Weld line behaviour of exfoliated and toughened polypropylene layered silica nanocomposites

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Abstract: Exfoliated and toughened polypropylene nanocomposites prepared by an introduction of a rubber in the form of compatibilizer toughener: ethylene propylene diene based rubber grafted with maleic anhydride (EPDM-g-MAH) were studied in terms of weld line properties and morphology. Effects of addition of rubber and nanolayer on weld line strength under tensile loading condition of polypropylene matrix were investigated. Data showed that in the absence of either EPDM or nanolayers, a sharp decrease in weld line strength cannot be avoided whereas in the presence of each in optimum ratio, the drastic increase in both toughness and weld line strength values can be easily reached. The beneficial effect is believed to come from the selective placing of nanolayers around the rubber droplets and making them smaller in size which contributes to diffused weld line regions with high mechanical strength.

Introduction

Polymer/layered silicate or clay nanocomposites possess attractive properties when compared with neat polymers and micro-composites [1]. Among the nanofillers, layered silicate have drawn a lot of attention because of their small size or large surface with nanoscale dimension resulting in tremendous improvement in mechanical properties, [2-5] barrier properties [6-7] and thermal stability, and fire retardancy [8-11].

Polypropylene (PP)/clay nanocomposites, on the other hand, are especially very interesting because of their attractive potential applications in automobile industry. But because of its extremely non-polar molecular structure, the homogeneous dispersion of layered clay within PP matrix is rather difficult to achieve. Literature has some studies regarding the preparation of PP-organoclay nanocomposites having a mixture between intercalated and partially exfoliated structures [12-13]. Moreover, although some benefits are gained with these structures, decrease in tensile ductility of the resultant nanocomposites especially at low temperatures was tried to be overcome via poly(ethylene-co-octene) (PEOc) copolymer addition for forming rubber toughened PP [14]. However, even the optimized amounts of the organoclay, PP-g-MAH and PEOc did not give both the desired impact resistance and exfoliation to the nanocomposites.
Quite recently, as an original solution to the above mentioned drawbacks, the results on synthesis of new exfoliated PP nanocomposites with much more toughened structures via incorporation of a rubber toughener in the form of compatibilizer was published [15]. It has been found that the desired exfoliated nanocomposite structure as well as improved thermal and dynamic mechanical properties could be achieved in all compatibilizer to organo-clay ratios and clay loadings.

It is well known that the plastic materials are often molded into complicated parts by injection molding, compression molding and extrusion. In fact molding of such parts usually produces a weld line once the melt fronts have joined either by impingement flow or around an insert. Weld line is undesirable when the strength, long term durability and surface quality is a concern. The losses in abovementioned performances with presence of weld line for composites usually much more pronounced than that for their counterparts owing to much more complicated morphology in the weld line region. There is no doubt that it might be possible to overcome these drawbacks through development of a special weld line morphology via molding temperature, injection velocity, holding pressure at various degrees depending on materials [16-17].

Despite the tremendous growth of polymer nanocomposites, only few studies has been reported on the weld line behavior of them. Edward et al [18] published their results on the effect of weld lines in injection moldings of Nylon 6 nanocomposites as the first report on weld line behavior of nanocomposites. It has been found that nanocomposites containing organically modified montmorillonite exhibited low weld line strength due to the presence of notches at the weld line region, interference with molecular diffusion across the boundary, or variation in orientation or type of crystallinity because of the clay platelets. The significance of the process factors on welded samples and the effects of weld strength were then determined and discussed. Variation of crystallinity which may be responsible from weak weld line strengths were also investigated by Akkapeddi et al [19] and found that flow induced orientation of the platelets near weld line region and an apparent nucleation promotes faster crystallization of nylon 6 leading the difficulties in diffusion of the molecules resulting in formation of weak defect points. Pukanszky et al [20] studied polypropylene/montmorillonite (PP/MMT) nanocomposites prepared by using sieved bentonite, sodium and organophillic MMT. Specimens were injection-molded with various weak sites (weld lines, gate section) in the test area to see the performance of the nanocomposite under practically relevant conditions. The results showed that the weld line strength of PP nanocomposites is very low most probably clay particles orient parallel to tile weld line and strongly deteriorate the properties.

The purpose of this study was to investigate the weld line behavior in injection molded tensile specimens of successfully exfoliated and toughened PP/Org-MMT nanocomposites. Since these new and special nanocomposites have a multiphase character, emphasis will be placed on isotropic morphology development as a function of both the existence of toughener compatibilizer as well as nanofiller. It is believed that the results will also serve to understanding the weld line behavior of both binary and ternary phased PP nanocomposites in detail.

**Results and discussion**

Some tensile properties of normal (without weld line) and welded specimens of neat polypropylene (PP), PP nanocomposite (PPNC), toughened PP (PPNC0) and
toughened PP nanocomposite (PPNC3) are given in Table 1 summarizing the maximum tensile stress and impact strength values as well as all weld line factors for abovementioned samples both without and with weld lines.

**Tab. 1.** Some mechanical properties of normal and weld line specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max. Stress, normal (MPa)</th>
<th>Max. Stress, weld, (MPa)</th>
<th>Weld Line Factor</th>
<th>Impact Strength, normal (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>33.25 (0.42)</td>
<td>31.71 (0.45)</td>
<td>0.95</td>
<td>2.89 (0.09)</td>
</tr>
<tr>
<td>PPNC</td>
<td>32.50 (0.32)</td>
<td>24.50 (0.37)</td>
<td>0.75</td>
<td>2.75 (0.11)</td>
</tr>
<tr>
<td>PPNC0</td>
<td>28.24 (0.27)</td>
<td>18.51 (0.32)</td>
<td>0.65</td>
<td>3.70 (0.12)</td>
</tr>
<tr>
<td>PPNC3</td>
<td>26.07 (0.35)</td>
<td>22.53 (0.45)</td>
<td>0.86</td>
<td>4.17 (0.15)</td>
</tr>
</tbody>
</table>

Data in parentheses represent standard deviations.

It is quite clear that in all cases weld line causes to a decrease in mechanical strength which can be also followed by low weld line factors. Neat PP is strong enough even with a weld line present, and the presence of weld line causes little variation in tensile yield property. Quite high weld line factor is most probably due to the extensive inter-diffusion of polymer molecules at the weld region which can also be easily observed by a smooth even hardly seen weld line in Figure 1.

**Fig. 1.** ESEM image of weld line region of PP.

The PP nanocomposites (PPNC), on the other hand exhibits weaker mechanical behavior than neat PP even without a weld line present. Reduction in weld line factor to 0.75 may have resulted from inherent size of organoclay leading to the agglomerate formation as well as organoclay orientation and location at the weld line region by acting as stress concentrators causing weakening. Insufficient exfoliation of organophilic montmorillonite in polypropylene matrix was previously reported [15].
Organoclay orientation, on the other hand, in a high shear flow field during injection molding can induce a high degree of PP chain orientation due to the fountain flow at the flow fronts having an extensional component normal to the overall flow direction. When both the flow fronts impinge at the weld line, the organoclay and polymer chains may orient perpendicular to the overall flow direction, making it a potential source of weakness. The poor weld line strength of micron-sized fiber-filled polymers have been reported to be due to perpendicular alignment of the filler at weld line plane and to their non-uniform distribution [21]. In the weld line region, the nanoparticles may also hinder molecular diffusion across the weld line interphase and/or promote planar molecular orientation parallel to weld line plane and hence lead to incomplete molecular entanglement [16]. The resultant weld line morphology in Figure 2 clearly presents the significantly large weld line region resulting from low degree of molecular diffusion. Similar results were also reported by Pukanszky et al [20] for polypropylene montmorillonite nanocomposites.

**Fig. 2.** ESEM images of weld line region of PPNC samples (a) and enlarged view (b).

Table 1 represents also the result of attempts of having better weld line strength in samples via using a rubber toughener in the form of compatibilizer both in the absence and presence of nanoparticle.

It is very well known that the mechanical strength loss for immiscible polymer blends due to the presence of the weld line is usually much more pronounced than that for their counterparts owing to complicated morphology. The situation is much more complicated by the presence of oriented domains and minor phase concentration gradients in the weld line regions [22]. In our study here, as it was previously determined via surface indentation force measurements in AFM [15], the existence of dispersed MAH grafted EPDM phase as rubbery droplets having MAH shells in PP matrix was evidenced. Moreover, ESEM data given in Figure 3 represent this phase morphology of binary blend, PPNC0, with dark holes resulting from etched EPDM
particles which are heterogeneously dispersed in PP matrix with ca 6 \( \mu \)m rubber domain size.

The quite low weld line factor in this toughened PP (PPNC0) can be attributed to the existence of abovementioned rubber domains in PP matrix. Figure 4 shows this weak weld line morphology in details as very deep, large and smooth weld line valleys indicating incomplete diffusion of the macromolecules in impingement flows. Moreover ca 6 micron sized rubber droplets can be observed in low pressure view (Figure 4d).

**Fig. 3.** ESEM image of etched PPNC0 sample.

**Fig. 4.** ESEM images of weld line region of PPNC0 sample (a), enlarged views of weld line region and weld line valley (b, c) and low pressure view (d).

On the other hand in the presence of a ternary system with additional organophilic montmorillonite in 3 to 1 compatibilizer to organoclay ratio, which was previously found to be an optimum composition for the best impact performance [15], weld line
strength increases considerably together with special narrowed and much more diffused weld line region morphology (Figure 5). Here, it is obvious that domain size decreases to ca 2 micron in the presence of nanolayers. Also, fractured and etched surface micrograph (Fig 6) exhibits almost the same dramatic decrease in size of more homogeneously distributed rubber domains to ca 2 μm and even less than 1 μm in the presence of nanolayers. Reduction in the domain size may be attributed to both the nano size directed domain morphology via reduction in the difference in melt viscosities of continuous polymer matrix and dispersed phase [23] resulting in improvement in the mixing properties gained by the presence of nanosilica layers, giving a sharper shear-thinning nature to the composites [24] as well as possible agglomeration of the compatible nanolayers around the EPDM particles and forming a diffused layer between PP and EPDM.

**Fig. 5.** ESEM images of weld line region of PPNC3 sample (a), enlarged views of weld line region and valley (b, c) and low pressure view (d).

**Fig. 6.** ESEM image of etched PPNC3 sample.
More homogeneous dispersion of EPDM rubber domains with a smaller size in PPNC3 nanocomposite is probably due to the deposition of nanosized silica platelets selectively around the dispersed rubber phase as given by AFM image (Figure 7a) and disruption of the continuity of this discrete phase via shear thinning. Surrounding of rubber domains with nanolayers are believed to have resulted from the strong hydrogen bonding between the hydroxyl groups of silicates and MAH groups of the rubber. Moreover, the dispersion of the nanolayers in the PP matrix is also obvious in a magnified image of the nanocomposite (Figure 7b).

![AFM phase image of non-etched PPNC3 sample](image.png)

**Fig. 7.** AFM phase images of non-etched PPNC3 sample [15].

In order to differentiate nanosilica morphology better, the etched surface of 3% clay-loaded nanocomposite, PPNC3 was scanned in tapping mode AFM. The nanoscale dispersion in the etched nanocomposite was easily observed as shown in Figure 8. Exfoliation is quite clear and partly nano-sized stacked silica platelets with a maximum thickness of ca 35 nm and less are largely separated from each other (ca
151.2 nm) and oriented in all possible directions to one another in the PP matrix. This result can be a further confirmation with XRD patterns exhibiting no diffraction peaks demonstrating the almost complete delamination or exfoliation of silica layers in PP matrix (Figure 9).

![AFM phase image of etched PPNC3 nanocomposite](image)

**Fig. 8.** AFM phase image of etched PPNC3 nanocomposite [15].

![XRD patterns](image)

**Fig. 9.** XRD patterns of organoclay (a) and PPNC3 sample(b).

It was previously reported that, in order to increase the weld line strength via reducing the minor phase dimensions, the dispersed phase viscosity is increased above that of matrix [25]. Similarly, in this study, selectively surrounded rubber particles with organophilic nanolayers are believed to be effective in increase in viscosity of the dispersed elastomeric phase which exhibits high complex viscosity around its relaxation temperature, -35 °C as it can be seen in DMA thermogram (Figure 10).
Moreover, the impact strength increase in PPNC0 sample in Table 1 can be explained as enhanced deformation of the PP due to the interactions between rubber particles and PP ahead of crack tip. The further increase in PPNC3 can be attributed to possible void formation around the nanoparticle during fracture. This increase in toughness related impact strength is not observed in PPNC as there is no relaxation of the crack tip constraint due to the lack of rubber particles [27].

It is also most interesting that the impact resistance of PP enhanced by almost 112 % with both rubber toughener and nanolayer addition occurs without any significant loss in weld line strength.

**Conclusions**

Exfoliated and tough layered silica based PP nanocomposites were prepared with melt blending of organically modified clay and EPDM-g-MA as compatibilizer. XRD and morphological studies showed that as compared to PP-EPDM binary blends, in all nanocomposites having different degree of loading and compatibilizer to organoclay ratios, the occluded rubber domains dispersed more homogeneously with much smaller size, ca 700 nm. By both decrease in rubber domain size surrounded with nanolayers as well as exfoliation of the nanolayers in PP matrix it was possible to achieve a major improvement in impact resistance.

These exfoliated and impact resistant PP nanocomposites are found to be safely produced with quite high weld line strength. The beneficial effect is believed to come from the selective placing of nano-layers around the rubber droplets which may probably resulting in increase in viscosity of discrete rubber phase and making them smaller in size which contributes to diffused weld line regions with high mechanical strength.

**Experimental part**

**Materials**

Table 2 shows specifications of the materials used in the study. Isotactic polypropylene (iPP) in granular form with melt-flow rate of 12.2 g/10 min. was
supplied by Basell Polyolefins. Maleic anhydride grafted thermoplastic elastomer, namely maleic anhydride grafted ethylene propylene diene monomer (EPDM-g-MA) was used as a compatibilizer. The organically modified montmorillonite (Nanofil-15) containing dimethyl dihydrogenated tallow quaternary ammonium (2M2HT) modifier with cation exchange capacity (CEC) of 100 meq/100 g was kindly provided by Süd-Chemie AG, Germany.

**Tab. 2.** Polymers and organoclay used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Commercial name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (PP)</td>
<td>Moplen-HE 125 MO</td>
<td>Basell Polyolefins</td>
</tr>
<tr>
<td>EPDM-g-MA</td>
<td>FUSABOND- MF 416 D</td>
<td>DuPont de Nemours</td>
</tr>
<tr>
<td>Organoclay</td>
<td>Nanofil-15</td>
<td>Süd-Chemie AG</td>
</tr>
</tbody>
</table>

**Preparation of PP nanocomposites**

All the compositions given in Table 3 were compounded by simultaneous addition of PP, EPDM-g-MA and organoclay to intermeshing co-rotating twin screw extruder (PRISM TSE24) a modular system, with 24 mm screw diameter (D) and 28:1 L/D ratio (shaft length over screw diameter). The barrel temperature profile adopted during compounding of all compositions was 70 °C at the feed section, increasing to 190 °C at the die head. The screw rotation speed was fixed at 500 rpm. The extrudate was quenched in a water bath, pelletized and then dried.

The composites were then injected into a special double-gated mould having three cavities by using Arburg Allrounder 320C Injection Molding Machine with a barrel temperature of 180 - 230 °C. The mold temperature was 25 °C. Cycle time, injection molding pressure and holding pressure were set to 55 s, 800 and 700 bar, respectively. The injection rate was 120 cm³/s. One of the cavities was suitable for tensile whereas other two for impact and flexural test specimens. The mould had two runner systems feeding two gates for each cavity. Gates were located opposite ends of cavities to form cold weld line in the middle. One of the runners was closed to produce specimen without weld line. Specimens containing weld line were produced by letting both gates of each cavity open. All test specimens were allowed to `condition` under ambient conditions for at least 48 hrs prior to testing.

**Tab. 3.** Polypropylene nanocomposites and their compositions.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PP (wt%)</th>
<th>EPDM-g-MA (wt%)</th>
<th>Organoclay (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PPNC</td>
<td>97</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>PPNC0</td>
<td>91</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>PPNC3</td>
<td>88</td>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>

**Characterization**

Typical stress strain curves for normal and weld line specimens were obtained at ambient temperature by using a Zwick Universal Tensile Testing Machine Z020.
Load indicator equipment was a 20 kN load cell and extension indicator was a mechanical long stroke extensometer. Test specimens were left at the air conditioned room (23 ± 2 °C and 50% relative humidity) for at least 48 h, and then measured in thickness and width before testing to obtain the cross section area of the sample. Afterwards, the specimen was fixed to self-aligning grips of the tensile test machine with 123 mm distance between grips. Test was performed at a constant speed of 50 mm/min and the stress and corresponding strain values were recorded at 0.1 second time intervals.

For the ease of comparing the effect of weld line on mechanical properties of molded material, the weld line factor $F_{wl}$ was defined as [26];

$$F_{wl} = \frac{\text{Property value of specimen with weld line}}{\text{Property value of specimen without weld line}}$$

where property value was chosen as maximum stress values in this study.

The impact strength of the normal (without weld line) nanocomposites was measured by Izod pendulum impact testing machine (Zwick impact tester) at room temperature. Injection molded test bars were in the dimensions ($t \times w \times l$) of $4 \pm 0.2$ mm, $10 \pm 0.2$ mm, $80 \pm 0.2$ mm. 2 mm notch with notch base radius $0.25 \pm 0.05$ mm was machined at mid-span of specimen.

Scanning electron microscopes (ESEM-FEG/EDAX Philips XL-30 (Philips, Eindhoven, The Netherlands) ) and Jeol JSM 35C instruments using an accelerating voltage of 10 kV were used to examine the morphology of the cryogenically fractured samples especially weld line regions from different sections.

In order to measure the basal spacing ($d_{001}$ reflection) of MMT clay in nanocomposites, X-ray diffraction (XRD) measurements were conducted on a Rigaku D/Max-2200 Ultimate diffractometer with CuK$_\alpha$ radiation and operating at 40 kV and 40 mA.

Atomic Force Microscopy (AFM) was performed by using Ambios Universal Scanning Probe Microscope (USPM) (Ambios Technology, Santa Cruz, CA). Hot pressed thin films were directly scanned to investigate dispersion of rubber particles in PP. Then, the samples were etched with hot n-heptane for 2 hours to remove EPDM particles so that clay particles were detectable on the surface. Phase mode imaging was performed using a silicon nitride cantilever probe (NSC16) with a spring constant of 25-60 N/m. Phase images were obtained in tapping mode in which the cantilever was oscillated at its resonance frequency of 170 kHz.

The dynamic mechanical properties of the nanocomposites were measured with a dynamic mechanical analyzer (DMA-Q800, TA Instruments, New Castle, DE, USA) in the single-cantilever mode at a frequency of 1 Hz and a heating rate of 5 °C min$^{-1}$ over a temperature range of -70 to 130 °C. The average dimensions ($t \times w \times l$) of the injected samples were $3 \times 10 \times 34$ mm$^3$.

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References