

Properties of Poly(ethylene 1-octene)-*g*-Maleic Anhydride Copolymers Prepared via Solvothermal Process

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ABSTRACT: The poly(ethylene 1-octene)-*g*-maleic anhydride copolymers (POE-*g*-MAH) with high grafting degree (GD) (>9%) have previously been obtained by a solvothermal method in our laboratory. It is found that the low GD (less than 2.5%) did not change the bulk properties of polyolefin elastomers (POE). Therefore, it is worth further understanding whether a high GD POE-*g*-MAH copolymer differs from the pure POE in its comprehensive properties and performance. In this article, POE-*g*-MAH with different GDs were synthesized and characterized by thermogravimetric analyze (TGA), differential scanning calorimetry (DSC), wide angle X-ray diffraction spectroscopy (WAXD), and dynamic rheological testing. The

results show that the thermal decomposition temperature, melting points, the crystallization temperatures, and the crystallinities were decreased by the increasing GD. By WAXD, three peaks respectively, attributed to the amorphous phase, the (110) and (200) interferences of the orthorhombic unit cell were detected, and they also decreased by the increasing GD. And the POE-*g*-MAH copolymers had higher storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) than those of pure POE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1069–1075, 2009

Key words: POE-*g*-MAH; thermal properties; rheological behavior; crystallization

INTRODUCTION

The development of metallocene catalyst technology¹ has recently led to the synthesis of a great variety of new polyolefins with different structures. Among them, poly(ethylene 1-octene) (POE) has attracted much attention due to its high octane content (more than 18%), unique uniform distribution of comonomer, and narrow molecular weight distribution. POE as a thermoplastic elastomer can compete against conventional elastomers in the production of polyolefin-based blends because it is produced in the pellet form, which allows for faster mixing and wider handling and compounding options.² Because of its good thermal stability, weather resistance, ageing resistance, and excellent toughness, POE can also be used as a good toughening modifier.^{3,4} However, POE with weak polar property is not a good modifier for polar polymers, for example, poly(butylene terephthalate) (PBT)⁵ and nylon.^{6–8} To improve the miscibility between polar and nonpolar polymers, POE was usually functionalized or modified by grafting some unsaturated low molecular com-

pounds inclusive of polar functional groups.^{9,10} As one of the most commonly used monomers having its high reactivity in successive reactions, maleic anhydride and silane have been successfully grafted onto the POE through molten method.^{8,11,12} Because of the increased solubility and reactivity of compounds and polymers under high temperatures and pressures, solvothermal reactions could be used to synthesize chemical compounds or copolymers which are hard to produce by traditional methods.^{13,14} Recently, our group has successfully prepared ABS-*g*-MAH¹⁵ and poly(ethylene 1-octene)-*g*-maleic anhydride copolymers (POE-*g*-MAH)¹⁶ copolymers via this method, and graft copolymers with higher grafting degree (GD) were obtained. Further studies demonstrated that the graft copolymerization could be carried out in both good solvents and poor solvents of POE (including less hazardous solvents). Especially, the POE-*g*-MAH copolymers with both higher GD and lower gel content could be obtained in good solvents. A number of authors have studied on the synthesis of polyolefin graft copolymers by reactive extrusion or other forms of melt phase processing. Primary concerns are the structures of the formed graft copolymers, the mechanisms of graft formation, and their relationship to processing conditions rather than an analysis of the reaction or reaction products. The few detailed studies of the grafting copolymers

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suggest that their properties strongly depend on their structures.

It is well known that a grafting polymerization will become efficient only when the number of grafted units is dominant and the side reactions (like crosslinking, degradation etc.) are negligible.¹⁷ The competition between the grafting and side reactions usually both leads to the significant changes of the grafted copolymers' properties such as the melt flow index, the soluble fraction of the graft copolymer,¹⁸ and the phase behavior.¹⁹ In general, the properties of the grafting copolymer with a low GD (<2.5%) are similar to those of the matrix, so little works on the properties of the grafting copolymers were reported up to now. In our previous work, the POE-g-MAH copolymers with both higher GD (>9%) and lower gel content (<15%) can be obtained by the solvothermal method. The high GD will change the polarity of the chain, the nature of the long chain branching, and the arrangement of the short chain branchings in the macromolecule, which leads to the modified properties of the grafting copolymer. As a compatibilizer of polymer blends, both the GD and the properties of grafting copolymers would have effect on the properties of immiscible polymer blends, so it is important to investigate the properties of grafted copolymers. On the other hand, it is critical to investigate the effect of the different GD on the properties of grafted copolymers. The GD of the copolymers prepared by the solvothermal method can be controlled in the range of 0–10%. Therefore, the article aims to investigate the thermal properties, crystalline behavior, and rheological properties of POE-g-MAH copolymers.

EXPERIMENT

Synthesis

POE with 18% 1-octene mixture (Engage 8003) was purchased from Dupont Dow Elastomer. The purified POE-g-MAH copolymers were prepared through the solvothermal process.¹⁶ The determination of the GD and the gel content of the POE-g-MAH were reported in our previous paper.¹⁶ The samples used have the 0–10% GD and less than 15% gel content.

Thermogravimetric analysis

The thermal-stability analysis was performed using a Perkin–Elmer TGA7 Thermogravimetric Analyzer at a heating rate of 20°C/min under nitrogen atmosphere.

Thermal analysis

Differential scanning calorimeter (DSC) measurements were conducted in a Perkin–Elmer PYRIS-1 DSC. Transition temperatures were calibrated using indium and zinc standards. Samples (about 5 mg) were heated from the room temperature to 125°C at a rate of 10°C/min and held for 5 min to destroy any residual nuclei before being cooled to room temperature at 10°C/min, and then reheated in the melting range at the same conditions. All DSC measurements were performed under an inert (N₂) atmosphere at a heating rate of 10°C/min.

X-ray diffraction

XRD patterns were obtained using a Philips PW1710 X-ray diffractometer equipped with a Ni-filtered Cu-K_α source. The voltage and the current of the X-ray tubes were 40 kV and 100 mA, respectively.

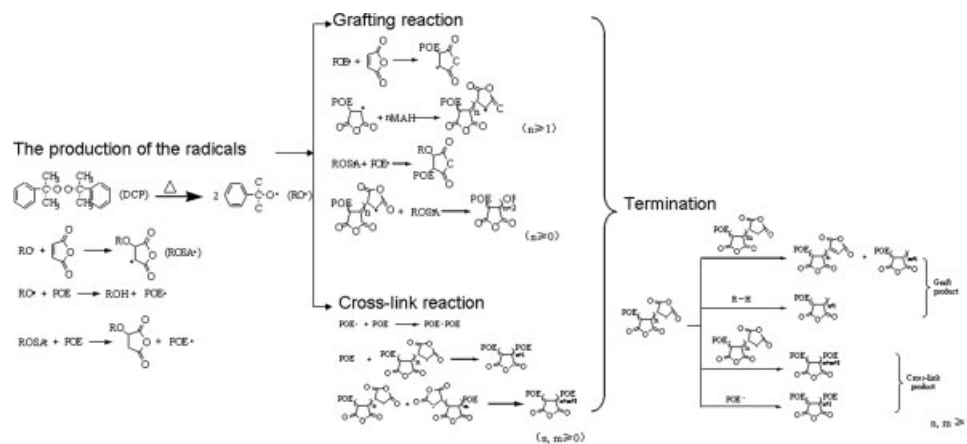
Rheological measurements

The rheological properties of the blends were measured in a rotational rheometer (Gemini 200HR Rheometer, Bohlin Instruments, UK) equipped with a parallel plate geometry. All tests were conducted under nitrogen atmosphere. Steady shear viscosities, η^* , were measured at 150°C. Rheological properties of the virgin POE and the POE-g-MAH copolymer were measured using 20 mm diameter parallel plates (the gap between two plates was 1.0 mm) in oscillatory shear mode. Dynamic storage modulus, G' , and loss modulus, G'' , were determined as a function of frequency (F), with strain of 5% at 150°C. The range of frequency was from 0.01 to 100 Hz. A fixed strain of 5% was used to ensure that measurements were taken within the linear viscoelastic regime of the materials.

RESULTS AND DISCUSSION

Thermogravimetric analysis

It is well known that the thermal stability of materials is related to their molecular chemical bond strength, structural rigidity and regularity, crosslink density, molecular imperfection, and so on.²⁰ When maleic anhydride (MAH) is grafted onto a POE backbone, its structural regularity (such as degree of branching) will be changed and thus leads to the differing thermal stability of POE. The reaction mechanism was listed in Scheme 1. From Scheme 1, it could be seen that the reaction is very complicated, which includes the production of radicals, grafting reaction, crosslinking reaction and the termination reaction. To eliminate the effect of the crosslink reaction, the different GD samples with the similar gel content



Scheme 1 The scheme of the reaction mechanism.

were selected. The thermal stability of a material is usually assessed by thermogravimetric analysis (TGA) where the mass loss due to volatilization of degraded by-products is monitored in function of temperature. When the heating is operated under an inert gas flow (nitrogen), a nonoxidative degradation occurs. Figure 1 shows TGA thermograms of the virgin POE and POE-g-MAH graft copolymers under nitrogen atmosphere. In Figure 1, pure POE and POE-g-MAH had the significant mass loss at about 460°C, and the onset degradation temperature decreased with the increase of the GD. Maleic anhydride can be grafted onto POE backbone in four ways as shown in Scheme 2. Structure 1 in Scheme 2 is very difficult to form because of stereo-hindrance effect. The tertiary carbon atoms have turned into the quaternary though the number of the side chains do not increase, which will affect the thermal stability. In Structure 2 and Structure 3, the number of the

side chains increases, resulting in the weakened thermal stability. In Structure 4, the number of the side chains hardly change so that the degradation temperature of POE is not affected. The results from Table I show that the degradation temperature of POE shifted from 469.6°C to 455.8°C with increasing the GD. From Figure 1, it can also be seen that several percentages of weight loss occur about 250°C, which could be assigned to the decomposition of the crosslink POE or the disaggregation of MAH in HDPE-g-MAH (in Scheme 1).

Melting and crystallization behaviors

Because the chain structure of the polymer will affect the characteristics of the crystallinity, crystallization, and melting behaviors, an evaluation of the structure and property relationship is important. In this part, melting and crystallization behaviors of pure POE and POE-g-MAH with different GDs were compared in Figures 2 and 3, and the results obtained from DSC analyses are summarized in Table II.

DSC heating thermograms of pure POE and POE-g-MAH samples are shown in Figure 2. Pure POE exhibited broad differential scanning melting endotherm, which could be due to the distribution in length of crystallizable ethylene sequence imposed

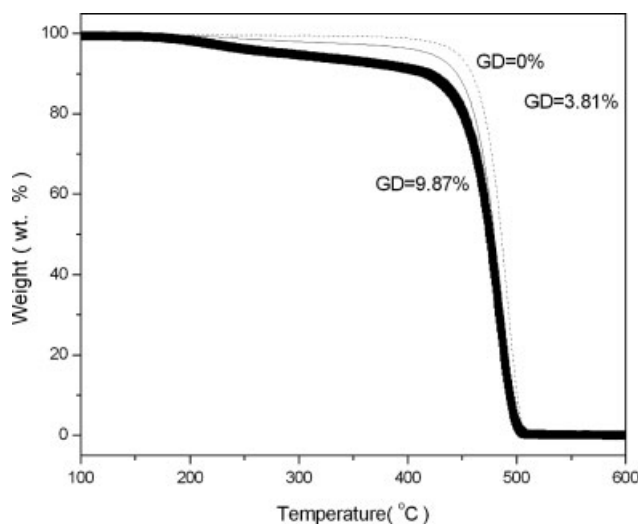
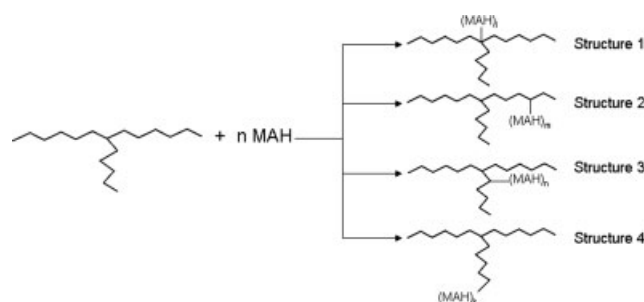


Figure 1 TGA curves of POE-g-MAH with different grafting degree.



Scheme 2 Different grafting structures of POE-g-MAH.

TABLE I
The Onset Degradation Temperature (T_d) of POE and POE-g-MAH from TGA

GD (%)	0	1.52	3.81	5.02	7.40	9.87
T_d (°C)	469.6	463.3	462.4	459.8	458.6	455.8

by the placement of noncrystallizable units along the chain, leading to a broad distribution of crystal sizes in this polymer.²² Different melting behaviors reflect from the melting temperature (T_m) of pure POE at 81.37°C that was much higher than those of POE-g-MAH ranging from 76.02°C to 67.32°C. The heat of fusion (ΔH_f) of pure POE (39.29 J/g) was also clearly higher than those of POE-g-MAH ranging from 25.81 J/g to 13.98 J/g in the order of increasing extent of grafting. In other words, T_m and the heat of fusion decreased as the extent of grafting increased. The structures of POE-g-MAH were listed in Scheme 2, from which it can be inferred that the more α -olefin was incorporated into the polymer chains so that the regularity of the chain structures was disrupted. On the other hand, the spacing between the chains was also increased due to the grafted branches.^{21,23–25} Consequently, T_m , ΔH_f , and X_c decreased with the increase of GD.

The crystallization temperatures as shown in Tab. 2 decreased from 61.38 to 41.66°C with the increase of the GD in the range of 0–9.87%, and the crystal peaks of POE-g-MAH were broader than that of pure POE, shown in Figure 3. The sharp peak of pure POE is attributed to thicker lamellae containing a high ethylene sequence length, whereas the broader peak of POE-g-MAH copolymers at lower temperatures, are attributed to thinner lamellae corresponding to groups of shorter and branching ethylene sequences.^{24,26} The physical structure and the

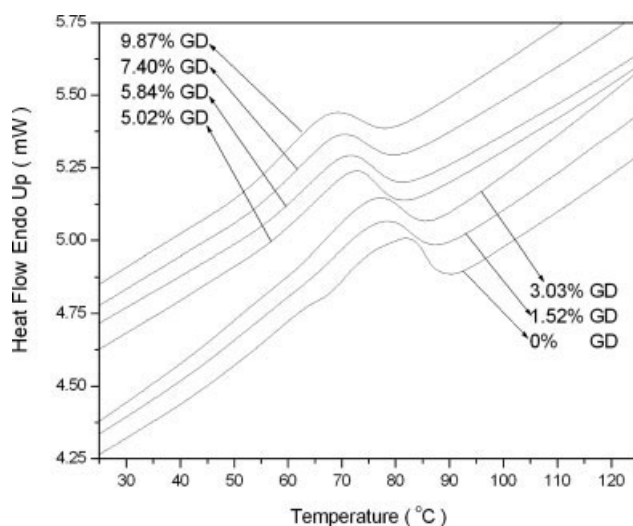


Figure 2 DSC heating thermograms of POE-g-MAH with different GD.

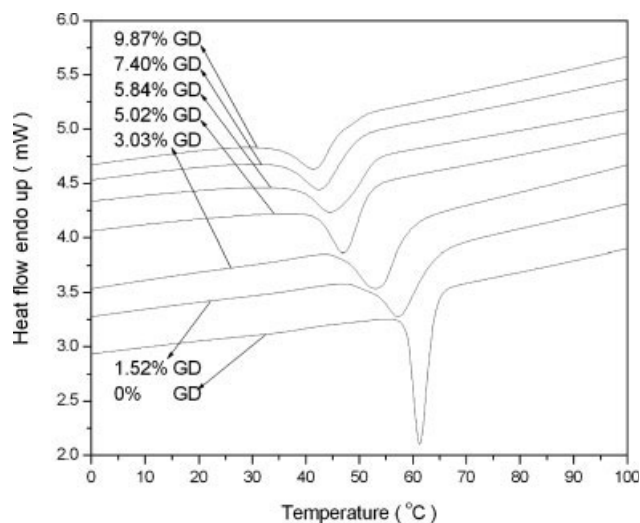


Figure 3 DSC cooling thermograms of POE-g-MAH with different GD.

properties of inter- and intramolecularly homogeneous poly(ethylene-co-1-octene) are mainly controlled by the constitution of the macromolecule.²⁷ Because the short-chain branches-MAH existed, the rigidity of the chains was improved, packing of the chains within the crystal was strongly hindered, and the physical parameters like degree of crystallinity and crystallization temperature were strongly influenced.²⁸ Therefore, the crystal temperature decreases with the MAH concentration.

X-Ray analyses

The results of WAXS studies are shown in Figure 4. As to pure POE, despite a broad halo at $2\theta \approx 19.58^\circ$ attributed to the amorphous phase, two peaks ($2\theta = 20.88^\circ$ and $2\theta = 23.14^\circ$, respectively) coming from the (110) and (200) interferences of the orthorhombic unit cell are detected, which is in good agreement with the Bragg d values assigned for

TABLE II
DSC Results of POE and POE-g-MAH

GD (%)	T_m (°C)	T_c (°C)	ΔH_f (J/g)	X_c (%) ^a
0	81.37	61.38	39.29	13.41
1.52	76.02	57.54	25.81	8.81
3.03	75.17	53.69	24.85	8.48
3.81	73.07	51.37	21.04	7.18
5.02	71.85	47.19	16.60	5.67
5.84	70.55	45.09	16.13	5.51
7.40	69.01	42.69	15.07	5.14
8.53	68.14	41.95	14.12	4.82
9.87	67.32	41.66	13.98	4.77

^a $X_c = \Delta H_f / \Delta H_f^0 \times 100\%$, where ΔH_f^0 is the enthalpy of fusion of perfectly crystalline POE was taken to be 293 J/g²¹, ΔH_f is the enthalpy of fusion of POE was taken by DSC.

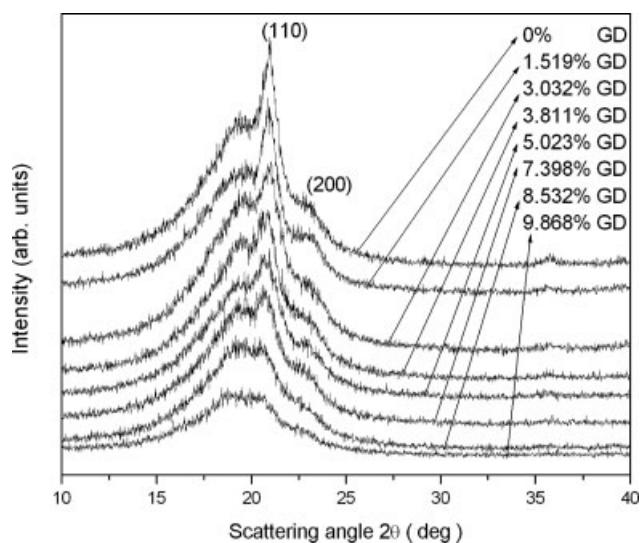


Figure 4 Wide angle X-ray diagrams of POE-*g*-MAH with different GD.

these reflections in the case of linear polyethylene, having the unit cell dimensions $a = 0.741$ nm, $b = 0.494$ nm, and $c = 0.255$ nm.^{27–29} In case of the POE-*g*-MAH copolymers, the θ_{110} and θ_{200} peaks decrease in their intensity with increasing GD and disappear almost completely at a GD of 9.87%, which indicates that imperfection (paracrystalline distortion, size of crystallites, and lattice defects^{30,31}) of the crystalline phase increased with the increase of GD. It can also be seen from Figure 5 that the peak in the $d_{\text{amorphous}}$, d_{110} , and d_{200} values increase with the rising GD, indicating the loose packing of the molecular chains in the orthorhombic unit cell. Relatively, loose packing of the chains in the unit cell could be attributed to the overall influence from the hexyl and MAH branches in packing of the ethylene sequence

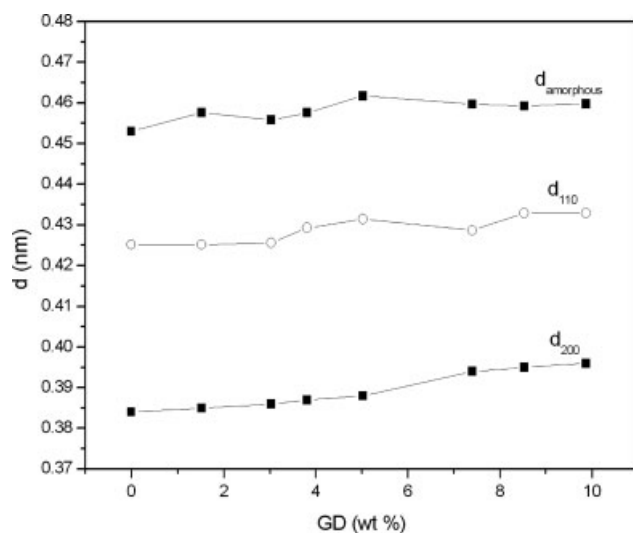


Figure 5 A series of two-dimensional X-ray diffraction patterns.

lengths. These physical features, strongly influenced by increasing MAH content, could be explained why the length of crystallizable ethylene sequences decreases with the increasing amount of branches. Moreover, chain mobility decreases with increasing rigid MAH content. This further resulted in the formation of smaller, less perfect, and less stable crystallites with increasing MAH contents.²⁸ The results are in agreement with those of our previous DSC analysis.

Rheological properties

In general, grafting processing of polyolefins is often accompanied by side reactions, that is, (a) radical-induced crosslinking of the polyolefin substrate, (b) radical-induced chain scission of the polyolefin substrate, (c) shear induced degradation of the polyolefin substrate, and (d) homopolymerization of the monomer.¹⁷ In our previous work,¹⁶ the results showed that the radical-induced crosslinking of the polyolefin substrate was the main side reaction in MAH and POE graft system. Therefore, the samples with 0–10% GD (GD) and <15% gel content were selected to exclude the crosslinking effects. The dependence of complex viscosity on the shear rate at 150°C for POE and POE-*g*-MAH is shown in Figure 6. In whole range of the frequency investigated, the pure POE and their graft copolymers exhibit a decrease in the viscosity value with increasing shear rate, which indicates that they present a typical pseudoplastic behavior. A Newtonian plateau was not observed in the frequency range investigated in this work. At low shear rates, the viscosity of POE-*g*-MAH is higher than that of pure POE, which proves that MAH can induce crosslinking reaction on POE backbone even at low gel content. Moreover, the viscosity of POE-*g*-MAH copolymers increased

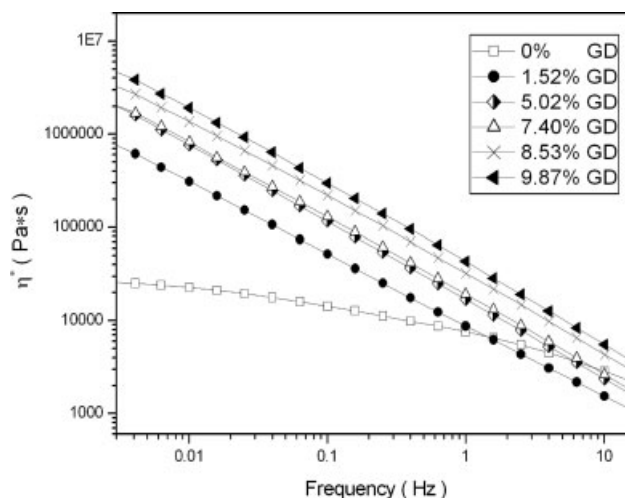


Figure 6 Complex viscosity versus frequency for POE-*g*-MAH with different GD.

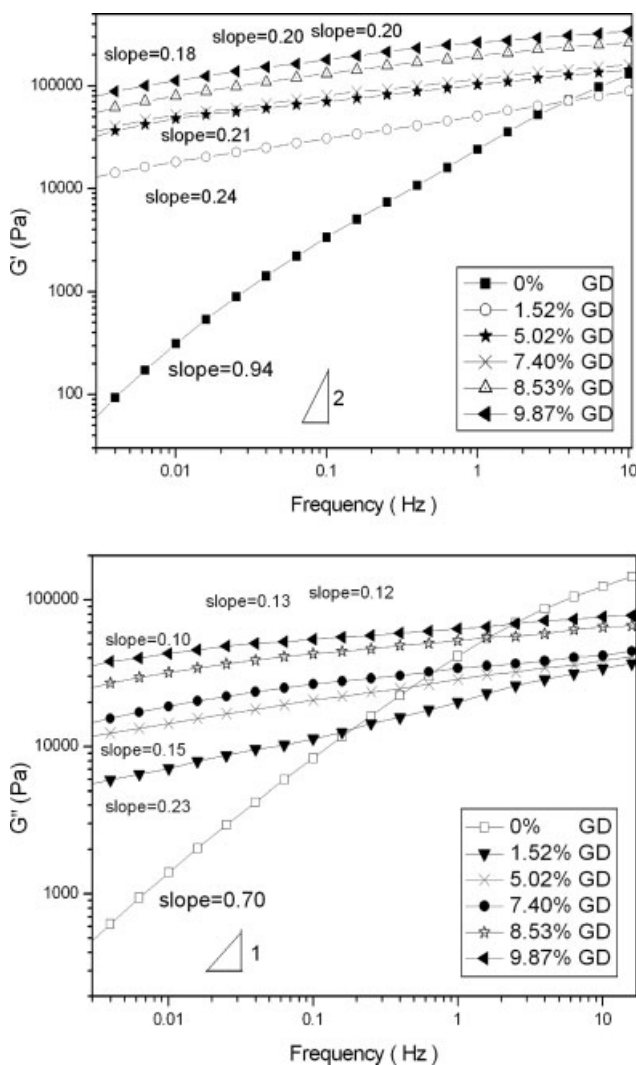


Figure 7 Storage modulus and loss modulus versus frequency for POE-g-MAH with different GD.

with increasing GD, which could be attributed to the strong interaction between the chains due to the improvement of the rigidity and the polarity of the chains when MAH was grafted onto POE backbone.³² In other words, the more MAH content added, the stronger the intermolecular interaction existed. At the higher frequency, the viscosity of POE-g-MAH with 1.52% and 5.02% GD is lower than that of pure POE, which could be because the non-Newtonian behaviors could be enhanced due to MAH, and further lead to the transitions from the Newtonian plateau to the non-Newtonian regime shifted to lower frequency.

The dynamic storage modulus, G' , is related to the elastic behavior of the material and may be considered as the storage energy. The dynamic loss modulus, G'' , represents the dissipated energy. The dependence of G' and G'' on the frequency measures the relative motion of all molecules in the bulk and can give important information about the flow

behavior of melts.^{33,34} Figure 7 showed the dependence of storage and loss moduli on the frequency. G' and G'' of POE and POE-g-MAH increased with increasing frequency. At low frequencies, G' and G'' values increased with the increasing GD, POE-g-MAH with 9.87% of the GD presented the highest G' and G'' values and pure POE had the lowest one, which proved the appearance of gel in the copolymers (The results are agreement with our previous work¹⁵). The increase in elastic modulus may result from the improvement in rigidity and the interaction between polymer chains. If the polymer chains is fully relaxed, they exhibit characteristic homopolymer-like terminal behavior, that is, $G' \propto F^2$, $G'' \propto F^1$. The slope of G' versus frequency (F) in log-log plot for pure POE is 0.94 at low frequency regime, which deviates from the terminal slope, 2.0, of the monodispersed linear polymer and indicates polydispersed molecular weight. It should be noted that the terminal zone slopes for POE-g-MAH copolymers are lower than that of pure POE, and decrease with increasing MAH content. The differences in slopes may be attributed to differences in extent to rigidity or polarity of the chains and little crosslinking structure.¹⁶ The frequency dependence of G'' also progresses a monotonic increase with an increasing GD. The low-frequency-regime dependence of the loss modulus decreases monotonically with increased MAH content when the slope changes from 0.70 to 0.10. As a consequence, the POE-g-MAH copolymer provided the polydispersity. Therefore, polar MAH branches are important parameters that affect the shear sensitivity of POE-g-MAH copolymers.

CONCLUSIONS

POE-g-MAH products with high GD (about 10%) have been successfully obtained by the solvothermal method. The properties of neat POE have clearly been changed when MAH was grafted onto POE backbone. The effect of the different GD on the properties of POE copolymers were systematically studied in terms of their thermal stability, melting and crystallization behaviors, and rheological properties. The important results are summarized herein:

1. The thermal stability denoted as T_d , T_m , T_c , and crystallinity (X_c) of POE-g-MAH decreased as the GD increased.

2. The intensity of the (110) and (200) peaks of the orthorhombic unit cell decreases with the increase of GD, whereas $d_{\text{amorphous}}$, d_{110} , and d_{200} spacings slightly increases as the MAH contents increase.

3. The POE-g-MAH has higher storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) than those of pure POE at low frequencies. And the

polar MAH branches pose important impact on shear sensitivity of POE-g-MAH copolymers.

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