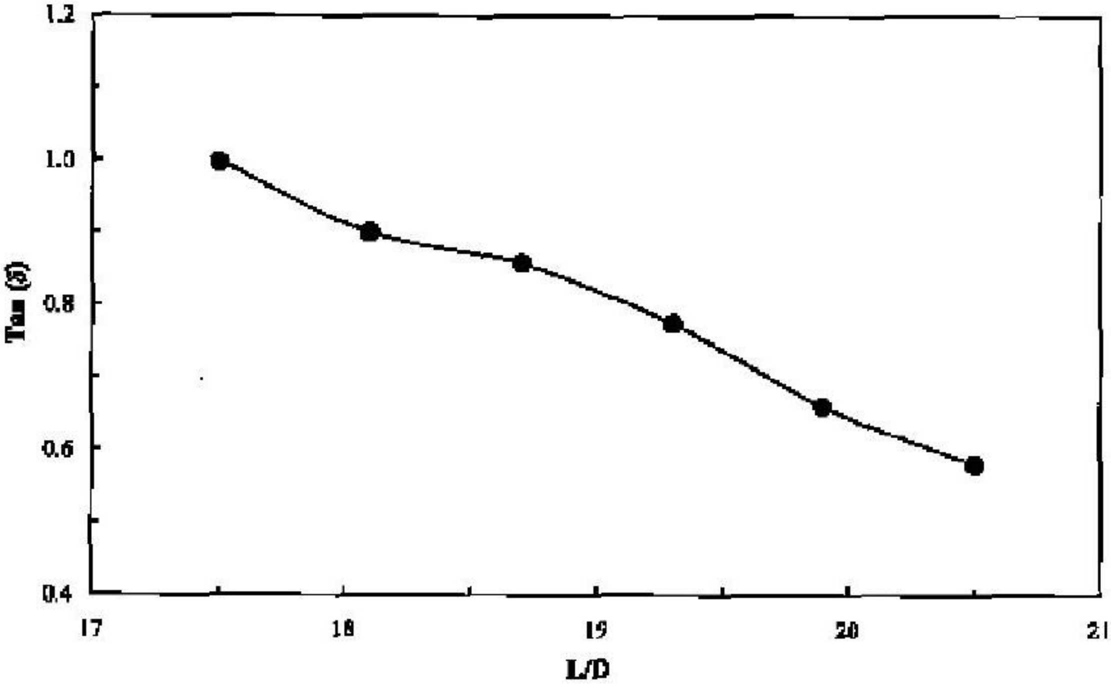

Figure 4. Viscoelastic response (tan δ) of the blend at a fixed frequency of 0.03 Hz . long and 5 to 10μ m wide, essentially aligned in the flow direction. This alignment is not visible in the last valve. In this case, the time required to collect samples was higher than that for the remaining valves, due to the low pressure of the melt at this location (upstream from the lefthanded transport element). Therefore, some elastic recovery could have occurred. Generally, the sequence of micrographs seems to indicate that the number of smaller particles of PET and the homogeneity of the dispersion increases along the screw, due to the progressive breakage of the larger droplets into smaller particles. Consequently, there is a large increase in the interfacial area, which is probably responsible for the increase of the viscoelastic character of the melt shown in Figure 4. Since PET and HDPE are incompatible, it would be possible for interfacial slip to occur. However, as was shown in a previous paper (Covas et al., 2001), the viscosity increases along the extruder, i.e., with the increase in interfacial area. This is a clear indication that it is not interfacial slip that is occuring, but increased friction. Experiments with other lower speeds induced the development of distinct morphologies, characterized by a unimodal distribution of the PET particles with a larger average size. However, drawing of the blend was only possible for a screw speed of 100 rpm , which seems to indicate that drawability is essentially dependent on average particle size.

Conclusions

During the manufacture of microfibrillar composites the evolution of the blend morphology along the extruder can be correlated with its viscoelastic response. The results show that, although there is a bimodal distribution of the disperse phase, drawability is mainly dependent on its average particle size.

Thermoplastic/LCP Blends

The addition of liquid crystalline polymers, LCP, to engineering plastics is well known to lead not only to a viscosity reduction, but also to an improvement of the mechanical properties (see, for example, Seppällä et al., 1992 and Choi et al., 1996) and of the thermal and dimensional stability (Seppällä et al., 1992). This is related to the morphological structure that is developed in this type of blends, i.e., a fibrillar LCP phase, oriented along the flow direction. Previous works have reported on the morphological, rheological and mechanical characteristics of extruded blends (see, for example, Heino et al., 1994, and Li et al., 1994) but it would be clearly desirable to evaluate the evolution of the morphology along the extruder, in order to optimize the processing conditions with a view to increasing the final mechanical properties of the blends. This work is currently in progress, this section aiming to highlight the type of information that it is possible to obtain. Thus, results are shown for morphological and rheological measurements performed on samples collected along the barrel length of the Leistritz corotating twin-screw extruder, as well as for the extrudate.

Experimental

The materials used for this work were polypropylene, Stamylan P (12E62) from DSM, and a commercial liquid crystalline polymer (a $80/20\%\text{w/w}$ blend of para-hydrobenzoic acid/PET), Rodrun LC 3000, from Unitika. Blends with 10%, 20% and 40% w/w were produced in the extruder, using a set temperature of $220^{\circ}\mathrm{C}$ and a screw speed of 150 rpm and a flow rate of 4.0 kg/h. The screw comprised a block of 11 kneading discs staggered at -60°, melting of the material having occurred upstream due to the presence of a left-handed element (see Figure 5).
Rheological measurements were carried for all the blends and pure components, again using a Reologica StressTech HR rheometer. The experiments were performed in oscillatory shear at 10% strain and for a frequency range between 0.01 and 316 Hz . The gap was set at 1 mm and the temperature was $220^{\circ}\mathrm{C}$. The morphology was studied using a ZEISS DSM 962 Scanning Electron Microscope.

Results and Discussion

Results are shown in Figure 5 (blend $10\%\text{w/w}$) for SEM micrographs of samples collected from the middle of the mixing block onwards. The globular structures seen at this point (labeled I in Figure 5) will orient progressively along the flow direction, due to the increase in the total applied strain and higher shear stress levels, giving rise to droplet-like structures (labeled II in Figure 5). As the material progresses downstream along transport elements some relaxation occurs and the disperse phase takes again the form of globular structures (labeled III in Figure 5). Finally, at the die exit, the LCP domains are again highly oriented and the maximum fibrillar formation is achieved (labeled IV in Figure 5). Furthermore, the LCP domain dimensions vary in each valve, decreasing as the material progresses along the mixing section.

The rheological measurements show clear differences in the viscoelastic behavior for samples collected at different locations along the extruder, as can be seen in Figure 6, where the elastic modulus, G', and the dynamic viscosity, η', are depicted. Both the viscosity and the elastic modulus decrease along the axial length of the extruder, a minimum value being reached for the final extruded blend. This fact can be explained taking into consideration that the formation of fibrillar LCP structures achieves its maximum point when the material crosses the die, i.e., when the elongational forces are highest. Thus, the decrease in average droplet size seems to yield a bigger effect on the rheological properties than the relaxation that occurs in the transport section prior to the die.

Conclusions

Samples of PP/LCP blends collected along the extruder barrel were analyzed in order to establish possible relationships between morphological and rheological properties. The highest viscosity and elastic modulus values are obtained for the

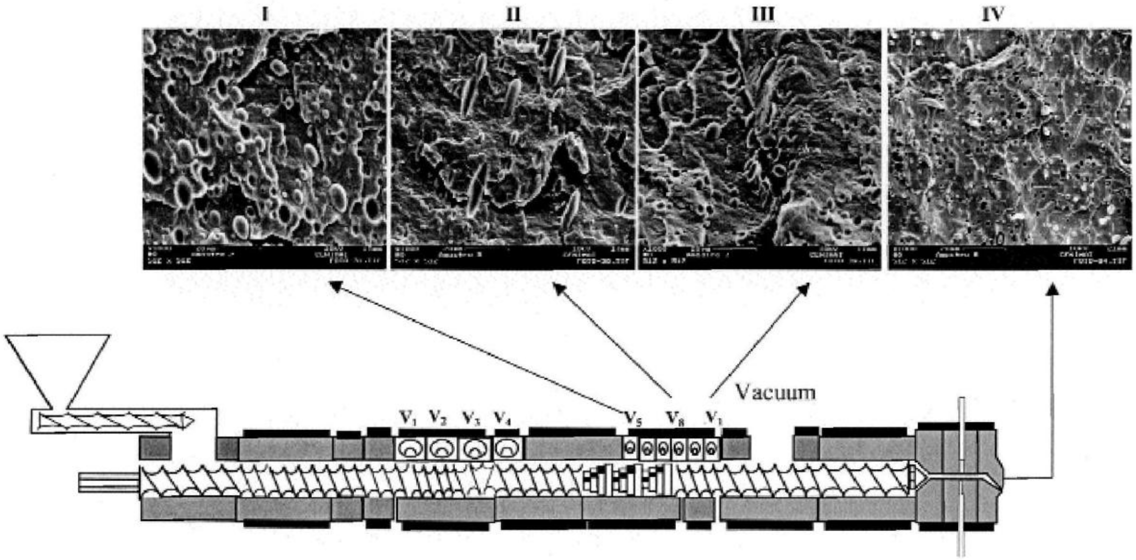

Figure 5. Screw configuration and SEM images of the 10% wt LCP blend along the cylinder extruder. Labels are: I - Valve 5 (mid-mixing block), II - Valve 8 (end of mixing block), III - Valve 10 (beginning of final transport section) and IV - Extrudate.

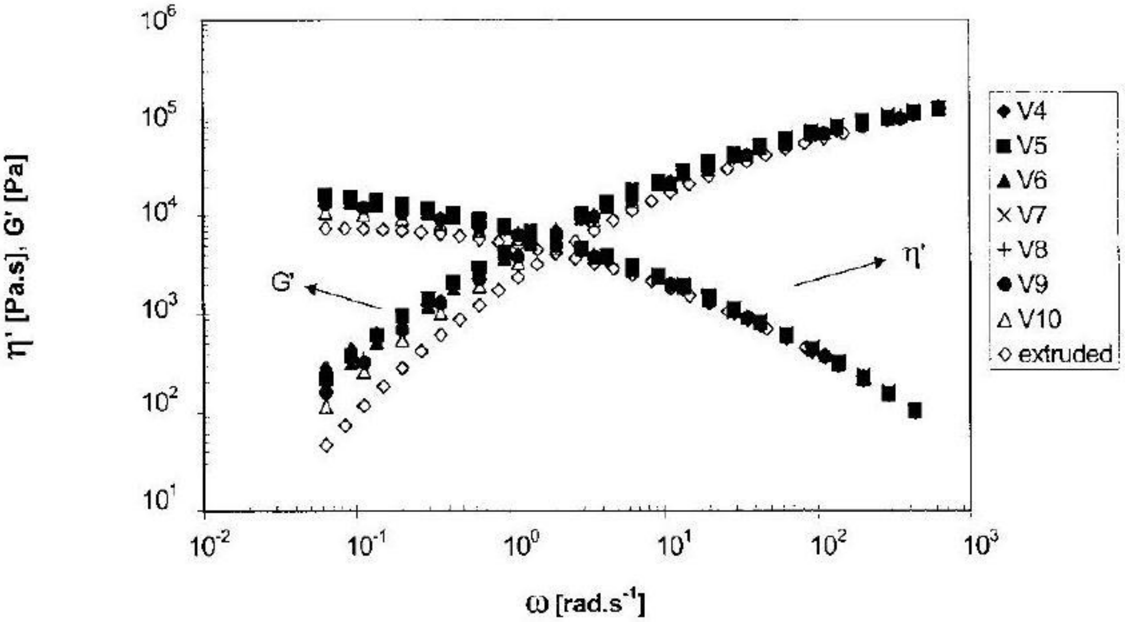

Figure 6. Elastic modulus and dynamic viscosity for samples collected along the cylinder of the extruder.

samples in which the LCP exists essentially as spherical domains. In contrast, when a fibrillar LCP structure is present (as it can be observed for the final extruded blends), the LCP orients along the flow direction and both the viscous and elastic responses decrease.

Polyamide-Rubber Blends

Although polyamides (PAs) are extensively used in engineering applications due to their excellent chemical and abrasion resistance and relatively high toughness, the latter deteriorates significantly at low temperatures. It has been shown that PA's toughness can be improved by adding a small amount of a functional rubber (Utracki, 1994; Datta and Lohse, 1996), for example, Maleic anhydride (MA) modified ethylene/propylene elastomers (EPM-g-MA) (Borggreve and Gaymans, 1989; Kim and Kim, 1991). It is now well established that the morphology and the interphase characteristics determine the physical/mechanical properties of the blends (Crespy et al., 1992; Kim and Kim, 1991).

It has also been demonstrated that the geometry of the compounding equipment and the operating conditions selected have a strong effect on the resulting mixing quality, chemical conversion, and morphology (Willis et al, 1990). Therefore, it is important to investigate how these interact during the preparation of the blend, i.e., along the extruder axis. This will be done in the next sections.

Experimental

Commercial PA-6 (Akulon ® K123) and EPM (Keltan ® 740), both from DSM, were used. EPM-g-MA (Exxelor VA 1801 containing 0.49wt. % of MA) was kindly provided by Exxon, Spain. Blends of 80% PA-6 and 20% EPM (non-reactive blend) or EPM-g-MA (reactive blend) w/w were prepared in the Leistritz co-rotating extruder, the screws rotating at 200 rpm , the flow rate set at 6 kg/h and the temperatures at 220°C to 230°C in the barrel and at 220°C at the die. Figure 7 presents the configuration of the screws and the axial location of the sampling devices. The material was collected at zones where the melt was being subjected to more intensive mixing, hence significant changes in morphology and/or chemistry could be anticipated (i.e., at staggering kneading blocks and at left-handed screw elements). Immediately after collection the samples were quenched in liquid nitrogen in order to prevent further reaction or coalescence.

Milled samples were hydrolyzed with refluxing 6 N hydrochloric acid during 6 h and subsequently filtered, washed with water and dried for one hour at 180°C, in order to convert dicarboxylic acid back to anhydride. Compression-molded thin films of the residues were analyzed by FT-IR (Perkin Elmer 1720 spectrometer), the residual MA content being quantified using the anhydride carbonyl absorption at 1785 cm^{-1} after IR calibration with a set of references. The MA conversion (in %) is defined as [(MAoriginal - MAresidual)/MAoriginal] × 100. After fracture of the samples in liquid nitrogen, etching with boiling xylene to remove the rubber from the surface and gold plating, the morphology of the non-reactive blend was studied using a Jeol JSM 6310F SEM. In the case of the reactive blend, samples were trimmed (in 0.1 × 0.2 mm bits) at room temperature and stained with a 50/50 osmium tetroxide/formaldehyde mixture. Cryo-coupes of about 70 nm were cut at −100°C and studied with a Philips EM420 Transmission Electron Microscope at 120 kV. The size and the size distribution of the dispersed phase were determined using a Leica Quantimet 550 image analysis system.

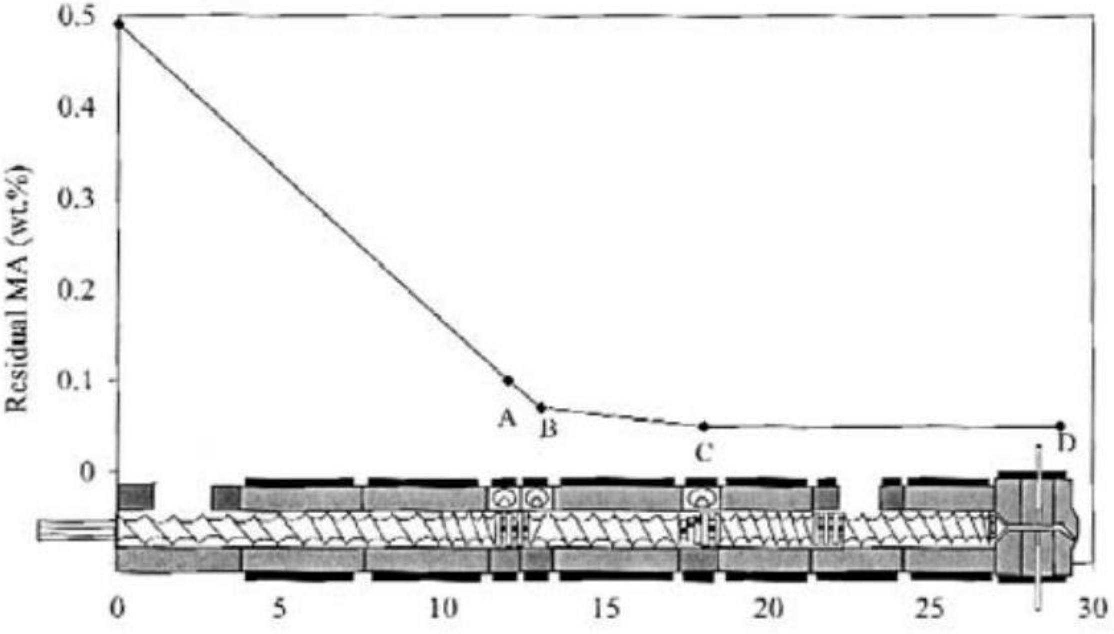

Figure 7. MA conversion of PA-6/EPM-g-MA blend along the screw.

Results and Discussion

Figure 7 shows the evolution of the residual MA content of the PA6/EPM-g-MA blend along the extruder, as determined by FT-

IR. It decreases significantly from its original value until location A and remains unchanged thereafter. This means that the MA content is reduced up to the first kneading zone, i.e., upon melting of the material.

Data on the morphology evolution of the non-reactive and reactive blends is gathered in Figure 8. SEM (after extraction of the rubber) and TEM micrographs are shown for the nonreactive and reactive blends, respectively. No information for location A is included, as PA is still partially solid and each specific blend is not yet produced. The PA-6/EPM blend exhibits a rather large average particle size and no visible interfacial adhesion. Although the particle size decreases along the extruder, the most significant changes occur during and immediately after melting. The same type of evolution was observed with the PA-6/EPM-g-MA blend, but now a much finer morphology is present. Initially, the disperse phase contains both spherical particles and ribbons or threads, but towards the die fine regular spherical particles can be noticed. The occlusions that can be noticed in the rubber particles are probably formed upon melting of the PA-6 pellets (a more detailed discussion can be found at Machado et al, 2001).

Given the above results, a correlation between melting of the blend components, chemistry conversion and morphology evolution for the reactive blend seems to exist. The high amount of interfacial area generated upon melting induces chemical conversion and morphology evolution. However, since the staggered kneading blocks downstream will not induce significant changes in morphology / chemical conversion, the graft copolymers formed earlier at the interface seem to provide sufficient steric stabilization against coalescence of the dispersed phase particles. In the case of the non-reactive blend, along with the progressive decrease in average particle size, some coalescence could also be observed, thus indicating poor morphology stability.

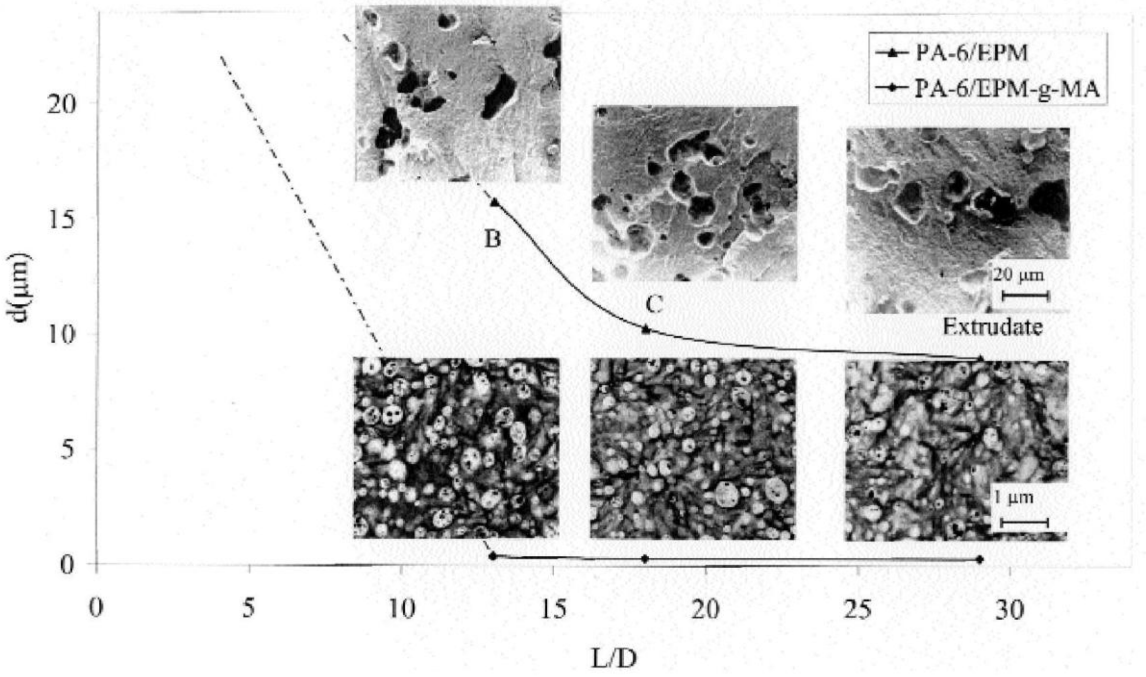

Figure 8. Morphology evolution along the screws for PA-6/EPM and PA-6/EPM-g-MA blends.

Conclusions

The results showed that a correlation between chemistry, morphology and thermo-mechanical stresses exist. Major changes occur upon melting, when interfacial area is generated. Further mixing will modify the morphology depending on the stability of the interface.

PVC Dry Blends

Suspension PVC powder has a complex particle hierarchy and a small degree of structural order (Gilbert and Vyvoda, 1981; Covas et al, 1988). Upon processing and due to the combined action of stresses, residence time and temperature, this morphology is progressively changed into a more conventional network of molecular entanglements, together with the survival of some supermolecular entities. Cooling downstream will induce the formation of some secondary structural order (Gilbert and Vyvoda, 1981; Gilbert, 1985). This process is known as 'gelation', the degree of gelation defining how much progress has been made towards the formation of a homogeneous molecular network. It has been unambiguously shown that the degree of gelation relates to the mechanical performance of the final part and, obviously, to the thermo-mechanical environment created upon processing (Benjamin, 1980; Gilbert, 1985; Covas et al., 1988).

The aim of this section is to study the influence of key PVC resin characteristics on the processing behavior in a counterrotating twin-screw extruder (which is normally used for the production of rigid pipes and profiles), as this would facilitate the development of new polymer grades. Representative samples of material from inside the extruder were obtained during the normal operation of the machine. They were subsequently characterized in terms of morphology, rheology and gelation level.

Experimental

Five commercial resins (denoted A to E in Table 1), with different k values (i.e., average molecular weight), apparent density, dioctyl phthalate (DOP) absorption and morphology (for example, sample E is a skinless-type resin) were selected. A typical tin stabilized commercial formulation used for the production of indoor profiles was adopted (Table 2). The corresponding compounds were prepared in a Thyssen Henschel KM 120 high intensity mixer. The solids were initially fed and mixed at 2200 rpm until reaching 70°C; after adding the liquid stabilizer, mixing continued until 115°C, followed by cooling down to 50°C in a second chamber.

The compounds were processed in the Leistritz LSM 30.34 extruder referred to in the previous sections, but now in counter-rotating mode. The screws rotated at 30 rpm for an output of 7 kg/h, the set temperatures ranging from 180°C to 195°C in the barrel and 205°C in the die. Figure 9 illustrates the screw profile and shows the location of the sampling devices. After removal from inside the extruder, the material samples were immediately quenched in liquid nitrogen for subsequent analysis.

The surface of specimens fractured at low temperatures was observed using scanning electron microscopy (Cambridge Stereoscan 360 and Jeol JSM-6301F). Gelation levels were quantified using, among others, a method based on DSC results

Table 1. Main characteristics of the PVC resins selected.

Resin	*K* value	DOP absorption (%)	Bulk density (g/mL)
A	68.1	19.3	0.550
B	68.5	23.3	0.556
C	66.2	25.2	0.550
D	65.7	22.8	0.538
E	65.9	22.7	0.538

Table 2. Formulation.

Component	p.h.r.
PVC	100.0
Calcium carbonate	5.0
Tin thermal stabilizer	1.5
External lubricant	0.6
Polyethylene wax	0.2
Calcium stearate	0.6
Processing aid	0.7
Titanium dioxide	3.0

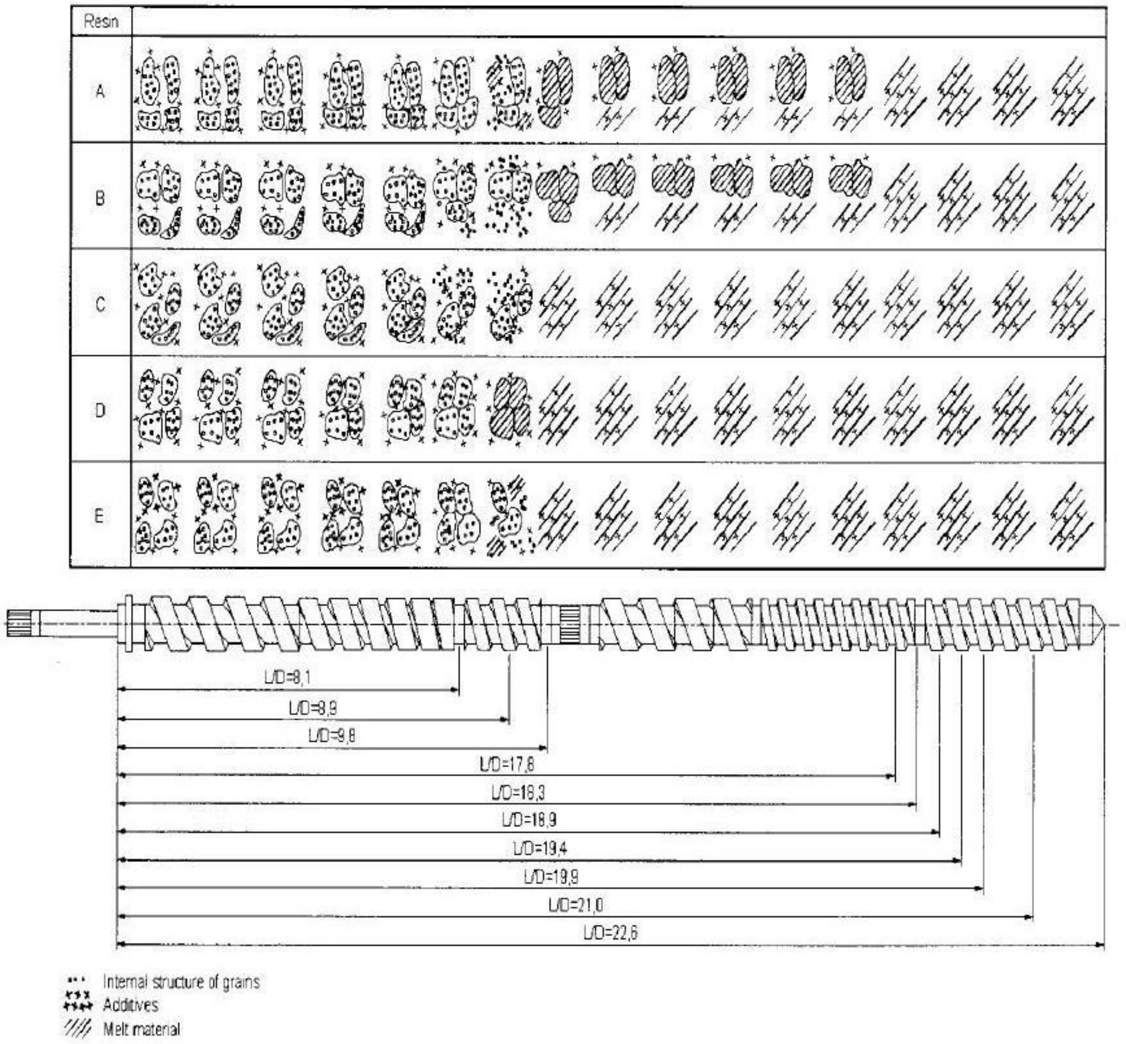

Figure 9. Comparison of the morphology evolution along the screws for the various PVC compounds.

(Gilbert and Vyvoda, 198;, Gilbert, 1985). This uses the enthalpy of a broad endotherm ranging from above Tg to approximately the processing temperature, that is present in the traces of PVC samples that are heated from 30°C to 230°C at 20°C/min (in this case, in a Perkin Elmer DSC 7).

Results and Discussion

The evolution of the morphology of the various compounds along the extruder was identified using scanning electron microscopy. The general differences in the behavior of the various compounds are schematized in Figure 9. Up to $L/D = 8$ the grains of compounds A, D and E preserve their particle characteristics, even if some decrease in porosity is evident,

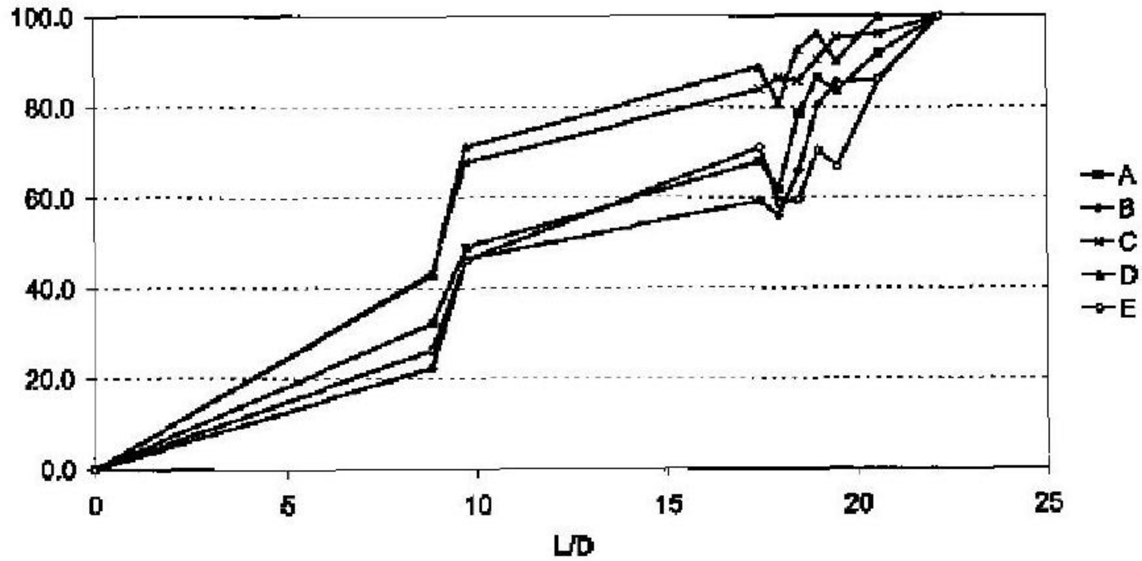

Figure 10. Evolution of gelation (in percentage, %) along the screw (DSC).

while the grains of compound C and, to a lesser extent, those of compound B, appear compacted and broken. The melting process is relatively rapid but heterogeneous, with the coexistence of individual grains, compacted grains still preserving their original contours and molten material. Melting of compounds C, D and E is completed by $L/D = 10$, whereas the remaining two extend this process until $L/D = 18$. Upon melting, the internal porosity of compound D seems to be eliminated and the grains are significantly elongated (the length increases from circa 150μ m to around 500μ m). Compounds A and B followed generally the same route, denoted as CDFE (compaction, densification, fusion and elongation) by Allsopp (Allsopp, 1982; Covas et al., 1988). Conversely, in the case of compounds D and E primary particles were also clearly identified, i.e., gelation seems to involve a progressive decrease in particle size (which is usually associated with the development of higher shear stresses). No significant morphology evolution could be perceived further downstream.

The various methods proposed to quantify gelation are indeed complementary, since each one assesses the existing morphology/structure at a different scale. The evolution of gelation along the screws, as measured by DSC, is shown in Figure 10. This Figure together with Figure 9 provides an overall view of the structural/morphological changes taking place, since they encompass scales with different orders of magnitude.

The rate of gelation seems to be higher prior to $L/D = 10$. The mixing rings located immediately downstream create a pressure profile, with local residence times and stresses well above those that would be expected from simple conveying elements. Higher gelation rates (resins C and D) are related to lower k values. Surprisingly, porosity does not influence the gelation level, only the gelation mechanism, as higher porosity facilitates grain rupture.

Conclusions

Commercial PVC resins used for the extrusion of PVC profiles may follow different gelation routes under identical operating conditions. Differences in rate can also be perceived and correlated with characteristics of the individual resins, namely k value and porosity.

General Conclusions

This work discussed the physical and chemical phenomena involved in the preparation of various polymer-based systems in a twin-screw extruder. The ability to collect relevant samples of the materials being processed without affecting the normal operation of the machine, provided the opportunity to understand the morphological, rheological and chemical evolution along the extruder and, consequently, to understand the ongoing physical and chemical processes. Hopefully, this information will provide the opportunity for optimizing the corresponding compounding conditions, both in terms of operating conditions and equipment geometry, in order to maximize the materials performance.

Nomenclature

G'	elastic modulus, (Pa)
L/D	ratio length/diameter
M_0	torque corresponding to entry effects, $(\mathrm{N} \cdot \mathrm{m})$
$\tan\,\delta$	tangent of phase shift in oscillatory experiments

Greek Symbols

η' dynamic viscosity, $(\mathrm{Pa} \cdot \mathrm{s})$
ω frequency, (rad/s)

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