ORIGINAL PAPER

Enhancing Maleic Anhydride Grafting onto Low-Density Polyethylene via Synergistic Incorporation of Phenolic-Based Initiators and Peroxides during Reactive Melt Blending

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Received: 27 April 2026, Revised: 31 August 2026, Accepted: 7 September 2026

DOI: 10.22063/poj.2026.35869.1392

ABSTRACT

This study investigates the reactive melt grafting of maleic anhydride (MAH) onto low-density polyethylene (LDPE) using dicumyl peroxide (DCP) as a radical initiator, with particular emphasis on the effect of Irganox 1010 on grafting efficiency and gel formation. The effects of MAH and DCP concentrations, together with Irganox 1010, dimethylformamide (DMF), and methanol, were systematically evaluated. Grafting increased with increasing MAH and DCP contents; however, the addition of Irganox 1010 produced a pronounced increase in MAH grafting, despite its conventional role as a phenolic antioxidant. This finding indicates that Irganox 1010 can facilitate the grafting reaction under reactive melt-processing conditions, potentially through a synergistic interaction with DCP-generated radicals. Importantly, the increased grafting in the presence of Irganox 1010 was accompanied by suppression of gel formation, demonstrating a favorable shift in the competition between MAH grafting and polyethylene crosslinking. Aromatic additives and their combinations further affected grafting efficiency, with the synergistic additive systems yielding the highest grafting levels. FTIR spectroscopy confirmed successful MAH incorporation through the characteristic carbonyl absorption bands of grafted anhydride groups. The melt flow index decreased progressively with increasing grafting degree, reflecting increased molecular weight, chain entanglement, and the contribution of crosslinked structures, particularly in samples with higher gel fractions. Overall, the results establish Irganox 1010 as an effective additive for enhancing MAH grafting onto LDPE while limiting undesirable gel formation, highlighting its potential to improve the efficiency and controllability of reactive melt functionalization processes.

Keywords: LDPE; Grafting; Maleic anhydride; Phenolic-based materials; reactive extrusion.

INTRODUCTION

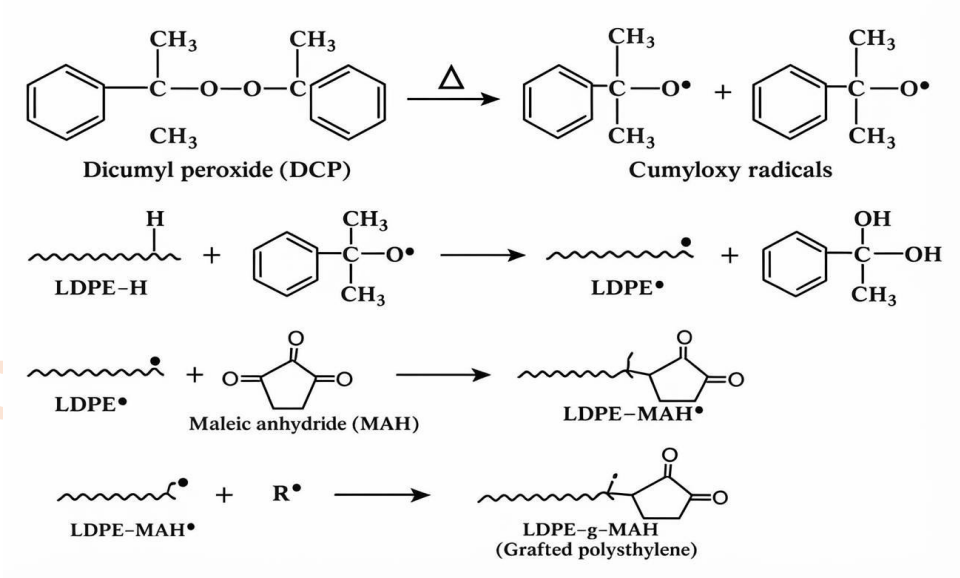
In recent years, extensive research has been dedicated to enhancing polymer properties and developing new polymers tailored for specific applications. This pursuit aims to optimize their characteristics and, at times, cater to specialized needs. However, despite polyolefins' amalgamation of chemical, physical, and processability traits, their lack of reactive groups presents significant limitations in various fields of application, particularly concerning their interfacial reactions with other materials [1].

Environmental concerns have driven efforts towards eco-friendly processes, particularly in polymer modification during the melt phase. Various techniques, such as solvent-free processes, have been developed to enhance stability and dispersion within polymeric matrices, reducing volatile organic compound emissions [2]. Chemical modification using coupling agents has been employed to improve compatibility among blend components, preventing excessive coalescence and strengthening adhesion [3]. Grafting procedures, commonly utilizing maleic anhydride due to its reactivity, enhance compatibility in polymer alloys [4]. Functionalization through grafting aims to enhance polyolefin properties, although side reactions such as chain secession or cross-linking need to be managed [1]. The free-radical reaction process is widely utilized for polymer modification, particularly in grafting maleic anhydride onto polyolefins [5]. Industrial applications often involve melt grafting in extruders or internal mixers, while solution-based reactions provide deeper mechanistic insights. Reactive extrusion, favored for material synthesis, benefits from polyethylene's widespread applicability [6].

Modifying thermoplastics in twin-screw extruder systems is deemed suitable for cost-effective material production and expeditious acquisition of new commercial polymers [7]. The performance of twin-screw extruders as continuous flow reactors significantly influences high performance thermoplastic polymer production [8]. Considerable research has been conducted in these two domains. Extensive research has been conducted in these areas. The grafting of maleic anhydride enhances polyethylene's compatibility with other polymers and fillers, particularly benefiting industries such as automotive and construction materials [9]. Furthermore, such modifications can be advantageous in the packaging industry by improving barrier properties and mechanical strength, thereby expanding the use of polyethylene in specialized applications. Although numerous studies have investigated the grafting of maleic anhydride onto polyethylene, most have primarily focused on improving grafting efficiency or optimizing processing parameters. Comparatively limited attention has been devoted to systematically evaluating the influence of radical inhibitors, polar solvents, and antioxidants on simultaneously controlling grafting efficiency, gel formation, and rheological behavior during reactive extrusion. Therefore, a comprehensive understanding of the individual and combined effects of these additives remains incomplete. The novelty of the present work lies in the systematic investigation of the effects of dimethylformamide (DMF), methanol, and Irganox

1010 on the reactive extrusion grafting of maleic anhydride onto low-density polyethylene using dicumyl peroxide as the radical initiator. Unlike previous studies, this work not only evaluates grafting conversion but also correlates the effects of these additives with gel formation and melt rheological properties, providing practical insight into producing functionalized polyethylene with high grafting efficiency and minimal gel content.

In this study, samples were prepared using dicumyl peroxide as the initiator through the reactive extrusion process [10]. These samples comprised grafted low-density polyethylene and maleic anhydride. Dimethylformamide, methanol, and phenolic-based compounds were employed as inhibitors in certain examples, while Irganox 1010 served as an antioxidant. The primary aim of this study is to investigate the conversion of maleic anhydride grafting onto low-density polyethylene chains, aiming for minimal gel formation in the samples. The combination of maleic anhydride and dicumyl peroxide was chosen for their established role in initiating grafting via free radical mechanisms. Scheme 1 shows the free radical mechanisms of grafting. In addition, dimethylformamide (DMF) and methanol were selected as polar solvents with known inhibitory effects on radical reactions, allowing investigation of their role in suppressing gel formation. Irganox 1010, a phenolic antioxidant, was included to explore its stabilizing effect on the grafting process and its potential synergistic role in controlling radical activity. This formulation enabled a systematic analysis of how such additives influence grafting efficiency, gel formation, and polymer rheology.



Scheme 1. Reaction scheme for the free-radical grafting of maleic anhydride onto LDPE, initiated by dicumyl peroxide (DCP).

EXPERIMENTAL

Materials

The LD0020, a variant of LDPE (Low-Density Polyethylene), exhibits a melt flow index of 2 g/10 min (2.16 kg at 190°C) and a density of 0.920 g/cm³, with an average molar mass of 150,000 g/mol. This specific LDPE variant was procured from Bandar Emam Petrochemical Co. in Iran.

Throughout the study, various chemicals were utilized, including maleic anhydride sourced from Sadr Shimi Gostaran Yazd, Iran, and methanol and dimethylformamide acquired from Sigma Aldrich USA. Additionally, Irganox 1010 (pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate), molecular formula: $C_{73}H_{108}O_{12}$, CAS No. 6683-19-8) was obtained from Merck (Germany). Irganox 1010 is a sterically hindered phenolic antioxidant containing four phenolic hydroxyl groups attached to a pentaerythritol core.

Sample preparation

The sample preparation method involves the introduction of low-density polyethylene (LDPE) into a reaction extrusion machine via a funnel, where it is melted. Additives, including dicumyl peroxide, dimethylformamide, methanol, a phenol-based cyclic compound, and ethanol, are then added to the molten LDPE. To ensure product purity, suctions are installed in the device to remove any unreacted maleic anhydrides and solvents. Additionally, a solvent mixture comprising maleic anhydride, dimethylformamide, methanol, and Irganox 1010 in acetone is prepared in a doublewalled container with water circulation to prevent evaporation or fire risks. Substances like methanol are carefully transferred to the device using a narrow interface. The suction solvent is cooled by a distillation tower to maintain optimal conditions. The blending process occurs in a fully intermesh corotate twin-screw extruder (ZSK 25, Werner & Pfleiderer, 2002 Germany) with a screw diameter of 25 mm and an L/D ratio of 40. Extrusion takes place at a screw speed of 600 rpm and temperatures ranging from 130°C to 230°C. Specifically, thermal zones are set at 130°C (doubled), 135°C, 160°C, 175°C, 180°C, 190°C, and 230°C. These parameters are carefully chosen to optimize processability and achieve the desired sample quality.

Table 1 presents the compositions of various samples prepared with different proportions of Irganox 1010, methanol, DMF, DCP, and MAH. The table lists the specific parts per hundred resin (PHR) values for each component across thirteen different samples. The compositions vary performed to investigate the effects of these components on the properties of the resulting materials, providing a detailed matrix for analysis. The

analysis performed on these samples aimed to evaluate the impact of varying concentrations of each additive on the material properties. Key properties such as thermal stability, mechanical strength, and chemical resistance were measured and compared across the samples. The variation in the additive levels allowed for the identification of optimal compositions that enhance desired properties while minimizing any adverse effects.

Table 1. Combination of weight percentages of produced samples.

Sample	Mah (PHR)	DCP (PHR)	DMF (PHR)	Methanol (PHR)	Irganox1010 (PHR)
1	0	0	0	0	0
2	1.5	0.05	0	0	0
3	1.5	0.1	0	0	0
4	1.5	0.12	0	0	0
5	1.5	0.15	0	0	0
6	1	0.05	0	0	0
7	1	0.1	0	0	0
8	1	0.12	0	0	0
9	1	0.15	0	0	0
10	1.5	0.12	0.5	0.5	0.2
11	1.5	0.12	0.25	0.25	0.2
12	1	0.12	0.5	0.5	0.2
13	1	0.12	0.25	0.25	0.2

Characteristics gel content determination

The gel content in the samples was measured following the ASTM D 2765 test method. Initially, a 5 g sample was refluxed in 250 cc of xylene for 240 minutes at approximately 130°C. Subsequently, the resultant hot solution underwent filtration using multiple fine-textured fabric filters. To precipitate the polymer soluble in xylene but insoluble in acetone, one liter of cold acetone was introduced into the substrate solution. The separation process was executed through filter paper and vacuum. The fabric filter, of a cheese cloth type and containing polymer insoluble in xylene, was rinsed with acetone and subjected to a temperature of 75 to 80°C. Following this, the fabric filter was dried at 70-80°C until weight loss occurred, ultimately determining the quantity of gel.

Titration Method

In order to determine the maleic anhydride grafting in LDPE, titration method was used. In this method, the acid number method was used. 1 g of polymer was refluxed in 150 ml of xylene saturated with water for 90 min. Then, the hot solution was titrated with 0.05 N alcoholic potassium hydroxide in the presence of thymol blue in 1% DMF to give a color change from yellow to blue, then the blue solution was titrated with dissolved chloridric acid in 0.05 N isopropanol. Potassium hydrogen phthalate was used to standardize the KOH solution.

The acid number was obtained from the following equation:

$$(mg\ KOH/g\ ) = \frac{mL\ KOH\ \times NKOH\ \times\ 56.1}{Polymer\ weight}$$

The maleic anhydride percentage of the grafting was obtained from the following equation:

$$Maleic\ anhydride(\%) = \frac{Acid\ number\ \times 98}{2 \times 56.1 \times 10}$$

Melt flow index analysis

The melt flow index (MFI) test was conducted to evaluate the melt output of the samples over a ten-minute period. The test, performed in accordance with ASTM D1238, was carried out using an SMF-300 model (SANTAM) melt flow tester, with a set temperature of 180 °C and an applied load of 2.16 kg.

FTIR spectral studies

Evidence of functionalization was analyzed using FTIR spectroscopy. Thin films were obtained by compression molding between metal sheets covered with refractory sheets at 180°C. The test was performed by a Nexus FT-IR device model B70 in the wavenumber range of 400-4000 cm^{-1}

Rheological analysis

The rheological tests were carried out using an Anton Paar RheoCompass rheometer equipped with parallel plate geometry (25 mm diameter, 2 mm gap). A frequency sweep test was conducted at 180 °C to identify the linear viscoelastic region of the samples. In accordance with ASTM D4440, the dynamic melt properties—including complex viscosity, storage modulus (G'), and loss modulus (G")—were measured over a frequency range of 0.01 to 1000 rad/s at a constant strain amplitude of $\gamma = 0.1$.

RESULTS AND DISCUSSION

Gel content

The gel test results, summarized in Table 2, serve as a pivotal insight into the underlying mechanisms governing gel formation in polymer synthesis. It's imperative to note that gel formation, a manifestation of extensive crosslinking, is intricately influenced by various factors intrinsic to the polymerization process. The meticulous calculation of gel percentages, with an error margin of 0.01, underscores the precision required in elucidating these phenomena. Notably, the presence of Irganox1010, coupled with inhibitors, emerges as a potent mitigating factor against gel formation, evident from the negligible gel percentages observed in these samples. This phenomenon can be attributed to the inhibitory action of Irganox1010 on free radicals, effectively diverting their reactivity towards branching processes rather than crosslinking, as corroborated by titration tests. Consequently, samples enriched with Irganox 1010 exhibit a higher degree of branching, reflected in elevated grafting percentages compared to counterparts lacking Irganox 1010. An intriguing observation arises from the comparison of Samples 10–13, containing Irganox 1010, with the corresponding formulations without Irganox 1010 (Samples 1-8). Although all these formulations contained inhibitors, gel formation was absent in Samples 10–13, highlighting the pivotal role of Irganox 1010 in suppressing crosslinking reactions [11]. Although Irganox 1010 effectively suppresses undesirable crosslinking, its radical-scavenging activity can also reduce the concentration of active macroradicals available for MAH grafting. Consequently, Samples 12 and 13 exhibited a slight decrease in grafting percentage compared with the corresponding formulations without Irganox 1010. This behavior indicates that excessive stabilization of radicals partially suppresses the grafting reaction while effectively preventing gel formation. These findings highlight that inhibition mechanisms in polymer chemistry can vary based on chemical structure and mode of action. For example, Irganox 1010 acts as a radical scavenger, reducing the availability of radicals for crosslinking, while polar solvents such as methanol and DMF modulate the solubility and distribution of reactive species, indirectly affecting the extent of gelation. This underscores the need to consider both chemical reactivity and physical effects when evaluating the role of additives in grafting systems.

Table 2. Characterization results of the prepared samples, including gel content, titration, and melt flow index (MFI).

Samples	1	2	3	4	5	6	7	8	9	10	11	12	13
Gel%	0	0	0.5	0.7	1	0	0	0.2	0.6	0	0.1	0	0
Graft%	0	1	1	1	1.2	0.6	0.6	0.65	0.7	1.3	1.2	0.9	0.8
MFI	2	1.6	1.2	0.8	0.6	1.8	1.5	1.3	1	0.3	0.5	0.7	1

The influence of solvents, exemplified by Methanol and DMF, further accentuates the intricate interplay between reactants and reaction environments. Solvents, acting as reaction mediators, can modulate the solubility and distribution of reactants, thereby influencing reaction kinetics and gel content. Samples subjected to solvent-rich environments, as evidenced in samples 10 to 15, exhibit nuanced gel formation behaviors, underscoring the complexity inherent in polymerization processes [12]. This holistic analysis, integrating data from Table 1 and Table 2, offers profound insights into the nuanced mechanisms governing gel formation in polymer synthesis. It underscores the imperative of judicious compound selection, inhibitor incorporation, and concentration control in orchestrating desirable polymerization outcomes.

Titration

The titration tests, as summarized in Table 2, offer a comprehensive view of the grafting degrees across various samples, highlighting the impact of chemical composition on the modification of polymers. For instance, Sample 1, which contains no additives, shows a grafting degree of 0%, serving as a control to underscore the essential role of initiators in the grafting process. A progressive increase in the concentration of DCP (Dicumyl Peroxide) from 0.05 PHR to 0.15 PHR across Samples 2 to 5 corresponds with an increase in grafting degrees from 1% to 1.2%, confirming the initiator's critical role in facilitating the generation of free radicals needed for grafting. Moreover, samples that incorporate solvents like Methanol and DMF, along with Irganox1010 (Samples 10 to 13), display higher and more variable grafting degrees, with the peak observed in Sample 10 at 1.3%. The solvents influence the solubility and mobility of radicals and monomers, significantly affecting the grafting degree. These results are consistent with previous studies on peroxide-initiated maleic anhydride grafting of polyolefins, which have reported that increasing initiator concentration generally enhances grafting efficiency by increasing the concentration of macroradicals available for MAH addition [13]. However, the present results further demonstrate that the combined use of Irganox 1010 and polar inhibitors can modify this behavior and influence the balance between grafting and undesired crosslinking.

Surprisingly, Irganox1010, typically known for its antioxidant properties, seems to support rather than inhibit the grafting process by possibly stabilizing free radical intermediates, thus enabling more controlled reactions[14]. This analysis underscores the nuanced role of formulation parameters like initiator concentration and the presence of solvents and stabilizers in defining the properties of modified polymers, essential for designing targeted polymer functionalities.

FTIR spectral analysis

Fourier-transform infrared (FTIR) spectroscopy was utilized to analyze the grafting of maleic anhydride onto polyethylene. The FTIR spectrum, as illustrated in Figure 1, revealed notable absorption peaks at 1712

cm^{-1}, indicative of both symmetric and asymmetric C=O carbonyl vibrations typically found in maleic anhydride. Additionally, the detection of a peak at 1492 cm^{-1} was indicative of C-H vibrations in methylene groups characteristic of low-density polyethylene [15]. The spectrum also showed peaks between 2800–3000 cm^{-1}, representing C–H stretching vibrations of methylene groups typical of LDPE. No characteristic absorption related to C–C stretching is expected at 2150 cm^{-1}, since C–C single bonds are generally IR inactive; furthermore, this spectral region is typically associated with triple bonds (C≡C or C≡N), which were not observed in the present system [16]. It should be noted that hydrogen bonding interactions cannot be conclusively determined from a single FTIR spectrum, as such analysis requires comparison of band shifts or peak broadening relative to a reference sample. Therefore, no definitive claim regarding hydrogen bonding is made based solely on the present spectrum. The spectrum also exhibited a peak at 720–735 cm^{-1}, corresponding to the rocking vibration of long – CH_2– sequences, confirming the polyethylene backbone structure [17]. The appearance of characteristic anhydride carbonyl peaks together with the preserved LDPE backbone signals confirms the covalent grafting of maleic anhydride onto polyethylene, in agreement with titration results [18].

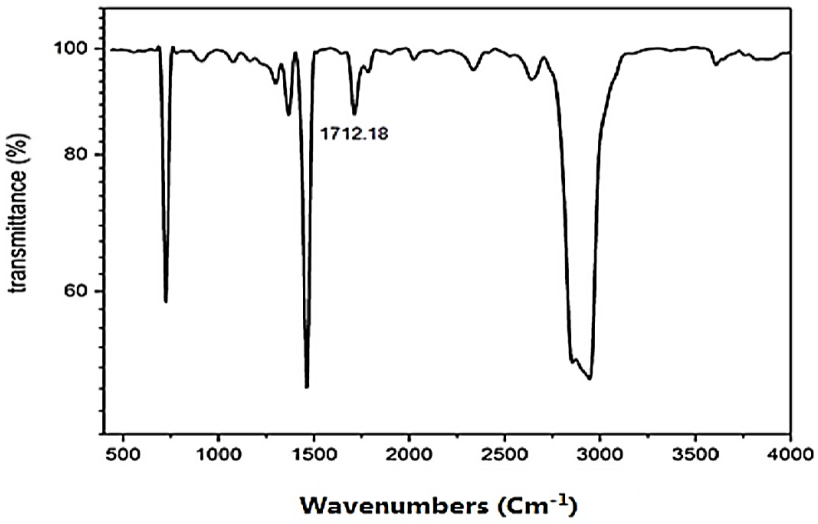


Figure 1. diagram percentage of passage against the wave number of the infrared spectroscopy test.

Melt flow index

The melt flow index (MFI) is a critical parameter for assessing the processability of thermoplastic polymers, indicating how easily a polymer can flow under heat and pressure. Test results from Table 2 show a clear trend where the melt flow index decreases as the grafting amount increases.

This is highlighted by the addition of maleic anhydride (MAH) to polyethylene, which results in grafting that introduces additional side chains and increases the molecular weight. Such molecular modifications lead to increased entanglements within the polymer matrix, restricting the mobility of polymer chains and consequently lowering the melt flow index [19]. Although samples 3 and 4 exhibit grafting percentages similar to sample 2, they show lower MFI values. This behavior is attributed to differences in the grafted structure rather than the grafting percentage alone. Variations in graft chain length, branch distribution, or molecular architecture can increase chain entanglement and melt viscosity, thereby reducing polymer flow despite comparable grafting levels. The most extensively grafted sample exhibits the lowest melt flow index, demonstrating that extensive molecular changes significantly impact polymer flow characteristics. This trend is in agreement with previous reports on maleic anhydride-grafted polyolefins, where increased grafting and associated changes in molecular architecture were found to restrict chain mobility and consequently reduce melt flow. The present results therefore support the established relationship between the degree of functionalization and melt processability [20].

Additionally, the inclusion of phenolic-based compounds as stabilizers and inhibitors in the polymer matrix affects the melt flow index. These compounds are known for their radical interacting capabilities, potentially leading to further cross-linking or branching within the polymer structure. The resulting increased entanglement from this cross-linking reduces the polymer's ability to flow under the application of heat and pressure. The stabilizing effects of phenolic compounds not only enhance thermal stability and mechanical properties but also significantly reduce the melt flow index, as evidenced by the lower values observed in samples containing these additives [19]. This interaction between polymer chemistry and material processing characteristics illustrates how modifications intended to improve specific properties can inversely affect others, like melt flow, essential for manufacturing processes.

Rheology

The plot of complex modulus versus frequency is commonly used in polymer research **to evaluate** variations in complex viscosity, particularly in the low-frequency region, where the response is highly sensitive to molecular architecture. Figure 2 presents the complex viscosity (η^*) as a function of frequency. An increase in the zero-shear complex viscosity (η_0^*) generally suggests an increase in molecular weight due to enhanced chain entanglement. An overall increase in (η_0^*) was observed for all samples subjected to the maleic anhydride grafting process. However, this increase may also be attributed to other structural factors, such as chain branching, partial crosslinking, or enhanced intermolecular interactions induced by grafting, which can restrict chain mobility and increase melt resistance [20]. In addition to the grafting of maleic anhydride onto the polyethylene backbone, evidence of chain scission reactions was inferred from the rheological response. Specifically, samples 1 and 2 exhibited a reduction in zero-shear complex

viscosity (η_0^*) and a downward shift of the low-frequency plateau compared to the neat polyethylene, indicating a decrease in molecular weight. Such a reduction in η_0^* is consistent with chain scission occurring during the grafting process. Therefore, the increase in viscosity should not be attributed exclusively to MAH grafting. The rheological response indicates that grafting-induced branching and partial crosslinking can increase viscosity, whereas chain scission can counteract this effect by reducing molecular weight and chain entanglement. Thus, the final viscosity reflects the competition between these simultaneous structural changes during reactive processing.

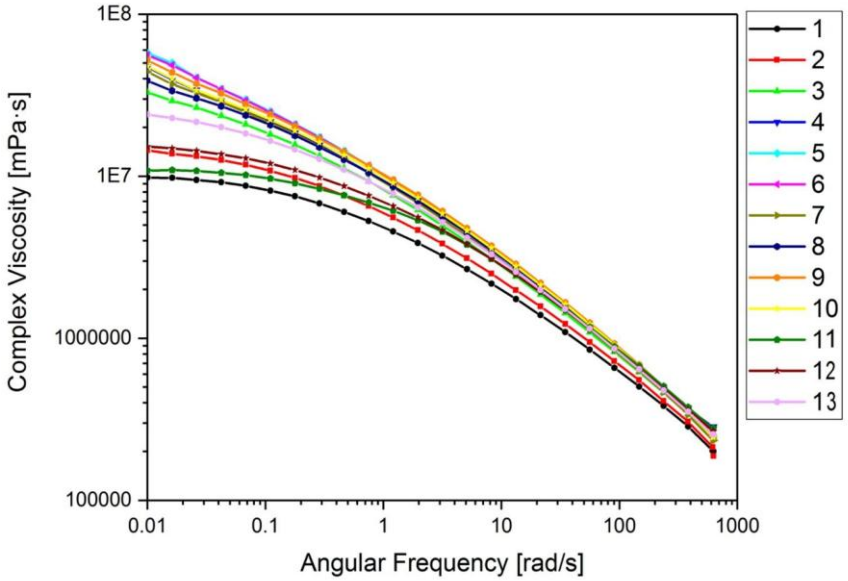


Figure 2. Viscosity complex chart versus angular frequency.

In addition to the grafting of maleic anhydride onto the polyethylene backbone, evidence of chain scission reactions was also observed, suggesting the occurrence of competing radical-induced processes during reactive extrusion[21]. Moreover, a clear rise in chain entanglement is evident. Figure 3 shows the storage modulus (G') as a function of angular frequency for the studied samples. At low frequencies, G' exhibits a plateau whose magnitude increases with molecular weight, reflecting stronger chain entanglements. At higher frequencies, the decline of G' is less pronounced for samples with higher molecular weight, indicating that the polymer chains resist deformation more effectively under rapid oscillatory shear. Overall, the observed upward shift in G' across all frequencies suggests enhanced molecular entanglement and increased stiffness of the polymer matrix due to the grafting process.

Simultaneously, a moderate upward shift in storage modulus is evident, which reflects enhanced molecular entanglement and increased stiffness of the polymer matrix.

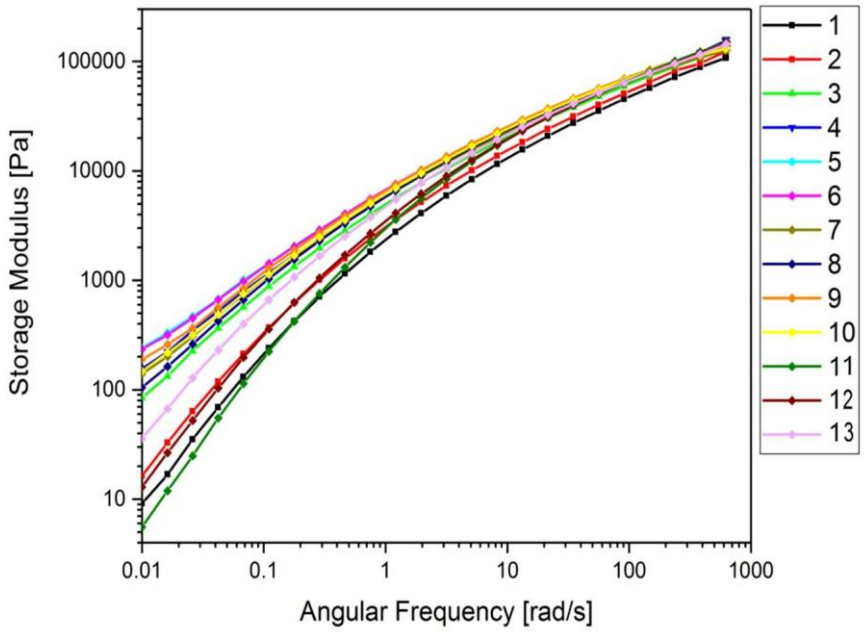


Figure 3. Storage modulus chart versus angular frequency.

The high degree of maleic anhydride grafting does not necessarily result in greater chain entanglement. The results indicate that grafting percentage alone cannot be considered the determining factor for entanglement density. However, the significant difference observed between samples 10 (1.3% grafting) and 11 (1.2% grafting with 0.1% gel content) requires further clarification. Although their grafting percentages are very close, sample 10 exhibits markedly higher complex viscosity, whereas sample 11 shows a much lower viscosity comparable to sample 1. This discrepancy cannot be attributed solely to the minor difference in grafting level. Notably, sample 11, despite exhibiting a relatively high grafting percentage comparable to sample 10 and low gel content, presents the lowest entanglement among the evaluated samples. One possible explanation is that sample 11 may have undergone partial chain scission during reactive processing, resulting in a reduction in effective molecular weight and consequently lower melt viscosity. Even at relatively high grafting levels, molecular weight reduction would significantly

decrease entanglement density and elastic response. This finding suggests that chain entanglement is governed not only by grafting level but also by parameters such as molecular weight distribution, chain architecture, and the effectiveness of intermolecular chain coupling within the melt.

Furthermore, the very low reported gel content in sample 11 may indicate insufficient branching or ineffective intermolecular coupling reactions. Since rheological behavior is highly sensitive to network formation, re-evaluation of gel content is recommended to confirm its accuracy, as even a small experimental deviation could significantly affect the interpretation. On the other hand, samples 4, 5, and 9, which exhibit higher gel contents indicative of increased crosslinking, show the highest viscosity and storage modulus values. This behavior reflects the formation of a more developed three-dimensional network structure that restricts long-range chain mobility and enhances elastic response. Therefore, rather than indicating lower entanglement, the rheological response suggests that the dominant contribution arises from chemical crosslinks and network formation, which override the effect of physical chain entanglements within the melt. Additionally, samples containing phenolic-based inhibitors, which suppressed gel formation, also demonstrated lower entanglement—likely due to the absence of the branching mechanisms facilitated by radicals [22]. The results confirm that grafting percentage alone cannot be considered the determining factor for viscoelastic performance; instead, the combined effects of molecular weight evolution (including possible degradation), branching efficiency, and actual gel/network formation must be taken into account.

Figure 4 shows how the loss modulus (Pa) changes with angular frequency (rad/s) across various polymer formulations. Each formulation reflects a specific combination of additives and processing conditions, including different concentrations of Irganox 1010, methanol, DMF, DCP, and MAH. The loss modulus—an indicator of viscous behavior—consistently increases with frequency in all cases, highlighting improved energy dissipation at high frequencies, characteristic of viscoelastic materials.

Formulations 1 to 9, which exclude Irganox 1010, methanol, and DMF but vary in DCP and MAH concentrations, exhibit a steady rise in loss modulus. Notably, those with higher DCP (0.15 PHR) and MAH (1.5 PHR) contents show the highest values, suggesting enhanced crosslink density or improved phase compatibility. In contrast, only formulation 10, containing Irganox 1010, methanol, and DMF, exhibits a relatively higher loss modulus across the entire frequency spectrum, whereas formulations 11 to 15 show lower loss modulus values compared to the reference sample.

The distinct behavior of formulation 10 may be attributed to the stabilizing role of Irganox 1010 and the solvent action of methanol and DMF, which can promote improved dispersion and enhanced chain interactions. These findings highlight the significant impact of DCP and MAH on viscoelastic properties,

further improved by additives such as Irganox 1010, methanol, and DMF. The increasing loss modulus with frequency emphasizes the critical role of formulation in finetuning the performance characteristics of polymer materials.

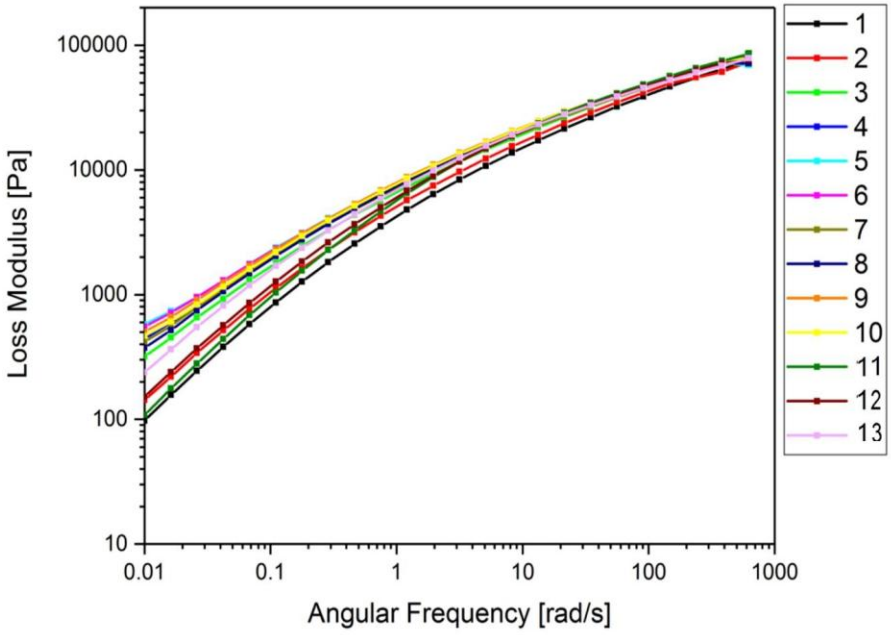


Figure 4. Loss modulus diagram compared to the angular frequency Figure.

Figure 5 presents the collision coefficient chart, where the observed intersection points become more pronounced with increasing grafting percentage and the incorporation of maleic anhydride into the polymer backbone. The presence of maleic anhydride promotes additional intermolecular interactions and possible chain extension or branching reactions. As a result, the polymer samples exhibit a broader molecular weight distribution, indicating increased structural heterogeneity [23]. [23], indicating not only more frequent grafting but also significant structural changes. The addition of phenolic-based compounds further expanded this distribution, whereas samples without Irganox 1010 showed this effect to a lesser degree. Gel test results corresponded with the broader molecular weight distribution observed in some samples. However, in cases where gel was not present, the broadened molecular weight distribution could be attributed to chain scission mechanisms [24].

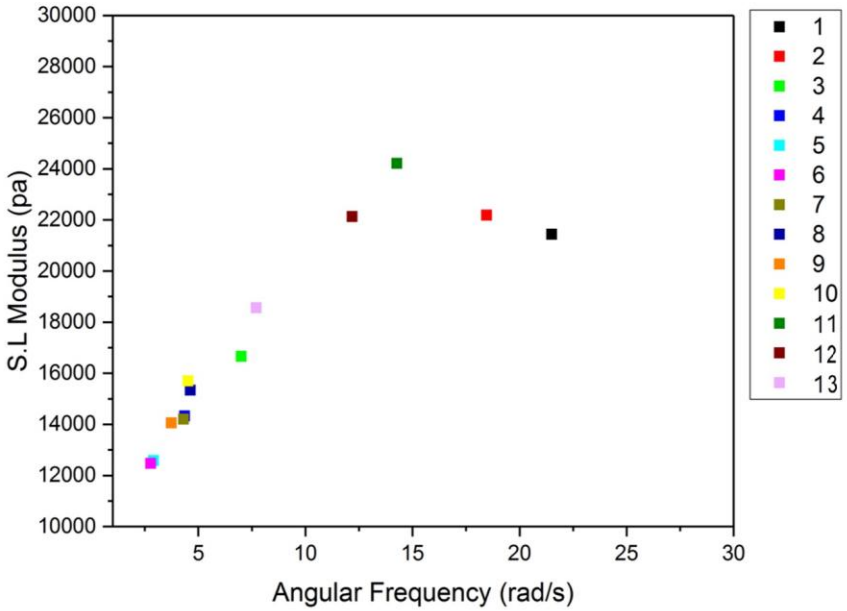


Figure 5. Collision coefficient chart.

CONCLUSION

The different properties of the samples containing the antioxidant Irganox1010 along with methanol and dimethylformamide as inhibitors in different weight percentages were evaluated, and the results showed that by increasing the weight percentage of maleic anhydride and dicumyl peroxide, the percentage of grafting in the samples increased. Also, the presence of the antioxidant compound with the inhibitor increased the amount of maleic anhydride monomer sitting on the polymer chains, and as a result, the degree of grafting in the samples increased. An increase in the amount of maleic anhydride leads to an increase in the gel content of samples, but in the samples containing Irganox1010, the gel formation in the samples was prevented as much as possible, and the free-radicals produced by the initiator were used to graft the maleic anhydride onto the polyethylene chains. Increasing the number of grafting resulted in a decrease in the molten flow index, and the presence of Irganox1010 in the samples resulted in further increase in viscosity in the samples. Infrared spectroscopy test confirmed the presence of maleic anhydride in the sample structure. The grafting process leads to an increase in the molecular weight as well as an increase in the rate of grafting in the polymer chains, which may cause the formation of gels in the samples. The grafting process widened the molecular weight distribution of the samples as well, but the presence of Irganox1010 reduced it, and also led to a decrease in chain secession in the samples.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

ETHICAL APPROVAL

This article does not contain any studies with human participants or animals performed by any of the authors.

ACKNOWLEDGEMENGTS

This research was supported by the Science and Research branch of Islamic Azad University and also Iran polymer and petrochemical institute.

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