Grafting of Ethylene–Ethyl Acrylate–Maleic Anhydride Terpolymer with Amino-Terminated Polydimethylsiloxane during Reactive Processing

N. T. McManus, S.-H. Zhu, C. Tzoganakis, A. Penlidis

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

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ABSTRACT: An ethylene–ethyl acrylate–maleic anhydride copolymer (EEAMA) is grafted with aminopropyl polydimethylsiloxane (PDMS) via melt reactive mixing at 140°C. The materials produced split into two components based on their solubility in acetone. The acetone soluble material is highly enriched in PDMS, whereas the insoluble material contains levels of PDMS that are lower than the proportions added to the reaction mixture. It was found that for all reaction mixtures the PDMS content in the acetone insoluble solids increases with mixing time. Molecular weight distributions of materials become narrower as the amount of PDMS increases. Rheological testing shows that the level of PDMS in the mixtures and the presence of the acetone soluble fractions give rise to significant changes in the complex viscosity and elastic moduli for the polymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4230–4237, 2006

Key words: PDMS; maleic anhydride-modified polyolefin; processing aids; grafting

INTRODUCTION

Polymeric materials consisting of low surface energy polymers play important roles in polymer material engineering and design as well as in polymer processing because of their tailored surface properties[1–11] and their utility as processing aids.[8,9] Polydimethylsiloxane (PDMS) is a classic example of low surface energy material. To expand its range of utility, PDMS may be incorporated into polyolefin to modify surface and processing properties[1–3,8–11] because of its unique low surface energy. However, in mixtures of PDMS and polyolefin, PDMS tends to migrate onto the surface because of poor compatibility. This blooming effect results in a liquid PDMS surface and causes undesired contamination.

To solve this problem, chemical bonding between PDMS and polyolefin can be introduced to generate block or graft copolymers. Copolymerizing a vinyl monomer with a cyclic siloxane in the presence of catalyst can achieve this goal.[3] Another approach is to introduce functional groups into modified polyolefin, which can react with terminal functional groups of PDMS. e.g., polypropylene (PP) with terminal double bonds, which are generated by a controlled peroxide degradation process, has been developed to be capped with PDMS through catalytic hydrosilylation reaction of hydride-terminated PDMS.[10,11] This hydrosilylation can be further applied to produce PP–PDMS–PP block copolymer in a multistep synthesis.[12]

More frequently obtained are polyolefin-*graft*-PDMS copolymers[1–3,7,8,13–17] by reaction between modified polyolefin and PDMS. The copolymerization of vinyl monomers with acrylate or maleic anhydride (MA) yields modified polyolefin that are able to react with PDMS of hydroxyl or amine terminal groups. In this way, PDMS branches are grafted onto polyolefins.[1–3] Vinyl silanes[13–17] are also possible to be attached to polyethylene molecules by peroxide grafting. Multiple vinyl groups in the silane, attached on polyethylene in this way, make it possible to crosslink the saturated polyolefin by water moisture. Usually, these reactions between modified polyolefin and PDMS can be accomplished in the melt, eliminating the need for solvent and the subsequent solvent removal.

Grafting modification of polymers gives rise to changes in a number of properties. The degree of grafting can be not only detected by analytical techniques such as nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC),[18–24] but also is reflected in changes of the rheological properties, which are very sensitive to the molecular architecture, the polydispersity of the molecular chain length distribution, and homogeneity.[25–32] It is often necessary to combine the results from different tech-

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Correspondence to: N. T. McManus (nmcmanus@cape.uwaterloo.ca).

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niques to piece together a full picture of polymer structures.

In this study, we synthesize a silicone-containing polyolefin that could find potential applications as a processing agent or surface property modifier. The material is obtained by reacting a commercial copolymer of ethylene, ethyl acrylate, and maleic anhydride with an amine terminated PDMS in the melt phase. The reaction was studied with respect to the amount of PDMS and the reaction time. In addition, the structure and the composition of the derived polymers were analyzed by GPC, NMR, and rheological techniques.

EXPERIMENTAL

Materials

The terpolymer of ethylene–ethyl acrylate–maleic anhydride (EEAMA) was Lotader 8200 (6.5 wt % EA and 2.85 wt % MA) from Atofina. The aminopropyl terminated polydimethylsiloxane (PDMS) was PS512, from United Chemical Technologies (contained 0.0776 mmol equivalents of amine per gram ($M_W \approx 26{,}000$) and had a viscosity of about 800–1200 cS.).

Reactive mixing

Lotader 8200 was melted in a Haake Rheocord 3000 batch mixer at 140°C. In the different mixes, 10, 25, and 50 parts by weight of PDMS per hundred parts of EEAMA (phr) were added in the melt and reacted for a certain time period. The mixer rotors were run at 30 rpm. In runs where the reaction kinetics was followed, samples were taken at preset reaction times from the compounds to analyze the PDMS content attached to the EEAMA.

Precipitation of EEAMA/PDMS compounds

One gram of sample taken from the product compounds was dissolved in 20 mL toluene at 100°C to obtain clear solutions. The solutions were cooled and 200 mL of acetone were added to precipitate the reacted EEAMA copolymer. The precipitated suspensions were filtered and dried for further analysis. The soluble component (sol) was obtained from the filtered solution after evaporation of acetone.

Infra-red spectroscopic analysis

IR spectra of the samples were collected with an IR spectrometer (Excalibur, Bio-rad). Films for IR measurements were obtained by casting a 1–2% solution of the samples in toluene on a sodium chloride disk. A uniform and continuous film of ~0.1 mm in thickness was formed after evaporating the toluene at 60°C. Because of the sensitivity of peak height to the IR film thickness, six spectra were collected for each sample at different spots on the disk, and the averaged peak heights and deviations are obtained. Peak heights in a spectrum were obtained using a universal baseline for the whole spectra. For the purpose of calibration, eight PDMS/EEAMA mixtures with prescribed PDMS contents were prepared and their IR spectra collected. Calibration curves relating to the peak height ratio and PDMS contents were constructed using the relative heights of those peaks in the IR spectra from EEAMA and PDMS (see below).

^{1}H and ^{13}C nuclear magnetic resonance

Samples (0.1 g) were dissolved in 5 mm NMR tubes in 1 g of deuterated toluene (toluene-d_8, Aldrich) at a temperature of 100°C. ^{1}H and ^{13}C NMR spectra were acquired on a NMR spectrometer (AVANCE 300, Bruker) using a high temperature module. A 1D one pulse program and an inverse-gate pulse program were used to acquire ^{1}H and ^{13}C spectra, respectively. The pulse delay times between scans were 6 and 10 s for ^{1}H and ^{13}C, respectively. Peak integration was conducted for quantitative analysis.

Gel permeation chromatography

The molecular weight distribution (MWD) of the reacted EEAMA copolymers was measured by a GPC (Alliance GPCV 2000, Waters) equipped with a refractive index detector and a viscometer, and the number (M_n), weight (M_w), and viscosity (M_v) average molecular weights were calculated. Samples were dissolved in 1,2,4-trichlorobenzene at 140°C and the eluent flow rate through the column (Styragel® HT6E, Waters) was 1 mL/min. Universal calibration and calibration using polyethylene standards (SRM 1475a, NIST) were applied to determine the molecular weight averages.

Rheological measurements

The linear viscoelastic properties of the samples were measured using a rheometer (AR 2000, TA Instrument) with a cone-and-plate fixture (40 mm in diameter, cone angle = 1°) at 140°C. The frequency sweep tests (from 0.001 to 100 Hz) were carried out at a strain of 8% under a N_2 purge at 10 mL/min.

RESULTS AND DISCUSSION

Torque change during melt reaction

Figure 1 shows the reaction scheme between MA in EEAMA and amine groups in PDMS. The reaction leads to the formation of amide links between EEAMA and PDMS molecules. Carboxyl groups in the maleic

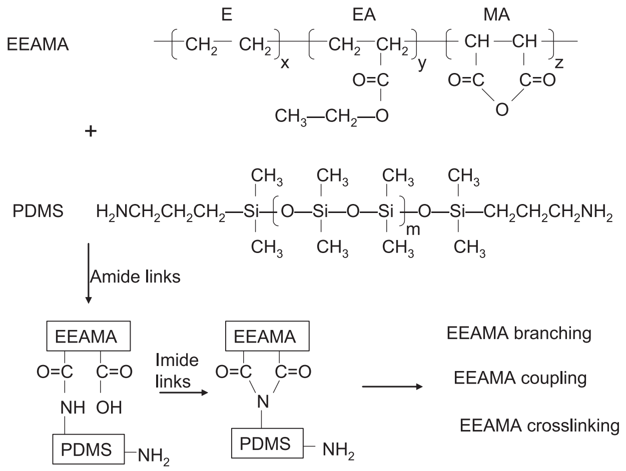

Figure 1 The reaction scheme for EEAMA and PDMS.

TABLE I
The PDMS Content Calculated from IR Spectra and ^{1}H/^{13}C NMR Spectra of PDMS/EEAMA Compounds

Sample	FTIR (phr)	^{1}H NMR (phr)	^{13}C NMR (phr)
10 phr PDMS			
Precipitated	5.0	5.7	
Sol		22.1	
25 phr PDMS			
Precipitated	15.8	14.9	
Sol		56.9	
50 phr PDMS			
Precipitated	21.6	25.5	19.9
Sol		127.8	158

acid are only intermediate products of the amide formation, which can further react with either amide or the amine to form imide and amide links between EEAMA and PDMS. The attachment of PDMS onto EEAMA by amide and imide links forms the branching grafts. The terminal amine groups in the PDMS can couple EEAMA molecules or crosslink the EEAMA molecules with multiple MA units. This kind of branching, coupling, and crosslinking are expected to increase the viscosity of the melt.

Figure 2 shows the torque change during the mixing of EEAMA with 10, 25, and 50 phr PDMS. The torque increases significantly at the initial stage of mixing after the PDMS is added, then decreases slowly to level off. The level-off torque value increases with the amount of PDMS added up to 25 phr, because of the reaction between PDMS and EEAMA molecules. However, this value becomes smaller when the compound contains 50 phr PDMS, but it is still larger than that of pure EEAMA. The smaller level-off torque in 50 phr than 10 and 25 phr PDMS/EEAMA compounds is attributed to a better lubricating effect of the sol component in 50 phr compound that has a much higher concentration of PDMS than those in the other two compounds (cf. Table I).

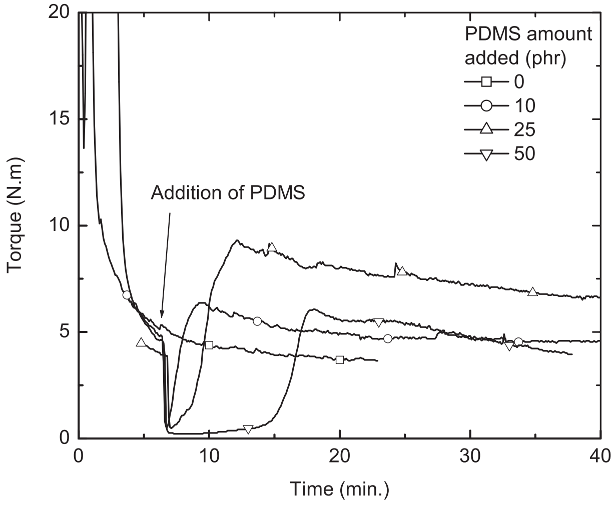

Figure 2 The torque during the melt reactive mixing of 0, 10, 25, and 50 phr PDMS/EEAMA.

Reaction kinetics

The reaction between amine and anhydride end groups of polyethylene has been reported in melt reactive mixing at 200°C.[33] The conversion of the functional groups is shown to reach over 50% within 2 min. The reaction of MA in an EEAMA with the terminal amine group in polyamide-66, as reported in Ref. 34 is also found to complete in 5 min. The same reaction employed in this study is also rapid, with the torque during melt mixing reaching a maximum after addition of PDMS. Increase in torque during mixing because of the grafting reaction have been observed by other researchers in studying the melt grafting of PDMS onto polyethylene.[4] At the initial stage of the mixing, PDMS molecules are expected to attach to EEAMA by chemical bondings. Compound samples taken from the melt after the torque maximum appear to be solid without any visible sign of liquid PDMS. The PDMS/EEAMA compounds completely dissolve in toluene at elevated temperatures with no apparent gel presence. Addition of acetone to the solution causes precipitation; the minor component is soluble in acetone. The acetone soluble component turns out to be a gummy substance after drying. It is expected to contain not only liquid PDMS but also the EEAMA bonded to the PDMS.

The torque decreases gradually after the maximum, as shown in Figure 2, are probably due to the dispersion of the sol in the precipitated fractions of the compound, along with possible exchange reactions of PDMS with the EEAMA molecules in the sol and precipitated fractions. These two effects can change

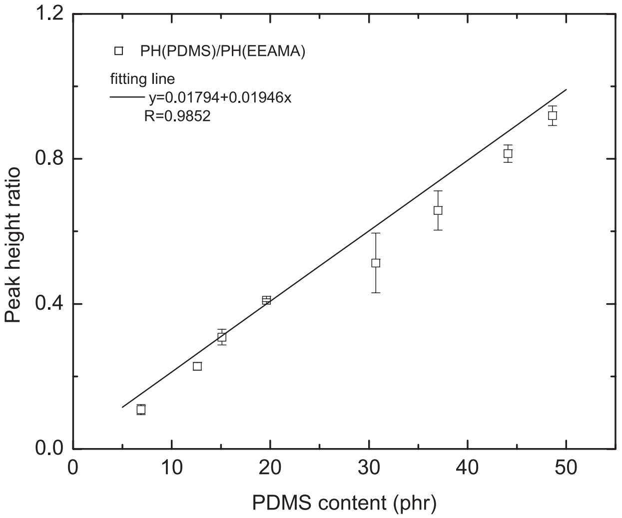

Figure 3 The height ratios of the PDMS peaks to the EEAMA peaks in the IR spectra of the eight mixtures of EEAMA and PDMS.

the PDMS content in the precipitated portion as the reaction time increases. Thus, the effect of reaction on the PDMS content in the precipitated fraction of the compounds is investigated as a function of mixing time.

Reaction time

An IR method was used to measure the PDMS content in the precipitated compounds using a calibration line.

IR calibration

In the IR spectra of EEAMA, PDMS, and their mixtures, EEAMA and PDMS show distinct characteristic peaks which do not overlay each other. The EEAMA peaks occur at 2919 and 2850, 1782 and 1735, 1463 and 1473, 731 and 720 cm^{-1}, while the PDMS peaks appear at 1261, 1093, and 1021 and 802 cm^{-1}.[35,36] Since peak heights vary according to their relative concentration, the IR spectra of the PDMS/EEAMA mixtures or compounds yield the PDMS content once the relative peak heights are calibrated with regards to the concentration. The sum of height for all four PDMS peaks was compared against sum of all eight EEAMA peaks, as shown above, in the IR spectra of the EEAMA/PDMS compounds. This height ratio was related to the PDMS content by the calibration line as shown in Figure 3. This shows the height ratios as a function of the PDMS content in eight PDMS/EEAMA mixtures. The linearity in the calibration data is good and the fitting line has an $R^2 = 0.9847$. By using the calibration fitting equation, the PDMS content in a compound is obtained from the height ratio of PDMS peaks with respect to EEAMA peaks in their IR spectra. The PDMS contents in the precipitates of several PDMS/EEAMA compounds thus calculated are shown in Table I. They are in good agreement with those obtained independently from ^{1}H/^{13}C NMR measurements, listed also in Table I.

PDMS content of the precipitated compounds as a function of reaction time

Samples were taken at different reaction times for a 50 phr PDMS/EEAMA compound. The PDMS contents in the precipitates were determined using the above IR method. Figure 4 shows the PDMS contents in the precipitates as a function of reaction time. The PDMS content increases with time and reaches 34 phr after about 40 min. As the mixing proceeds, the PDMS-concentrated sol fraction is dispersed more evenly in or reacted with the precipitated fraction in the PDMS/EEAMA compound, leading to an increase in the PDMS content of the precipitated samples, which accompanies the slow decrease in the viscosity (as shown on the torque curve in Fig. 2). In other words, the liquid PDMS is initially consumed readily by the sol fraction EEAMA and serves as a reservoir to provide the PDMS for further reaction during the melt mixing, which results in an increase in the PDMS content of the precipitated samples with time.

Effect of added amount of PDMS on final product

In the three PDMS/EEAMA compounds used, 10, 25, and 50 phr PDMS correspond to only 1.6, 3.88, 5.82 mmol of NH_2 groups in comparison with 28.7 mmol of

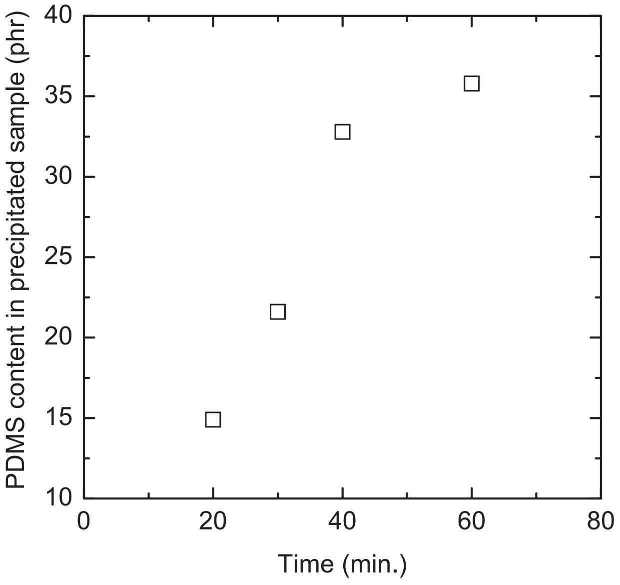

Figure 4 The PDMS content in the precipitated sample, as calculated from the IR peak ratio by means of the calibration line, as a function of reaction time for a 50 phr PDMS/EEAMA compound.

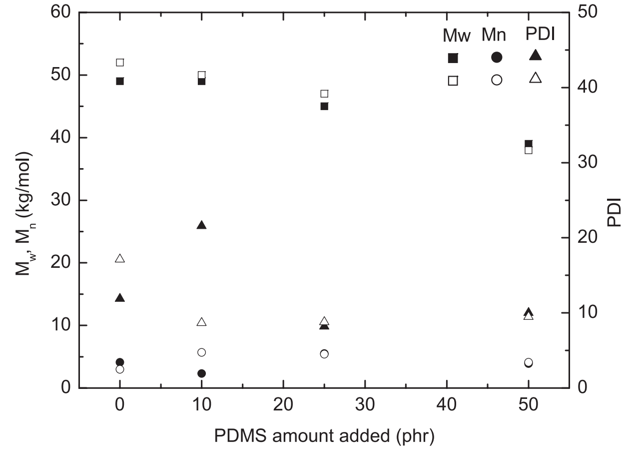

Figure 5 Effect of PDMS amount added on the molecular weights (M_n, M_w, and PDI) of the EEAMA/PDMS compounds.

MA in the 100 parts of EEAMA. The MA amount is, therefore, in excess in the reaction between the MA and the amine. Increasing the amount of PDMS would involve more MA, and thus more EEAMA molecules would be grafted by PDMS.

Figure 5 shows the changes in molecular weight characteristics as a function of the PDMS amount. The filled and open symbols represent two measurements for each sample. The number average molecular weight, M_n, is essentially constant while weight average molecular weight, M_w, and polydispersity index (PDI) decrease slightly as the amount of PDMS is increased.

The changes in the molecular weight averages should only be regarded as qualitative since the chemical composition of the products changes in parallel with any changes in molecular weights. It had been assumed that a larger amount of PDMS would lead to a high degree of branching and chain coupling thus increasing molecular weights. This was not observed in the molecular weight as measured by GPC, which is perhaps not surprising since the GPC measures the hydrodynamic volumes of polymer in solution which is related not only to the chain length but also chemical composition. Quantitative comparisons of molecular weight averages should only be made for polymers whose chemical structures and architectures are similar.[18–23]

PDMS has different solubility from the base EEAMA polymers and the three mixtures have differing levels of PDMS and so it is likely that, grafting of PDMS onto EEAMA would result in a significant change in the hydrodynamic volume for a given molecular weight. This is illustrated by examining a plot of the product intrinsic viscosities, [η], in relation to M_w (Fig. 6). This clearly shows that as the level of PDMS in the mixture increases there is an increase in curvature for the log [η] versus log M_W plot. In compounds with a similar chemical composition this would be indicative of increased branching but here is likely a compounded effect from increased branching and differences in chemical structure.

This could obscure any change in the molecular chain length after reaction of EEAMA and PDMS. The effect of chain branching and coupling between EEAMA and PDMS also has a marked effect on the compound rheological properties, which will be discussed later.

^{1}H/^{13}C NMR spectra analysis

The compound samples, both precipitated and sol, show peaks in their ^{1}H and ^{13}C spectra which can be readily assigned to the protons in PDMS and EEAMA. In the ^{1}H NMR spectra, the methyl protons in the PDMS ($Si{-}CH_3$) register a major peak around chemical shift $d = 0.21$ ppm.[19,20,37–41] The major peak at 1.32 ppm is attributed to the methylene protons in the backbone EEAMA. Another diagnostic signal for the EEAMA is the signal at 4.1 ppm for the OCH2 from the ethyl-acrylate component. In the ^{13}C spectra, the carbons ($Si{-}CH_3{-}CH_2{-}$, $Si{-}CH_3$, and $Si{-}CH_2{-}$) in the PDMS produce the major signal peaks at 0.8 ppm. The major EEAMA peaks occur around 29.8 ppm.

The integrations of the signals in the NMR spectra allow for evaluation of PDMS content in the PDMS/EEAMA compound. For the ^{1}H spectra, the peaks at 0.21 and 1.32 ppm were chosen to represent PDMS and EEAMA. The conversion factor from integral ratio of ethylene to $Si(CH_3)_2$ phr should be (unit mass ratio) $\times$ (proton ratio) $= (28/74) \times (1.5) = 0.5675$. In the ^{13}C

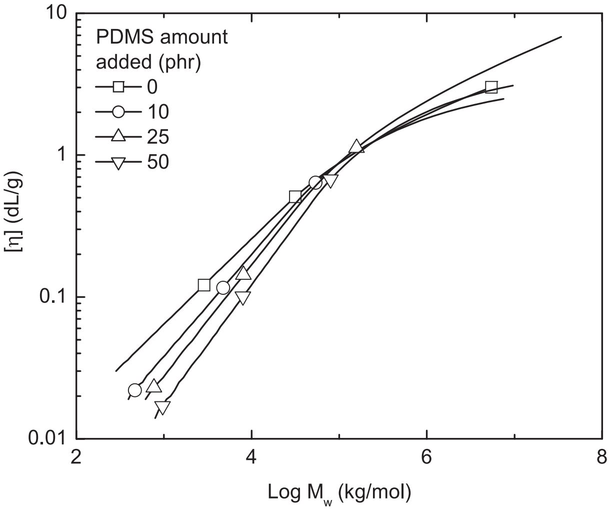

Figure 6 The hydrodynamic volume, measured by viscometry, as a function of molecular weight for 0, 10, 25, and 50 PDMS/EEAMA compounds.

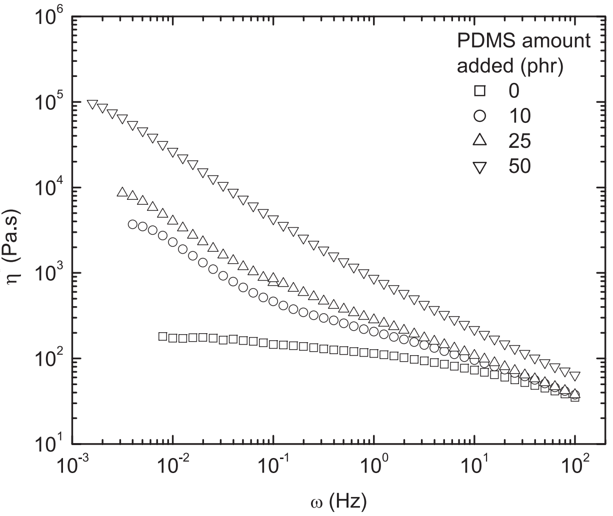

Figure 7 Linear viscosity, η^*, versus frequency, ω, of EEAMA and EEAMA/PDMS compounds with 10, 25, and 50 phr PDMS (unprecipitated).

spectra, peaks at 0.8 and 29.8 ppm are representing the PDMS and EEAMA, respectively. The ratio of the peak integrations are multiplied by the unit mass ratio of PDMS and averaged EEAMA: (unit mass ratio) × (carbon ratio) = (30.97/74) × (1) = 0.4185. The values obtained are listed in Table I along with the values determined from the IR method. The PDMS amount in the acetone soluble fraction is greater than double of the original PDMS amount added for all the three compounds.

The sol component is a concentrated PDMS/EEAMA compound which is soluble in acetone. The EEAMA in the sol probably comes from the high molecular weight portion. From the weight fraction of EEAMA, the molar ratios of units are: $x/z = 111$, $x/y = 49.8$, and $y/z = 2.23$ (for meaning of x, y, z, see Fig. 1). According to the number average molecular weight measured for Lotader 8200, one EEAMA molecule has on average one MA unit. Therefore, the portion with higher than average molecular weight reacts preferentially with more PDMS because of a higher local MA concentration, and hence may produce a higher degree of grafting which would tend to be part of the acetone-soluble fraction.

Rheological analysis

Effect of PDMS amount

Figure 7 shows the complex viscosity, η^*, of PDMS/EEAMA samples as a function of frequency. After addition of PDMS, the viscosity plateau of the pure EEAMA in the low frequency region is replaced by the increasing slopes in the compound samples with higher levels of PDMS. This implies that the structure of EEAMA undergoes marked changes (branching and crosslinking) due to the grafting of PDMS.

Effect of sol component

Figure 8 shows the linear storage, G′, and loss, G″, moduli of three compounds with and without precipitation treatment. In 10 phr PDMS/EEAMA compounds, the values of G′ for the precipitated samples are much lower than the unprecipitated samples at low frequencies. They merge together at high frequencies (cf. Fig. 8). As PDMS content increases, this difference between the precipitated and unprecipitated samples becomes smaller at 25 phr, and disappears at 50 phr. Note that this is actually the effect of sol component in the compound samples because the precipitation treatment washes away the sol component in the precipitated samples. However, the precipitation treatment does not affect very much the values of G″.

Figure 9 shows the plots of double log G′ versus G″ for EEAMA and three EEAMA/PDMS compound samples. For pure EEAMA, a linear line is capped by an upswing at low values of G″. In the case of compound samples, similar trends are observed: as the

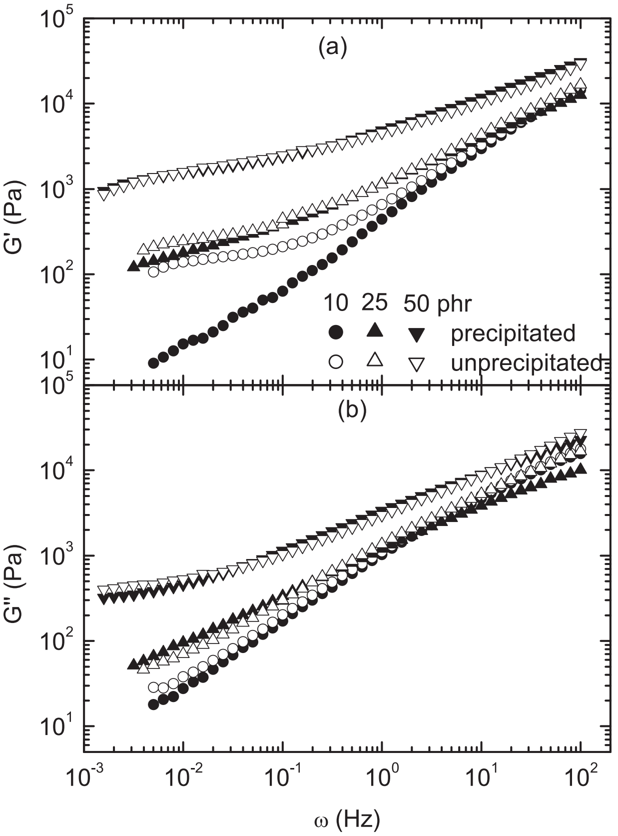

Figure 8 Storage, G′, and loss, G″, moduli as function of frequency, ω, of EEAMA/PDMS compounds with 10, 25, and 50 phr PDMS (precipitated and unprecipitated).

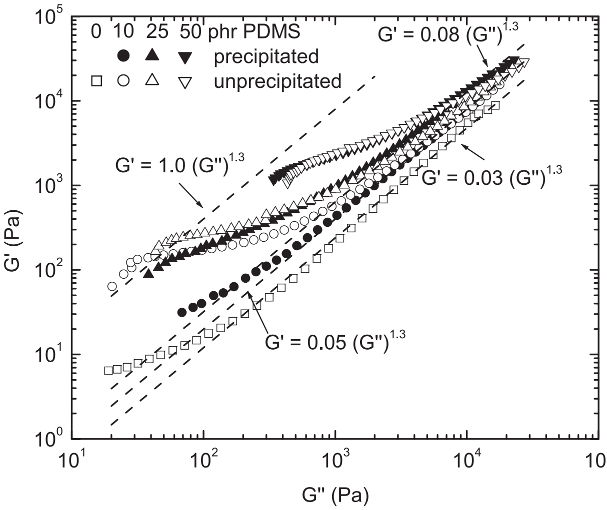

Figure 9 Log G′ versus log G″ plots of EEAMA and EEAMA/PDMS compounds with 10, 25, and 50 phr PDMS (precipitated and unprecipitated).

PDMS content increases, the linear part shows almost parallel upshifts to higher G′ levels; and the upswing at the end moves to higher G″ values. The difference between the unprecipitated and the precipitated samples is apparent from the position of the upswing in 10 phr, becomes smaller in 25 phr, and unnoticeable in 50 phr PDMS/EEAMA compound. For linear polymers, G′ and G″ are related by[42]

$$G' = J_e^0(G'')^2 \tag{1}$$

where J_e^0 is the linear equilibrium recoverable compliance. It is well-known that J_e^0 is a material function dependent on the molecular weight and its distribution. In polybutadiene blends of two different molecular weights,[42] increasing the fraction of the high molecular weight component can give rise to higher values of J_e^0. It has been reported that for metallocene polyethylene with long chain branching, higher degree of branching causes an upshift in the log G′ versus log G″ plot,[43] where a relation was obtained (eq. (2))

$$G' = 0.00541(G'')^{1.42} \tag{2}$$

We fit the linear part of our results in Figure 9 and the relations between G′ and G″ are shown with the fitting lines (dashed lines). The estimated value of the power exponent is 1.30 in agreement with typical values for most polymers ranging from 1.26 to 1.50. The values of J_e^0 (m^2/N) obtained is shown in Figure 9. An increase in the amount of PDMS leads to higher levels of J_e^0, suggesting an increase in the molecular weight and degree of grafting.

Degree of grafting

It has been noticed that a higher degree of grafting on the rubber particles of ABS lead to pronounced increases in both G′ and G″ values.[26] An increase in the degree of branching in metallocene polyethylene gives rise to parallel upshifts of the lines to higher elastic region.[43] For the graft copolymers from EEAMA and PDMS, the precipitated samples contain less PDMS than the unprecipitated sample from the same compounds. A higher amount of PDMS in the sample implies a higher degree of grafting, which increases the complex viscosity and the elastic modulus at low frequency (Figs. 7 and 8) and causes upshifts in double logarithmic modulus plots (Fig. 9). This can be explained by the higher elasticity due to the higher degree of grafting.

CONCLUSIONS

A PDMS grafted polyolefin, which can be potentially applied as a processing agent or a surface property modifier, is synthesized via reactive melt mixing of EEAMA and aminopropyl PDMS. The reaction between MA and NH_2 occurs readily during melt mixing of EEAMA and PDMS. It is likely that the higher molecular weight portion of EEAMA contains more MA units and thus reacts preferentially with PDMS. This fraction of the PDMS/EEAMA compound forms a component that is soluble in acetone. The larger fractions from different mixtures are insoluble in acetone and have lower PDMS levels with respect to the amount of PDMS in the original mixtures. The PDMS content of the acetone insoluble fraction from PDMS/EEAMA compound increases with mixing time. Higher levels of PDMS added in the compounds result in a narrower MWD as measured by GPC, and a significant increase in the linear viscosity, elastic, and loss moduli. Rheological data verifies that the sol component in the PDMS/EEAMA compound is very elastic presumably because of high PDMS content and high degree of grafting.

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References

1. Corning, D. Brit. Pat. 1,286,460 (1972).
2. Yakes, K. P. WO 9810724 (1998).
3. Smith, S. D.; Wnuk, A. J.; Gerber, M. S. U.S. Pat. 5,476,901 (1995).
4. Pattanakul, W.; Magaraphan, R.; Grady, B. P. J Appl Polym Sci 2001, 82, 519.
5. Ginic-Markovic, M.; Choudhury, N. R.; Dimopoulos, M.; Matisons, J.; Kumudinie, C. J Appl Polym Sci 2001, 80, 2647.
6. Garcia, M.; de Rooij, M.; Winnubst, L.; van Zyl, W. E.; Verweij, H. J. J Appl Polym Sci 2004, 92, 1855.

7. Munoz, P. M. P.; Vargas, M. D.; Werlang, M. M.; Yoshida, I. V. P.; Mauler, R. S. J Appl Polym Sci 2001, 82, 3460.
8. Yilgor, I.; Yilgor, E.; Suzer, S. J Appl Polym Sci 2002, 83, 1625.
9. Yilgor, E.; Sinmazcelik, T.; Yilgor, I. J Appl Polym Sci 2002, 84, 535.
10. Malz, H.; Tzoganakis, C. Polym Eng Sci 1998, 38, 1976.
11. Long, J.; Tzoganakis, C.; Chen, P. J Appl Polym Sci 2002, 88, 3117.
12. Fu, P.-F.; Glover, S.; King, R. K.; Lee, C.-L.; Pretzer, M. R.; Tomalia, M. K. Polym Prepr 2003, 44, 1014.
13. Sen, A. K.; Mukherjee, B.; Bhattacharyya, A. S.; De, P. P.; Bhowmick, A. K. J Appl Polym Sci 1992, 44, 1153.
14. Palmlof, M.; Hjertberg, T.; Sultan, B. A. J Appl Polym Sci 1991, 42, 1193.
15. Konar, J.; Bhowmick, A. K. J Appl Polym Sci 1993, 48, 1579.
16. Shieh, Y.-T.; Tsai, T.-H. J Appl Polym Sci 1998, 69, 255.
17. Ghos, P.; Chattopadhyay, B.; Sen, A. K. Polymer 1998, 39, 193.
18. Yang, L.; Zhang, F.; Endo, T.; Hirotsu, T. Polymer 2002, 43, 2591.
19. Boileau, S.; Bouteiller, L.; Kowalewska, A. Polymer 2003, 44, 6449.
20. Cai, G.; Weber, W. Polymer 2004, 45, 2941.
21. Storey, R. F.; Donnalley, A. B.; Maggio, T. L. Macromolecules 1998, 31, 1523.
22. Seo, Y.; Kim, Y. Polymer 1994, 35, 4163.
23. Crouzet, P. A.; Martens, M.; Mangin, A. J Chromatogr Sci 1971, 9, 525.
24. Lederer, K.; Beythollahi-Amtmann, I.; Billiani, J. J Appl Polym Sci 1994, 54, 47.
25. Tuminello, W. H. Polym Eng Sci 1986, 26, 1339.
26. Aoki, Y. Macromolecules 1987, 20, 2208.
27. Han, C. D.; Kim, J. J Polym Sci Part B: Polym Phys 1987, 57, 1605.
28. Vega, J. F.; Santamaria, A. Macromolecules 1998, 31, 3639.
29. Harrel, E. R.; Nakajima, N. J Appl Polym Sci 1984, 29, 995.
30. Han, C. D. J Appl Polym Sci 1986, 32, 3809.
31. Ha, M. H.; Kim, B. K.; Kim, E. K. Polymer 2004, 93, 179.
32. Graebling, D.; Muller, R.; Palierne, I. Macromolecules 1993, 26, 320.
33. Jones, T. D.; Macosko, C. W.; Moon, B.; Hoye, T. R. Polymer 2004, 45, 4189.
34. Moan, M.; Huitric, J.; Mederic, P. J Rheol 2000, 44, 1227.
35. Silverstein, R. M.; Bassler, G. C.; Morril, T. C. Spectrometric Identification of Organic Compounds, 5th ed.; Wiley: New York, 1991.
36. Noto, V. D. In Spectroscopic Techniques in Biophysics; Gacometti, G. M., Giacometti, G., Eds.; IOS: Amsterdam, 2001; p 149.
37. Ibbett, R. N. NMR Spectroscopy of Polymers; Blackie: Glasgow, 1993.
38. Tonelli, A. E. NMR Spectroscopy and Polymer Microstructure: The Conformational Connection; VCH: New York, 1989.
39. Wang, W.-J.; Ye, Z.; Fan, H.; Li, B.-G.; Zhu, S. Polymer 2004, 45, 5497.
40. Dutta, N.; Karak, N.; Dolui, S. K. Prog Org Coat 2004, 49, 146.
41. Heinen, W.; Rosenmoler, C. H.; Wenzel, C. B.; de Groot, H. J. M.; Lugtenburg, J.; zan Duin, M. Macromolecules 1996, 29, 1151.
42. Berger, L.; Meissner, J. Rheol Acta 1992, 31, 63.
43. Su, Z.; Zhao, Y.; Xu, Y.; Zhang, X.; Zhu, S.; Wang, D.; Wu, J.; Han, C. C.; Xu, D. Polymer 2004, 45, 3693.