Polyethylene Nanocomposite Heat-Sealants with a Versatile Peelable Character

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Figure S1. Schematic representations of polymer microstructures (chain architectures) of selected polyethylenes used in this study. LLDPE: linear low density polyethylene; LDPE: low density polyethylene; LDPE-random-VA: LDPE-ethyl vinyl acetate copolymer at moderate (20-30%) VA content, also referred to simply as EVA; LLDPE-graft-MAH: maleic anhydride grafted linear low density polyethylene at very high (2-3%) MAH content; HDPE: high density polyethylene. Most of the sealants used in the study are blends of the above polymers; for example, the commercial grade PE/EVA sealant is a blend of 56/14/30 (w/w) of LLDPE/ LDPE/ LDPE-random-VA, whereas the PE/EVA/MMT is a blend of 50/13/27/4/6 (w/w) of LLDPE/ LDPE/ LDPE-random-VA/ LLDPE-graft-MAH/ organo-montmorillonite.
Figure S2. (a) Bright field Transmission Electron Microscopy (TEM) characterization of the composite structure of the PE/EVA/MMT nanocomposite sealant (specimen shown is from a multilayer blown film with about 7-10 µm of nanocomposite sealant co-extruded on a HDPE). The observed filler dispersion is typical of well-dispersed MMT in melt-processed polyolefin/MMT nanocomposites. (b) X-Ray Diffraction (XRD) patterns focusing on the montmorillonite d_{001} basal spacing. The two organo-montmorillonite masterbatches (MB) based on LDPE-graft-MAH and LLDPE-graft-MAH (LDPE MB and LLDPE MB respectively), the two respective PE/MMT nanocomposites (made by dilution of each masterbatch by the 80/20 LLDPE/LDPE sealant), and the PE/EVA/MMT nanocomposite made from the LLDPE MB masterbatch diluted by sealant and 30% EVA copolymer. The increase in intensity and the sharpening of the diffracted peak for the PE/EVA/MMT system is not due to an increased number of diffracting moieties (i.e., there are obviously much fewer intercalated montmorillonite tactoids in the PE/EVA/4 wt% MMT nanocomposites compared to the two masterbatches containing 25 wt% MMT). Rather, the sharper and more intense 001 diffraction peak is due to better tactoid alignment and especially due to an increased coherence length (i.e., the tactoids are flow-aligned in the blown films, and the MMT platelets adopt better parallel stacking upon EVA introduction); increased coherence (better stacking) also accounts for the appearance of strong 002 and 003 reflections in this system.
**Figure S3.** Seal strength for serrated seals defined by a bench-top impulse thermal sealer (materials as in fig. 1 of the paper). The same seal trends (fused vs. peelable) observed at high pressures and long dwell times are reproduced here, despite the much shorter dwell times, the very low pressures, and the serrated seal geometry, which substantially increases the weld seal strength. All PE/EVA/MMT seals still remain peelable and with comparable seal strengths over the whole range of impulses (cf. the whole range of sealing temperatures) independently of the second surface of the seal. It is remarkable that the peelable strengths of the nanocomposite sealant maintain comparable values for this serrated seal geometry, a clear indication that the seal strength is an inherent property of the nanocomposite sealant. The serrated pattern consists of five parallel 2 mm wide line-seals separated by 2 mm wide unsealed spacings. The impulse sealer (KF-300H model by GHL Packaging Inc.) operates at a constant power of 146 W, thus the temperature at the seal interface increases with the impulse duration, albeit in a non-linear fashion and in a different manner for each film composition and/or thickness.

**Figure S4.** ATR-FTIR of fracture seal surfaces (25.4 mm wide flat seals, 1000 psi/8 s). Spectra from peelable seals between PE/EVA and PE/MMT, where MMT nanofillers are detected on the PE/EVA side whereas no EVA is detected on the PE/MMT side. This result qualitatively indicates that the PE/MMT interfacial adhesion, mediated by LLDPE-graft-MAH, is weaker than the adhesion between PE and EVA, mediated by polymer entanglements and, to a smaller extent, by co-crystallization.

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S-4
Figure S5. Seal strengths as a function of the PE-based sealant composition, for unfilled sealants and nanocomposite systems. The data clearly cluster in three distinct groups for unfilled sealant blends (black symbols, fused above 100°C) for 4 wt.% MMT nanocomposites (red triangles, peelable with lower seal strength) and for 2 wt.% MMT nanocomposites (blue circles, peelable with higher seal strengths). The peelable behavior of the nanocomposites is also compared against an optimized commercial peelable sealant, which is based on a similar LLDPE/LDPE blend and includes EVA copolymer and polybutylene (PB). The composition was varied to include 30 or 60% w/w EVA copolymer/PE, with 18 or 9 molar% vinyl acetate comonomer in the EVA, and 4 or 2 wt.% MMT inorganic loading (corresponding to 6 or 3 wt.% of ogano-MMT), as indicated in the legend. All seals were 25.4 mm wide flat seals, made on an ASTM F2029 compliant Sentinel thermal sealer, operated with both sealing jaws heated, at 40psi and 0.5s dwell time. The short dwell time –dictated by the ASTM protocol– may not allow for full equilibration of the sealing interface, thus, the sealing strengths are plotted versus the sealer temperature (cf. platen temperature) rather than versus sealing temperature (cf. fig. 1).

Figure S6. Differential scanning calorimetry (DSC) traces of the melting peak from bulk (bottom traces) and blown film (top traces) specimens, comparing the unfilled PE sealants (LLDPE/LDPE blends) and their respective nanocomposites. In agreement with typical polyolefin/MMT nanocomposites behavior, there is no marked change of the melting temperature upon addition of the MMT fillers, and despite the LLDPE-graft-MAH polymer in the masterbatch used for the nanocomposite formation (a more detailed discussion in refs. 9–11,16).

In contrast, the introduction of EVA copolymer in PE sealant blends and in PE/EVA/MMT nanocomposite sealants is primarily responsible for lowering the melting point of the PE, and thus lowering the onset sealing temperature. This effect of EVA is discussed in detail in refs. 6,7 of the manuscript.