Reactive compatibilization of poly(methyl acrylate-*ran*-acrylonitrile)/poly(ethylene) blends through amine–anhydride coupling

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ABSTRACT: Methyl acrylate/acrylonitrile copolymers (MA/AN) were reactively compatibilized as the dispersed phase into poly(ethylene) (PE) for potential hydrocarbon barrier materials. The MA/AN was made reactive by including *p*-aminostyrene (PAS), yielding terpolymers (MA/AN/PAS) with pendant primary amine functionality (number average molecular weight $\bar{M}_n$ = 65–133 kg mol^{-1}, dispersity ($Đ$) = 1.83–2.53, molar composition of PAS in copolymer F_{PAS} = 0.03–0.14, molar composition of AN = F_{AN} = 0.27–0.52). The non-functional MA/AN and amino functional MA/AN/PAS were each melt blended into PE that was grafted with maleic anhydride (PE-*g*-MAnn) at 200 °C at 70:30 wt % PE-*g*-MAnn:co/terpolymer. After extrusion, the dispersed phase particle size (volume to surface area diameter, $\langle D \rangle_{vs}$) was coarse (12.6 μm) for the non-reactive blend whereas it was much lower for the reactive blend ($\langle D \rangle_{vs}$ = 1.2 μm). Coarsening after annealing at 150 °C was slow, but the domain sizes increased only slightly for both cases. The reactive blend was deemed sufficiently stable and thus was suitable as a candidate barrier material for further testing against olefins. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44177.

INTRODUCTION

Barrier polymers are used to prevent penetration of liquids, gases, or vapors in materials used often for storage containers and food packaging.[1] Materials such as ethylene-vinyl alcohol copolymers, poly(acrylonitrile) (PAN), vinylidene chloride copolymers, poly (chlorotrifluoroethylene), polyesters, and polyamides are just some common polymers used for barriers (sometimes in blends with other polymers) against certain gases, liquids, and/or moisture.[1] Traditionally, metals were the choice to fabricate storage/transport containers. However, the light-weight nature of polymers in addition to relatively low processing temperatures compared to metals made them attractive alternatives. Consequently, polymers such as poly(ethylene) (PE) or poly(propylene) (PP) have been used.[1,2] However, using polyolefins such as PE or PP, despite their attractive mechanical strength, physical properties, and cost, may not be effective as barrier materials solely and thus requires the addition of other polymers in the form of a blend.

While blending can deliver a material combined with the desirable properties of two or more polymers, it often leads to phase separation upon further processing due to incompatibility between the constituent polymer phases.[3,4] Phase separation is indicated by coalescence, leading to large dispersed phase particle sizes, low interfacial area, and subsequent poor mechanical and other physical properties. To overcome coalescence and improve phase stability, compatibilization is used.[4–6] Many groups have shown that adding compatibilizers to polymer blends reduces the size of the dispersed phase significantly (which is crucial for many properties) and reduces coalescence.[3,7–23] By far, the most common method to compatibilize polymer blends is reactive compatibilization.[4,6]

Reactive compatibilization uses complementary functional groups on the respective polymers to reduce the interfacial tension and suppress coalescence, resulting in stable morphologies.[5] Examples of compatibilization reactions are amine–anhydride, amine–carboxylic acid, amine–epoxy, isocyanate–hydroxyl, oxazoline–carboxylic acid, and epoxy–carboxylic acid.[24] The coalescence rate is dependent on, among other variables, the kinetics of the coupling reaction.[6,25–27] It is therefore important to choose a reaction that has a relatively rapid coupling rate compared to the residence time of the extrusion process. Out of these reactive pairs, the kinetics of the amine-anhydride (primary amine to be specific) coupling is the fastest.[24]

PAN has been extensively studied as a barrier material against oxygen and carbon dioxide.[28] Furthermore, in the food industry, it has been used to block the permeation of aromas and/or flavors along with other hydrophobic compounds.[28] Its hydrophilic structure however, limits its absorption against water vapor.[11]

However, this hydrophilicity is useful as a barrier against hydrocarbon liquids such as the case of dispersing nylon into PE as dispersed, elongated domains to prevent hydrocarbon penetration.[29] Using nylons or polyesters is useful, as the terminal functional groups left as residues from the step-wise polymerization mechanism used to make the polymers can be applied toward reactive blending. PAN, in contrast, is made most often by a free-radical polymerization mechanism, and is further amenable to controlled polymerization methods, which provide the potential for more sophisticated microstructures and consequently, opportunities for more extensive tailoring of mechanical and physical properties. The only missing component is the inclusion of a functional group in PAN for reactive blending. Further, acrylonitrile is often copolymerized with another monomer to improve thermal stability; often styrene and methyl acrylate are used.[30] Indeed, styrene/acrylonitrile (SAN) and methyl acrylate/acrylonitrile (MA/AN) copolymers are commercially available as barrier materials synthesized by conventional radical polymerization, however little is mentioned how these are compatibilized.[30] We previously made SAN copolymers where we placed a single reactive amine group at the chain end.[31] The amine-terminated SAN was effective in compatibilization with maleic anhydride grafted PE (PE-g-MAn) and we were able to form elongated SAN domains in the PE.[31] However, the dispersed phase particle size was limited to about 2 μm and further modulation could potentially be accessed by making the acrylonitrile-containing copolymer with many pendant functional groups and perhaps diluting it with cheaper non-functional SAN. The following study first describes the conventional radical polymerization of methyl acrylate, acrylonitrile, and p-aminostyrene terpolymers (MA/AN/PAS) to give pendant amino functionality and then describes its reactive blending and phase stability after blending with PE-g-MAn. Others have attempted pendant amino functional by several methods. We note that p-aminostyrene has been incorporated into styrene/glycidyl methacrylate/p-aminostyrene terpolymers, which were crosslinked by UV-irradiation.[32] Lukey et al. made poly(4-aminostyrene) by post-polymerization modification from poly(styrene).[33] Here we made linear copolymers with acrylonitrile and 4-aminostyrene directly to obtain the copolymer with ostensibly the desired mechanical properties and pendant functionality. We will use the data obtained to select the appropriate coupling chemistry (comparing against an epoxy/acid reaction for example) to make stable blends and eventually test a formulation for its barrier properties in succeeding studies.

EXPERIMENTAL

Materials

Methyl acrylate (MA) (99%) and acrylonitrile (AN) (99%) were obtained from Sigma–Aldrich (Oakville ON Canada), purified by passing the monomers through a column of basic aluminum oxide (Brockmann, Type 1, 150 mesh) and calcium hydride (90–95% reagent grade) (5 wt % CaH$_2$: 95 wt % Al$_2$O$_3$), which were also obtained from Sigma Aldrich), and stored under a head of nitrogen prior to use. Azobisisobutyronitrile (AIBN) was obtained from DuPont (Wilmington DE), and purified by re-crystallization from methanol before use.

p-Aminostyrene (PAS) was obtained from Oakwood Chemicals Estill, SC and used as received. Deuterated chloroform (99.8 atom %) (CDCl$_3$), deuterated dimethylsulfoxide (DMSO-d_6), trimethylsilyldiazomethane in 2 M hexanes solution, and phenyl isocyanate (98%) were obtained from Sigma Aldrich and were used as received. N,N-Dimethylformamide (DMF) certified grade (99%) was obtained from Fisher and used as received. HPLC grade DMF (99.5%) was obtained from Fisher (Ottawa, ON Canada) as the mobile phase for gel permeation chromatography (GPC). Lithium bromide was added to the DMF at a concentration of 1 g L^{-1} for GPC.[34] PE-g-MAn (1.70 wt % grafted maleic anhydride) with a melt flow index (MFI) of 1.5 g (10 min)$^{-1}$ at 190 °C, density of 0.91 g mL^{-1}, and melting point of 123 °C was obtained from Arkema (Exton, PA) and used as received. Other chemicals such as acetone (99.5%) and methanol (99.8%) were obtained from Fisher and used as received.

Methods

Synthesis of Methyl Acrylate/Acrylonitrile Copolymers. MA and AN were copolymerized using DMF as the solvent in a three-necked 50 mL reactor with a nitrogen purge, thermocouple/thermowell, and reflux condenser. The reactor sat on top of a stirring plate and heating mantle. Appropriate amounts of AIBN, MA, AN, and DMF were measured out and poured into the reactor with the formulation for MA_AN_Exp1 (see Table I) shown as an example. For this particular experiment, 0.1137 g (0.692 mmol) AIBN, 5.1163 g (59.43 mmol) MA, 3.3177 g (62.53 mmol) AN, and 7.9164 g (108.31 mmol) DMF were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 min prior to starting the reaction and maintained throughout the reaction. The reactor set point was 65 °C to ensure adequate decomposition of AIBN.[35] The chiller was set to 4 °C. Once the reaction was complete (reaction time of about 3–4 h), the polymer was precipitated the first time in about 300 mL of deionized water, re-dissolved in a minimum amount of solvent, and precipitated a second time in about 50 mL of deionized water to remove unreacted monomers. Finally, the polymer was vacuum dried in the oven at 50–60 °C overnight. This particular copolymer had a number average molecular weight (M_n) of 90.9 kg mol^{-1} and Đ of 2.71 relative to poly(methyl methacrylate) (PMMA) standards in DMF at 50 °C. The copolymer had a MA molar composition of 0.51, which was determined by proton nuclear magnetic resonance (^{1}H-NMR) (300 MHz, DMSO-d_6, δ): 3.6 (s, 3H, O—CH$_3$), 1.2–2 (m, 2H, backbone CH$_2$). Qualitative analysis was done by FTIR 1650–1750 (s; ν(C—O)), 2250 (s; ν(C≡N)).

Synthesis of Methyl Acrylate/Acrylonitrile/p-Aminostyrene Terpolymers. MA, AN, and PAS were terpolymerized in a three-necked 50-mL reactor with a nitrogen purge, thermocouple/thermowell, and reflux condenser. The reactor sat on top of a stirring plate and heating mantle. The solvent was DMF. Appropriate amounts of AIBN, MA, AN, PAS, and DMF were measured out and poured into the reactor, with the formulation for MA_AN_PAS_Exp1 (see Table II) shown as an example. For this particular experiment, 0.107 g (0.652 mmol) AIBN, 7.1598 g (71.46 mmol) MA, 1.335 g (25.16 mmol) AN, 0.6016 g (5.05 mmol) PAS, and 9.7982 g (134.06 mmol) DMF were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 min prior to starting the reaction and maintained throughout

Table I. Characterization of Methyl Acrylate (MA)/Acrylonitrile (AN) Non-functional Copolymers Synthesized by Conventional Radical Polymerization

Experiment I.D.	Feed composition				Characterization		
	[AIBN] $\times 10^2$ (M)	[MA] (M)[a]	[AN] (M)[a]	$f_{MA,0}$[b]	F_{MA}[c]	M_n (kg mol^{-1})[d]	$Đ$[d]
MA_AN_Exp1	3.88	3.33	3.50	0.48	0.51	90.9	2.71
MA_AN_Exp2	3.73	1.58	5.03	0.24	0.14	29.3	2.54
MA_AN_Exp3	3.36	4.84	1.48	0.77	0.71	52.0	4.23
MA_AN_Exp4	3.57	4.27	1.83	0.70	0.66	61.2	2.46

[a] 50:50 wt % monomers:solvent.
[b] Initial molar feed composition of MA.
[c] Copolymer molar composition of MA calculated using ^{1}H-NMR.
[d] Obtained by GPC using DMF as mobile solvent with respect to linear PMMA standards at 50 °C.

the reaction. The set point of the reaction was set to 65 °C to ensure sufficient initiator decomposition.[33] Once the reaction was complete (reaction time of 1.5 h), the polymer was precipitated initially in about 300 mL of deionized water, re-dissolved in a minimum amount of solvent and precipitated a second time in about 50 mL of deionized water to remove unreacted monomers. Finally, the polymer was dried overnight in a vacuum oven at 50–60 °C. This particular terpolymer had M_n of 114.1 kg mol^{-1} and $Đ$ of 2.14 relative to PMMA standards in DMF at 50 °C. The terpolymer had a MA and AN molar composition of 0.68 and 0.24 respectively, which were calculated by ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.9–7.5 (m, 4H, Ar H), 0.8–2 (m, 3H, CH—CH$_2$), 3.6 (s, 3H, O—CH$_3$). Qualitative analysis was done by FTIR 1650–1750 (s; ν(C=O)), 2250 (s; ν(C≡N)), 3300(d; ν(NH$_2$)).

Characterization

Proton Nuclear Magnetic Resonance. ^{1}H-NMR (Varian 300 MHz) was used to characterize the composition of all copolymers and terpolymers. The peaks of interest for MA/AN copolymers were at δ = 3.6 ppm for the methyl protons for MA and δ = 1.2–2 ppm for the backbone protons. The peaks of interest for MA/AN/PAS terpolymers were at δ = 3.6 ppm for the methyl protons for MA, δ = 0.8–2 ppm for the backbone protons, and δ = 6.5–7 ppm for the styrenic protons of PAS. For all polymers, the AN content was calculated using the backbone protons, rather than solely the proton on the α-carbon.[36,37] CDCl$_3$ was used for ^{1}H-NMR analysis for the terpolymers, whereas deuterated DMSO-d_6 was used for the copolymers.

Gel Permeation Chromatography. All polymers were analyzed using a Waters Breeze system equipped with two ResiPore (3

μm MULTI pore type 250 × 4.6 mm^2) columns along with a ResiPore guard column (3 μm, 50 × 4.6 mm^2) from Polymer Laboratories. The flow rate was 0.3 mL min^{-1}. The gel permeation chromatography (GPC) was equipped with a differential refractive index (RI 2410) detector. MA/AN copolymers and MA/AN/PAS terpolymers required DMF with 1 g L^{-1} lithium bromide as the mobile phase and a column temperature of 50 °C. The molecular weights were measured relative to linear PMMA standards. Prior to analysis, polymer samples containing PAS were quenched with phenyl isocyanate to prevent sticking of the amine groups onto the column.[5,38]

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy. A Perkin–Elmer spectrum TWO with UATR accessory (also from Perkin-Elmer) and diamond as the ATR crystal was used to qualitatively analyze MA/AN and MA/AN/PAS co/terpolymerizations. The peaks of interest for MA/AN copolymers were at ν = 1600–1800 cm^{-1} for the carbonyl stretch of MA and ν = 2200–2400 cm^{-1} for the nitrile stretch in AN.[37] The peaks of interest for MA/AN/PAS terpolymers were at ν = 1600–1800 cm^{-1} for the carbonyl stretch of MA, ν = 2200–2400 cm^{-1} for the nitrile stretch for AN and ν = 3300–3500 cm^{-1} for the N—H stretch of the primary amine of PAS.[39]

Thermal Gravimetric Analysis. A thermal gravimetric analysis (TGA) Q500 (TA Instruments) was used to determine the minimum degradation temperature and degradation profiles of the MA/AN/PAS terpolymers. The analysis began at ambient temperature (35–40 °C) and proceeded to 550 °C at a heating rate of 10 °C min^{-1}. The analysis was done under oxygen rather than nitrogen to simulate the environment in an extruder.

Table II. formulations for Methyl Acrylate (MA)/Acrylonitrile (AN)/*P*-aminostyrene (PAS) Terpolymerizations in DMF Solution at 65 °C

| Experiment I.D.	[AIBN] $\times 10^2$ (M)	[MA] (M)[a]	[AN] (M)[a]	[PAS] (M)[a]	$f_{MA,0}$	$f_{AN,0}$
MA_AN_PAS Exp1	3.23	3.54	1.25	0.25	0.70	0.25
MA_AN_PAS Exp2	4.02	4.14	0.59	0.25	0.83	0.12
MA_AN_PAS Exp3	5.29	3.15	2.18	0.31	0.56	0.39
MA_AN_PAS Exp4	3.03	3.56	1.26	0.26	0.70	0.25
MA_AN_PAS Exp5	2.90	3.94	0.81	0.28	0.78	0.16
MA_AN_PAS Exp6	2.95	3.99	0.47	0.28	0.84	0.10
MA_AN_PAS Exp7	3.35	3.67	1.30	0.19	0.71	0.25

[a] 50:50 wt % monomers to solvent ratio.

Differential Scanning Calorimetry. A differential scanning calorimetry (DSC) Q2000 from TA Instruments was used to approximate the glass transition temperature (T_g) of the MA/AN/PAS terpolymers. The analysis was comprised of two heating cycles and one cooling cycle. Heating cycles began at $-20\,°C$ and went to $180\,°C$ at a rate of $20\,°C\ \mathrm{min}^{-1}$. The cooling cycle began at $180\,°C$ and went to $-20\,°C$ at a rate of $20\,°C\ \mathrm{min}^{-1}$. The measurements were done in an aluminum t-zero pan and were calibrated to an empty aluminum t-zero pan.

Rheology. Sample discs (~ 0.7 g) of MA/AN copolymer and MA/AN/PAS terpolymer were prepared in a Carver Model 3857 hot press at $200\,°C$. The discs were 1 mm in thickness and 25 mm in diameter. The discs were prepared between teflon plates at a clamping force of 12 tons. The pressing time was 10 min with quick releases at 3 min intervals to remove any gas bubbles. The discs were cooled to room temperature at rate of about $35\,°C\ \mathrm{min}^{-1}$.

Rheological measurements were performed on the prepared discs using an Anton Parr MCR 302 parallel plate rheometer. A frequency sweep was employed at $200\,°C$ for MA/AN copolymers and MA/AN/PAS terpolymers discs under nitrogen to avoid decomposition. The strain was kept below 10% to stay within the linear viscoelastic regime and the angular frequency was varied between 0.01 and $300\ \mathrm{s}^{-1}$.

Extrusion and Scanning Electron Microscopy. MA/AN/PAS terpolymers and MA/AN copolymers were melt blended with PE-g-MAnn in a Haake MiniLab II twin-screw extruder in counter-rotating mode. A 70:30 mass ratio of PE-g-MAn;co/terpolymer was used. The mixture was mechanically mixed by hand with a spatula prior to feeding it to the extruder. The operating conditions were set at $200\,°C$ at 50 rpm. The material was passed through the extruder a total of three passes before the product was collected (a total residence time of about 2–3 min). The product was quenched in liquid nitrogen within the first 10–20 seconds as it exited the extruder (after the third pass) to freeze the morphology. A sample of the product was then freeze-fractured and was put into a beaker of DMF (and stirred) for a minimum of 36 h to ensure the dispersed phase was etched. The samples were dried and glued onto aluminum stubs with cyanoacrylate glue. The samples were then coated with a 2 nm layer of platinum to make the sample conductive for SEM analysis. A FEI Inspect F-50 FE SEM was used to analyze the morphologies from the freeze-fractured surfaces of the extruded polymers at 1–2 kV (significant charging occurred at higher settings). Finally, ImageJ software was used to analyze the images. A minimum of 350 particles was used in determining the volume to surface area diameter ($\langle D\rangle_{\mathrm{vs}}$). The particles were manually selected using the ROI manager rather than letting the software automatically detect particles. The background was subtracted before adjusting the threshold.

Since a 2D surface of a 3D sample was analyzed by SEM, the calculated diameter does not represent the true size of the domains. Stereological corrections are necessary but previous studies have shown that a relatively small increase of 10–15% in
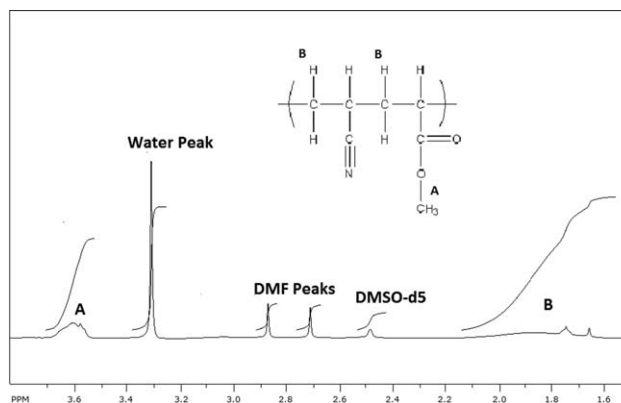
Figure 1. ^{1}H-NMR spectrum of the non-functional poly(methyl acrylate-*stat*-acrylonitrile) copolymer (MA_AN_Exp1 listed in Table I).

domain sizes is typical and thus were not done here.[6,16,38] $\langle D\rangle_{\mathrm{vs}}$ was calculated by using eq. (1)[6]:

$$\langle D\rangle_{\mathrm{vs}} = \frac{\sum_{i=1}^{k} n_i D_i^3}{\sum_{i=1}^{k} n_i D_i^2} \tag{1}$$

where n_i is the number of particles and D_i is the diameter of the spherical particle extracted from its area. $\langle D\rangle_{\mathrm{vs}}$ estimates the ratio of volume to interfacial area and is thus a useful measure in polymer blends of the concentration of compatibilizing copolymer required, for example. $\langle D\rangle_{\mathrm{vs}}$ was calculated by assuming that the particles were spherical (in 3D) and circular (in 2D) so that their diameter could be extracted from their area.

RESULTS AND DISCUSSION

Synthesis of Methyl Acrylate/Acrylonitrile Copolymers

MA was copolymerized with AN using AIBN as the initiator. Such copolymers were previously studied for carbon fiber applications.[36,37] The goal for our synthesis was to make copolymers (and ideally terpolymers by inclusion of a monomer with a reactive functionality such as an amine) that had a sufficiently high AN composition to be useful as a barrier material (typically ~ 40–50 mol % AN based on SAN copolymers for barrier against oxygen and carbon dioxide[30]) and to use the binary system as the model non-reactive polymer for blending studies with PE-g-MAn. Feed compositions were thus varied to cover a broad composition range as seen in Table I. Table I shows that varying the feed compositions still results in significant AN incorporation. The compositions were calculated using ^{1}H-NMR with a typical spectrum shown in Figure 1 as an example.

The spectrum shows residual DMSO-d_5 at 2.5 ppm indicating that the solvent used was not 100% pure.[40] Furthermore, the appearance of the water peak at 3.3 ppm has two possible sources. It is either residual water that did not evaporate during the drying step or it is residual water present in the solvent.[40]

The compositions were calculated by examining the peak areas of the methyl protons of MA labeled in Figure 1 as "A", and the backbone protons labeled as "B" using the following previously published method[37]:
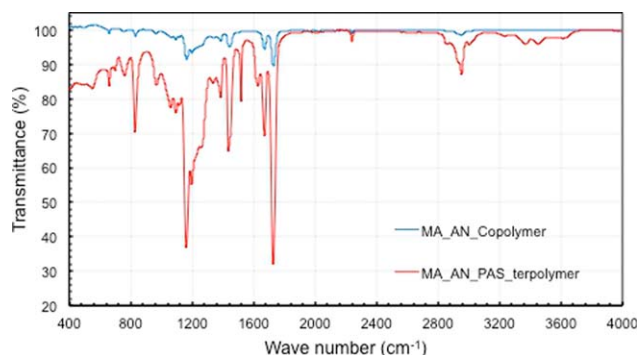
Figure 2. Superimposed ART-FTIR spectrum of MA/AN copolymer (blue; MA_AN_Exp1 in Table I) and MA/AN/PAS terpolymer (red; MA_AN_PAS_Exp4 in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$n = \text{moles of MA present in copolymer} = \frac{A}{3} \quad (2a)$$

$$m = \text{moles of AN present in copolymer} = \frac{B}{2} - n \quad (2b)$$

Molar compositions of MA and AN in the copolymer, F_{MA} and F_{AN}, respectively, were calculated using the following.

$$F_{MA} = \frac{n}{n+m} \quad (3)$$
$$F_{AN} = 1 - F_{MA}$$

Table I shows that the copolymer compositions are similar to the feed compositions. The reported reactivity ratios are $r_{AN} = 1.29$ and $r_{MA} = 0.96$ implying that a statistically random copolymer was likely, which seems to be in fair agreement with our results.[36] With the incorporation of AN confirmed, terpolymerizations were attempted to also incorporate functional amine pendant groups into the copolymer, which is necessary for reactive compatibilization into the PE matrix.

Synthesis of (MA/AN/PAS) Terpolymers
Terpolymers using a feed of MA, AN, and PAS were polymerized with AIBN as the initiator. Others have polymerized PAS in its protected form by anionic polymerization, conventional radical polymerization, and even by atom transfer radical polymerization.[41–43] According to these previous studies, there is a possible resonance structure where the electron density from the amino group shifts through the aromatic group, leaving a negative charge on the α-carbon of the vinyl group.[42,43] This is the reason why polymerizing PAS in its unprotected form is difficult to a significant conversion. PAS was chosen as its amine group can couple to anhydrides, acids, and epoxies.[24] The different formulations are listed in Table II.

Compositions were limited to contain a fairly low concentration of PAS (5–10 mol %) since it is required only for compatibilization during blending while AN composition should be sufficiently high to be an effective barrier material. Excessive AN incorporation may make processing difficult (which is why MA was incorporated).[44–47] Qualitative analysis using ATR-FTIR was done to confirm the presence of the amino group from PAS. Figure 2 is a typical spectrum of a terpolymer compared to binary copolymer without PAS.

In Figure 2, the overlapping spectra of the copolymer and terpolymers are identical except for two peaks. The peak at about $\nu = 1500\ cm^{-1}$ represents the N—H bend and the doublet at $\nu = 3400\ cm^{-1}$ represents the signature N—H stretch of the primary amine.[39] Figure 3 shows no residual PAS monomer (no vinyl peaks) in the ^{1}H-NMR spectrum and therefore, it can be concluded that PAS was incorporated into the terpolymer. ^{1}H-NMR was then used to quantitatively estimate the terpolymer composition.

The polymer compositions were determined examining the peak for the styrenic protons of PAS (A at $\delta = 6.5–7$ ppm), along with the peak for the methyl protons of MA (B at $\delta = 3.6$ ppm) and the backbone protons (D at $\delta = 1.2–2.2$ ppm). The approach is outlined below:

$$X = \text{moles of PAS in terpolymer} = \frac{A}{4}$$

$$Y = \text{moles of MA in terpolymer} = \frac{B}{3}$$

$$Z = \text{moles of AN in terpolymer} = \frac{D}{3} - X - Y$$

It should be noted that the doublet at $\delta \sim 3$ ppm represents the solvent, DMF. The terpolymers had to be washed several times to reduce the solvent trapped in the resin. The characterization of all of the terpolymers is shown in Table III.

The AN content of the terpolymers varied from 27 to 52 mol % and the PAS content varied from 3 to 14 mol %. The AN content may seem quite low to be effective for a barrier material. For the reactive terpolymer we used for reactive blending $F_{AN} = 29$ mol % (MA_AN_PAS) to ensure that processing was relatively easy. This gives a reduction in permeability of 7–8 times compared to a polymer without any AN, using tabulated permeability against gases like CO_2 and O_2 as a guide.[48]

Furthermore, there are approximately 30–290 amino groups per polymer chain. In most cases the polymer compositions are relatively consistent when similar feed compositions are used. The slight differences in copolymer compositions can be attributed to the polymers having different conversions (different M_n). Therefore, repeatability does not seem to be an issue despite the high reactivity of PAS. In summary, the functional monomer can be incorporated in relatively low concentrations into the terpolymer
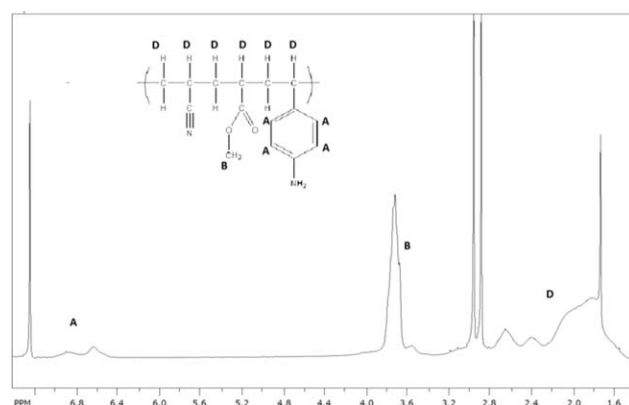
Figure 3. ^{1}H-NMR spectrum of the functional terpolymer MA_AN_PAS_Exp1.

Table III. Characterization of MA/AN/PAS Terpolymers

Experiment I.D.	F_{MA}[a]	F_{AN}[a]	M_n (kg mol^{-1})[b]	Đ[b]	T_g (°C)
MA_AN_PAS Exp1	0.68	0.24	114.1	2.14	11.2
MA_AN_PAS Exp2	0.67	0.27	117.1	1.95	4.2
MA_AN_PAS Exp3	0.44	0.52	66.9	2.23	28.3
MA_AN_PAS Exp4	0.70	0.27	65.8	2.58	7.0
MA_AN_PAS Exp5	0.47	0.39	162.5	1.83	21.0
MA_AN_PAS Exp6	0.69	0.20	133.0	2.09	10.2
MA_AN_PAS Exp7	0.63	0.29	102.4	2.51	9.0

[a] Obtained by ^{1}H-NMR.
[b] Obtained by GPC using DMF as the mobile phase relative to PMMA standards at 50 °C.

(3–14 mol %, 30–290 amino groups per chain). TGA was done to determine the degradation profiles of the terpolymers in order to determine a reasonable extrusion/process temperature. Figure 4 shows a typical TGA spectrum.

There is an immediate mass loss at about 50–100 °C, which can be attributed to the moisture absorbed by the polymer from the humidity in the air. There is further weight loss up to 140 °C, which is the residual DMF solvent that was not removed during the vacuum drying stage. For further evidence of this, the ^{1}H-NMR does show DMF peaks at about δ = 2.8–3 ppm. Previous work has indicated poly(MA) to begin to slowly degrade at about 200 °C under oxygen and vacuum conditions, so it is was not expected to degrade much before 200 °C.[49] From 300 °C and onwards, degradation of MA and AN in the polymer is most likely occurring,[49,50] with most of PAS in the polymer not being degraded at all, as it is reported to degrade after 500–550 °C.[51] Therefore, the upper limit that these terpolymers can be extruded at without significant decomposition occurring is about 250–275 °C. T_gs were also analyzed using DSC (see Table III). The analysis showed that the T_g of the terpolymers varied between 4 and 28 °C. This was expected as PMA, the major component, has a T_g of 8 °C.[52] It is also worth noting that the higher the MA composition, the lower the T_g, as expected, which could be problematic for barrier materials. Too low of a T_g would result in difficult to orient biaxially in a film. However, the range of compositions we studied was intended to see how sensitive the PAS incorporation was as a function of MA and AN composition. For scale-up to barrier testing, we intend to use higher AN composition to boost the T_g.

Extrusion and SEM Analysis
Blends of the amine functionalized terpolymer and the non-functional MA/AN copolymer were prepared with PE-g-MAn at 200 °C at 30 wt % of the dispersed phase. Blend miscibility can be determined theoretically by evaluating a blend pair's interaction parameter (χ_{blend}), which can be calculated by the eq. (4)[53]:

$$\chi_{blend} = \chi_{A/B} = \frac{v}{RT} \times (\delta_A - \delta_B)^2 \qquad (4)$$

where χ_{blend} is the interaction parameter between PE-g-MAn (A) and the co/terpolymer (B), R is the gas constant, T is absolute temperature of the blend, v is the molar volume, and δ is the

Hildebrand solubility parameter. The solubility parameter for PE-g-MAn was estimated by compositionally averaging the individual solubility parameters of PE and MA from literature estimates. This provides $\delta_{PE\text{-}g\text{-}MAn} = 8.0$ cal$^{1/2}$ cm$^{-3/2}$.[54] Furthermore, δ for the MA/AN copolymer was determined by using a weighted average (using the polymer compositions as the weights) of the solubility parameters found in the literature for the homopolymers.[55] The solubility parameter of PAS was not found in the literature so a group contribution method was used to estimate it according to the approach described by van Krevelen.[56] For the non-functional MA/AN copolymer, $\delta_{MA/AN} \approx 10.5$ cal$^{1/2}$ cm$^{-3/2}$ while for the reactive MA/AN/PAS terpolymer, $\delta_{MA/AN/PAS} \approx 10.3$ cal$^{1/2}$ cm$^{-3/2}$ (using the composition of the terpolymer used for subsequent blending experiments: MA/AN/PAS-Exp7, which had 8 mol % PAS in the final terpolymer). The molar volumes were calculated from the mass of the repeat units and the literature densities. The molar mass of the polymer repeat unit (using the polymer compositions as the weights) was approximately 75 g mol^{-1} and 78 g mol^{-1} for the non-reactive and reactive blends respectively. The densities were calculated to be 0.90 g mL^{-1}–0.91 g mL^{-1} for the non-reactive and reactive blends, respectively, using a composition average of the monomers constituting the copolymers. χ_{blend} for both the non-reactive and reactive blends was quite high, being 0.5–0.6, indicating that the blends were indeed immiscible.[56]

Table IV summarizes the blends studied. The matrix was PE-g-MAn in all cases, and the dispersed phase consisted of varying levels of functional terpolymer (MA_AN_PAS_Exp7) with a non-functional copolymer (MA_AN_Exp4). The cases with 100% MA_AN_PAS_Exp7 or with only MA_AN_Exp4 were also done with the latter serving as the non-reactive blend. Figure 5 shows the SEM images of the reactive and non-reactive blends.

From Figure 5(a–c), the non-reactive blend has much larger dispersed phase domains, compared to the reactive cases, being greater than 10 μm. The particle size is nearly halved when the dispersed phase consists of 50:50 wt % MA/AN/PAS terpolymer:MA/AN copolymer. When the dispersed phase is solely the MA/AN/PAS terpolymer, the particle size is 10 times smaller
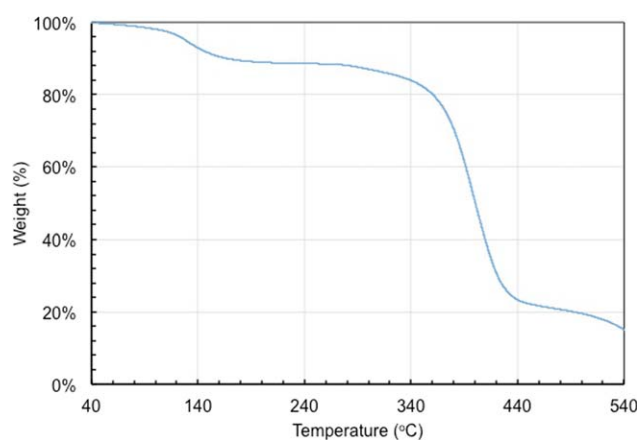
Figure 4. Thermal degradation shown via thermal gravimetric analysis (TGA) of an MA/AN/PAS terpolymer under atmospheric conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Particle Sizes Obtained from SEM Images of Various Reactive and Non-Reactive Blends of PE-g-MAn with Methyl Acrylate/Acrylonitrile Copolymers

SEM Image[a]	Blend ratio				$\langle D \rangle_{vs}$ (µm)
	PE-g-Man (wt %)	MA/AN/PAS (wt %)	MA/AN (wt %)	Annealing conditions	
A	70	0	30	None	12.5
B	70	15	15	None	4.6
C	70	30	0	None	1.2
D	70	0	30	20 h at 150 °C	14.1
E	70	15	15	20 h at 150 °C	5.1
F	70	30	0	20 h at 150 °C	1.4

[a] The letters in the SEM image column correspond to the images in Figure 5.

compared to the non-reactive case, being about 1.2 µm after extrusion. Thus, the effect of reaction was substantial. Since the polymers did not have a common solvent for GPC, possible, SEM was used to infer the effect of reaction (see Table IV).

Seeing that $\langle D \rangle_{vs}$ for the functionalized blends decreased relative to the non-functionalized blend, it shows that morphology was stabilized due to the coupling reaction as was suggested by previous studies.[5,26,27,33,57] Conversely, the small increase in $\langle D \rangle_{vs}$ after annealing indicates that coalescence was very slow at the temperature used, and that slight variations in $\langle D \rangle_{vs}$ were more likely to be caused by particle analysis, rather than the coalescence process.[31] To compare the particle sizes with theoretical or semi-empirical predictions, estimates of the blend interfacial were necessary. The interfacial tension of the blends was estimated using eq. (5), a method previously used for the blending of immiscible polymers.[58]

$$\Gamma = \left(\frac{\chi}{6}\right)^{1/2} \times p_o b k T \qquad (5)$$

Here, χ is the enthalpic interaction parameter, k is the Boltzmann constant, T is the temperature, b is the statistical segment length, and p_o is the average monomer density. The monomer density and the statistical segment length were estimated using a weighted average with the weights as the polymer compositions and blend ratios. The statistical segment lengths were calculated using eq. (6) with the following tabulated data for $r_o M^{-1/2}$ ([=] nm (g/mol)$^{-1}$: poly(acrylonitrile) = 0.093; poly (methyl acrylate) = 0.059; poly(p-aminostyrene) = 0.067, and poly(ethylene) = 0.10.[59]

$$b = \left(\frac{r_o}{M^{\frac{1}{2}}}\right)(MW_{avg})^{\frac{1}{2}} \qquad (6)$$

Here, MW_{avg} is the weighted average molecular weight of the polymer using the composition as the weights.

The interfacial tensions calculated for the functionalized and non-functionalized blend were 18 mN m^{-1} and 17 mN m^{-1}, respectively. Previous studies have shown that the interfacial tension for blends containing PE, copolymers of styrene and acrylonitrile or polymers structurally similar to these varies significantly depending on composition, blend ratio, and temperature.[60–68] These reported values are lower than those approximated by eq. (3). Note that eq. (3) assumes the polymers are symmetric and assumes incompressibility and an infinite degree of polymerization.[58]

The interfacial tensions can be used in conjunction with eq. (7), Taylor's equation,[69] to compare the theoretical particle size with the observed domain sizes.

$$\langle D \rangle_{vs} = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma} \eta_m (\frac{19}{4}\eta_r + 4)} \qquad (7)$$

Here, Γ is the interfacial tension, η_r is the viscosity ratio between the dispersed phase and the matrix, $\dot{\gamma}$ is the shear rate, and η_m is the viscosity of the matrix polymer. The estimated particle size by eq. (5) at a maximum shear rate of 27 s^{-1} for the functionalized and functionalized blends was 0.25 µm and 0.28 µm, respectively. The shear rate was found using the rotational speed (50 rpm), along with the known gap of about 1.40 mm between the barrel and the screws by eq. (8), where D is the diameter of the screw and N is the rotational speed of the screw.

$$\dot{\gamma} = \frac{\pi D N}{gap} \qquad (8)$$

These estimates are lower than the observed particle sizes as Taylor's equation does not take into account coalescence in the blend. Therefore, the observed particle sizes were compared to Wu's semi-empirical equation [eq. (9)].[70]

$$\langle D \rangle_{vs} = \frac{4\Gamma \eta_r^{-0.84}}{\dot{\gamma} \eta_m} \qquad (9)$$

The estimated particle size by eq. (9), at the maximum shear rate in the extruder (27 s^{-1}), for the reactive and non-reactive blend, was 4.4 µm and 2.0 µm, respectively, which is relatively close to that of the observed data. It should be noted that the conditions to use eq. (9) are limited to dispersed phase concentrations of 15 wt % and $\dot{\gamma} = 100$ s^{-1}. The η_m and η_r used in Wu's equation for our blends was taken from the rheological data shown in the next section.

Rheology

Blend rheology is important, as the viscosity ratio is a parameter that can dramatically alter mixing and thus dispersion of the one polymer in the other.[71–74] Complex viscosity measurements versus frequency are shown in Figure 6 and we applied the Cox–Merz rule[75] to relate it to the steady conditions of our actual blending experiments.

For the particular extruder used, the shear rate was approximated using the largest and smallest sections of the screws. The
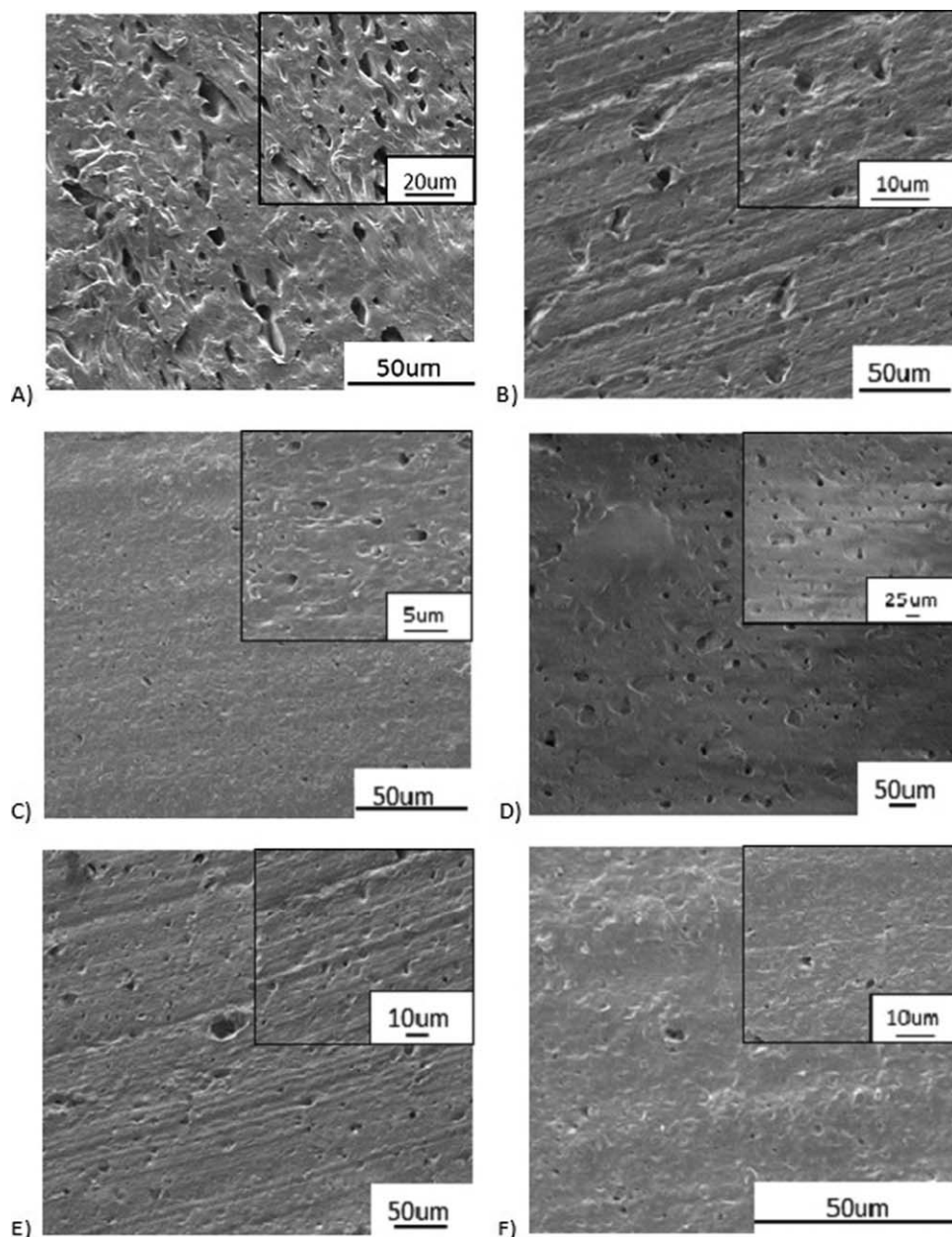
Figure 5. SEM micrographs of the various reactive and non-reactive blends: (a) non-reactive (PE-g-MAn/MA_AN) after extrusion; (b) reactive blend with diluted functional groups in MA co/terpolymers (PE-g-MAn/MA_AN/MA_AN_PAS) after extrusion; (c) and reactive (PE-g-MAn/MA_AN_PAS) after extrusion. The annealed blends are shown in (d) non-reactive PE-g-MAn/MA_AN blend, (e) reactive blend with diluted functional groups in MA co/terpolymers (PE-g-MAn/MA_AN/MA_AN_PAS), and (f) reactive PE-g-MAn/MA_AN_PAS. All blends were 70/30 wt % of PE-g-MAn/dispersed phase AN containing copolymer and extrusion was done at 200 °C in all cases. The non-reactive AN copolymer was MA_AN_Exp4 and the reactive AN terpolymer was MA_AN_PAS_Exp7. Table IV summarizes the particle sizes and blending ratios for the blends.

shear rates were approximated as 9 and 27 s^{-1} at 50 rpm in the region with the minimum and maximum diameter, respectively, by using the screw speed, gap distance and, screw diameter. Using the data obtained and data previously measured,[31] it can be seen that the η_r of the non-reactive system copolymer: PE-g-MAn = 0.19–0.23 and that of the reactive terpolymer: PE-g-MAn was 0.3–0.6 at the low and high shear rates estimated in the extruder. η_r approaching unity should theoretically result in the minimum domain sizes.[76] Previous studies demonstrated

that the amine-maleic anhydride coupling with similar chain lengths achieved a sub-micron domain size in other blend systems, even with relatively low η_r ($\eta_r < 0.05$).[38,57,77] Even using completely functional terpolymer, without dilution with non-functional copolymer, and having η_r close to unity, we were not able to achieve sub-micron dispersions. Further, we had several amino groups per chain and we were still unable to reduce the particle size as we did earlier with a single amino group at the end of a styrene/acrylonitrile copolymer chain.[31] One key
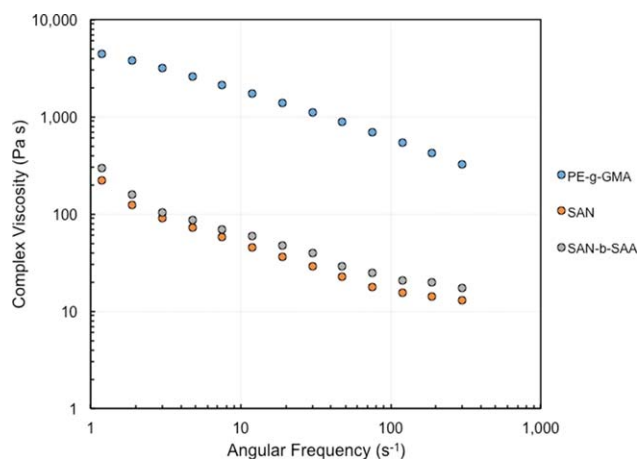
Figure 6. Complex viscosity measurements of MA/AN (blue; MA_AN_Exp4—see Table I for characterization data), MA/AN/PAS terpolymer (orange; MA_AN_PAS_Exp7, see Table III for characterization data) and PE-*g*-MAn at 200 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difference that may explain our results is that the amine on the *p*-amino styrene monomer was an aniline, which does not react as quickly as a primary aliphatic amine.[77–79] With slower coupling rates, the interface cannot be stabilized as rapidly, leading to slightly larger final domain sizes.

CONCLUSIONS

In this study, AN-containing polymers with and without an amine functionality were synthesized and were melt blended with PE-*g*-MAn, a poly(ethylene) grafted with maleic anhydride. The domain size of the dispersed phase was 1.2 µm for the reactive blend and 12.5 µm for the non-reactive blend. Upon annealing, evidence of a slow coalescence rate was seen for all blends. We concluded that the reaction coupling was responsible for the stable morphology and smaller domain sizes. We were unable to achieve sub-micron domain sizes as observed in other blends using the amine-anhydride reaction, and this was ascribed to the use of an aniline instead of a primary amine in the coupling reaction, which was earlier shown in the literature to be slower in coupling kinetics with anhydrides.

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