STUDIO E SVILUPPO DI COMPOSITI A MATRICE TERMOPLASTICA PER APPLICAZIONE NEL SETTORE DEI TRASPORTI

Napoli, 15.12.2008

Tutor
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Schematic

Micro/Nano Matrix

Glass Fiber Woven fabric

Micro and Nano fillers

Glass-Fiber composite

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Outline

- Preparation of nano- and nano/micro-composite matrix
- Morphological, structural and rheological characterization of the matrix
- Preparation of Glass Fiber Nano/Micro composites (GF-NM)
- Mechanical properties of the GF-NM
- Study of a high-performance thermoplastic blend (PC/ABS)
- Glass fiber composite with PC/ABS matrix
- Conclusions
Motivations

- Improved specific mechanical properties
- **Reduction of final polymer content**
- Cost and weight reduction
- Increased thermal resistance
- Better barrier properties and flame stability
Automotive needs

- Need to improve the performances of materials
- Need to arrange materials and various structures for the realization of “multiperformance” systems

Structural function
- Assure flexural and torsional rigidity of components
- Assure structural performance reckon with localized strain
- Satisfy the security performances
- Assure fatigue toughness of components
Thermoplastic composites

High impact strength

Recyclability
Abrasions and water resistance
Unlimited shelf life
Ability to be assembled by welding
Lower moisture absorption

Poor creep resistance
Poor solvent resistance
High processing temperature and pressure

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Why Polypropylene?

- Lower process temperature with respect to PA
- Low cost
- Better processability
- Lower water moisture sorption
- Great recyclability

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Polypropylene nanocomposite issues

- Difficult to produce by extrusion or melt blending
- Lack of affinity between hydrophobic PP / hydrophilic clay
- Low fracture toughness

Use of compatibilizer: PPgMA

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Materials

- PP: Moplen HP500J (supplied by Basell)
- Compatibilizer: Polybond 3200 (1 wt% MA functionalized PP, Crompton)
- Organoclay: Dellite 72T (Laviosa), Nanofil 5 (Süd-Chemie) both organo-modified by using an ammonium salt
- Inorganic filler: CaCO$_3$ micron sized particles
Processing procedure

Processing parameters

Temperature = 170 °C
Time = 7 min
Speed of rotation = 70 rpm

<table>
<thead>
<tr>
<th>Material</th>
<th>from</th>
<th>to</th>
<th>With respect to</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPgMA</td>
<td>0</td>
<td>25</td>
<td>wt% of PP</td>
</tr>
<tr>
<td>Clay</td>
<td>0</td>
<td>7</td>
<td>wt% of polymer</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0</td>
<td>22</td>
<td>wt% of polymer</td>
</tr>
</tbody>
</table>

Haake reomix
Matrix characterization

- X-ray Scattering (degree of intercalation and/or exfoliation)
- DSC (effect of nanoparticles on crystallinity)
- TGA (thermal stability)
- Rheological tests (degree of intercalation and/or exfoliation)
- Mechanical properties

Evaluate the effect of nanoclay addition on mechanical and rheological properties

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Mechanical properties – PPgMA effect

Young modulus increases with the PPgMA content up to 15 wt%, due to its better compatibility with platelets. Young modulus decreases with further increase of PPgMA content, due to the lower molecular weight of the compatibilizer.

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Mechanical properties – Filler effect

Young modulus increases with the nanoclay content up to 3-5%
Both nanocomposites show a young modulus increase of 50% with 3 wt% of clay.

The matrix with Nanofil5 shows a further increase with 7 wt% of clay.

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Mechanical properties – nano/micro

The Young modulus changed very slightly with the micro.

Small amount of nanoclay determined an increase of about 50%.

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A rheological characterization was conducted in order to evidence the influence of the composition on the flow behaviour of the nano/micro-composites.

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Modelling rheological behaviour

The rheological behavior was described in terms of the Carreau-Yasuda four parameters model

- Good agreement of the model with experimental data
- \(\lambda\) and \(a\) decreased as the clay content increased, exhibiting a non-Newtonian behavior
- Shear thinning is more evident for high wt% nanoparticles content

\[
\eta^*(\omega) = \eta_0 \left[1 + (\lambda \omega)^a \right]^{(n-1)/a}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\eta_0) (Pa s)</th>
<th>(\lambda) (s)</th>
<th>(a)</th>
<th>(n)</th>
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<tr>
<td>PP/15/0/0</td>
<td>2301</td>
<td>0.14</td>
<td>0.42</td>
<td>0.20</td>
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<td>0.25</td>
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<td>1.57</td>
<td>0.43</td>
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<td>0.34</td>
<td>0.18</td>
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<td>0.18</td>
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<td>0.29</td>
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<td>1.1</td>
<td>0.32</td>
<td>0.27</td>
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</tbody>
</table>
TPC – Impregnation techniques

Film stacking

thermoplastic matrix reinforcing fibre
(a)

thermoplastic film reinforcing fibre fabric
(b)

thermoplastic fibre reinforcing fibre
(e)

thermoplastic powder reinforcing fibre
(c)

thermoplastic powder reinforcing sheath reinforcing fibre
(d)

thermoplastic fibre reinforcing fibre
(f)

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Glass Fiber Nano/Micro composites

Glass fiber composites were produced by film stacking technique

GF content between 30wt% to 35wt%

Closed mould

Temperature

Pressure

Matrix ply (4 ply)
Fiber glass (3 ply)

200 °C
900 seconds
15 bar

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# Glass fiber nano/micro composites

<table>
<thead>
<tr>
<th>Name</th>
<th>$v_p$ [wt%]</th>
<th>$t_{0m}$ [mm]</th>
<th>$t_{fm}$ [mm]</th>
<th>$t_{fc}$ [mm]</th>
<th>$v_f$ [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE_30_03</td>
<td>30</td>
<td>0.30</td>
<td>0.16</td>
<td>1.35</td>
<td>35</td>
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<tr>
<td>CE_40_03</td>
<td>40</td>
<td>0.30</td>
<td>0.20</td>
<td>1.40</td>
<td>35</td>
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<tr>
<td>CE_40_04</td>
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<td>0.40</td>
<td>0.30</td>
<td>1.47</td>
<td>32</td>
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<td>CE_40_05</td>
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<td>0.50</td>
<td>0.40</td>
<td>1.75</td>
<td>30</td>
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<td>50</td>
<td>0.30</td>
<td>0.26</td>
<td>1.41</td>
<td>35</td>
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<tr>
<td>CE_NM_03</td>
<td>7 nano + 15 micro</td>
<td>0.30</td>
<td>0.12</td>
<td>1.20</td>
<td>35</td>
</tr>
</tbody>
</table>

The increase of matrix viscosity influenced the fiber impregnation, however it can be considered that the fibers were fully impregnated.

These values are obtained by a qualitatively analysis of cross section microphotography.
Glass fiber micro/nano composites
Glass fiber nano/micro composites

40% CaCO₃ - 32 wt% GF
Matrix ply thickness 400 μm
GF thickness 250 μm
Pre consolidation thickness
Composite thickness 1.47mm

≈300 μm
Glass fiber nano/micro composites

40% CaCO₃ – 30 wt% GF
Matrix ply thickness 500 μm
Composite thickness 1.75mm

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Glass fiber micro/nano composites

40 wt% CaCO₃ – 35 wt% GF
Composite thickness 1.40mm

7 wt% Clay + 15 wt% CaCO₃ – 35 wt% GF
Composite thickness 1.20mm

Better impregnation with respect to micro-composite

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Mechanical properties

ASTM D790-03
Mechanical properties

Effect of filler content

The GF-NM composite sample exhibits higher flexural modulus

The GF-NM composite sample exhibits higher flexural modulus

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The flexural strength increases with content of filler. GF-NM exhibits the maximum value.
Dynamical mechanical analysis

The $G'$ value decreases with filler increase, probably due to bigger interlayer thickness.

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Dynamical mechanical analysis

GF-NM exhibits higher storage modulus in the entire temperature range investigated. This effect is due to the greater contribution to mechanical reinforcement of nanoparticles.

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Dynamical mechanical analysis

The analysis of $\tan \delta$ confirm that the higher interlayer thickness gets worse the elastic modulus, but give to composite a "damping ability"
**PolyCarbonate / ABS commercial blends**

### Cycoloy C3100

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>2200 MPa</td>
</tr>
<tr>
<td>Tensile Stress</td>
<td>45 MPa</td>
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<tr>
<td>Flexural Modulus</td>
<td>2100 MPa</td>
</tr>
<tr>
<td>Density</td>
<td>1.15 g/cm³</td>
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<tr>
<td>Mold Temperature</td>
<td>240-260 °C</td>
</tr>
</tbody>
</table>

### Cycoloy XCM850

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>4650 MPa</td>
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<tr>
<td>Tensile Stress</td>
<td>45 MPa</td>
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<tr>
<td>Flexural Modulus</td>
<td>4450 MPa</td>
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<tr>
<td>Density</td>
<td>1.3 g/cm³</td>
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<tr>
<td>Mold Temperature</td>
<td>260-290 °C</td>
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</table>

PC/ABS is an amorphous resin blend that is widely used for fabricating thin-walled plastic packaging for communication and electronic devices.

PC/ABS blends result in a useful balance in toughness and stiffness as compared to conventional high impact PC or ABS alone, heat resistance, and better processing capabilities than PC alone.

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PC/ABS characterization

- Differential scanning calorimeter (DSC)
- TGA (thermal stability)
- Rheological tests
- Dynamic mechanical analysis (DMA)
- Fourier Transform Infrared Spectroscopy (FTIR)
- SEM/EDS on residual calcined of XCM850
The DSC analysis shows the presence of two $T_g$, although not very obvious, corresponding to the two components: ABS at about $118^\circ$ C and PC at about $150^\circ$ C.

There aren’t any difference between the two materials, probably because the calorimeter is unable to correctly get the transition.
PC/ABS – TGA analysis

Thermograms show a better stability of XCM850 probably due to the presence of nanoclay

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The nanoclay also influenced the rheological behaviour at lower frequencies. The $G'$ curves evidence a pseudo-solid like behaviour for XCM850.
PC/ABS – Dynamic Mechanical Analysis

DMA analysis evidences the shift towards higher value of Tg for XCM850

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The FTIR spectra shows a peak at 1078 cm\(^{-1}\) corresponding to Si-O bond stretching, that suggests the presence of silicate.
The presence of silicates is confirmed by SEM/EDS analysis that shows peaks corresponding to presence of Mg, O and Ca atoms.

The filler of XCM850 is probably a Silicate of Mg and Ca distinctive of a natural mineral.
Glass fiber composites were produced by film stacking technique.

- Matrix ply (12 ply)
- Fiber glass (11 ply)

**GF content between 28 vol% to 33 vol%**

**Temperature and Pressure Graphs**
- Temperature: 280 °C for 900 seconds
- Pressure: 15 bar for 900 seconds

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The higher viscosity of XCM850 probably influences the impregnation of fiber that results to lower $G'$ values.
The SBS analysis confirms that the Cycoloy C3100 seems to have a better compatibility with glass fiber, in spite of XCM850 that shows the best mechanical properties.

This behaviour is probably due to the lower viscosities of C3100 matrix.
Glass Fiber vs Carbon Fiber - DMA

Carbon fiber composite exhibits a higher modulus, but the Tg shifts towards lower value.

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The CF composite has a higher MaxLoad value, but the Short Beam Strength (SBS) is lower than the GF composite.

This behaviour is probably due to the minor compatibility between carbon fibers and PC/ABS matrix, that results in a worse impregnation.
The basal spacing of MMT increased from 12.6 to 19.6 Å. When MMT was modified by $^{16}$Me$^+$Br, the gallery of MMT was intercalated and was expanded by the molecular chain of $^{16}$Me$^+$Br.
The FTIR spectra shows, for the OMT, the presence of peaks corresponding to stretching of C-H bond (wave number=2629, 2853 cm⁻¹).
Conclusions

Nanocomposites and nano/micro-composites young modulus increased for all the concentrations of clay (from 1 to 7 wt% with respect to PP) being more than 30% higher than that of the nanoclay free PP

The replacement of a small amount of microfiller with the corresponding amount of nanofiller effectively allow a strong increase of the Young modulus

Both micro and nano-composites exhibited enhanced rheological properties at low strain rates, when compared to bulk material, but zero shear properties of nano-filled composites are higher

The same effect was observed on mechanical flexural properties of glass-fiber composite prepared with nano/micro-composite matrix at the same GF wt% content.
The DMA evidences a behavior strongly influenced by the interlayer thickness; the $G'$ value for the GF-NM is up to 6 times greater than CE_30_03 (30 wt% of CaCO$_3$).

The analysis of $\tan \delta$ confirms that the higher interlayer thickness gets worse the elastic modulus, but gives to the composite a "damping ability".

The damping properties of this structure can be therefore designed by tuning the initial composition of the particulate reinforced composites and its thickness in the multilayered structure.

Finally, it has been studied and characterized a commercial PC/ABS blend and a Na$^+$ Montmorillonite is modified by organic cations and becomes organophilic montmorillonite (OMT).

To further this study, as future development, is scheduled to implement the know-how acquired until now, on high performances polymers that can be employed like matrices for thermoplastic composites to use in transport and automotive industry.
Thank you for your attention!
The use of PPgMA increased the basal spacing of platelets (signal peak shifted to lower 2θ values) when compared to the PP/clay blend, where the peak is slightly shifted to the right.

The use of a compatibilizer is effective to enhance the intercalation/exfoliation process.

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The use of PPGMA allowed the intercalation in nanocomposites, regardless of the clay concentration.

The peak (if existent) is shifted to $2\theta$ values lower than 2 (corresponding to a basal spacing higher than 4.5nm).
Thermal stability

The effective intercalation of clay strongly enhanced the thermal stability of the nanocomposite.
Effect of clay on crystallization

As expected the crystallization kinetics is slightly enhanced, due to both the clay and compatibilizer content.

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Nano/micro - Stress-strain behavior

The nano-/micro-composites behavior outside elastic region should be better understood and clarified.

All nano-/micro-composites exhibit slightly higher yield stress values compared to micro-composites, but the effect of clay content is not clear.

3wt% Nanofil 5 allowed to enhance the Young modulus, the yield stress and ultimate strain.

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PC/ABS – Rheological analysis

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