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The use of nano and micron –sized particles to enhance the interlayer adhesion in self-reinforced, single polymer composites

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Delamination; D. Scanning Electron Microscopy (SEM)

Abstract

Recent work has shown that the interlayer adhesion of single polymer composites produced by the Leeds hot compaction process can be significantly improved by either introducing interleaved films of the same polymer between the layers of woven oriented tapes that make up the composite or by the incorporation of carbon nanofibres (CNF) into the oriented tapes prior to hot compaction, or by a combination of these two approaches to produce a synergistic effect.

Following on from these findings, we have now investigated the changes in the interlayer peel strength caused by incorporating other micron and nano-scale fillers into polypropylene films which are interleaved into the interlayer region of the hot compacted composite. The filler initially chosen for this study was talc, but a number of other fillers have also been investigated. Scanning electron microscopy has been used to image the peel surfaces and to undertake a preliminary study of the effects of particle size and shape on the peel strength.

1 Introduction

Recent research on the self-reinforced single polymer composites produced by the Leeds hot compaction method has been focused on the enhancement of the material properties, both through modification and enhancement of the hot compaction technique [1] and also through trials of new materials, including the incorporation of nanoscale fillers [2-4]. In addition to improving the more usual mechanical properties (e.g. Young's modulus), a key objective has been the enhancement of the interlayer peel strength of these composites.

The hot compaction process can be widely applied to oriented polymers for the production of polymer/polymer composites [5, 6]. In this process, an assembly of oriented fibres or tapes (often in the form of a woven cloth) is taken, under a small constraining pressure, to a critical temperature, where a thin skin on the surface of each oriented element melts. On cooling, this skin recrystallises to form the matrix of a single-polymer composite, with the remaining oriented fraction acting as the reinforcing phase. The virtue of this technique is that the matrix phase is produced around each fibre by melting and recrystallisation, negating the need for infiltration of a second matrix phase.

Alternative methods for the production of single polymer composites which can also result in improved interlayer adhesion can be obtained either through co-extrusion of tapes or filaments with a high melting point core and lower melting point sheath [7] or through film stacking techniques [8]. A complete review of these techniques and other single polymer composites can be found in ref [9].

In typical fibre reinforced composites, the volume fraction of the reinforcement phase is normally a maximum of 50-60%. In the hot compaction technique, since the

matrix phase is produced from the reinforcement fibres, a higher volume fraction of reinforcement is achievable. Analysis of the structure [5, 6] has shown that the optimum properties of the final composite are achieved at 30% of melting, i.e. 70% oriented phase remaining.

Hot compacted composites are produced by compacting layers of woven PP tapes in a laminate-type structure. Whilst there is excellent bonding within each of the woven layers, because only the outer skin of the tapes is melted, there is just a thin layer of matrix material, a few microns thick between each woven layer. Thus the interlayer adhesion, which can be quantified by measuring the force required to peel apart the layers, is of crucial importance. One way to improve the strength of this interlayer bond is to increase the thickness of the interlayer region (i.e. increase the amount of matrix material) by raising the compaction (processing) temperature; however this leads to a reduction in the mechanical properties of the material.

It has been previously reported that the incorporation of carbon nanofibres (CNF) into hot compacted polypropylene woven tapes (without interleaved films) resulted in an improved peel strength [2]. Another study [1] has shown the advantage of using unfilled thin film layers, of the same polymer, interleaved between the woven tape layers, resulting in greatly enhanced peel strength since the film layer introduces more matrix material at the point required – the interlayer region. It was subsequently shown that a synergistic effect could be achieved by combining these two approaches to result in greatly enhanced peel strengths [10]. A key finding of this latter study was that it was discovered that the nanoscale filler (CNF) did not need to be present in the woven tapes, and that similar peel loads could be achieved by only incorporating the filler into the film layers.

Here, we report on the enhancement of the peel strength in these composites when fillers other than CNF are incorporated into the interleaved films, with a particular focus on talc, initially chosen since it is a cheap and readily available filler. A preliminary effect of the size of the particulates on the peel strength has also been investigated, using scanning electron microscopy (SEM) to examine the post-test peel surfaces.

2 Experimental

2.1 Materials

The polymer used in this work was a polypropylene (PP) homopolymer with a weight average molecular weight (M_w) of 360,000g/mol, number average molecular weight (M_n) of 78,100g/mol, density of 910kgm⁻³, and unconstrained peak melting point of 163°C. For the hot compaction process, woven PP fabric composed of the same base PP resin was obtained from Propex Fabrics GmbH and was the same as used in previous studies (cloth E in [11, 12]).

Blending of materials was achieved using a twin-screw extruder, with length to diameter ratio of 40. The blending conditions used were as determined in previous study [4], with a blending temperature of 200°C and a screw speed of ~70rpm.

Talc powder was obtained from Sigma Aldrich. The particle size is estimated to be between 10 and 20µm. Nanoclay was also obtained from Sigma Aldrich, and was a montmorillonite clay surface modified with 15-35% w/w octadecylamine and 0.5-5% w/w aminopropyltriethoxysilane, grade I.31PS. The typical agglomerated particle size is in the range 15-20µm. Carbon black was supplied by Cabot Corporation and was the Vulcan PF grade, with a particle size in the range 24-36µm.

The flyash was a standard commercially available example of this material and was sourced from the University of Bradford. The exact composition of flyash can vary between batches; however the particles are generally spherical and vary between 0.5 and 100µm in size.

2.2 Film casting

Film layers were cast using the cast film line at the University of Bradford. The extruder was set at 185°C for the Pure PP and 20% w/w talc filled films or 200°C for the remainder of the films, with a haul-off speed of 5.3m/min and the chill rollers set to 5°C. The cast-line was started with pure PP before the filled material was fed in. The thickness of the films was measured as shown in Table 1.

Film thickness varied due differing viscosities of the blended composite materials, because the particles were all of different loadings, shapes and sizes. It was difficult to optimise the film casting process, because only a relatively small amount of each composite material was produced.

2.3 Hot compaction

Hot compaction was performed by layering the woven PP fabric and interleaving the filled PP films in between each set of woven layers. The construction was composed of four layers of PP fabric with three interleaved films in between (i.e. one layer of film between each of the woven layers). A thin piece of aluminium foil was placed along one edge of the construction to allow a peel crack to be initiated. The assembly was then placed under pressure in a hot hydraulic press and taken to the compaction temperature for a set dwell time (10 min) before fast cooling. A compaction pressure of 4.9MPa was used. Woven samples were approximately 300mm x 320mm and 0.5mm thick.

2.4 Peel Testing

T-Peel tests (after ASTM D1846) were performed on an RDP-Howden servo-mechanical tensile testing machine. Aluminium foil was placed along one edge of the hot compacted sample, located between the central two layers of fabric, prior to compaction and was used as a starting crack in order to test the sample. Samples were cut directly from the hot compacted sheet in 10mm wide strips. Peel tests were performed at a rate of 80mm/min (rate as in previous work [2, 3]), at a room temperature of $21\pm 1^\circ\text{C}$ and RH of 50%. The peel load was determined as the average force required to propagate the delamination of the hot compacted layers for the 10mm wide strip.

3 Talc filled composites

3.1 Filler Loading

Three different talc-filled films were produced, at loadings of 10, 20 and 30% by weight (% w/w), and samples were produced with these interleaved films. The latter two loadings were compacted at 193.9°C and the 10% w/w sample was compacted at 192.8°C . The peel loads obtained from these samples are shown in Table 2.

From these results, it was determined that incorporating the talc into the hot compacted sheet results in an increased peel load over a sample compacted with a pure PP interleaved film ($\sim 10\text{N}/10\text{mm}$), although not as pronounced as seen previously with the incorporation of CNF [10]. These results suggest that there is little difference in the peel strength of samples loaded up to 20% w/w, and at a loading of 30% w/w, there is no overall improvement obtained by incorporating the talc. It is thought that this is due to the interlayer region becoming saturated with the talc filler. In order to obtain a strong interlayer bond both the surface of the particles must be wetted to ensure no

voiding in the interlayer region and the layers must be bonded together by the matrix material in the interlayer region. At high particle loadings, there is less PP within the film layer and so there is not enough material to fulfil both of these criteria.

Further to these results some samples were produced in the trial phase of this study, with a 20% w/w film that gave even higher peel loads (~17N/10mm) than those in Table 2. Later work has therefore concentrated on studying samples produced with this loading, although it has been found that the results in Table 2 are more consistent.

3.2 Compaction Temperature

Initial trials at compaction temperatures similar to those used with filled film previously [10], showed that there was no increase in peel strength with an interleaved talc-filled film over that of a pure PP interleaved film, as can be seen in Figure 1. As the compaction temperature was increased, although the peel load trended upwards (as expected, since there is more matrix material generated by melting the woven layers), the samples compacted with a pure PP interleaved film tended to plateau out to a value of approximately 10N/10mm, whereas the samples with talc-filled interleaved films increased up to a peel strength of 14N/10mm.

In order to peel the samples apart, a piece of aluminium foil is placed along one edge of the peel sample, creating “end tabs” that can be placed into the grips on the tensile testing machine and the sample pulled apart. A sample produced with a 20% w/w talc-filled interleaved film and compacted at 195°C could not be peeled apart but instead failed along the point where the “end tabs” rejoined the main bulk of the sample. From this result, it can be inferred that the peel strength has been increased over the cohesive strength of the samples, but because the peel strength decreases with

increasing temperature, this indicates that a compaction temperature of 195°C is too high.

Figure 1 thus indicates that that the optimum compaction temperature for compaction with micron-sized particles is in the range 193-194°C, where the peel strength is increased by the incorporation of the particles, yet the cohesive strength of the compacted sheet is not significantly reduced. This optimum compaction temperature range is higher than that seen with the carbon nanofibres (CNF) reported previously [10], and is thought to be because the particle size of the talc is much greater than that of the CNF. In order to achieve a strong interlayer bond, not only does the particle surface need to be wetted with PP in order to obtain a good bond between PP and particle, it is also appears that enough of the woven material surface must be melted in order for the particles to embed themselves into the edge of this layer. If this does not occur, then the peel crack can simply run along the edge of the woven layer. In order to accommodate the larger talc particles, more material from the woven layer must be melted and thus a higher compaction temperature may be required.

3.3 Scanning electron microscopy (SEM)

Examination of the peel surfaces reveals a number of interesting details. Figure 2 shows SEM micrographs of the sample in Table 2 with a 20% w/w talc filled PP interleaved film. Figure 2 (a) shows an overview of the peel surface, and there are a number distinct regions visible. First, as reported previously [10], widespread fibrillation is visible across the surface (A) and tape fracture (B) and pull-out can also be seen. Not seen previously is the ‘pock-marked’ region of the surface (C). A higher magnification image of a similar region can be seen in Figure 2 (b). This does not cover the whole surface, but shows the region where the talc filled film has not been peeled

away from the woven tape surface. Underneath the talc-filled film, there are still signs of fibrillation (D), but also smoother sections of pure PP (E).

Noticeably, it is difficult to see any evidence of talc platelets in these images, and although some relatively large particles can be seen on the surface (F), there should be a much greater number of these particles visible. It is thought that since the talc platelets are very soft, they can be squashed during the compaction process due to the high pressure used to constrain the sample. When peeling the surfaces apart, the PP around each of the squashed platelets is pulled apart, and as a consequence pulls the squashed talc platelets apart, leaving the 'pock-marked' surface seen in Figure 2.

4 Other fillers

In addition to talc, a number of other potentially commercially useful fillers were screened to see if the effect of improving peel strength can be obtained with these materials. These results can be seen in Table 3.

Examination of the peel surfaces of these materials using SEM, and comparison with the talc-filled material (Figure 2) helps to explain the differences in the observed peel loads of the different fillers in Table 3. As with the talc-filled material and the carbon nanofibre filled composites reported previously [10], all samples showed tape fracture and pull-out, together with widespread fibrillation. The interesting differences in the micrographs reported here appear to be directly related to the filler particles used.

Figure 3 shows the peel surface with an interleaved nanoclay filled PP film. The similarity between this surface and that seen with the talc-filled (Figure 2) is immediately obvious. As with the talc-filled sample, there were regions of fibrillation (where the nanoclay-filled film had been pulled off the tapes) and regions that were

'pock-marked' as in Figure 3. It is also extremely difficult, as with the talc, to see any distinct signs of nanoclay platelets, although it is possible that a larger particle can be seen at A. It is thought that because the nanoclay is also a soft particle, a similar process of the platelets being squashed during the compaction process and then pulled apart during peeling has taken place, making it very difficult to observe single platelets. This could explain why the talc-filled and nanoclay-filled materials showed the same peel load.

Figure 4 (a) shows that the particles in the carbon black-filled material are much more distinct, with a number of particles clearly protruding from the peel surface (B). Noticeably, these particles are also present in a region where there is a high degree of fibrillation of the peel surface. Figure 4 (b) shows a higher magnification image of the leftmost particle indicated in (a). There are a number of fibrils that can be seen extended from the surface of the carbon black particle, and although these are small, they do indicate that there is some form of bonding between the particles and the PP. Because PP is chemically inert, it is speculated that the bonding relates to penetration of the PP into the porous carbon black particles. The fibrils are only small, because these pores are also small. This would then explain the difference in measured peel strength between the carbon black and talc, which have nominally the same size particles. Since talc is not porous, there can be no penetration of PP into the particle surface.

This may explain the effectiveness of the carbon nanofibres (CNF) in improving peel strength as reported previously [10]. The smaller size of the CNF means a greater surface area and therefore more chance for the PP to penetrate the particles, thus a higher measured peel load was obtained. In addition, the penetration of PP may also occur at the open ends of the CNF. It was not possible to image this behaviour in CNF,

since the particles are so small that they are difficult to observe in amongst the widespread fibrillation across the sample surface.

Figure 5 shows the peel surface of the sample with the lowest measured peel load -that with a flyash-filled interleaved film. As with other samples, there are regions of fibrillation visible across the surface, for example that seen at D. However the fibrillation taking place on the adjacent tape to D, i.e. at E and F is quite clearly prevented from expanding further by the presence of the large particles seen at G. It is believed that the size of the particles prevents good bonding in that particular region of the sample and thus the peel crack travels around these particles, through the PP matrix rich regions. It should be noted that the particles at D, and across the surface are quite distinct, and that there is no sign of any bonding or interaction between the particles and the PP.

5 Discussion

The images obtained from these peel surfaces have allowed an insight into the potential mechanisms responsible for the improved peel strength seen in these composites. Perhaps the most obvious reason is the increase in surface area that must be separated from the polymer during the peeling process, and so it is suggested that those particles with the greatest surface area should result in the highest peel load. It should be noted that the surface area is clearly linked to both the particle size (and size distribution) and shape, and that these dependencies have only been examined broadly in this study.

The interaction between the particle surface and the polymer is also of crucial importance in determining the peel load. The greater the degree of adhesion the polymer

has to the surface, the more difficult it is to remove from the particle surface, and so increasing the amount of energy that can be absorbed in the peeling process. This, of course, reaches a limit where the amount of energy required to extricate the polymer from the particle is greater than that required for the peel crack to simply move through the polymer matrix itself. Chemical modification of the particles or polymer to improve adhesion is perhaps the most obvious route therefore to obtain improved peel strength for these composites, however the base polymer used in this study, polypropylene, is generally chemically inert and as such it is difficult to achieve improvements of this kind. An alternative to this is to obtain some form of mechanical interlocking between the particle surface and polymer chains, such that the polymer is able to infiltrate the particle surface. In order to obtain this kind of interaction therefore, the particles used must have some form of surface roughness, or alternatively must be porous. This type of mechanical interaction obviously improves the peel load, since it requires more energy to extricate the embedded polymer from the particle.

Whilst these factors are somewhat speculative, the particles investigated in this study, and in previously [10], have demonstrated a combination of these factors. Perhaps, most interestingly is the effect seen with the carbon black, where a small amount of polymer seemed to have penetrated the particle surface, allowing a good mechanical bond between the polymer and particles. It was difficult to image talc and nanoclay particles in the peel surface, and it is thought that platelets may have been pulled apart during the peel test since they are extremely soft. The flyash, the filler with least effect, showed larger particles on the surface of the sample, with no bonding of any kind with the PP, and these seemed to prevent fibrillation across parts of the surface.

6 Conclusions

It has been demonstrated that the interlayer adhesion of hot compacted self-reinforced single polymer composites can be improved with a number of different fillers, in addition to carbon nanofibres.

Preliminary studies with talc-filled interleaved films have shown that there is an effect due to the concentration of filler used and also that the compaction temperature used is also important. This could be due to a particle size effect, in order to allow the particles to embed themselves into the woven tape surface. Testing of other materials blended into films: nanoclay, carbon black and flyash have all resulted in greater measured peel loads compared to a pure PP film.

SEM imaging of the peel surfaces has suggested that there are a number of potential reasons for the improved peel strength, including surface roughness of the particles, particle-polymer adhesion (mechanical and chemical) and particle shape, size and surface area.

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Figure 1 Peel load versus compaction temperature for samples produced with 20% w/w talc/PP film, pure PP film and with no film or filler.

Figure 2 SEM micrographs of peel surfaces of a sample compacted with a 20% w/w talc-filled interleaved film. (a) shows an overview of the sample surface showing areas of fibrillation and also some that are 'pock-marked.' (b) shows a higher magnification image of the 'pock-marked region. For details of the labels see the text.

Figure 3 SEM micrograph of peel surface of sample compacted with a 20% w/w nanoclay filled PP interleaved film. See text for details of annotation.

Figure 4 SEM micrographs of peel surface of a sample compacted with a 20% w/w carbon black filled PP interleaved film. (a) shows a number of particles embedded in a region of fibrillation and (b) is a higher magnification image showing PP fibrils attached to the surface of larger particle. See text for details of annotation.

Figure 5 SEM micrograph of peel surface of a sample compacted with a 20% w/w flyash filled PP interleaved film. The particles can be seen clearly on the surface and interfere with fibrillation. See text for details of annotation.

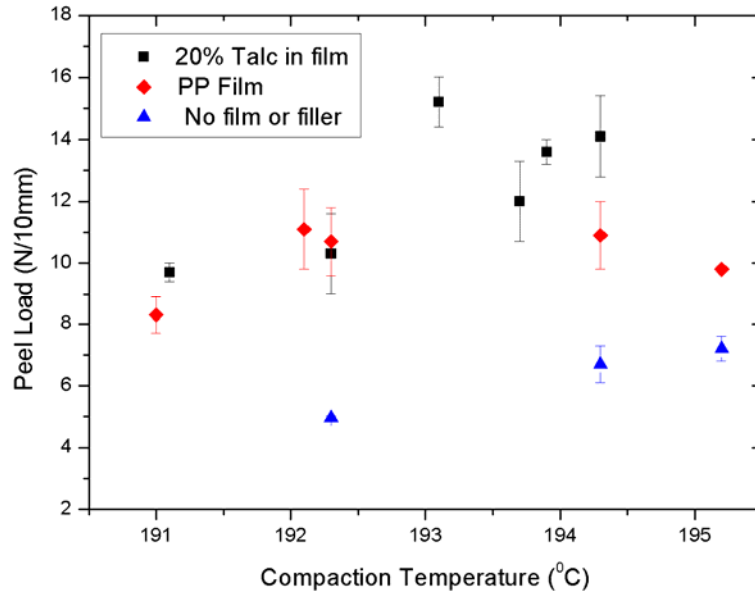


fig.1

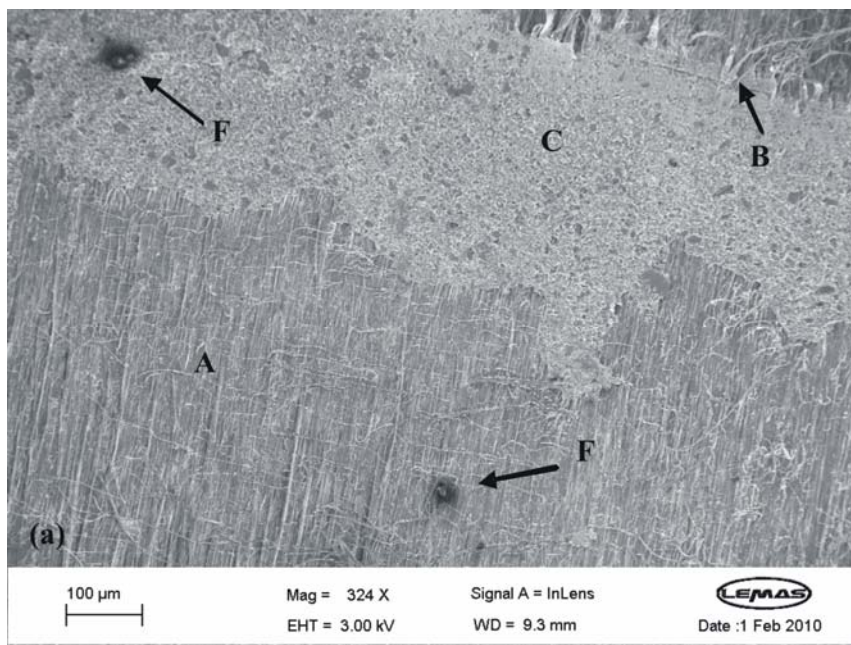


FIG.2a

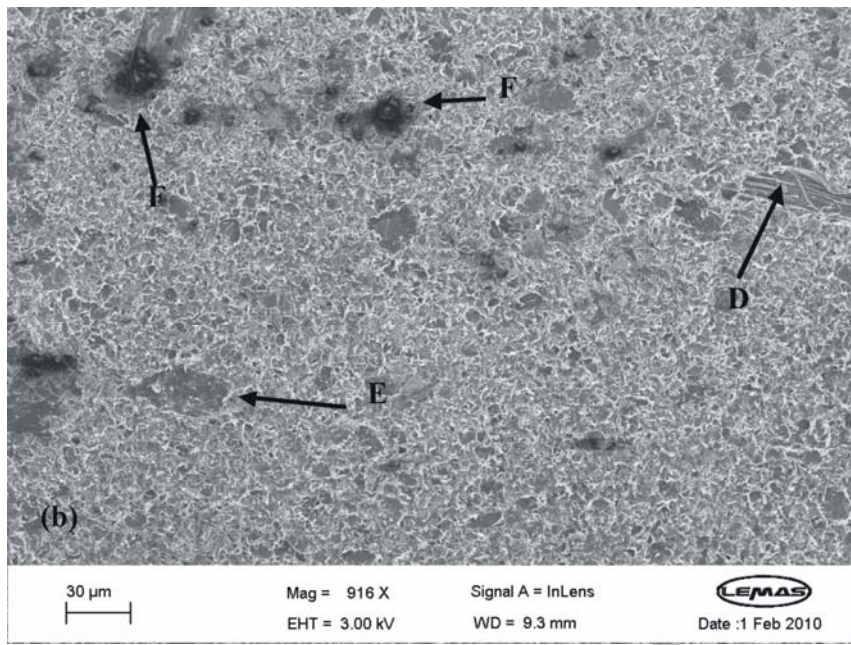


Fig.2b

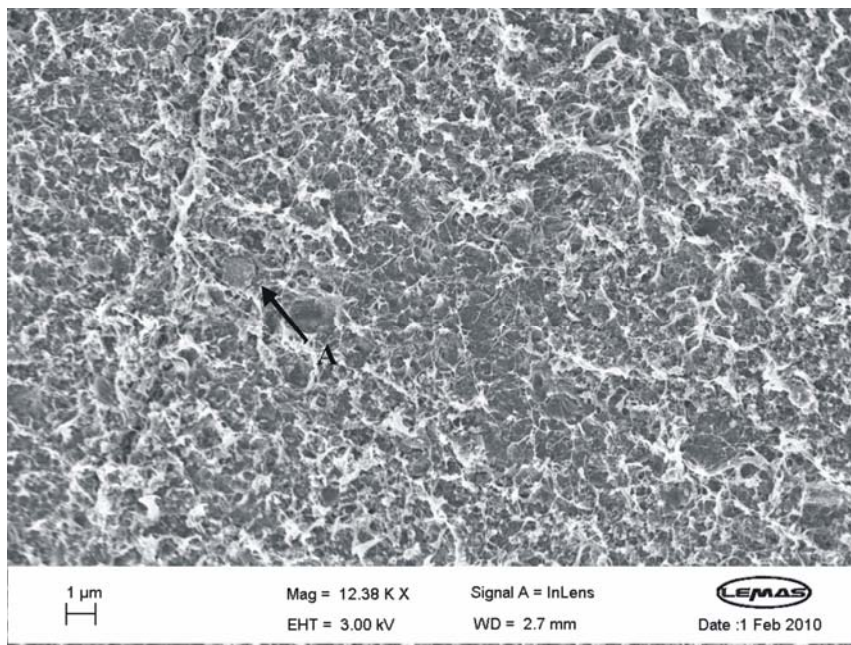


Fig.3

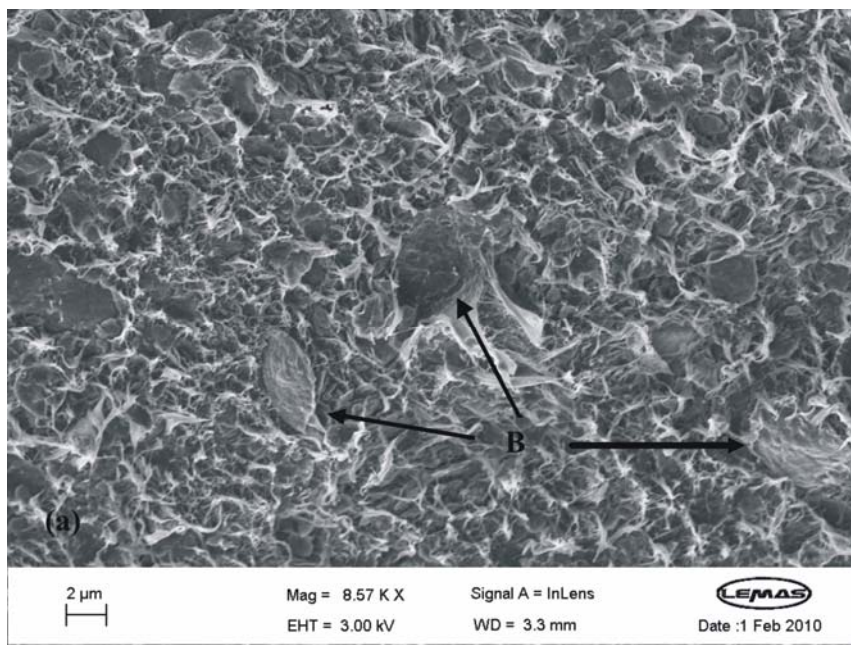


Fig.3

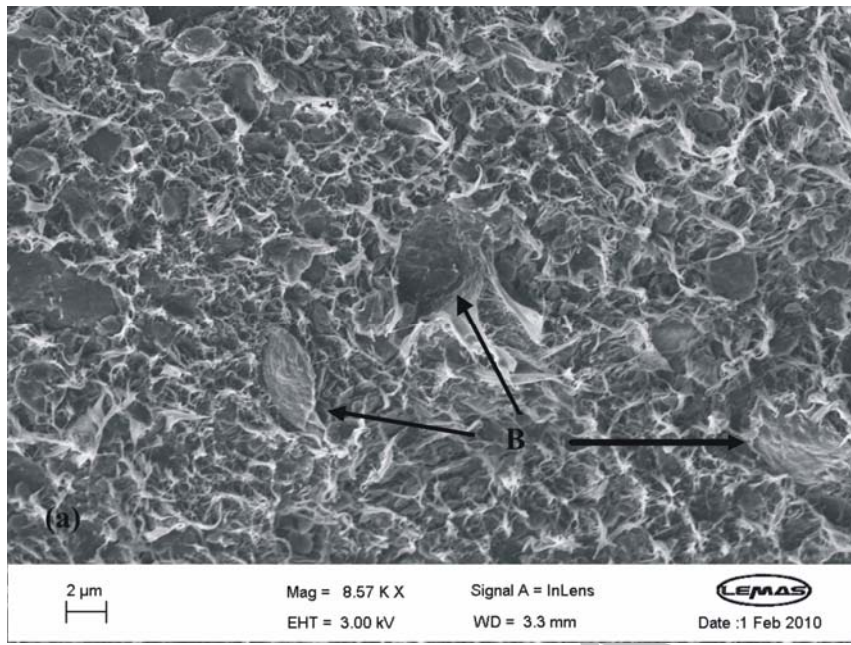


Fig.4a

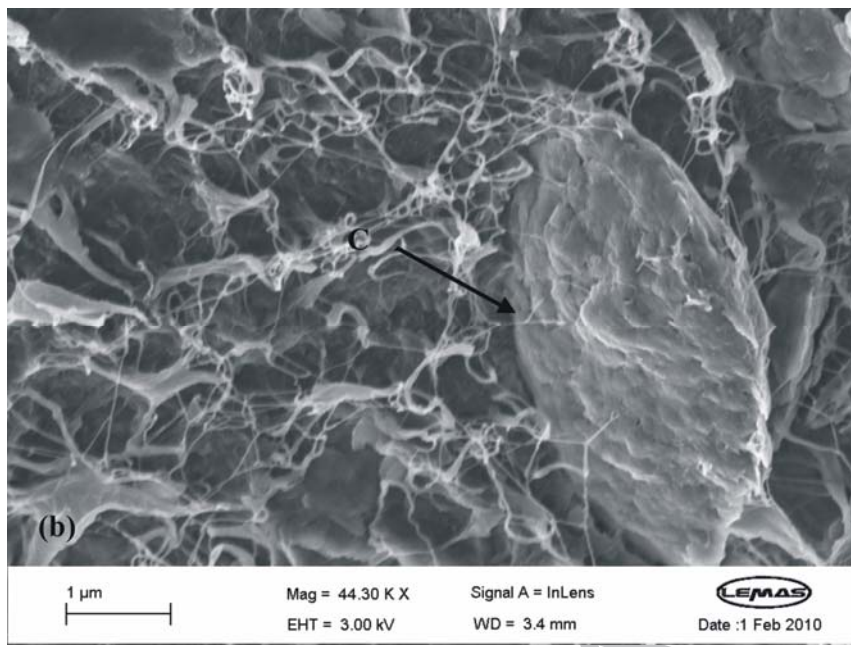


Fig.4b

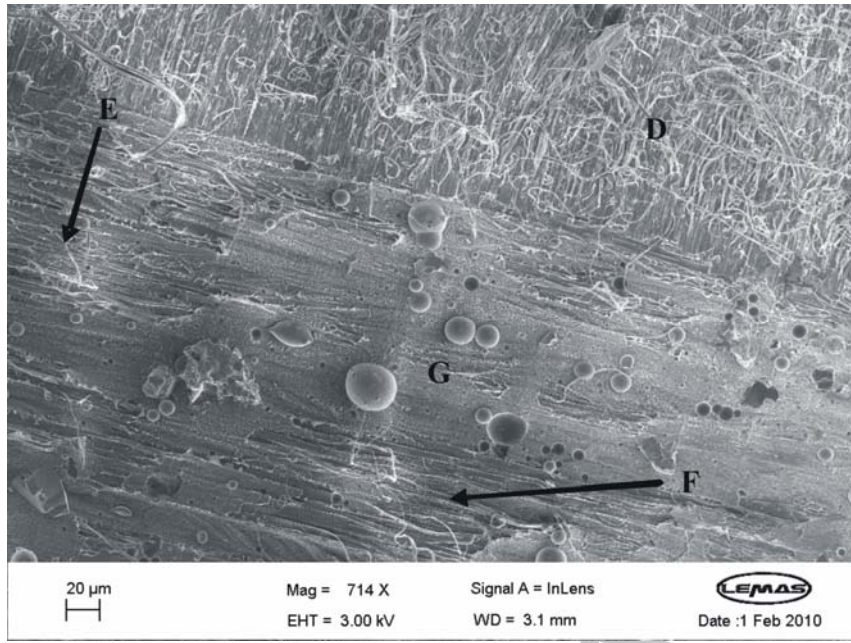


Fig.5

Table 1. Thickness of pure and filled PP films produced on cast film line.

<u>Film</u>	<u>Thickness (μm)</u>
<u>Pure PP Film</u>	<u>56\pm8</u>
<u>20% w/w talc filled PP film</u>	<u>83\pm8</u>
<u>30% w/w talc filled PP film</u>	<u>50\pm4</u>
<u>20% w/w nanoclay filled PP film</u>	<u>99\pm13</u>
<u>20% w/w flyash filled PP film</u>	<u>79\pm5</u>
<u>20% w/w carbon black filled PP film</u>	<u>26\pm3</u>

Table 2. Peel loads of samples produced with different filler loadings of talc in the interleaved films.

<u>Loading of talc in film (% w/w)</u>	<u>Compaction temperature (°C)</u>	<u>Peel load (N/10mm)</u>
<u>10</u>	<u>192.8</u>	<u>14.5±1.7</u>
<u>20</u>	<u>193.9</u>	<u>13.6±0.4</u>
<u>30</u>	<u>193.9</u>	<u>10.4±0.7</u>

Table 3. Peel loads of samples produced with different fillers. A loading of 20% w/w was used for all films and a compaction temperature of 193.9°C was used

<u>Filler</u>	<u>Peel load (N/10mm)</u>
<u>Nanoclay</u>	<u>13.1±0.6</u>
<u>Carbon black</u>	<u>14.5±0.5</u>
<u>Flyash</u>	<u>11.7±0.5</u>