Blends of Ethylene–Methyl Acrylate–Acrylic Acid Terpolymers with Ethylene–Acrylic Acid Copolymers: Mechanical and Thermomechanical Properties

Nutthakan Pongrakananon,[1] Nathaporn Somrang,[1] Worakanya Visitsart,[1] Pitt Supaphol,[1] Manit Nithitanakul,[1] Brian P. Grady[2]

[1]*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand*
[2]*School of Chemical Engineering and Materials Science, The University of Oklahoma, Sarkeys Energy Center, 100 East Boyd, T-335, Norman, Oklahoma 73019-1004*

Received 2 December 2002; accepted 16 July 2003

ABSTRACT: The effect of methyl acrylate content in ethylene–methyl acrylate–acrylic acid (E–MA–AA) terpolymers and acrylic acid content in ethylene–acrylic acid (E–AA) copolymers was investigated in blends of these two materials. The E–MA–AA terpolymer with 8 mol % methyl acrylate was not miscible with any E–AA material no matter what the AA content, whereas the terpolymer with only about 2 mol % methyl acrylate was miscible, at least to some extent, with the E–AA copolymer at high acrylic acid contents. Evidence supporting this conclusion derived from gloss, differential scanning calorimetry testing, and dynamic mechanical measurements. For the E–AA polymer material with the highest acid content, there was a synergistic effect for some properties at low added amounts of E–MA–AA copolymer; the tensile strength and hardness were 10% higher than values for the E–AA copolymer, even though the E–AA copolymer was much stiffer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2216–2222, 2004

Key words: blends; ethylene–acrylic acid copolymer; ethylene–methyl acrylate–acrylic acid terpolymer; mechanical properties; calorimetry

INTRODUCTION

To develop new polymeric materials for both scientific and commercial purposes, the blending of two or more different polymers is often used. Industrially, the blending process is almost always carried out in the molten state. At equilibrium, the amorphous components of both polymers may exist as a single homogeneous phase that would, in turn, mean that the two polymers are miscible; that is, the two materials are compatible. In most cases, however, the amorphous components of the two polymers will separate into distinct phases consisting primarily of the individual components. Further, if there exists sufficiently long uninterrupted blocks of one repeat unit on both copolymers, then the two blocks can cocrystallize. Cocrystallization has recently been the subject of investigations for ethylene copolymers made with metallocene or Ziegler–Natta catalysts.[1–4] In this article, we were primarily interested in blends of polyethylenes made without the use of site-selective catalysts; studies of blends of these materials where cocrystallization was reported are not very prevalent in the literature.

To promote miscibility in amorphous regions, typically strong interactions are necessary between the components. In the context of this article, the term miscibility is used loosely—in the sense that the two components may not be truly mixed at the segmental level and have true thermodynamic miscibility. Rather, the two components are mixed to the point where a macroscopic characteristic, such as the glass transition, does not clearly show features characteristic of the individual components. Some of the strongest interactions available are hydrogen-bonding interactions. Ethylene–acrylic acid copolymers have such interactions between the neutralizing hydrogen of the acid group and a carbonyl oxygen of another acid group. The ability to hydrogen bond has meant that ethylene–acrylic acid copolymers are popular as one part of a blend (e.g., with polyamides[5] or polyacetals[6]). The carboxylate group also has the capability of reacting, which in turn can enhance blend compatibility; for example, the carboxylic acid can react with the terminal amine group on a polyamide.[7,8] If carboxylate groups are found on two different chains, as in our case, the possibility of compatibilization attributed to interchain anhydride formation exists, although for the conditions used in this study the formation of anhydrides should be limited or not occur at all.[9]

Correspondence to: B. Grady (bpgrady@ou.edu).
Contract grant sponsor: Chulalongkorn University.
Contract grant sponsor: NSF CARRER; contract grant number; DMR-9733068.

Journal of Applied Polymer Science, Vol. 91, 2216–2222 (2004)

TABLE I
Copolymer Compositions[a]

Grade	Ethylene	Methyl acrylate	Acrylic acid
310	0.950	0.023	0.027
320	0.893	0.070	0.028
EAA1	0.988	—	0.012
EAA2	0.974	—	0.026
EAA4[b]	0.974	—	0.026
EAA5	0.961	—	0.039

[a] All values are in mole fractions.
[b] EAA4 has a lower average molecular weight than that of EAA2.

Infrared spectroscopic studies of our materials confirmed this assumption.

The commercial usefulness of ethylene–acrylic acid arises from its combination of toughness, clarity, gloss, and adhesion to polar substrates. One purpose of this study was to investigate whether a more flexible polymer, a terpolymer made from ethylene, acrylic acid, and methyl acrylate, could be used to lower the relatively high glass-transition temperature of the ethylene–acrylic acid copolymer, without sacrificing desired properties such as relatively high hardness and optical clarity. We chose not to investigate the adhesive ability of these materials because the adhesive characteristics depend on rheological properties that we were not attempting to control and because the acrylic acid contents were roughly identical in the terpolymers. We also wanted to explore whether it was possible to create a blend that appeared to be miscible according to the macroscopic characteristics listed earlier, and add to the growing list of pairs of polymers having apparent miscibility.

EXPERIMENTAL

Ethylene–acrylic acid copolymers were manufactured and graciously supplied by ExxonMobil Chemical. These particular materials were experimental; similar commercial materials are sold under the trademark ESCOR in areas outside of North America. Two grades of ESCOR terpolymers were also graciously supplied by ExxonMobil Chemical. Samples referred to in this article as 310 and 320 are ESCOR AT 310 and 320, respectively. Molar compositions are shown in Table I and were supplied by the manufacturer.

Polymer blends were prepared in a Collin Model T-20 twin-screw extruder operated at 50 rpm and zone temperatures at either 125 or 130°C. The melt was extruded through a single-strand die, solidified in cold water (the temperature was ~ 25°C), and pelletized. Pellets were dried in a hot air oven at 60°C for 2 days and kept in sealed plastic bags before compression molding to minimize moisture absorption.

Samples for mechanical and physical property tests were prepared from compression-molded sheet using a Wabash V 50 H compression press machine. The pellets were placed in a picture-frame mold and the mold was preheated at 160°C for 5 min. The mold was then compressed under a force of 10 tons for 3 min. The compression-molded sheet was then cooled to 40°C at a cooling rate that was fitted well by an exponential decay with a time constant of 3 min. Test specimens for each test were cut from the molded sheets using a die cutter.

A solids analyzer RSA II (Rheometric Scientific) was used to measure storage and loss moduli as a function of temperature. The film and fiber fixture was used to mount the samples and 3 K temperature steps were used. All experiments were performed with a 10 Hz frequency, 0.1% strain, and with static force tracking dynamic force.[10]

A Perkin–Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) was used to measure the melting point and the fractional crystallinity of the blended materials. The sample was heated from 30 to 140°C at a heating rate of 5°C/min and cooled to 30°C at a cooling rate of 5°C/min and reheated again to 140°C. Enthalpies of melting (ΔH_m) and melting temperatures (T_m) were collected from the second scan. Tensile properties, impact strengths, and hardness values of the blends were determined from the average of 10 samples. An ASTM D1708 microtensile die was used to cut the samples for tensile testing, and an Instron universal testing machine (Instron, Canton, MA) was used to measure tensile strength and elongation at break using a crosshead speed of 1.30 mm/min. A Shore D durometer was used to measure hardness of the blends according to the ASTM D2240 test procedure.

X-ray diffraction (XRD) patterns of all 310/EAAs blends were collected on a Rigaku (Japan) R2000 diffractometer equipped with a graphite monochromator and a Cu tube operated at 40 kV and 30 mA. First, the samples were subjected to the same treatment as DSC samples, then the sheet sample was put onto a glass slide specimen holder using petroleum jelly as a binder between sample and glass holder. The sample was examined between 5 and 35° (2θ) at a scanning rate of 2°/min in 0.02° increments. The XRD patterns of the crystalline and amorphous scattering in the diffraction pattern were separated from each other and were used for determination of the crystalline fraction. The degree of crystallinity (χ_c) is equal to the ratio of the crystalline scattering intensity to the total scattered intensity.

RESULTS AND DISCUSSION

Figure 1 shows the gloss for all samples blended with the higher methyl acrylate containing terpolymer

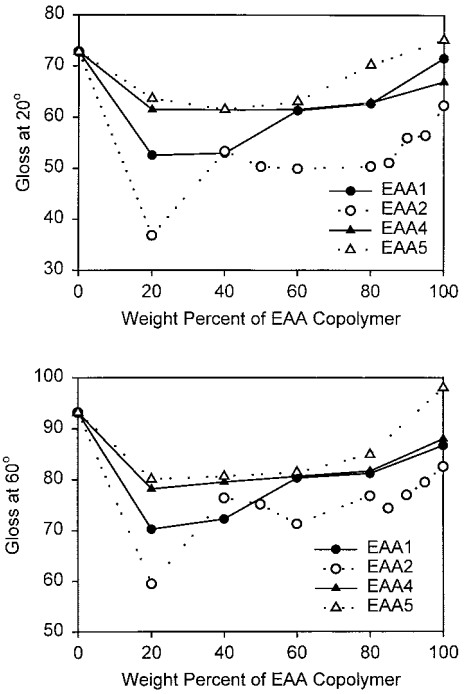

Figure 1 Gloss measurements for EAA copolymer and 320 terpolymer blends.

(320) and Figure 2 shows the tan δ versus temperature for the sample blended with EAA5. EAA5 has the highest acrylic acid content, so if miscibility can be achieved, it would be with this sample (as it was for the 310 samples). As Figure 1 implies and Figure 2 shows, the amorphous phases are clearly phase separated. Tan δ values of the blends are best described as the sum of two peaks weighted by the appropriate weight fractions as opposed to two peaks that become

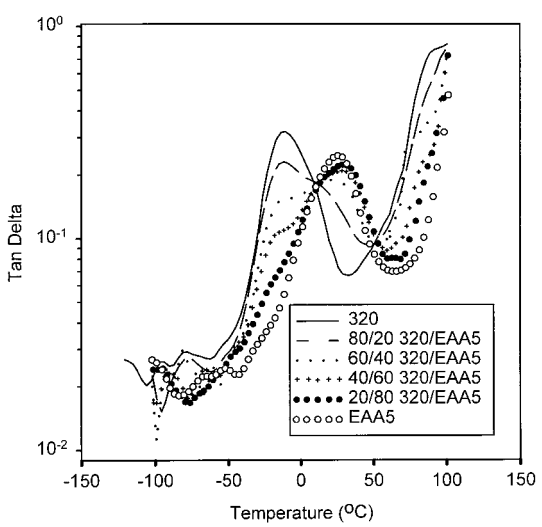

Figure 2 Representative DMA spectra for immiscible blends with 320 terpolymer. The copolymer shown is EAA5, the copolymer with the highest acrylic acid content.

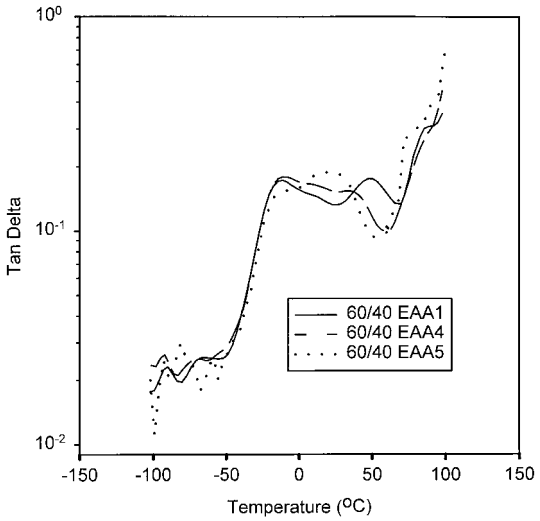

Figure 3 Tan δ versus temperature for EAA/320 terpolymer blend compositions that have constancy of tan δ over a wide temperature range near room temperature.

one peak upon blending. Tan δ spectra of the other materials (not shown) also show phase separation. Figure 2 shows that it is possible to blend the two materials at roughly equal proportions and have a material that has a very flat tan δ versus temperature profile over a range of about 40°C centered at a temperature that is around room temperature. The exact location of the center of this flat region depends on the frequency of testing, whereas the exact percentage and width vary slightly with the acrylic acid content, as shown in Figure 3. A flat tan δ with temperature centered near room temperature is a desirable attribute for materials used as dampeners (e.g., vibration or sound dampeners).

Much more miscible materials were formed from blends of the terpolymer with a lower methyl acrylate content. Dynamic mechanical spectra are shown in Figures 4–7. These spectra are much more difficult to interpret; determining which systems are phase separated is not a trivial matter. Not surprisingly, because the number of interchain interactions is expected to be higher with larger mole fractions of acrylic acid, blends of the terpolymer with EAA1, having the lowest acid content, are phase separated, whereas blends with EAA5, having the highest acid content, are the most phase-mixed. Figures 5 and 6 are not distinctly different, even though the molecular weights are different (the melt flow index of EAA4 is about twice that of EAA2). In terms of applications, whether the blend is thermodynamically phase mixed is not really important; it is the behavior of the various mechanical and optical properties that is important. Further, these properties can provide important clues regarding phase separation versus phase mixing.

Gloss is a fairly sensitive measure of phase mixing; if, over all concentrations negative deviations

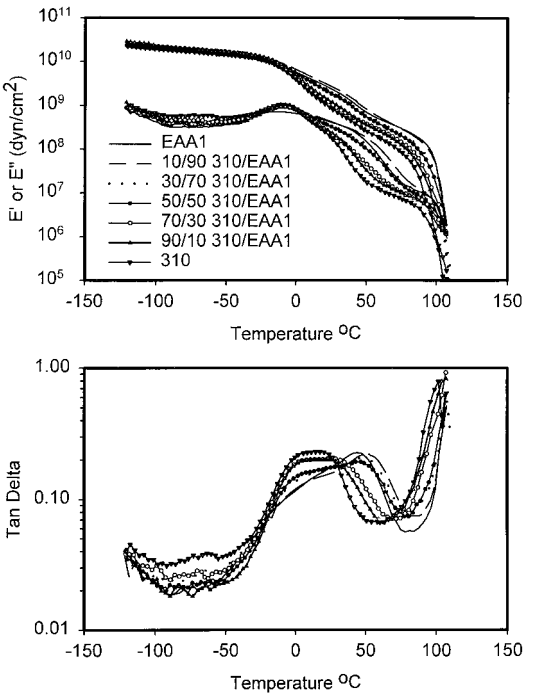

Figure 4 DMA spectra for EAA1/310 terpolymer blends.

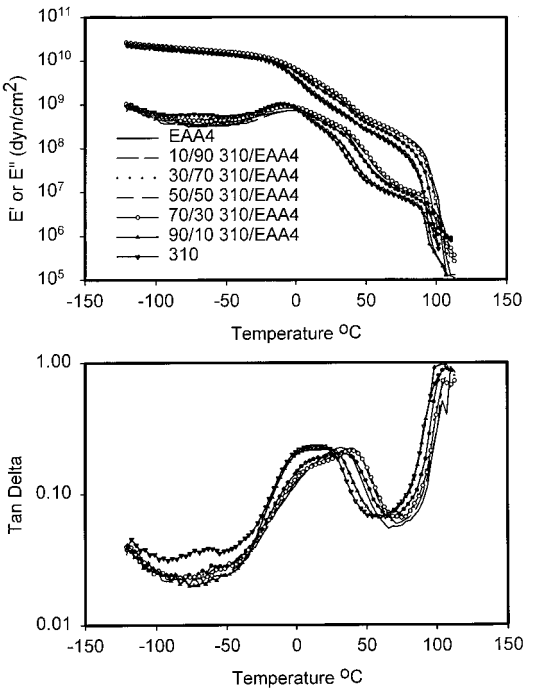

Figure 6 DMA spectra for EAA4/310 terpolymer blends.

from the rule of mixing occur, one can be fairly certain that phase separation is occurring. Figure 8 shows that results for all blends are much better than those shown in Figure 1 (i.e., the negative deviations from the law of mixing are much less significant than the deviations in Fig. 1). Except for the 20/80 310/EAA blend, the gloss for the 310/EAA5 blends follows almost exactly the rule of mixtures. This result does not mean that the two materials are miscible; however, this result does imply that if phase separation is occurring, the domain sizes are small.[11]

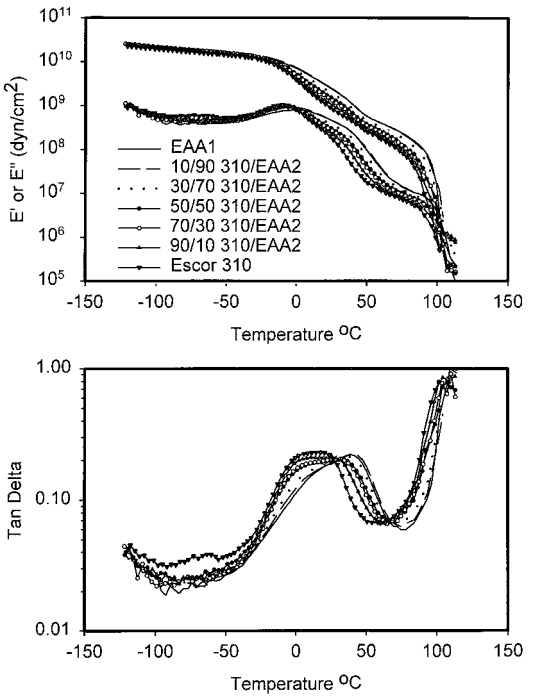

Figure 5 DMA spectra for EAA2/310 terpolymer blends.

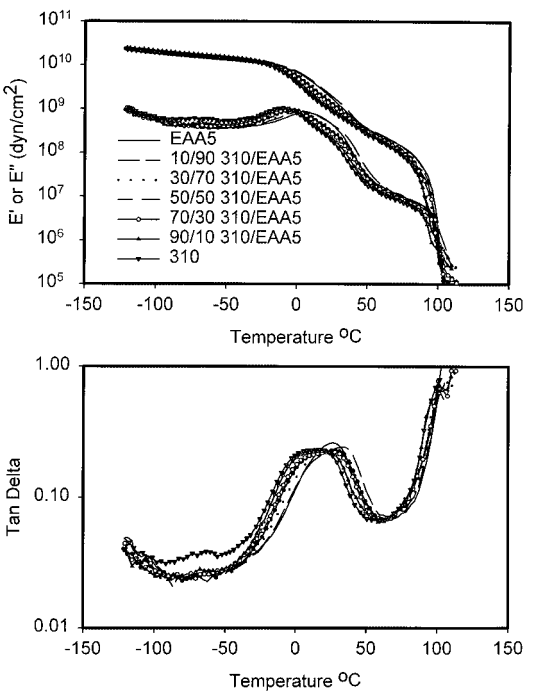

Figure 7 DMA spectra for EAA5/310 terpolymer blends.

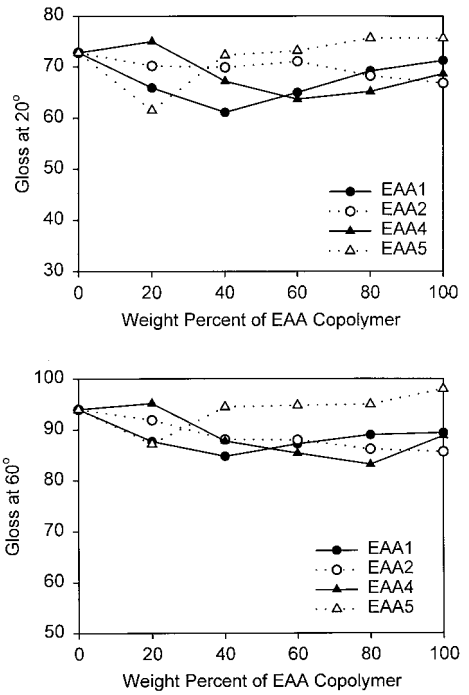

Figure 8 Gloss measurements for EAA/310 terpolymer blends. The same scale is used as in Figure 1 to facilitate comparison between the two figures.

The tensile properties of the 310/EAA blends are also characteristic of a system that is not highly phase separated. The properties shown in Figure 9 are for

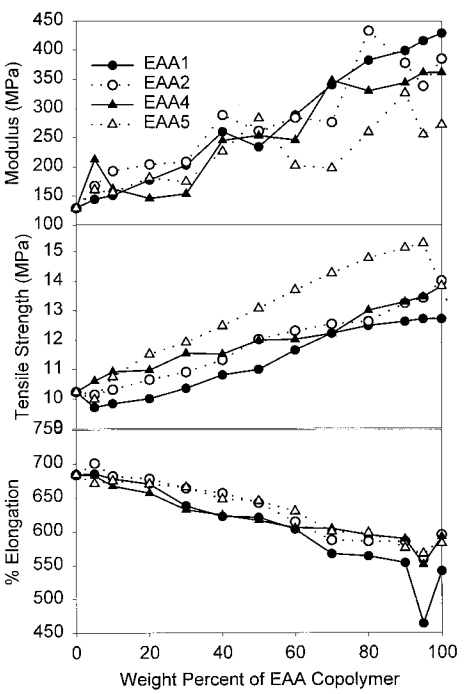

Figure 9 Tensile properties for EAA/310 terpolymer blends.

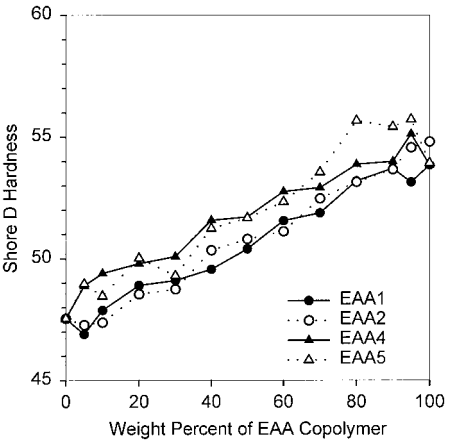

Figure 10 Shore D hardness for EAA/310 terpolymer blends.

the most part well described by the sum of the properties weighted by the fraction of each component. One significant exception to this is the tensile strength for the EAA5 blend; there is a clear synergistic behavior at high copolymer contents. This synergistic behavior was not found for either the modulus or elongation, although the sample-to-sample variation in the former means that even if such an effect were present, it could not be identified. The hardness, shown in Figure 10, also shows the same synergistic effect at high EAA contents. However, the crystallinities are not higher, as shown in Table II, so this data does not support increased crystallinity as the cause of the synergistic effect, however these samples do have a different thermal history than samples tested mechanically.

The only sample that showed clear evidence of two separate melting transitions in DSC experiments was EAA1. Spectra for blends with EAA1 are shown in Figure 11 along with a representative sample that showed no clear evidence of two distinct crystallite phases, sample EAA2. The results of melting temperature measurements are shown in Table II; however, baseline determination was deemed to be too difficult to obtain accurate crystallinity measurements from these DSC curves. Hence, the fractional crystallinity was determined by X-ray crystallography experiments, where the sample thermal history was chosen to mimic that in DSC experiments. This statement also highlights an important point: the thermal history of samples in the DSC and XRD measurements was different from that for all other measurements; additional thermal processing detailed in the experimental section was performed on the samples used for DSC and XRD measurements.

Based on the location of the melting transitions, the two crystalline populations in EAA1 are clearly terpolymer-rich and copolymer-rich, with the latter pre-

TABLE II
Properties of Polyethylene Crystallites for 310 Blended with Various EAAs

	EAA1		EAA2		EAA4		EAA5	
% EAA	T_m[a]/(°C)	% Crystallinity[b]	T_m[a]/(°C)	% Crystallinity[b]	T_m[a]/(°C)	% Crystallinity[b]	T_m[a]/(°)	% Crystallinity[b]
0.0	86.3	11.8	86.3	11.8	86.3	11.8	86.3	11.8
20	89.3	12.5	92.8	5.2	92.8	11.5	87.5	8.0
40	89.2[c]	13.2	95.4	9.7	95.5	14.0	90.7	10.1
50	89.8[c]	11.7	96.8	12.8	94.8	11.2	92.5	9.7
60		13.8	97.6	10.4	96.6	13.1	93.1	10.8
70		15.3		12.0		10.3		8.8
80		16.1	98.1	16.0	97.2	14.9	93.7	12.6
90		18.0		15.0		13.3		9.8
100	101.1	20.1	97.8	18.2	97.2	15.6	94.6	10.8

[a] These values represent the temperature where the maximum heat flow occurred and was calculated from DSC measurements. The error bars on these measurements are approximately ±1°C.
[b] These values are from XRD measurements. The error bars on these measurements are approximately ±2%.
[c] In these samples, there were two crystalline peaks corresponding to a phase containing primarily 310 and a phase containing primarily EAA. The melting temperatures corresponding to the latter were identical for all samples and were 101.1°C within experimental error, as shown in Figure 11.

sumably containing ethylene segments from only EAA1, given that the melting temperature did not shift with the amount of 310 in the material. For the other EAA copolymers, the rule of mixtures did not work well for the single melting temperature; there was a clear bias toward higher temperatures, that is, toward the melting temperature of pure EAA copolymer. However, given the clear lack of two peaks in the DSC spectra, even at very high terpolymer contents, one can almost be sure that the two materials are cocrystallizing. With respect to percentage crystallinity, the behavior of EAA2 was especially surprising; the crystallinity clearly declined and went through a minimum upon blending. The only significant known difference between EAA2 and EAA4 was the molecular weight of the polymer; hence this effect is most likely attributable to crystallization kinetics. Currently, we are exploring the crystallization behavior more closely, using a series of isothermal and nonisothermal kinetic experiments.

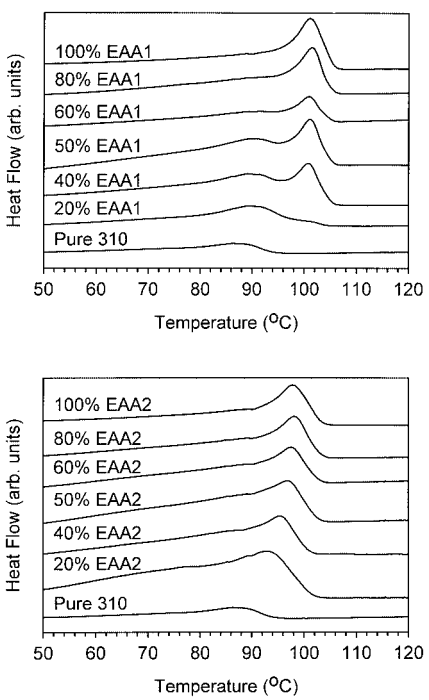

Figure 11 DSC spectra for selected EAA/310 terpolymer blends. These spectra were not normalized by sample weight. Note the difficulty in baseline determination that eliminates the ability to determine fractional crystallinity.

CONCLUSIONS

Blends of ethylene–methyl acrylate–acrylic acid terpolymers and ethylene–acrylic acid copolymers form apparently miscible blends if the terpolymer has sufficiently low methyl acrylate content and the copolymer has sufficiently high acrylic acid contents as evidenced by one glass-transition temperature and one crystallization melting point. For the highest acrylic acid content copolymer, there was a synergistic effect in tensile strength and hardness attributed to the higher crystallinity versus either pure component. Although the phenomenon of cocrystallization in LDPE copolymers has not been investigated in detail, this cocrystallization is perhaps the most interesting features of these blends.

The authors thank Ken Gant for measurements of many of the dynamic mechanical spectra presented in this article. Financial support for P.S. was provided by Chulalongkorn University through the Development Grant for New Faculty/Researcher. Financial support for B.P.G. was provided by an NSF CAREER Grant DMR-9733068. The authors also thank Dr. Joe Domine of ExxonMobil Chemical for helping to procure the materials used in this work.

References

1. Chen, H. Y.; Cheung, Y. W.; Hiltner, A.; Baer, E. Polymer 2001, 42, 7819.
2. Xu, J. T.; Xu, X. R.; Chen, L. S.; Feng, L. X.; Chen, W. Polymer 2001, 42, 3867.
3. Tanem, B. S.; Stori, A. Thermochim Acta 2000, 345, 73.
4. Galante, M. J.; Mandelkern, L.; Alamo, R. G. Polymer 1998, 39, 5105.
5. Valenza, A.; Visco, A. M.; Acierno, D. Polym Test 2002, 21, 101.
6. Horrion, J.; Cartasegna, S.; Agarwal, P. K. Polym Eng Sci 1996, 36, 2061.
7. Wang, X. D.; Li, H. Q. J Mater Sci 2001, 36, 5465.
8. McKnight, W. J.; Lenz, R. W.; Musto, P. V.; Somani, R. J. Polym Eng Sci 1985, 25, 1124.
9. McNeill, I. C.; Alston, A. Angew Makromol Chem 1998, 261/262, 157.
10. DMA spectra were recorded for all samples and only a fraction of these are shown in this article; interested parties are welcome to contact the corresponding author for a full set of DMA spectra.
11. There is one other possibility, that extreme surface segregation is occurring. However, we can confidently reject this hypothesis based on both the qualitative similarity of the gloss measurements and the behavior of EAA2 and EAA4.