

Effect of Grafting Ratio on Rheological and Mechanical Properties of High Density Polyethylene-graft-Maleic Anhydride/Polyamide 6 Blends

¹CHENGZHI CHUAI, ¹MAHMOOD IQBAL*, ²MUHAMMAD AIJAZ,
MANZOOR IQBAL AND ¹LIU HIU

¹*School of Materials Science and Chemical Engineering,
Tianjin University of Science and Technology, 13th Street Tianjin, 3004571, China.*

²*Polymer and Plastic Center, PCSIR Labs Complex Karachi 75280.*

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Summary: Graft copolymerization of high density polyethylene with a maleic anhydride was carried out using intermeshing co-rotating twin screw extruder in the presence of benzoyl peroxide (BPO). The HDPE/PA6 and HDPE-g-MAH/PA6 blends were prepared in a co-rotating twin screw extruder. The melt viscosity of the grafted HDPE was measured by a capillary rheometer. The grafted copolymer was characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The influence of the variation in temperature, benzoyl peroxide (BPO) and maleic anhydride (MAH) concentration and temperature on the grafting degree and on the melt viscosity were studied. The grafting degree increased appreciably up to about 0.4 phr, and then decreased continuously with an increasing BPO concentration. Furthermore, the results revealed that the tensile strength of the blends increases linearly with increasing polyamide 6 content. The results of scanning electron microscopy (SEM) and mechanical test showed that the blends have good interfacial adhesion and good stability of the phase structure, which is reflected in the mechanical properties.

Introduction

Manufacturing high-performance polymers is a main objective for polymer scientists and engineers. The manufacturing of multiphase plastics generally offers a way to combine several properties of individual polymer components. It can be achieved by mixing two or more polymers leading to the formation of polymer blends or an alloy. The possibility of compounding polyolefins (HDPE) with polar polymers such as polyamide has resulted in the development of available HDPE/polar polymer blends [1-4]. However, HDPE and polyamide are thermodynamically immiscible and phase-separated upon blending because of poor adhesion. Improvement of the adhesion between the phases is possible to obtain chemical compatibility of the blend, *i.e.* by the introduction of the third component into the two-polymer blend [5-11]. Most common compatibility can be promoted through block or graft copolymers containing group capable specific interaction with the blend component. These copolymers are synthesized separately which can react with the functional group of polyamide during blending [12]. Generally, the functionalization of low

density polyethylene has been successfully obtained using solutions, [13, 14], melts [15, 16], and even solid-state route [17]. Special attention has been paid on the reactive extrusion [18]. For the peroxide-initiated functionalization of polyethylene in melted state, which is often called the "reactive extrusion method" it is generally observed that cross-linking and/or chain scission may occur simultaneously with the reaction. For polyethylene, the dominant side reaction is cross-linking; for polypropylene, the prominent side reaction is chain scission [19-22]. In the case of the ethylene-propylene rubber, both cross-linking and chain scission may be important and lead to a very wide distribution of chain structure from highly degraded short chains to partially cross-linked chains and a plateau value of gel content ($\sim 50\%$) [21]. As interfacial properties are expectedly improved with increasing of the polar moiety, the side reactions may certainly alter the rheological nature and processing characteristics along with the mechanical properties of the functionalized polymer [23-25]. Therefore, the functionalization of HDPE *via* grafting unsaturated

*To whom all correspondence should be addressed.

monomers such as maleic anhydride (MAH) and acrylic acid has received a great deal of attention during the last several decades [26-29]. The modifications of PE with MAH through a free radical reaction in both solution and melt processes have been widely investigated [30]. Recently, Heinen *et al.* [31] synthesized [2, 3-¹³C₂] PE- g-MAH both in solution and in melt systems including high-density polyethylene (HDPE) and low-density polyethylene (LDPE). From noise-decoupled and 1D inadequate ¹³C NMR spectroscopy they found that MAH groups grafted onto HDPE and LDPE are in the form of single succinic anhydride and short oligomeric succinic anhydride, the average chain length is about 1-2, when the grafting is administered with an MAH amount of 10 wt % PE. Covas and co-workers [32] studied the free-radical melting grafting of MAH onto PE with an emphasis on the physicochemical phenomena developing along the screw axis of a twin screw extruder for different PEs.

In this study, the co-rotating twin-screw extruder is employed to study the grafting of MAH onto a HDPE chain. FT-IR technique is used to evaluate the grafting degree and another objective is to investigate the combined effects of maleic anhydride, benzoyl peroxide and temperature on grafting degree, melt viscosity and tensile strength of reaction product.

Results and Discussion

The FT-IR analysis is an analytical tool frequently employed to follow the maleation reaction. In Fig. 1(a, b, c), three spectra are depicted; they are respectively referred to as the following: pure HDPE (spectrum a), purified products of HDPE -g-MAH (spectrum b), and HDPE-g-MAH/PA6 sample after a formic acid extraction procedure (spectrum c). It can be observed from spectrum (b), that new absorptions appear in comparison to spectrum (a). These new absorptions are located at 1735 and 1783 cm⁻¹, and are assigned to the asymmetric and symmetric stretching of the carbonyl bond (C=O) of the grafted anhydride, and were found to support further the morphological observations. The band observed at 720 cm⁻¹ is attributed to the rocking vibrations of the -CH₂ bonds in HDPE. These results are consistent with the experiment of Hayes and McCarthy [33]. In spectrum (c), characteristic peaks

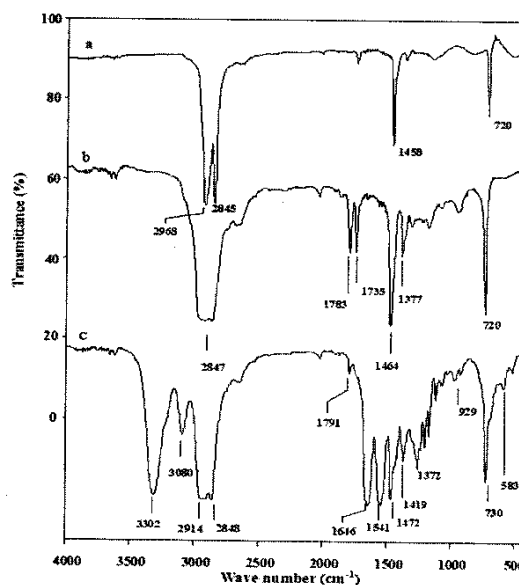


Fig. 1: FT-IR spectra of (a) virgin HDPE, (b) HDPE-g-MAH (c) HDPE-g-MAH/PA6.

for PA6 absorption are as follows: at 1646 cm⁻¹ C=O stretching vibrations, at 1541 cm⁻¹ N-H bending vibrations and at 3302 cm⁻¹ N-H stretching vibrations respectively.

Morphology

The SEM micrographs of the pure HDPE, MAH grafted HDPE, HDPE/PA6 and HDPE-g-MAH/PA6 70/30 blends are shown in Fig. 2(a-d). It is clear from Fig. 2(a) that the dispersed HDPE particles with an average size of about 5µm have almost completely smooth surfaces. On the other hand, HDPE-g-MAH surfaces are very rough and the shape of the MAH particles is irregular which indicates that MAH monomers were grafted onto HDPE as shown in Fig. 2(b). The blends without added HDPE-g-MAH display low interfacial adhesion and poor dispersion of the minor phase droplet size. The interface between PA6 and HDPE phases is very clear [Fig. 2 (c)]. As it was shown in the work of Filippi *et al.* [12], addition of 0.4 phr BPO into blends brings about a considerably improvement of compatibility. In fact the two phases of the blends become practically indistinguishable [Fig. 2 (d)]. This indicates that the addition of 0.4 phr BPO increases the interfacial adhesion, which

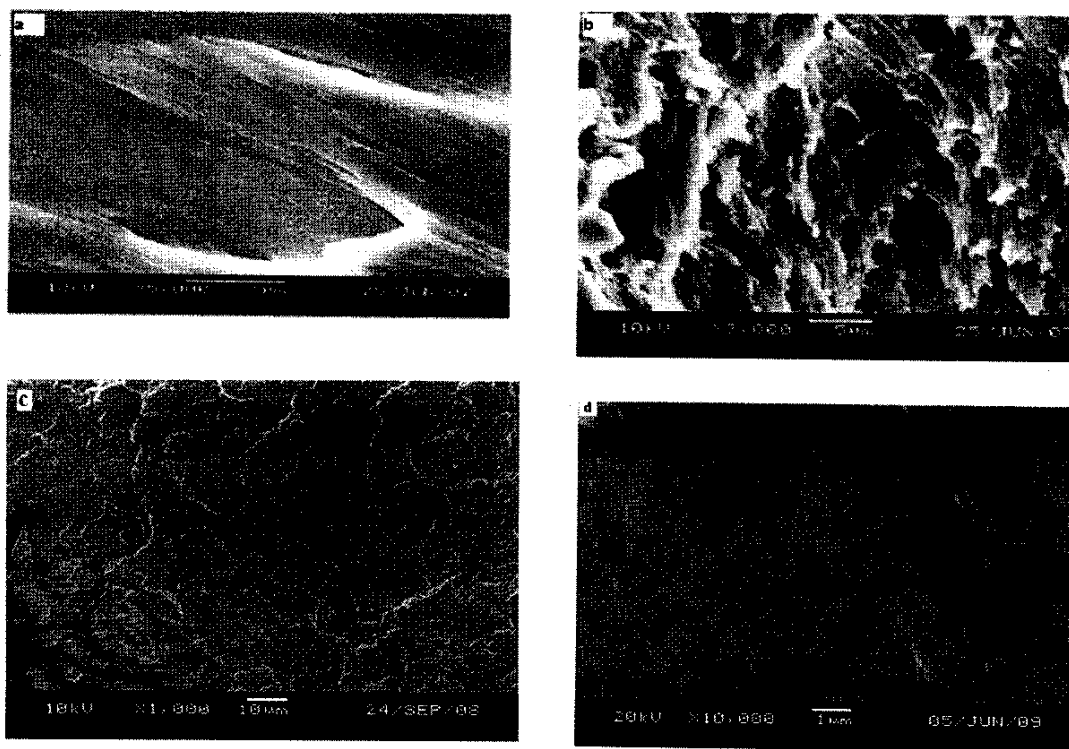


Fig. 2: SEM photograph of (a) virgin HDPE. (b) HDPE-g-MAH. (C) HDPE-g-MAH. SEM/PA6 (d) SEM photograph of the HDPE/PA6 /BPO/MAH blends with composition, 70/30/0.4/0.3.

promotes fusion of different phases. This increased interfacial adhesion for the blends was believed to be attributed to the chemical reaction of MAH group with amine end group in PA6 main chain molecule and consequently, improve the mechanical properties of the blends. Better dispersion and improved interfacial adhesion were attributed to formation of a HDPE-g-MAH/PA6 copolymer during the melt mixing

Effect of Maleic Anhydride Concentration

The accurate evaluation of the form of the grafted anhydride was beyond the scope of this investigation. Indeed, even if a mathematical elaboration of FT-IR spectra could be of help in discriminating among the two cyclic forms, our spectroscopic characterizations were addressed only with the aim of determining the amount of cyclic carbonyl compound grafted to the polymer as this

method was proved to be more effective than acid group titration when the polymer is analyzed in the form of a film and is properly treated for the removal of unreacted anhydride. A set of experiments was performed to investigate the influence of the initial concentration of MAH on the grafting process. Table-1 reflects the variations of the grafting degree of MAH with HDPE. From the same Table-1, it is observed that the grafting degree increases systematically up to about 0.3phr but later decreases linearly with increasing MAH concentration. A similar behavior was reported by Yang *et al.* [34]. In their experiment, it was found that the grafting degree increases linearly with increasing MAH content, then decreases with the increase of the MAH content. Interestingly the grafting degree of our laboratory grafted HDPE is higher than that of the work described by other researchers [23, 38]. Additionally, the molecular weight (M_n) of grafted PE increases markedly with increasing MAH content until 0.3phr

Table-1: Effect of MAH content on grafting degree.

S. NO	MAH (phr)	BPO (phr)	Grafting degree (%)
1	0.1	0.4	1.4
2	0.2	0.4	2.6
3	0.3	0.4	3.8
4	0.4	0.4	2.7
5	0.5	0.4	1.2

and later the percentage of grafted MAH levels off or decreases and therefore, contributes to increasing the melt viscosity of the materials. The results demonstrate that the chemical reactions for the grafting almost terminate at 0.3phr if the thermal degradation is neglected.

The influence of MAH concentration on the melt viscosity of MAH grafted HDPE is displayed in Fig.3. The melt viscosity of HDPE-g-MAH showed an increased tendency while increasing the amount of MAH. According to Gaylord³⁰ the cross-linking reaction results from the generation of radical sites on the polymer backbone followed by coupling. When MAH is present, the number of these sites is increased and therefore, the extent of crosslinkage is increased. In addition, the inter-polymer polar interaction between anhydride groups in the grafted HDPE may contribute to the melt viscosity increase.

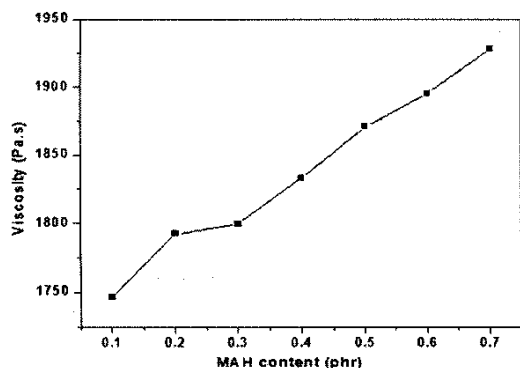


Fig. 3: Effect of MAH concentration on maleated HDPE melt viscosity.

Effect of Benzoyl Peroxide Concentration

Fig. 4 shows the influence of BPO concentration on the melt viscosity at a constant MAH content (0.3phr). In the absence of BPO, no

grafting occurred. As expected, the amount of grafted MAH increased when the initiator concentration was increased up to 0.4 phr; further increment behind this value did not lead to an improvement in the amount of grafted maleic anhydride. However the crosslinking side reaction increased with increasing BPO content in the MAH grafted HDPE, the extent of which was reflected by the increase in the melt viscosity [35].

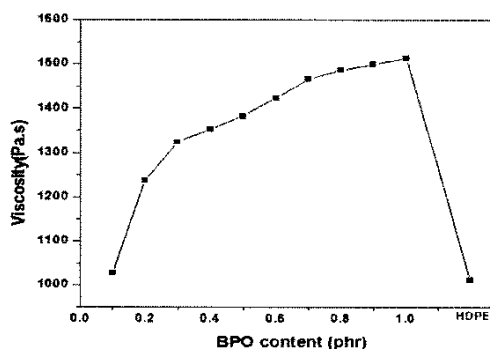


Fig. 4: Effect of BPO concentration on maleated HDPE melt viscosity.

The influence of BPO concentration on the grafting degree is summarized in Table-2. It is observed from the results that increasing the initiator concentration at a constant MAH content of 0.3phr resulted in an increase in the grafting degree up to about 0.4phr but later it drops continuously with increasing BPO concentration. Moreover, the molecular weight (Mn) of grafted HDPE increases systematically with increasing BPO concentration and therefore, contributes to a net enhancement in the melt viscosity of the material [36]. It is suggested that the chemical reactions for the grafting are almost complete at 0.4phr if the thermal degradation is ignored.

Table-2: Effect of BPO concentration on grafting degree.

S. NO	MAH (phr)	BPO (phr)	Grafting degree (%)
1	0.3	0.1	0.4
2	0.3	0.2	1.1
3	0.3	0.3	2.8
4	0.3	0.4	3.7
5	0.3	0.5	2.7
6	0.3	0.6	1.2
7	0.3	0.7	0.9

Effect of Temperature

The influence of reaction temperature was also a source of investigation. In fact, quite obviously, when the temperature is increased the rate of generation of free radical species is made faster owing to the faster decomposition of the initiator. We have observed that at fixed BPO and MAH ratios the grafting level initially increases with increasing reaction temperature until about 170°C, then decreases continuously with further increasing temperature. The results are reported in Table-3. It is clear from the experimental results that the decrease in grafting level was due to a chain scission of HDPE at higher reaction temperatures

Table-3: Effect of temperature on grafting degree.

S. NO	Temperature (°C)	MAH/BPO (phr)	Grafting degree (%)
1	150	0.3/0.4	1.1
2	160	0.3/0.4	2.6
3	170	0.3/0.4	3.5
4	180	0.3/0.4	1.0

The results of temperature dependence on melt viscosity of HDPE-g-MAH are depicted in Fig. 5, with an observation that the melt viscosity of the sample appears some first increase with increase of the reaction temperature and then obviously decreases above 170°C of reaction temperature. The decrease in the melt viscosities caused by generation of free radical species was made faster owing to the faster decomposition of BPO which led to the chain scission of HDPE at high temperature [37].

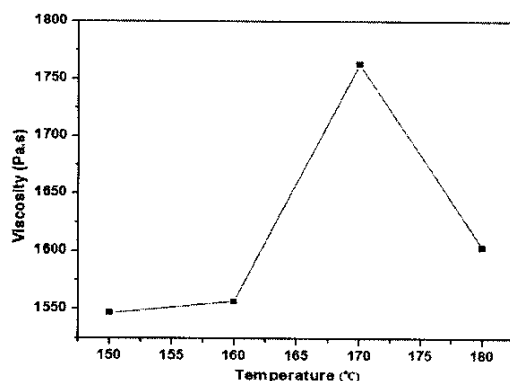


Fig. 5: Effect of temperature on the maleated HDPE melt viscosity (HDPE 100phr, MAH 0.3phr, BPO 0.4phr).

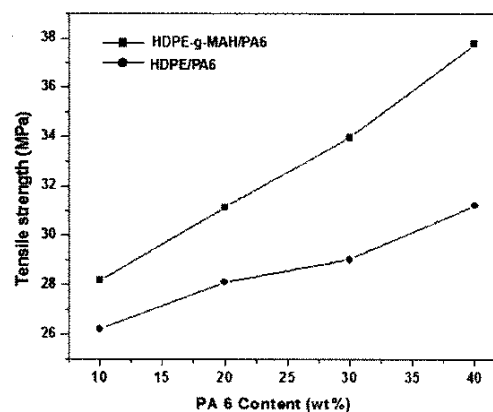


Fig. 6: Effect of PA6 content on the tensile strength of HDPE/PA6 and HDPE-g-MAH/PA6 (HDPE 100phr, MAH 0.3phr, BPO 0.4phr)+.

Mechanical Properties

A further part of our study was oriented to evaluate the end-use properties of the grafted and ungrafted HDPE and their blends with different content of PA6 are illustrated in Fig.6, and were found to support further the morphological observations. It is observed that HDPE-g-MAH/PA6 exhibit higher tensile strength than HDPE/PA6. From Fig.6 it is found that blending of PA6 with HDPE-g-MAH obviously improves the mechanical properties and the mechanical properties of blends increases as the miscibility of the HDPE and PA6 improves. The tensile strength of the blended polymer was found to depend exclusively on PA6 loading. The results revealed that tensile strength increased almost linearly with increasing PA6 contents in a gradient way. This increased is due to both particle size reduction and an improvement of the interfacial adhesion caused by the formation of HDPE-g-PA6 copolymers that appear to lead to the improvement of mechanical properties [38].

Experimental*Materials*

Polyethylene sample used for preparation of blend was a high density polyethylene (HDPE) grade (6063 M), supplied by SINOPEC Petrochemical Co Ltd. Beijing, China. Polyamide six was purchased from UBE Industry, Ltd. Japan with density of 1.12

g/cm^3 and melting point of $220\text{ }^\circ\text{C}$ and MFI ($220\text{ }^\circ\text{C}$, 2.1kg) = $2.0\text{ g}/10\text{ min}$. Benzoyl peroxide (BPO) was purchased from Tianlian Fine Chemical Company, Shanghai with a melting point of $102\text{-}106\text{ }^\circ\text{C}$ and was used as received. Maleic anhydride (MAH) was obtained from Tianjin Yong Da Chemical Reagent Development Centre, China of reagent grade and was used without further purification. All other chemicals including xylene and acetone were of reagent grade and used as received. All the polymers were carefully dried under vacuum before use.

Grafting Procedure

The grafting reaction was performed at Hebei Light Industry Ltd. China in a co-rotating twin-screw extruder (screw diameter: 30mm , length: 706mm). The BPO and MAH were dissolved in acetone and mixed with HDPE granules. After vaporizing the acetone, MAH and BPO adhered onto the granules homogeneously. The temperature profile of the extruder from the feed zone to the die varied at $150/170/170/160\text{ }^\circ\text{C}$ and the rotation speed of the screws was constant at 60 rpm . The extrudate was obtained in the form of a strip which was quenched in cooling water and palletized.

Blending

Both the high density polyethylene and polyamide 6 raw materials were in the form of pellets. The polyamide 6 pellets were dried at $110\text{ }^\circ\text{C}$ under a vacuum of 24 h .

Blends of HDPE/PA6 and HDPE-g-MAH/PA6 with a composition ratio of $70:30\text{ w/w}$ were prepared by means of a co-rotating twin-screw extruder. The temperature profile of the extruder varied at $150/220/220/215\text{ }^\circ\text{C}$ and the rotation speed of the screws was constant at 60 rpm . Pure PA6 was passed into the extruder to compare materials with the same thermomechanical history. The strip from the extruder was quenched in cooling water and separated into granules about 4 mm long.

FT-IR Analysis

The grafted samples were purified by dissolving in boiling xylene by precipitation of soluble part in acetone. Grafted polymers were

separated by filtration, washed several times with acetone, and then dried at $60\text{ }^\circ\text{C}$ under vacuum to obtain a constant weight. The HDPE-g-MAH/PA6 blend samples were purified using formic acid and hot xylene as selective solvents. The blend samples were treated first with formic acid and the insoluble fraction was separated by centrifugation of the suspensions, washed with the pure solvent, pure methanol, dried and weighed. The dried sample was extracted further by repeated treatments with hot xylene to obtain a xylene soluble and a xylene insoluble fraction. The insoluble fractions were washed several times with acetone, and then dried at $60\text{ }^\circ\text{C}$ under vacuum, until the weight of the product was constant.

The purified products of HDPE functionalized blends obtained were compression molded into thin films with a thickness of about 0.05 mm for Fourier transform infrared (FT-IR) characterization using a Bruker Vector -22 spectrophotometer (Germany). Grafting degree of MAH on HDPE was determined in comparison with a peak responsible for asymmetric and symmetric stretching vibrations of a C=O in MAH at a wave number 1783 cm^{-1} , 1735 cm^{-1} in comparison to $-\text{CH}_2$ rocking vibrations in HDPE at 720 cm^{-1} , which was used as the internal reference for the normalization of spectra [16, 39-41].

Morphological Analysis

The surface morphology of the copolymers was investigated by scanning electron microscopy (SEM, JEOL/EO and model JSM-6380, Japan) at an accelerating voltage of 10 kV . The samples were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before SEM examination.

Rheological Characterization

Rheological measurements of the grafted copolymers were made with a capillary viscometer, RH 2000-BOHLIN Instrument using a die with a 1 mm diameter and $L/D = 40$, at $180\text{ }^\circ\text{C}$.

To prepare a sample for the mechanical characterization blends were molded both by injection molding (JDH50 P Series Model).

The strength of the blend samples was measured by using computer-operated materials testing machine (Shenzhen Sans Model CMT4503 China) using a dumbbell specimen according to ASTM D415-80 at $20 \pm 3^\circ\text{C}$ with a cross-head speed of 50 mm min^{-1} . The data presented are the average of five tests in each case.

Conclusions

The reactive extrusion process has been developed for chemical modification of high density polyethylene using BPO as an initiator. It is evidenced from experimental results that the grafting degree increases systemically to a peak value, then dropped sharply with increasing BPO concentration. Moreover, the results showed that the molecular weight (M_n) of grafted HDPE increased linearly with increasing BPO content up to 0.4phr but later the percentage of grafted levels off or decreased and therefore contributed to an increase in the melt viscosity of the materials. The results revealed that the grafting degree increased appreciably with increasing MAH concentration up to about 0.3phr, then decreased continuously with further increasing MAH content. Furthermore, the experimental results indicated that melt viscosity increased almost linearly with increasing MAH contents.

The mechanical properties of the PA6/HDPE blends increased as the miscibility of the HDPE and PA6 improved. Proper selection of the operative conditions, we obtained a grafting degree higher than 3.8 %. The whole experimental picture suggested that maleation of HDPE can be successfully performed by the reactive extrusion in twin-screw extruder, therefore, allowing the achievement of a high grafting level in the presence of limited molecular degradation of the polymer.

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