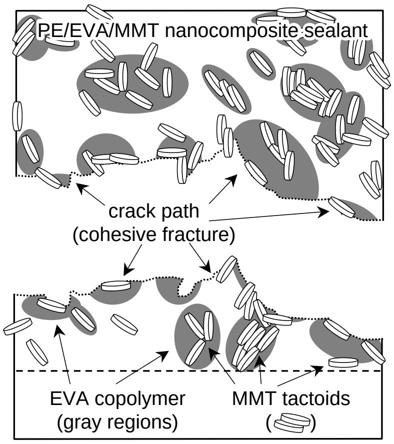
Polyethylene Nanocomposite Heat-Sealants with a Versatile Peelable Character

Evangelos Manias,* Jinguo Zhang, Jin Young Huh,
Kiattikhun Manokruang, Ponusa Songtipya, Maria del Mar Jimenez-Gasco

A novel heat-sealing performance is achieved by polyethylene (PE) nanocomposites reinforced by ethylene vinyl acetate (EVA) and montmorillonite (MMT). Appropriate nanocomposite design leads to hermetic seals with a general peelable/easy-open character across the broadest possible sealing temperature range. Observations of the fracture seal surfaces by infrared spectroscopy and electron microscopy reveal that this behavior originates from a synergistic effect of the EVA copolymer and the montmorillonite clay nanofiller. Namely, the combination of EVA-copolymers and MMT nanofillers provides sufficiently favorable interactions for nanocomposite formation and mechanical robustness, but weak enough interfacial adhesion to promote a general cohesive failure of the sealant at the EVA/MMT interfaces.



Introduction

Research efforts in polyolefin/layered-silicate nanocomposites have achieved many breakthroughs, and have yielded several examples of high performance materials, including more than a dozen commercialized examples.[1] With the exception of improved flame retardancy,[2] these polyolefin nanocomposites mostly rely on straightforward reinforcement by nanoscale, and hence high surface area, fillers to enhance selected property-sets,[1] while opportunities for nanocomposites with directed morphologies or genuine "nano"-functionalities still remain largely untapped.[3,4] At the same time, development and optimization of polyethylene (PE) heat sealants for plastic packaging applications has a long tradition, and these materials currently have the dominant market share of sealants for flexible packaging.[5] However, to date there has been no attempt to exploit the new functionalities afforded by the nanocomposite formation toward the development of PE heat-sealants with novel behaviors.

In this work, we report the design principles behind a new class of PE/montmorillonite nanocomposites, where appropriate functional polymers were employed to evoke versatile broad-range peelable heat seals. Specifically, a synergy of ethylene vinyl acetate (EVA) copolymer and montmorillonite nanofillers — appropriately incorporated

E. Manias
Polymer Nanostructures Lab – Center for the Study of Polymer Systems (CSPS), Pennsylvania State University, 325D Steidle Bldg, University Park, PA 16802, USA
E-mail: manias@psu.edu
E. Manias, J. Zhang, J. Y. Huh, K. Manokruang, P. Songtipya
Department of Materials Science & Engineering, Pennsylvania State University, 228 Steidle Bldg, University Park, PA 16802, USA
J. Y. Huh
Current Address: Chemicals R&D Center, Samsung Cheil Industries Inc., Uiwang-Si, Gyeonggi-Do 437-711, Korea
P. Songtipya, M. M. Jimenez-Gasco
Department of Plant Pathology Pennsylvania State University, 309 Buckhout Lab, University Park, PA 16802, USA

---

[a] Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at http://www.mrc-journal.de, or from the author.

Macromol. Rapid Commun. **2009**, *30*, 17–23

DOI: 10.1002/marc.200800553

in a commercial PE-based sealant — mediate a general cohesive failure, which macroscopically manifests in peelable seals across a very broad range of sealing temperatures.

Results and Discussion

Fused PE heat seals are well established and are straightforward to manufacture, simply by employing neat PE sealed at temperatures above its melting point. In contrast, peelable PE seals necessitate sealant modifications, typically addition of an immiscible and lower softening temperature polymer — such as polybutylene, methyl acrylic acid or methyl acrylate ethylene-copolymers, ionomers, and/or EVA copolymers.[5,6] Such blends, beyond the obvious decrease in seal initiation temperature, also lead to an apparent reduction in area of bonding, and thus to reduced seal strengths. This affords for peelable seal strengths to form over a broader temperature range (5 to 15 °C wide) compared to the much narrower (less than 5 °C wide) range for the respective PE.

Given the ability to independently control different properties in nanocomposites, one could devise strategies for PE nanocomposite sealants that broaden even more the temperature range of peelable heat-sealing strengths, while maintaining a mechanically robust character and a reduced melting point: for example, in this study we design nanocomposites sealants that fail predominately at the filler/polymer interfaces, and consequently exhibit a general cohesive failure during peeling. Their seal strength can thus be tailored at a peelable value by tuning the nanofiller/polymer interfacial adhesion, their melting point can be determined by the type and concentration of functionalized polymers, and their mechanical properties can be improved by the appropriate dispersion of the nanoscopic fillers. Ethylene vinyl acetate copolymers of low density PE — referred hereafter as EVA — were chosen as the functional polymers to achieve such a property set since: (i) they reduce the melting point of a typical PE sealants[6] — usually blends of linear low density and low density PE[7] (LLDPE/LDPE); (ii) even at low VA content (e.g., below 9 mol-%) they contain sufficient numbers of polar groups to disperse common organo-clay nanofillers[8,9] (such as alkyl-ammonium modified montmorillonite); and (iii) the combination of their random copolymer architecture and of the LDPE chain microstructure does not stabilize polymer-bridged networks of nanofillers, in contrast to the more commonly used maleic anhydride graft PE copolymers,[10,11] thus facilitating weaker interfacial strengths and resulting in a weaker cohesion for the nanocomposite.

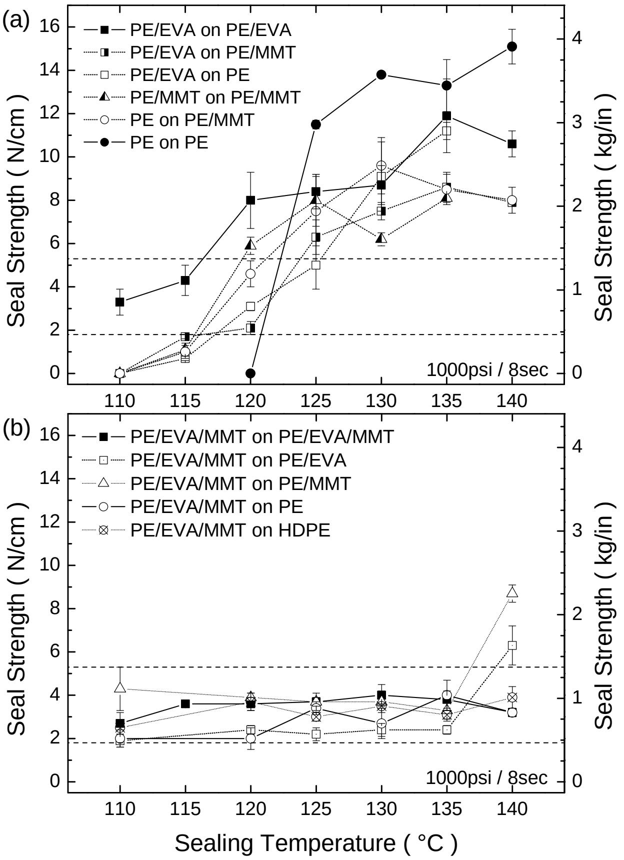


Figure 1. Seal strengths for 25.4 mm-wide flat seals, using 1 000 psi pressure and 8 s dwell time to fully equilibrate the sealing interface. The horizontal dashed lines indicate the range of peelable seal strengths. (a) Commercial grade PE and PE/EVA sealants, as well as the respective PE/MMT nanocomposite, show the typical[6,7] heat sealing curve, progressing with increasing temperature from no-seal (seal strength below $1\ N \cdot cm^{-1}$), to peelable seals over a narrow temperature range, to weld/fused seals at higher temperatures. (b) The PE/EVA/MMT achieves peelable heat seals over a very broad range of sealing temperatures,[14] independent of the substrate sealed on. (PE: neat commercial sealant, an LLDPE/LDPE blend; PE/EVA: same PE sealant blend with 30% of LDPE–EVA copolymer (18% VA content); PE/MMT: nanocomposite of the same PE sealant with 6 wt.-% organo-montmorillonite via LLDPE-*graft*-MAH/MMT masterbatch; PE/EVA/MMT: the PE/EVA blend reinforced by 6 wt.-% organo-montmorillonite).

In Figure 1, we compare the seal curves of a nanocomposite sealant (denoted as PE/EVA/MMT in Figure 1b, and comprised of LLDPE/LDPE polymer, 30% LDPE-*random*-VA copolymer, and 6 wt.-% dioctadecyldimethyl ammonium-modified montmorillonite, MMT) against the ones obtained by the respective neat sealant (PE in Figure 1, the unfilled LLDPE/LDPE blend) and the respective PE/EVA sealant (unfilled LLDPE/LDPE containing the same amount and type of EVA copolymer as the nanocomposite). All seals were formed at high pressure and very long dwell times (1 000 psi and 8 s) to ensure that the sealing interface between the two films is fully equilibrated[7] at each sealing temperature. Empirically,[12,13] a seal strength of 0.77 N per cm width of seal (ca. 200 $g \cdot inch^{-1}$) is considered as the onset of hermetic seal formation,

DOI: 10.1002/marc.200800553

whereas seal strengths in the range of 1.8–5.3 $\mathrm{N \cdot cm^{-1}}$ (1–2.5 $\mathrm{lb \cdot inch^{-1}}$ or ca. 450–1150 $\mathrm{g \cdot inch^{-1}}$) are considered peelable (easy-open). With increase in temperature the seal strength reaches a constant value plateau and the seals are considered weld/fused.

Comparing Figure 1a versus 1b, it becomes obvious at the outset that there exists a clear qualitative difference in the sealing behavior of the PE/EVA/MMT nanocomposite and that of PE and PE/EVA blends: the unfilled blends show the typical sealing curve that progresses smoothly from non-sealing below an onset temperature, to peelable (over a range of 5 or 10 °C wide for PE or PE/EVA, respectively), to the plateau strength of a fused seal for higher temperatures. In contrast, the PE/EVA/MMT shows an almost constant seal strength throughout a very broad sealing temperature range, at least 25 to 30 °C wide and in most cases for all temperatures studied.[14] Moreover, the conventional sealants perform very differently when sealed on different surfaces; for example from Figure 1a the seal strengths of PE or PE/EVA are very different when heat-sealed on themselves rather than on each other, whereas neither forms a hermetic seal on high density PE (HDPE) for any of the temperatures shown. In contrast, the PE/EVA/MMT shows the same sealing behavior on all sealants, and also on HDPE.

The broad-temperature peelable sealing is obtained only when both EVA and MMT are present together in the nanocomposite (Figure 1a vs. 1b). Namely, sealants that do not contain both EVA-copolymer and montmorillonite behave similar to the typical commercial PE sealant (i.e., beyond any difference in absolute values, PE, PE/EVA, and PE/MMT all show essentially the same sealing trends, Figure 1a). In particular, comparing the seal behavior of PE/EVA/MMT nanocomposite versus that of PE/MMT nanocomposite (the same LLDPE/LDPE blend reinforced by 6 wt.-% MMT, but including PE-*graft*-maleic anhydride instead of the EVA–LDPE copolymer) definitively traces the peelable behavior to a synergy of the EVA copolymer and the montmorillonite nanofiller.

Furthermore, the constant value of PE/EVA/MMT nanocomposite's seal strength, throughout the temperature range studied[14] and independent of the other side of the seal (Figure 1b), strongly indicates that this behavior is an inherent property of the nanocomposite sealant, rather than of the sealing interface or process. Clues along these lines can be obtained by compositional analysis of the fractured seal surfaces, which can be done, in a first approach, via attenuated total reflection infrared (ATR–FTIR) spectroscopy. In Figure 2a ATR–FTIR spectra are provided for the fracture surfaces from various seals (spectra a–f) and for the corresponding unsealed/virgin films (spectra g–j). Focusing first on peelable seals formed when PE/EVA/MMT nanocomposite sealants are sealed on neat PE films, the ATR–FTIR spectra show traces of EVA and MMT on the PE side of the fracture surface, indicating that the fracture path was through the PE/EVA/MMT nanocomposite (cohesive failure of the nanocomposite sealant); this observation holds for seals formed both at low sealing temperature (Figure 2a/spectrum e) as well as at high sealing temperature (Figure 2a/spectrum f). For PE/MMT sealants, filler is detected on the other side of a fused seal (Figure 2a/spectrum b) indicating a cohesive failure within the PE/MMT sealants; much smaller amounts of MMT are detected on the opposite side of peelable PE/MMT seals (Figure 2a/spectrum a) indicating a mostly interfacial failure. In contrast, for the PE/EVA sealant, there is no evidence of EVA on the other side of the fractured seal (not even for fused seals, Figure 2a/spectrum c) indicating an adhesive failure of the PE/EVA at the seal interface. Given the long dwell time and high pressure of the sealing, which assure that there are no diffusion or thermal equilibration limitations,[7] these results demonstrate that fracture occurs preferentially at the interfaces of the montmorillonite clay fillers (Figure 2). Additionally, considered in combination with the corresponding seal strengths (Figure 1), these results further suggest weaker interfaces in PE/EVA/MMT, compared to the LLDPE-*graft*-MAH mediated PE/MMT interface, which, in turn, seems weaker than the adhesion between PE and EVA. This last remark is qualitatively shown also by the ATR–FTIR spectra of 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 (Figure S3 of Supporting Information, or in ref.[15]). This ranking of interfacial strengths is consistent with the recorded seal strengths (Figure 1) and the ATR–FTIR spectra (Figure 2), as well as in accord with theoretical considerations of how the nature of the copolymers (i.e., the EVA and MAH polar comonomers, and the difference in polymer architecture and branching between the LLDPE-*graft*-MAH and LDPE-*random*-VA) will affect the interfacial adhesion with the SiO_x surface of the fillers.[8,10,11,16]

Further, insights on the fracture behavior of the nanocomposite sealants can be obtained by direct observation of the fractured seals by environmental scanning electron microscopy (ESEM). In Figure 2b, the PE side of the fractured seal is shown, comparing PE/EVA sealed on PE against PE/EVA/MMT sealed on PE. Despite its higher energy of fracture (*cf*. larger seal strength) the PE/EVA on PE seal yields a much smoother fracture surface than the three-fold weaker PE/EVA/MMT on PE seal. This, at first glance, may seem at odds with the usual connection between crack path tortuosity and energy of fracture. Generally, a rougher fracture surface indicates a higher energy to break, since it corresponds to a more tortuous crack propagation and a larger effective fracture area. Thus, a rougher fracture surface for the weaker seal clearly denotes that the cracks in PE/EVA/MMT sealant deviate

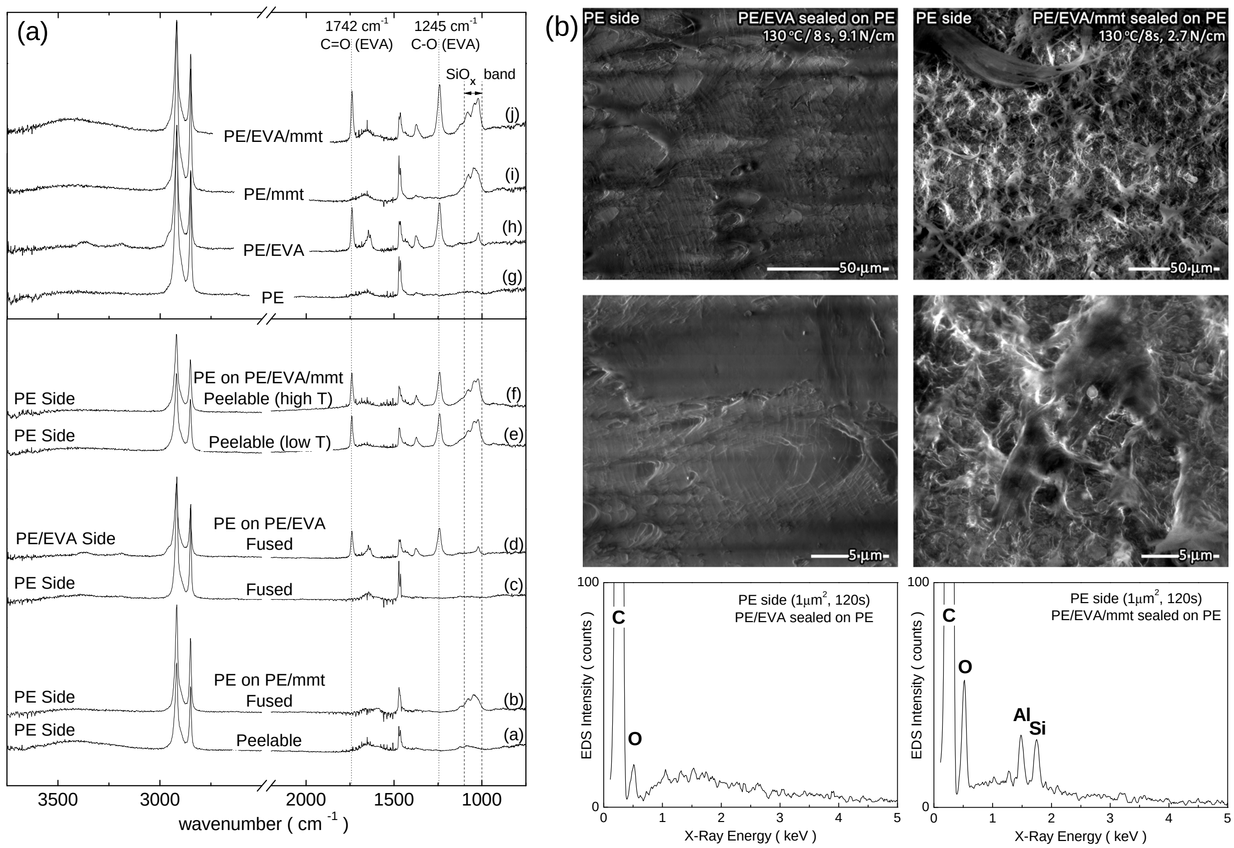


Figure 2. (a) ATR–FTIR spectra of virgin films (top) and fractured seal surfaces (bottom). The spectra from fracture surfaces of PE/EVA/MMT nanocomposite, detect MMT and EVA-copolymer on the opposite side of the broken seal, indicating a cohesive failure. Absence of similar transfers in PE/MMT and PE/EVA indicates that this behavior results from a synergy of EVA-copolymer and MMT nanofiller (all specimens were from 25.4 mm wide flat seals, 1 000 psi/8 s, temperatures vary to show peelable or fused seals, materials are termed as per Figure 1; spectra are from one (a, b, e, f) or both (c, d) fracture seal surfaces). (b) Secondary electron (topography) and corresponding energy dispersive X-ray spectra from environmental SEM of fracture seal surfaces: the PE side of PE/EVA sealed on PE (left) is relatively smooth and shows no appreciable transfer of sealant (adhesive seal failure). The PE side of PE/EVA/MMT sealed on PE (right) is much rougher despite the lower seal strength, and clearly shows aluminum and silicon traces, denoting appreciable amounts of MMT layered-silicate on the fracture surface (cohesive failure of the nanocomposite sealant).

from straight propagation in order to travel through weaker regions in the nanocomposite.[17] Inspection of the corresponding energy dispersive X-ray spectra (EDS, Figure 2b bottom) reveals that for the PE/EVA/MMT seal substantial amounts of the nanocomposite sealant transfer on the other side of the seal interface after fracture, as indicated by the characteristic EDS energies for Al and Si,[18] denoting a cohesive failure of the PE/EVA/MMT nanocomposite. In contrast, the smoother fractured surface from a PE/EVA seal shows limited, if any at all, transfer of the EVA-containing sealant to the other side of the seal.

From all the above, it becomes clear that fracture in the PE/EVA/MMT nanocomposite sealants preferentially occurs at the interface between EVA and MMT, i.e., between the LDPE-*random*-VA copolymer and the organically modified layered-silicate. A schematic of this mechanism is shown in Figure 3. More specifically, efficient nanocomposite sealants that operate in this manner necessitate that EVA-copolymers are preferentially located around the organically modified MMT nanofillers (as depicted by the gray regions in the schematic of Figure 3). This is intuitively expected to happen (since the vinyl acetate is polar and will interact more favorably with the organo-montmorillonites[8] than the apolar PE) and it is also experimentally confirmed by X-Ray diffraction (which shows further swelling of the intercalated MMT tactoids upon introduction of the EVA copolymer, Figure S2 of Supporting Information). The proposed mechanism of peelability is also consistent with the more tortuous fracture surfaces despite the lower fracture energies (*cf.* Figure 2b), since cracks in the PE/EVA/MMT nanocomposite sealant are expected to propagate through the weaker EVA/MMT interfaces, rather than the PE regions where polymer entanglement and crystallization occur. This mechanism is also consistent with the

DOI: 10.1002/marc.200800553

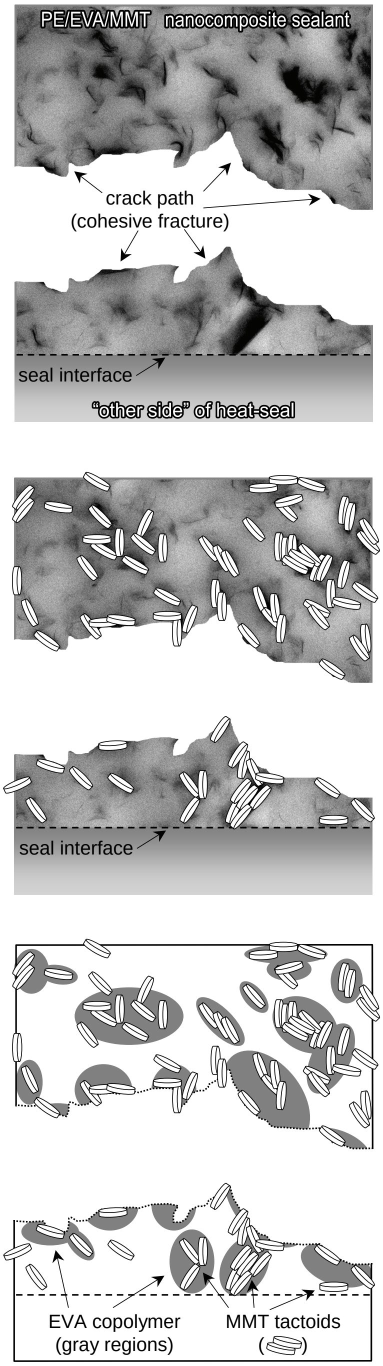


Figure 3. A schematic representation of the proposed mechanism for the general peelable character of the PE/EVA/MMT nanocomposite sealants. Incorporation of EVA copolymer and MMT in the nanocomposite sealant define regions with weak interfaces where cohesive failure of the nanocomposite is promoted, thus accounting for the behaviors reported in Figure 2. Cohesive failure upon sealant fracture, also accounts for constant-strength peelable heat seals across a broad range of sealing conditions and sealing surfaces (*cf*. Figure 1b).

almost constant — sealing-temperature independent — seal strength of PE/EVA/MMT shown in Figure 1b, since the seal strength is dictated by the interfacial adhesion of the EVA/MMT interfaces, an inherent property of the nanocomposites, which should be invariant under sealing temperature changes and independent of the material used for the other side of the seal. In support of this supposition, when PE/EVA/MMT is sealed on PE, PE/MMT, PE/EVA, or PE/EVA/MMT, a markedly independent seal strength of 3 $N \cdot cm^{-1}$ is obtained (with a spread of ± 1 $N \cdot cm^{-1}$, when materials and temperature are varied) compared to a spread of 15 $N \cdot cm^{-1}$ for the respective unfilled sealant (PE/EVA, for the same materials and temperature range).

Further, evidence of the seal strength being an inherent character of the PE/EVA/MMT nanocomposite can be obtained by employing different methods and conditions of heat sealing. For example, employing much shorter dwell times and smaller pressures, does not alter the broad temperature–range character of the peelable PE/EVA/MMT seals, nor does it alter their seal strength value. This was experimentally confirmed in a bench top impulse sealer under ultra-low pressures and heat-impulses of 0.2 to 1.0 s (Figure S3 of Supporting Information) and in an ASTM-conforming sealer (0.5 s dwell and 40 psi, Figure S5 of Supporting Information). Considering that such variations in the conditions of heat sealing, i.e., variations in dwell time and pressure, will mostly affect the temperature equilibration of the seal interface, the reproducibility of the sealing behavior under varied conditions is essentially equivalent to achieving a peelable seal over a broad range of sealing temperatures (*cf*. Figure 1b), and further endorses the proposed mechanism of a cohesive failure in PE/EVA/MMT. Also, variations in the composition of the PE/EVA/MMT nanocomposite sealant do not change qualitatively its peelable character (*cf*. Figure S5 of Supporting Information); quantitatively, the seal strength remains constant under substantial changes in the PE/EVA ratio and the EVA-comonomer fraction, whereas it shows small only changes with the MMT loading (Figure S5 of Supporting Information).

Finally, it is worth noting that PE/EVA/MMT also forms reproducible heat seals on HDPE, something that none of the standard sealants (e.g., PE or even PE/EVA) can achieve. Obviously, since PE/EVA blends do not form heat-seals on HDPE, this behavior is not solely due to the adhesive character of the EVA copolymer (a typical adhesion promoter of PE for polymers such as polyamides, polyesters, and polypropylene). Rather, this behavior is most probably a manifestation of the miscibility of the montmorillonite/EVA domains with HDPE.[16] This is an interesting observation, with important implications for flexible packaging applications, but its detailed discussion goes beyond the scope of this paper.

Conclusion

In summary, nanocomposite heat sealants based on LLDPE/LDPE blends reinforced by a combination of EVA copolymer and organically modified montmorillonite were made and studied. These materials exhibit a very versatile heat-sealing behavior, yielding hermetic but peelable heat-seals across the broadest possible temperature range. Their seals are characterized by almost constant seal strength, which is largely independent of sealing temperature. This novel performance originates from a synergy of the EVA copolymer and the montmorillonite nanofillers, which have an interfacial adhesion that is strong enough to promote mixing and maintain the sealant integrity, but is evidently weak enough to dictate paths of easy crack propagation upon seal peeling. This synergy results in a general cohesive failure of the nanocomposite sealant, and consequently in the formation of broad range peelable seals, bearing high promise for the flexible packaging industry.

Experimental Part

Materials

Commercial grade polymers and fillers were used throughout this study. PE was a Dow Integral polyolefin adhesive (an 80/20 blend of LLDPE/LDPE). Ethylene vinyl acetate was an ExxonMobil Escorene copolymer (LDPE-*random*-VA copolymer with 18% vinyl acetate content). The layered-silicates were commercial organo-montmorillonites (MMT) purchased from Nanocor, Arlington Heights (IL), with a cation exchange capacity (CEC) of *ca.* 1.0 meq $\cdot$ g^{-1} and modified by dimethyldioctadecyl ammonium. For the PE/MMT nanocomposites, the organo-MMT was first dispersed with a twin-screw extruder at 25 wt.-% inorganic loading in maleic anhydride (MAH) functionalized PE (an LLDPE-*graft*-MAH with 0.26 wt.-% MAH, $\overline{M}_{\rm w} = 67\,000$ g $\cdot$ mol^{-1} and $\overline{M}_{\rm w}/\overline{M}_{\rm n} = 6.1$). Nanocomposites were subsequently formed by dilution of these concentrates in the PE sealant in a twin-screw extruder. PE/EVA/MMT blown films were made of 10–20 μm sealant layer (LLDPE/LDPE with 30% EVA-copolymer and 6 wt.-% of organo-MMT, via a LLDPE-*graft*-MAH concentrate) on a ca. 50 μm thick HDPE substrate. Additional commercial-grade packaging films donated by Kraft Global Foods, Pliant Corporation, and Alcan Packaging were also tested as received.

Methods and Instrumentation

Twin-screw extrusion was done with a heating profile of 145, 145, 185, 185, 185, 185, and 185 °C from feed to nozzle (barrel diameter, $d = 30$ mm, $L/d = 36{:}1$) at a rate of 20 lb $\cdot$ h^{-1}. Blown films were produced on an industrial line (Pliant Corporation, Chippewa Falls, WI) to form both monolayer films of polymers, blends, and nanocomposites, and also multilayer blown films of sealants and nanocomposites coextruded on HDPE. Peel tests were performed according to the ASTM F88-00 unsupported protocol,[12a] on an Instron 5866 tensile tester, operated with pneumatic grips, at a testing speed of 200 mm $\cdot$ min^{-1}. Environmental scanning electron microscopy was performed in an FEI Quanta 200, operated under low vacuum, with no metal coating applied to the fracture surfaces; the microscope was equipped with an Oxford Inca energy dispersive X-ray system (EDS). ATR–FTIR spectra were recorded on a Scimitar 1000 (Digilab Global, Randolph, MA), at 2 cm^{-1} resolution, under ambient atmosphere.

Acknowledgements: Financial support and generous donations of materials by *Kraft Global Foods* are gratefully acknowledged. Additional financial support was provided to E. M. by the *National Science Foundation* (grant no. DMR-0602877, an MWN/Polymer division grant), and to M. M. J. G. by the *Penn State University Agricultural Experimental Station.*

Received: September 2, 2008; Revised: October 9, 2008; Accepted: October 9, 2008; DOI: 10.1002/marc.200800553

Keywords: adhesion; interfacial adhesion; PE; polyethylene heat sealants; polymer nanocomposites

[1] 1a] M. Tanniru, Q. Yuan, R. D. K. Misra, *Polymer* **2006**, *47*, 2133; [1b] S. S. Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, *28*, 1539 (and references therein); [1c] J. Zhang, E. Manias, C. A. Wilkie, *J. Nanosci. Nanotechnol.* **2008**, *8*, 1597; [1d] T. J. Pinnavaia, G. W. Beall, *Polymer-Clay Nanocomposites*, Wiley, New York 2000; [1e] Y.-W. Mai, Z.-Z. Yu, *Polymer nanocomposites*, Woodhead Publishing, Cambridge, UK 2006.

[2] [2a] J. Zhang, C. A. Wilkie, *Polymer* **2006**, *47*, 4537 (and 5736); [2b] J. Zhang, D. D. Jiang, C. A. Wilkie, *Polym. Degrad. Stabil.* **2006**, *91*, 298 (and 641); [2c] M. C. Costache, M. J. Heidecker, E. Manias, G. Camino, A. Frache, G. Beyer, R. K. Gupta, C. A. Wilkie, *Polymer* **2007**, *48*, 6532.

[3] [3a] R. Krishnamoorti, R. A. Vaia, *J. Polym. Sci. B: Polym. Phys.* **2007**, *45*, 3252; [3b] R. A. Vaia, J. F. Maguire, *Chem. Mater.* **2007**, *19*, 2736.

[4] E. Manias, *Nat. Mater.* **2007**, *6*, 9.

[5] D. S. Lee, K. L. Yam, L. Piergiovanni, *Food Packaging Science and Technology*, CRC Press, **2008**.

[6] C. Poisson, V. Hervais, M. F. Lacampe, P. Krawczak, *J. Appl. Polym. Sci.* **2006**, *99*, 974.

[7] [7a] P. Meka, F. C. Steling, *J Appl. Polym. Sci.* **1994**, *51*, 89; [7b] C. Mueller, G. Capaccio, A. Hiltner, E. Baer, *J Appl. Polym. Sci.* **1998**, *70*, 2021.

[8] [8a] R. A. Vaia, E. P. Giannelis, *Macromolecules* **1997**, *30*, 7990, 8000; [8b] E. P. Giannelis, R. Krishnamoorti, E. Manias, *Adv. Polym. Sci.* **1999**, *138*, 107.

[9] [9a] Q. Yuan, R. D. K. Misra, *Polymer* **2007**, *47*, 4421; [9b] X. Li, C.-S. Ha, *J. Appl. Polym. Sci.* **2003**, *87*, 1901; [9c] E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu, T. C. Chung, *Chem. Mater.* **2001**, *13*, 3516.

[10] [10a] F. P. La Mantia, N. T. Dintcheva, G. Filippone, D. Acierno, *J. Appl. Polym. Sci.* **2006**, *102*, 4749; [10b] J. Golebiewski, A. Rozanski, J. Dzwonkowski, A. Galeski, *Europ. Polym. J.* **2008**, *44*, 270.

[11] [11a] R. Krishnamoorti, K. Yurekli, *Curr. Opin. Colloid Interf. Sci.* **2001**, *6*, 464; [11b] F. R. Costa, M. Abdel-Goad, U. Wagen-

kneght, G. Heinrich, *Polymer* **2005**, *46*, 4447; [11c] M. J. Solomon, A. S. Almusallam, K. F. Seefeldt, P. Varadan, *Macromolecules* **2001**, *34*, 1864.
[12] [12a] ASTM F88-00, Standard Method for Seal Strength of Flexible Barrier Materials, *Annual Book of ASTM Standards*, **2000**, Vol. *8*; [12b] ExxonMobil standard #490, Crimp Seal Strength, Minimum Sealing Temperature, and Range, ExxonMobil Corporation **2001**.
[13] D. Aithani, H. Lockhart, R. Auras, K. Transpasert, *J. Plast. Film Sheeting* **2006**, *22*, 247.
[14] The temperature range studied for PE/EVA/MMT sealant in Figure 1 covers the complete range of seal formation: below 100 °C there is no systematic hermetic seal and above 150 °C the sealant films deform and fail/flow due to extensive polymer melting.
[15] J. Zhang, E. Manias, G. Polizos, J.-Y. Huh, A. Ophir, P. Songtipya, M. M. Jimenez-Gasco, *J. Adhesion Sci. Technol.* **2009**, in press.
[16] [16a] A. Morgan, C. Wilkie, *Flame Retardant Polymer Nanocomposites*, Wiley, Hoboken, NJ 2007, Ch. 2; [16b] Z. M. Wang, T. C. Chung, J. W. Gilman, E. Manias, *J. Polym. Sci. B: Polym. Phys.* **2003**, *41*, 3173; [16c] K. Strawhecker, E. Manias, *Macromolecules* **2001**, *34*, 8475.
[17] W.-J. Boo, L. Sun, G. L. Warren, E. Moghbelli, H. Pham, A. Clearfield, H.-J. Sue, *Polymer* **2007**, *48*, 1075.
[18] The SEM–EDS has adequate detection sensitivity to identify the traces of high atomic weight silicon and aluminum elements of the MMT inorganic nanoparticles (Si and Al detection limit ca. 0.1–0.25%, at 1.740 and 1.487 keV, respectively). However, the EDS sensitivity for the lighter nitrogen of the MMT organic modification is substantially smaller (N detection limit ca. 2–5% at 0.392 keV) mostly due to instrumental reasons: these softer x-rays are strongly absorbed in the sample (self-absorption), on oil/ice contaminations on the detector window, etc. Additionally, N is also much less abundant than either Al or Si in our systems, e.g., for a 6% organo-MMT nanocomposite there exists ca. 2% organic modification (i.e., 0.05% N, about two-orders of magnitude lower than its detection limit) and ca. 4% inorganic MMT (i.e., 1.1% Si and ca. 1% Al, about 5–10 times more than their EDS detection limit).