Thermoplastic elastomer · Blend compatibility · Atomic force microscopy

Tailor made Thermoplastic Elastomer (TPE) blends of commercial nitrile and acrylate rubbers with polyvinyl chloride, thermoplastic polyurethane and acrylonitrile styrene acrylate thermoplastic matrices, were investigated by Atomic Force Microscopy (AFM). Samples with surfaces flat at nanometric scale were prepared by injection and compression molding on freshly cleaved mica foils. The morphological and viscoelastic properties of the surfaces were mapped with nanometric resolution using the friction, tapping and phase contrast AFM modes. The AFM images show that in the investigated TPEs, the elastomers are homogeneously and finely dispersed within the thermoplastic matrix, thus confirming a high level of compatibility at the microscopic scale. The presence of rubber phase is identified at the outermost surface as well as in the bulk of the investigated blends. AFM is confirmed to be a very efficient tool for developing value added thermoplastic elastomer blends with better end use performances.

**Atomic Force Microscopy**

**Nanometric Scale Characterization of the Compatibility of Various Tailor-Made Thermoplastic Elastomers Blends**

Thermoplastic Elastomers (TPEs) are the fastest growing polymeric materials in the plastic and rubber industry. TPEs can be classified in many ways. One classification could be the differentiation of the “ready to use” materials (e.g. polypropylene/ethylene propylene diene monomer thermoplastic vulcanisates), from those that are “tailor made” (e.g. plasticized polyvinyl chloride/nitrile butadiene rubber - PVC/NBR blends) to meet specific end use requirements. Tailoring provides producers with greater flexibility in material design, cost optimisation, and the possibility to have a “unique” product for a specific application.

The functional properties of a tailor-made TPE blend depend not only on its composition and the properties of the constituent polymers, but also on its morphology. In the case of a material having a continuous and a dispersed phase, it is generally admitted that a fine particle size of the dispersed rubbery phase (below 1 to 2 microns) leads to the best end-use properties [1]. The morphology of polymers and rubber/plastic blends has already been extensively studied [2–7] and is known to depend on many parameters, such as concentration of the constituents and their relative viscosity and polarity. Melt-processing parameters like shear stresses and temperatures can influence the morphology as well. Both microscopic and thermal analysis techniques can be used to study the compatibility among the polymers in a blend [4]. The most used microscopic methods are optical and electron microscopy (SEM - Scanning Electron Microscopy, TEM – Transmission Electron Microscopy). More recently, AFM (Atomic Force Microscopy), has been compared to electron microscopy [7–9] and has been found to be a very efficient tool for studying the morphology and the viscoelastic properties of polymer blends [7, 10–15].

The purpose of the present paper is to report the possibilities offered by AFM mainly, to assess the compatibility and the excellent dispersion of the rubbery phase in various “tailor made” thermoplastic elastomer blends.

The materials taken here as study cases will be blends of nitrile and acrylate type rubbers with different thermoplastic matrices – plasticized PVC, TPU (thermoplastic polyurethane), and ASA (acrylonitrile styrene acrylate). The nitrile and acrylate rubbers used are commercial materials, made by emulsion polymerisation and available in powder form for ease of blending with thermoplastics. The company Eliokem markets those globally under the trade names of Chemigum and Sunigum. The nitrile rubbers used are acrylonitrile butadiene statistic co-polymers with 33% acrylonitrile content. The acrylate rubber is based on a unique acrylate styrene acrylonitrile terpolymer, that also contains carboxylic functional groups. Both these elastomers are pre-crosslinked materials, which have been specifically developed for wide use as plastics modifiers. The thermoplastic resins used are also commercial grades.

Commercial applications of the blends presented here are increasing steadily, as a result of the various benefits provided by the rubbery phase. These benefits are at the processing level compared to the thermoplastic alone, as well as for the physical end...
use properties provided by the rubber phase. Processing benefits provided by the NBR or acrylate rubber already evidenced include increased material melt strength, increased dimensional stability of finished parts, reduced viscosity at high shear rates and reduced sticking to metallic parts of processing machines. These can provide improved stability and easier transformation processes. In terms of properties, benefits include improved physical properties and/or chemical resistance, reduced hardness, reduced density, improved UV resistance as well as increased rubbery and soft touch properties. Such value added blends can be specifically formulated and produced by the compounder or end-user to meet existing or new requirements, enlarging the application scope of the mentioned resins.

Information on the raw material used, blends and samples preparation procedures and main characteristics is given in this paper.

Experimental and results

Blends with PVC resin

Nitrile rubber (NBR) blends with plasticised PVC have been successfully commercialised for more than 30 years in various applications, thanks to the great ability of PVC to be compounded and the wide range of properties obtained. The main reasons for blending nitrile rubber with plasticised PVC are that it significantly improves important physical properties such as abrasion, elasticity and crack resistance of the PVC. It also significantly enhances its chemical resistance and durability [16].

The PVC/NBR formulation used is shown in Table 1. It will be labeled as 40 phr PVC/NBR blend.

We prepared this compound by the so-called “dry-blend” technique [16]. In this technique the liquid plasticiser with plasticised PVC are absorbed by the PVC resin, which is heated by friction during a high speed mixing process. The powdered NBR is added in a second step in a cooling phase, and mixed for a short time with the powdered, plasticised PVC. We gelified the resulting free-flowing dry-blend was by two different techniques:

For the first one, it was introduced into the hopper of a single screw extruder (Farrel), equipped with a 3 rods die. The machine temperatures were set from 120 to 150 °C, the screw speed was progressively raised and stabilized at 50 rpm. The rods circulated into a water bath after die exit, before granulation. Molded plaques were then prepared with these granules by injection molding at 170 °C.

For the second gelification technique, the powdered PVC/NBR dry-blend was gelified by mixing of a compression molded 40 phr PVC/NBR blend observed by TEM on ultra thin samples (thickness from 0.08 to 0.1 micron) microtomed at room temperature with a glass knife, after staining the double-bonds of the rubbery phase with osmium tetroxide (OsO₄). The staining process increased sample hardness sufficiently to allow sectioning at room temperature.

Since this image was obtained on a sectioned sample, it is representative of the morphology in the bulk of the blend. As the staining affects the whole sample volume, the rubber phase represented is therefore given by the superposition of all the particles inside the sample and depends on sample thickness.

One can see a homogeneous distribution of round rubber particles, uniformly dispersed within the PVC thermoplastic matrix. The average particle size is centred around 97 nm, which indeed is the size of the rubber particles after polymerization as measured by light diffusion in the wet latex before coagulation.

Characterization by Atomic Force Microscopy (AFM) – The ability of the AFM technique to give complementary morphologi- cal data on these blends has been evaluated. The AFM measurements were performed with a multimode Nanoscope IIIA model from Digital Instruments (Santa Barbara, California, USA) working in contact – lateral force mode and in tapping-phase contrast mode.

In contact mode, the cantilever was in Si₃N₄ with an oxide sharpened tip and a stiffness close to 0,12 N/m (Nanoprobe). The sample is scanned at 90° relative to the axis of the cantilever to increase the friction of the tip on the surface. Two images were recorded, one in trace, the other in retrace. The friction images presented here are the subtraction of the two images (trace and retrace) in order to increase the friction signal and to minimise the morphological effect.

In tapping mode, we used a cantilever in silicon with a stiffness close to 50 N/m (Olympus), the oscillation frequency was around 270 kHz. Because of the high difference in viscoelastic properties between the polymers of the studied blends, the setpoint and the oscillation amplitude were chosen to work with a relatively soft tapping (r = A/V = amplitude set-point/free vibration amplitude = 0,7). This allows to obtain a very good contrast on phase contrast images without any damage of the sample surface.

A plasticized PVC/NBR sample with similar composition to that described above by TEM was investigated. The different sample preparation techniques described below allowed to obtain AFM images in depth as well as on the outermost surface of the samples.

Samples were first prepared by cryomicrotommy at – 20 °C with a diamond knife as pyramidal forms with a very flat surface. Similar preparation has already been successfully used on polymer blends and allows AFM imaging of the morphology in the sample bulk [6].

<table>
<thead>
<tr>
<th>Tab. 1. Formulation description</th>
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<tr>
<td>Product (tradename)</td>
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<td>PVCk (Solvin 271 PC)</td>
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<tr>
<td>Di isodeyl phthalate plasticiser (Jayflex DIDD)</td>
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<tr>
<td>NBR (Chemigum P83)</td>
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<td>Ba/Zn stabiliser (Baerlocht OE 69 MC)</td>
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Figure 1. TEM observation of PVC/NBR blend.
In the AFM tapping mode used for imaging the topography of the soft polymeric surface, both friction forces and excessive load are avoided, which could deform the softer phase of the sample during scanning. In figure 2 below, a well resolved population of nodules appears. They look as if they are protruding outside the surface, like elastic balls, in three dimensional space. Some pleats are however visible, which were probably formed during the preparation of the sample by cryomicrotomy. In the tapping AFM mode image, the NBR particles appear to have a spherical shape similarly to that revealed by TEM. Line scans analysis made perpendicularly to the image plan enable the diameter of the particles to be determined. The main part, which “comes out” of the surface, could be determined by using the analysis AFM module to be centred around 88 nm wide. This is in the range of the average particle size revealed by TEM (close to the original latex particle size), 97 nm. However, slightly lower values are found by AFM. The difference can tentatively be explained by the fact that only part of the particle protruding outside the sample surface is measured by AFM, and not the actual larger bulk diameter, as revealed by TEM. Such consistency between the morphologies revealed by respectively AFM and TEM techniques on plastic blends, rubber-modified plastics, or filled elastomers has already been reported [6, 7, 10].

Sample preparation by injection molding on mica foil – The following sample preparation allowed imaging directly the outermost surface of the samples. To obtain a flat surface at nanometric scale, the blend was compression molded directly onto a freshly cleaved mica surface, placed on the top of the sample inside the mold cavity. The relatively low viscosity of the melted blend prevents the mica foil from breaking during the process. Thus, the atomically smooth mica foil remained stuck to the molded plaque after demolding. Removing the mica foil allowed to obtain a nanometrically flat sample surface for AFM imaging. The different phases present at the surface of the observed sample could then be differentiated. The use of a mica surface to flatten polymer surfaces after melting for AFM imaging has already been described elsewhere [17].

Figure 3 is a topographic representation obtained for the surface of a 40 phr PVC/NBR blend prepared by compression molding. Spherical NBR nodules could also be detected at the outermost surface of the 40 phr PVC/NBR blends in the tapping mode, similar to those obtained in the bulk by using cryomicrotomy (see fig. 2). The images represented in figure 4 are observed for the compression molded 40 phr PVC/NBR blend surface with two other contrasts available in contact mode AFM, namely the height and friction imaging modes respectively. In the height mode (left image), dark (low) particles are observed which have approximately the same size and distribution as the rubber particles observed in the tapping mode (fig. 3). This observation means that the scanning tip is indenting more deeply into the soft rubber particles than into the harder PVC matrix. In the friction mode (right image) the rubber particles appear clear, which means that the friction forces experienced by the tip are larger on the softer and more indented rubber phase than on PVC.

This set of tapping and contact AFM images confirms those obtained previously by TEM concerning the fine and homogeneous dispersion of the NBR rubber in the PVC matrix. It provides further additional information on local viscoelastic properties such as relative hardness and friction forces characteristic of each phase.

Sample preparation by injection molding on mica foil – The morphology of the outermost surface of the 40 phr PVC/NBR blend was also checked on injection molded slab. In this operation, the flattening of the surface was obtained by fixing the mica foil directly inside the mold cavity (with a double-sided adhesive tape). Again the low viscosity of the injected material prevented breaking the mica, which remained stuck on the material after demolding and was removed for AFM imaging. The following AFM image (figure 5) was obtained on the 40 phr PVC/NBR blend surface prepared by the above injection

![Fig. 2. Tapping mode AFM observation of 40 phr PVC/NBR blend. Sample prepared by compression molding on mica foil. 5 microns scan, 0–50 nm height variation contrast.](image2)

![Fig. 3. Tapping mode AFM observation of the outermost surface of 40 phr PVC/NBR blend. Sample prepared by compression molding on mica foil. 2 microns scan, 0–30 nm height variation contrast.](image3)

![Fig. 4. Contact mode AFM observation (left: height image, right: friction image) of 40 phr PVC/NBR blend. Sample prepared by compression moulding on mica foil. 5 microns scan.](image4)
molding. It is indeed very similar to the image previously obtained on the compression molded sample. Spherical rubbery particles are again observed on this sample, however the surface roughness is more important than for the sample prepared by compression molding. Some ridges appear indeed that most likely may have been caused by the flow of the injected material.

These various TEM and AFM characterizations of the 40 phr PVC/NBR blend confirm the presence of NBR rubber particles finely dispersed into the PVC matrix. The AFM technique used to study the outermost surface of compression and injection molded samples, shows that the particles are also present at the extreme surface of the blend.

The extremely small particle size in the range of 100 nm observed in the 40 phr PVC/NBR blend confirms the excellent compatibility between PVC and NBR polymers, extending from the bulk up to the surface of the TPE blends.

In the PVC/acrylate rubber blend investigated hereafter, the acrylate rubber used (tradenamed Sunigum P95) is an acrylate styrene acrylonitrile terpolymer (ASA) with high acrylate rubber content. Compared to NBR, the acrylate rubber elastomeric modifier gives much improved resistance to UV and heat ageing. It can therefore be used in light coloured applications where UV or heat-ageing requirements are particularly demanding. This acrylate rubber can also be blended with many other plastics at melt temperatures up to 250°C.

To study the dispersion of the acrylate rubber in a plasticized PVC compound, the formulation and sample preparation were similar to those used previously for the NBR (see section 1-1), the NBR being replaced by the acrylate rubber.

The lack of double bonds in the acrylate rubber terpolymer does not allow staining by osmium tetroxide. This should prevent unambiguous identification of the rubbery domains inside the thermoplastic PVC matrix by TEM. In this case where the TEM technique can’t be used, morphological information can be obtained only by AFM thanks to its sensitivity to the “nanomechanical” properties of the blend [8].

Characterization by Atomic Force Microscopy. The outermost surface of this PVC/acrylate rubber blend was imaged in contact mode by AFM on compression molded sample prepared with the technique previously described of molding onto a mica foil (figure 6).

The morphology observed with this PVC/acrylate rubber blend is very close to the one reported previously for the PVC/NBR blend in the same formulation (figure 4).

The acrylate rubber phase softer than the matrix appears in the height mode as dark domains at a lower level than the matrix. Conversely in the right picture, the friction forces are observed to be larger (clear domains) in the acrylate phase than in the matrix.

These two images testify that this PVC/acrylate rubber blend also presents a very good dispersion and compatibility of the rubber at the microscopic level. The presence of polar acrylonitrile groups in this unique, pre-crosslinked acrylate elastomer powder provides an exceptional mixing behaviour with PVC, as shown by this outstanding level of compatibility at the microscopic level.

Blends with TPU resin
Nitrile rubber blend with TPU
In nitrile rubber/TPU blends, the former acts as a permanent and solid plasticiser, which reduces hardness whilst enhancing flexibility, soft touch and rubbery properties. It also improves the processing and rheological characteristics of the TPU resins.

We used the following procedure to prepare the TPU/NBR sample. A copolyester type TPU (tradenamed Avalon 75 AE supplied by the company Huntsman) was blended by melt mixing with a NBR rubber (tradenamed Chemigum P86F from Eikoki) in a co-rotating twin-screw extruder (Clextral), equipped with two gravimetric feeders (K-Tron) and a rod die. One feeder was used for the TPU in granulates, the other was used for the NBR in powder form. The hydroscopic TPU was first pre-dried in a ventilated oven for 3 hours at 90°C. For this extrusion/compounding process the materials were introduced simultaneously in the hopper and melt-mixed in the extruder barrel. For this operation the extruder temperatures were set from 170 to 185°C, the screws speed was progressively raised and stabilised at 250 rpm. The extruded rod was cooled into a water bath before granulation. Feeding rates of each material were adjusted to produce a blend of 60/40 TPU/NBR ratio. 0.5% of a phenolic antioxidant (tradenamed Irganox 1076 supplied by the company Ciba Specialty Che-
micals) was pre-mixed with the NBR in powder form to reinforce the thermal stability during the compounding operation. Plaques samples were then prepared by injection molding, with press temperatures set from 175 to 190 °C.

Characterization by Atomic Force Microscopy – The images shown in figure 7 below were obtained by contact mode AFM on a TPU/NBR sample, prepared by cryomicrotomy with a diamond knife at −120 °C. As previously the darker domains in the height mode (left picture) represent the soft NBR phase, and in the friction mode (right picture) this phase appears as clear domains. Some hard particles, clear in the height mode image and dark in the friction one, are also visible and most likely correspond to the mineral fillers that are used to cover this powdered NBR rubber to prevent agglomeration. Such contrast in a lateral force AFM image in a TPU containing polymer blend has already been observed [6]. The size of the rubbery domains varies from 100 nm to 1 micron approximately in this analysis.

Tapping mode AFM with phase contrast has also been successfully used to image soft polymer blends components [11, 12]. In such experiments, the phase contrast is sensitive to several experimental factors that affect the magnitude of tip-sample interactions [9]. The following image (figure 8) was obtained on this TPU/NBR blend by tapping mode AFM with phase contrast. At similar magnification, the same morphology is revealed in phase contrast mode with dark domains corresponding to the softer and/or more adhering dispersed rubbery phase compared to the continuous TPU matrix. Mineral fillers are also visible in the form of clear particles. Contact mode AFM at lower magnification (scan size: 30 microns) has been performed on this TPU/NBR blend. The images obtained (figure 9) confirm the homogeneity of the dispersion of the fine rubber domains in the TPU thermoplastic matrix.

The morphologies of the TPU/NBR blend revealed by AFM in contact mode, and phase contrast in tapping mode, appear to be in quite good agreement. Homogeneous and fine rubber particle sizes, below 1 micron, are observed, confirming an excellent compatibility for the blend produced. This can be explained by the polar character of both components and the shear forces acting in the mixing extruder to disperse the NBR into the TPU matrix. Acrylate rubber blend with TPU – The interest of such blends is to combine good mechanical strength with improved flexibility and UV resistance. The blends have a “rubbery” appearance and soft touch properties compared to the TPU alone. The acrylate rubber also enhances the TPU rheological properties and this makes processing of the blends easier (the viscosities at high shear rate are reduced and the melt strength is increased compared to the TPU resin alone). The sticking of these blends on metallic parts during processing is also significantly reduced [18, 19]. We prepared the blend of acrylate rubber (Sunigum P95) with TPU by melt mixing on the twin-screw extruder, in a procedure similar in principle to the one previously described with the NBR. The TPU used this time was a polyether type (tradenamed Elastollan 1180A supplied by the company BASF). A 80/20 ratio of TPU/ acrylate rubber ratio was used. 0,5% of phenolic antioxidant (Irganox 1010 from Ciba) was also added to reinforce the ther-
mal stability during the compounding operation. In this mixing process the extruder temperatures were set from 180 to 185 °C, and the screws speed was raised up to 250 rpm. Molded samples were then prepared by injection molding, with machine temperatures set from 190 to 205 °C.

Characterization by Atomic Force Microscopy – Contact mode AFM imaging on a TPU/ASA sample prepared by cryomicrotomy at −120 °C is presented in figure 10. The acrylate rubber phase is represented as dark and clear domains in respectively the height (left image) and the friction (right image) modes as for the NBR phase in the TPU/NBR rubber blend (see Fig. 7). The rubbery phase is softer and the friction forces are more important on this phase than on the matrix. Hard filler particles corresponding to the mineral partitioning agent are also visible as clear particles in the height mode and dark ones in the friction mode. There is a close similarity between these pictures and those obtained previously on the TPU/NBR blend, at the same level of magnification. The population of the acrylate rubber domains is smaller here due to the lower concentration of the acrylate rubber, only 20% compared to 40% for NBR. The size of the acrylate rubbery domains varies within a range from 100 nm to 1 micron approximately, similar to the TPU/NBR blend.

To assess the possible presence of these rubbery domains at the outermost surface of injection molded samples, another trial was conducted with a mica foil fixed into the mold to flatten the material surface. After removal of the foil the following pictures were obtained in AFM contact mode (figure 11).

The presence of acrylate rubber at the outermost surface of this sample is confirmed as shown by the darker (softer) domains seen in the height mode and clear domains in the friction one. Their average size appears much smaller (around 70 nm) than in the bulk of the sample prepared by cryomicrotomy. This difference observed between the bulk and surface rubbery domain sizes may be tentatively explained by the fact that only the smaller emerging part of the particles outside the matrix is observed at the surface. The bulk observation reflects the actual particle size distribution. Such difference between the surface and the bulk fraction of a component in a polymer blend has already been observed [13].

As the particle sizes observed by AFM in the sample bulk and at its outermost surface are lower than 1 micron, we can infer a very good compatibility between the TPU and acrylate rubber. A similar morphology in the bulk was previously also revealed by TEM after chemical staining of the TPU matrix [18].

It is important to point out that some acrylate rubber domains are present at the extreme surface of the TPU/acrylate rubber blend. This may explain that some surface properties are modified in these blends compared to the resin alone (reduced gloss, improved “soft touch” properties and UV resistance . . . ) [18, 19].

Blends with ASA resin

Acrylate rubber (Sunigum P95) and ASA resins are both characterised by excellent heat and UV resistance. Regarding the physical properties, the main effect of acrylate rubber when blending with ASA resin is to reduce hardness and increase elongation at break. It also modifies the aesthetics making the material more rubber like. Advantages for processing can also be expected thanks to the presence of the acrylate rubber in reducing viscosity at high shear rates and enhancing melt stability.

Acrylate rubber/ASA resin blends are formulated with two polymers based on the same monomers, respectively acrylate and styrene/acrylonitrile. None of those has any double bond readily reactive for chemical staining. The main difference between the ASA resin and the acrylate rubber composition is the acrylate rubber content which is much higher in the acrylate rubber (85% approximately) than in the ASA resin. Therefore the acrylate rubber is a much more elastic and softer material.
than the ASA resin. Because of the similar chemical structure of these two polymers, atomic force microscopy has been found as the only suitable method allowing a microscopic characterization of these blends, owing to its sensitivity to their respectively rigid and soft phases.

We prepared several blends of the acrylate rubber and ASA resin (tradename Luran S 7765E supplied by the company BASF) by melt-mixing in the twin-screw extruder in a similar procedure compared to the one used for the TPU/NBR and the TPU/ acrylate rubber samples. The hydroscopic ASA resin was first pre-dried in a ventilated oven for 3 hours at 80°C. The extruder temperatures were set from 200 to 230°C, the screws speed was raised up to 300 rpm. Samples for AFM analysis and some physical property testing were then prepared by injection molding at 240°C.

Samples formulations

To study the influence of the acrylate rubber in the ASA resin, two blends were prepared with different acrylate rubber amounts. The bulk shore D hardness was measured for these blends and compared to the ASA resin alone (see Table 1). A very significant drop in shore D hardness is obtained when blending ASA resin with increased acrylate rubber content as shown in Table 2.

Characterization by AFM

ASA resin and acrylate rubber/ASA blend samples were sectioned into the molded foils and surfaced by microtomy at 25°C with successively glass and diamond knives for AFM observations.

ASA resin alone – Since ASA resin initially already contains some acrylate rubber, two phases are expected to be observed for ASA resin alone. In contact mode AFM images of figure 12, the darker parts in height mode observed as lower domains should be representative of the softer phase of the resin, most likely the acrylate rubber domains dispersed in a more rigid SAN resin.

In this figure these soft domains appear as very small particles, uniformly dispersed into a rigid matrix. From the height mode image a size centred around 110 nm could be estimated for the acrylate domains.

ASA resin/acrylate rubber blend with concentration ratio 70/30 – The contact mode AFM image obtained on the 70/30 blend (figure 13) is characteristic of an excellent compatibility between the 2 materials. A high homogeneity is observed in the distribution of finely dispersed rigid and soft domains, no dispersed phase could be clearly identified. This could still be explained by the close similarity of chemical composition between the acrylate rubber and the ASA resin, and by an excellent mixing and dispersion of the acrylate and SAN phases of both products in the twin-screw extruder.

The amount of soft zones seen in height mode is more important here than on the pure ASA resin observed before, at the same magnification. This is obviously explained by a more important soft acrylate rubber phase in these samples, which is provided by the acrylate rubber.

ASA resin/acrylate rubber blend with concentration ratio 40/60 – The concentration ratio is now reversed with acrylate rubber as major constituent, 60% in the blend. The excellent level of compatibility between the acrylate rubber and ASA resin remains confirmed with the 40/60 composition, the level of dispersion still being excellent between the rigid resin and the soft rubber.

In this formulation with a majority of acrylate rubber content, the soft acrylate phase is larger than the rigid SAN domains that now appear more like dispersed rods in the height mode (see figure 14). The reduction of shore D hardness from 71 to 37 in these blends (see table 1), can be related to a greater soft acrylate phase content, which is revealed by AFM. This is particularly visible by comparing the pictures 12 to 14 in height mode where the

<table>
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<td>Acrylate rubber</td>
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Tab. 2. Hardness shore and mean roughness of ASA resin and ASA resin/acrylate rubber blends at different formulations.
softer acrylate phase appears as dark (low regions). Roughness parameters such as Ra (mean roughness) the mean value of the surface relative to the centre scan plane, can be obtained in tapping mode AFM. Values obtained for the two blend formulations and pure resin are included in Table 2. The surface roughness increases with soft acrylate phase content and Ra is indeed inversely related to the shore D hardness with a correlation coefficient $R^2 = 0.993$ (see figure 15).

Conclusions

On account of its outstanding spatial resolution and sensitivity to the differences in local viscoelastic properties at the microscopic level, it is confirmed that Atomic Force Microscopy is very well suited for the detailed characterization of bulk and surface morphologies of tailor-made TPE blends. The images obtained from the different AFM modes – the tapping mode with height and phase contrast, the contact mode with height and friction contrast – could be well correlated. By use of a specially adapted sample preparation (molding against a mica foil), AFM allows information to be obtained on sample composition at its outermost surface, which could be of high interest for practical applications.

Compared to TEM, AFM does not require the time consuming preparation steps of cryo-ultramicrotomy and staining of ultra thin samples. This technique is in addition particularly useful for identifying the elastomeric phases of TPEs made with rubbers, which do not contain easily reactive double bonds, such as acrylate rubbers. The blends of NBR and acrylate rubber with PVC, TPU and ASA resins that have been investigated in this work all show a very high level of compatibility at the microscopic level. This compatibility is generally characterized by an extremely fine particle size of dispersed rubbery domains, from 100 nm to 1 micron approximately, into a continuous thermoplastic matrix. This can be explained by the pre-crosslinked structure of the NBRs and acrylate rubber used, by the polar nature of both the elastomers and the resins, and by the shear forces encountered in the mixing processes that disperse the rubbers into the resins. Experience has shown that small modifications in the simple blends preparation procedures here described would not affect the quality of rubber dispersion into the thermoplastic resin, and the resulting benefits in properties and/or processing characteristics obtained. With plasticised PVC, the NBR and acrylate rubber particle sizes in the blends are found to be as small as they were just after polymerisation in the latex step, which means that the level of dispersion obtained is optimum. With TPU$s$, an extremely fine and homogeneous dispersed rubber phase has also been revealed, leading to the conclusion that TPEs with excellent properties can be easily obtained by melt blending TPU$s$ either with NBR or acrylate rubber. By adding increasing amounts of acrylate rubber to ASA resin, AFM analysis revealed a progressive change from a rigid towards a soft continuous phase, together with an excellent compatibility of the materials as could be expected from their chemically similar composition. In very close correlation with softness, surface roughness increases with acrylate rubber concentration.