New Aspects of the Reaction of HDPE with Maleic Anhydride

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ABSTRACT

The solution and bulk reactions of high density polyethylene (HDPE) with maleic anhydride (MA) with dicumyl peroxide initiator indicated a cyclical reaction. This cyclic reaction is expected to continue every 6 min in the mixer, depending on the concentration of monomer or the initiator. The reaction is chemosorption with novel fractal kinetics. The reaction conversion based on the percent MA grafted is cyclical both in solution and bulk. The torque of the mixer also reflects the same cyclical trend. The thermogravimetric and thermal analysis of the grafted product (MA-HDPE), prepared in the mixer and extruder, were used to measure the melting point. The effect of the initiatior, MA and rpm of the mixer on the melting point of the grafted HDPE are also reported.

Key Words: HDPE, maleic anhydride, grafting, cyclical reaction, thermal analysis

INTRODUCTION

The reactions of polymers with monomers in various media have been of interest for sometime. More recently, due to a new surge in production of grafted polymers and specifically the grafting of polyolefins; practical interest in the industrial application of these materials as compatibilizer of the heterogeneous polymer systems, and their reaction with more reactive monomers such as maleic anhydride has reached a new peak [1–5].

Furthermore, we are now directly concerned with the molecular design of the grafted polymers and the necessary conditions to make the desired product with a specific use without gellations or cross-linking. For this purpose we have introduced the concept of

active sites and the maximum free radical centers generated in the polymer system. We have also tried to optimize the conditions to reach the highest yield in a continuous process and adjust the kinetic parameters to the best possible yield. Since this is considered as an ultimate aim in industrial application of these materials, we have undertaken the kinetic study of reaction in bulk and we have tried to determine the important factors involved in reaction and its possible application in the process design, both in a continuous or discontinuous systems.

In this paper, we wish to report the grafting reaction of high density polyethylene (HDPE) with maleic anhydride (MA) in the bulk and report the formation of the maximum active sites generated upon the free radical reaction of polymer with the initiator

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during the desired mixing or extrusion processes. We also wish to report the cyclic conversion of this grafting reaction, and report further the crystallinity of the product with experimentally determined enthalpy and percent conversion of polymer during this reaction extrusion.

EXPERIMENTAL

HDPE was supplied from Arak Petrochemicals. The polymer grade is I₃, (MFI=23 and mp=144 °C). Maleic anhydride was obtained from Merck (mp=55 °C, 99% purity). Viscosity was determined in dichlorobenzene at 135 °C in a heating oil bath, using Ubbelohde viscometer.

Percent reaction rate of MA or grafting was determined according to procedures described earlier (titration with NaOH and FTIR films) [6]. The grafting was carried out in xylene and the bulk reaction was carried out in a Haake mixer, or a twin-screw co-rotating intermeshing extruder [7]. The melting points and the enthalpies were determined with TG from Perkin Elmer and DSC from Polymer Laboratories.

RESULTS AND DISCUSSION

Experiments were carried out within a short period of time, to show only the 1st cycle of the reaction conversion. The grafting process in the mixer or extruder, is expected to follow an alternating cycle of conversion. The first cycle in bulk, has been shown in Table 1. Similarly, the effect of the initiator dicumyl peroxide (DCP) in the solution reaction with 2% MA monomer with HDPE, after 60 min of grafting is shown in Table 2. The cyclic conversion reaction of HDPE with MA

Table 1. Conversion of grafted HDPE in the mixer[a].

No	Time (min)	MA Grafted (%)	[η] dL/g
1	2	15.1	0.530
2	4	25.0	0.510
3	6	34.5	0.504

(a) [η] of HDPE is 0.555 dL/g.

Table 2. Effect of DCP on grafting MA on HDPE t=60 min.

No	Dicumyl peroxide (%)	MA Grafted (%)
1	0.075	8.10
2	0.150	12.10
3	0.350	7.20

Reaction is in dichlorobenzene at 100 °C.

in solution is expected to depend on the concentration of free radicals and this effect has been shown in Table 3.

The reaction of HDPE with MA is expected to follow a free radical reaction in which the initiator DCP, decomposes upon heating to form free radicals, the radicals form the most stable active centers or sites in the polymer chain [4]. These centers are mostly located where the shortest or longest branches of HDPE in form of methyl, ethyl or higher alkyl groups are located. Once tertiary free radicals are generated they become reactive on the surface of the polymer or at its interface. The higher the concentration of the initiator the larger is the number of active centers, and the higher is the possibility of reaction of more reactive small monomer with these centers (reactions 1–3). If these centers stay in locations other than the surface, the reaction between reactive radical and polymeric anhydride increases (reaction 4), and therefore, further competition is caused between the active centers of the chain and the free radical polymerization of MA. Other free radical reactions involved are termination reactions or coupling reaction (reaction 5).

Reactions of HDPE with MA:

$$DCP \longrightarrow DCP \text{ radicals } (2I.) \tag{1}$$

$$HDPE + I. \longrightarrow \sim P. \tag{2}$$

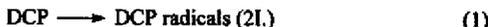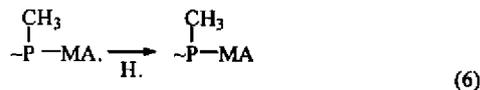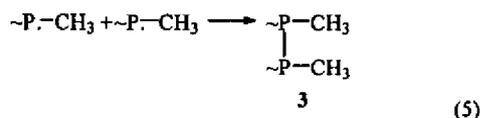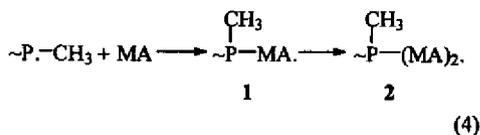$$2P. \longrightarrow \sim P–CH_3 + \sim P. \tag{3}$$

Table 3. Grafting conversion time of HDPE with MA (4% wt) and DCP (0.15% wt) in solution (xylene at 134 °C).

Time (min)	15	60	120	180
MA grafted (%)	34.1	40.8	54.5	35.9

$$\sim P.-CH_3 + MA \longrightarrow \sim \overset{\overset{\displaystyle CH_3}{|}}{P}-MA. \longrightarrow \sim \overset{\overset{\displaystyle CH_3}{|}}{P}-(MA)_2.$$

$$\underset{\mathbf{1}}{} \underset{\mathbf{2}}{}$$

$$(4)$$

$$\sim P.-CH_3 + \sim P.-CH_3 \longrightarrow \overset{\sim P-CH_3}{\underset{\underset{\sim P-CH_3}{|}}{}}$$

$$\underset{\mathbf{3}}{} \qquad (5)$$

$$\sim \overset{\overset{\displaystyle CH_3}{|}}{P}-MA. \underset{H.}{\longrightarrow} \sim \overset{\overset{\displaystyle CH_3}{|}}{P}-MA$$

$$(6)$$

$$MA + I. \underset{H.}{\longrightarrow} (MA)_n \qquad (7)$$

$$\sim P.-CH_3 \xrightarrow[\mathbf{3}]{1,2} \text{cross-linked HDPE} \qquad (8)$$

The grafted HDPE has been isolated and its FTIR and its intrinsic viscosity [η] of the grafted polymers in the extruder have been reported [6]. The reaction in mixer reaches its maximum after 6 min of mixing and 34.5% of maleic anhydride reacts by this time (Table 1). In the extruder the grafting depends on the rpm (Tables 4 and 5) and the grafting conversion reaches its maximum (20.1%) at 3.45 min.

In bulk, the molecular weight of HDPE decreases upon mixing with MA. The grafting does not seem to increase considerably with the concentration of monomer in this system (Tables 5 and 6). It seems that, grafting reaction is primarily a function of active centers, and these centers reach a constant level

Table 4. Grafting conversion time of HDPE with MA in bulk (extruder).

No	Time (min)	MA Grafted (%)
1	1.30	8.0
2	2.15	12.2
3	3.00	16.3
4	3.45	20.1

4% wt MA, 0.025% DCP, rpm is adjusted at 55, 45, 35 and 25, T₁=174, T₂=174, T₃=175, T₄=176 and T₆=176 °C.

Table 5. Grafting reaction conversion of HDPE with 4% wt MA and 0.025% DCP in bulk in the extruder.

No	rpm	Graft (%)	[η] dL/g	Time (min)	Active centers (mol/g)
1	55	8.5	0.540	1.50	1.869
2	45	12.2	0.531	2.25	3.054
3	35	16.3	0.530	3.00	3.190
4	25	20.1	0.528	3.45	3.460

in less than 4 min. It is reported that additional maleic anhydride may participate in gellation. More specifically, the effect of rpm and concentration of the monomer on the grafting have been shown in Tables 6 and 7. These tables show the concentration of monomer and the rpm of the extruder. It is clear that active centers generated in this system remain almost the same and its concentration is about 4 (mol/g). The increased active centers and the highest conversion are related to the low rpm.

Effect of Mixing Time on the Viscosity of the Polymer

The grafting reaction of HDPE, using DCP initiator and MA monomer in the mixer; has been studied in bulk and results are shown in (Tables 1 and 9). The chain scission and formation of active centers during mixing of HDPE with DCP, causes an alternating cycle that ultimately leads to a lower viscosity (Table 9).

The effect of the concentration of monomer and rpm of the mixer on the torque and the reaction time of HDPE with maleic anhydride in solution are shown in Figures 1 and 2. Tables 8 and 9 show that torque

Table 6. Grafting reaction conversion of HDPE with 6% wt MA and 0.025% DCP in the extruder.

No	rpm	Graft (%)	[η] dL/g	Time (min)	Active centers (mol/g)
1	55	9.1	0.542	1.50	1.6
2	45	13.4	0.535	2.28	2.52
3	35	17.1	0.532	3.00	2.92
4	25	20.9	0.530	3.76	3.19

Table 7. Effect of rpm and monomer concentration on HDPE grafting yield*.

No	rpm	MA (%)	Graft (%)	[η] dL/g
1	20	2	14.0	0.529
2	20	4	21.0	0.535
3	20	8	30.8	0.545
4	30	2	10.0	0.520
5	30	4	16.0	0.530
6	30	8	24.0	0.540

(*) Active centers are 1.23–4.57 mol/g.

Figure 2. Reaction conversion of HDPE and MA in solution.

increases, upon addition of DCP initiator, but this increase is in form of cycle for less than 6 min. The product isolated after 7 min shows 6.92 mol/g maximum number of radical chain ends or active sites. The cyclic trend of the reaction of HDPE with DCP, or its further reaction with monomer is led by similar reactions in form of propagation or termination of these active centers.

The rate constants for the reaction in the mixer and extruder are smaller, than the reaction in solution (Table 3). Our reported rates have been related to the earlier part of the reactions of HDPE [7].

These systems are considered to be dynamic because the monomer is not equally feasible to the larger polymer chains. Under these conditions the interface of the heterogeneous system of HDPE and

grafted PE controls the reaction. Based on a reported fractal kinetics the active sites on the surface of polymer interacts with monomer, and the reaction may follow a chemiodesorption process, (Appendix I-A) [4].

The grafting reaction and the viscosity of polymers during the continuous reaction with 4, 6 and 8% weight monomer are shown in Tables 5, 6 and 7. The probability of the reaction of monomer to generate the maximum active sites depends on the DCP concentration and the flow behaviour of the system. The flow behaviour in the extrusion is a complex process that may depend on the screw design, geometry, and its direction. The process is even more complicated when a polymer reacts with a monomer in a continuous or discontinuous form [10].

In this work, a double screw extruder has been used for the advantage of carrying out a fast reaction of polymer with monomer. In this process the entire

Figure 1. Effect of torque and time in the mixer.

Table 8. Effect of mixing time (min) on the torque (NM) and viscosity of the polymers, rpm=30*.

No	HDPE (g)	DCP (g)	MA (g)	Time (min)	T (°C)	Torque (NM)	[η] dL/g
1	60	–	–	4.54	–	4.4	0.554
2	60	0.09	–	5.00	175	5.5	0.534
3	60	0.09	–	7.00	181	8.1	0.509
4	60	0.09	2.4	7.00	181	8.2	0.510
5	60	0.09	2.4	8.24	182	8.0	0.504

(*) Active centers are 2.57 –6.92 mol/g.

Table 9. The cyclical nature of the HDPE reaction with DCP in the mixer.

No	Time (min)	Torque (N/M)
1	2.0	4.1
2	3.0	3.3
3	4.0	4.2
4	4.3	5.0
5	5.0	5.5

fluid flows from one channel of the screw to another and the reaction is influenced by this flow. At each section of the screw; the concentration gradient and the conversion equation for a multi-component system exist. The rate is related to the chemical kinetics and local thermodynamics of the reaction. (Appendix B).

However, the enthalpy used in the energy equation, may be estimated from DSC measurements. Since the conversion of HDPE to the grafted polymer for a given concentration of monomer and initiator is known, we can use the calculated crystallinity of the polymer from the grafting reaction, to estimate ΔH of the polymer. The percent weight reduction of HDPE with 4% weight MA and 0.15% DCP reacted in the mixer within 5 to 9 min indicated that $T_m = 137.8\ ^\circ C$ and $\Delta H \approx 46.54$ mcal/mg.

The thermographs of the grafted polymer are

Table 10. Enthalpy of the grafted HDPE from the bulk reaction with MA in the mixer (4% wt MA and 0.015% DCP).

No	Mixing t (min)	Polymer grafted (%)	ΔH (mcal/mg)	T ($^\circ$C)
1	6	–	45.40	137.91
2	4	1.00	48.48	141.42
3	6	1.38	46.94	137.43
4	–	2.50	40.56	138.53

Table 11. Enthalpy of the grafting HDPE bulk reaction with MA in the extruder.

No	rpm	ΔH (mcal/mg)	T_m ($^\circ$C)
1	25	45.99	139.15
2	35	47.88	139.92
3	45	49.02	138.26
4	55	49.14	139.46

shown in Figure 3. Table 10 shows the enthalpy of melting of HDPE-g-MA in the mixer and Table 11 shows the effect of rpm on ΔH of the polymer. DSC thermographs of HDPE-g-MA are shown in Figures 4 and 5.

CONCLUSION

The grafting of HDPE with MA and DCP in solution

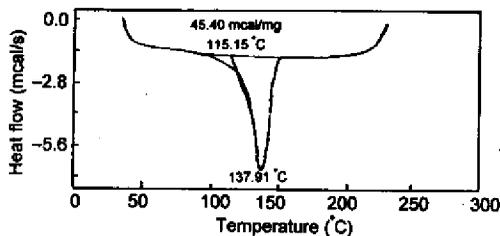**Figure 3.** Thermographs of the reaction of HDPE with MA in the mixer.
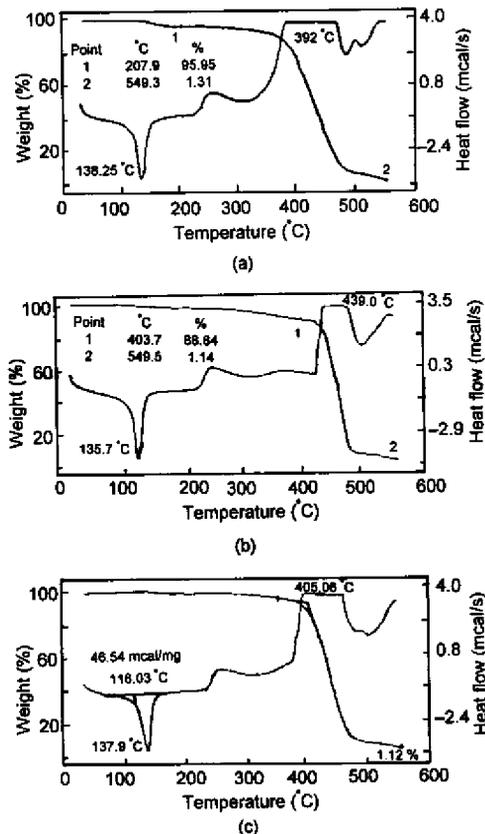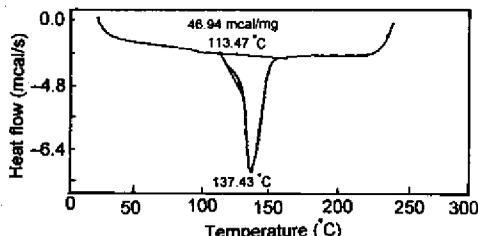
a = DCP = 0.15 wt%, MA = 8%, Reaction time = 5 min

b = DCP = 0.10 wt%, MA = 4%, Reaction time = 7 min
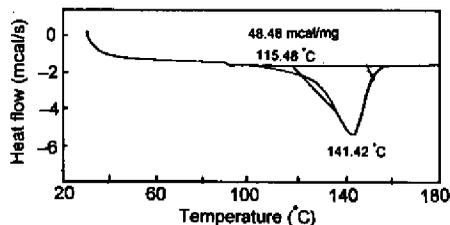
c = DCP = 0.10 wt%, MA = 4%, Reaction time = 9 min
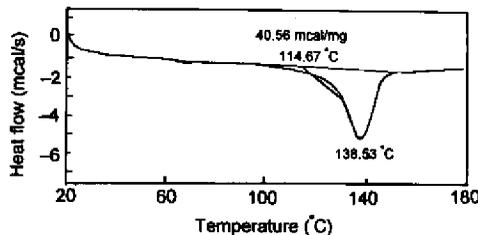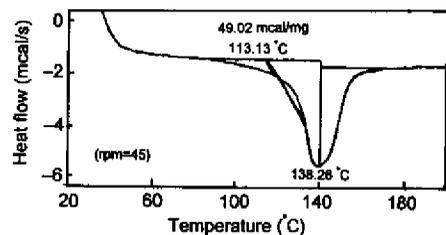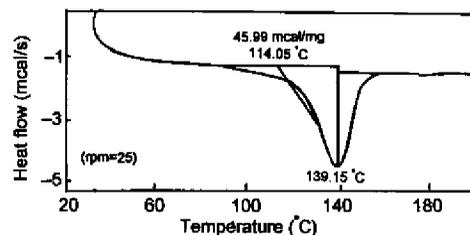
Figure 4. DSC Thermographs of HDPE-g-MA in the mixer.

and bulk is a cyclical reaction. The reaction of the polymer with MA in bulk depends on the rpm of
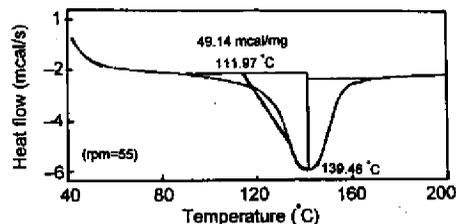
extruder and the grafting decreases with the increasing rpm of the extruder. The bulk reaction of HDPE with
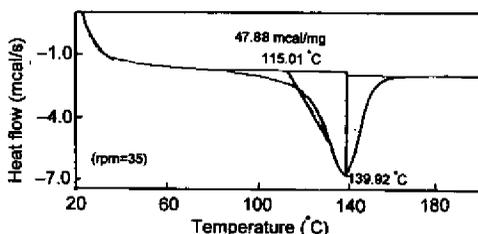

Figure 5. DSC Thermographs of HDPE-g-MA in the extruder.

DCP in the mixer also indicates a cyclical change in torque.

APPENDIX (A)

I-A: The equations for fractal kinetics are:

$$r_d = k_d(t).\Theta \qquad (1)$$

$$k_d = k_o.t^{-h}, \qquad h = 1-Ds/2 \qquad (2)$$

Where: k_d is the chemidesorption constant; h is the heterogeneity parameter, Θ is the coating, Ds is the parameter related to molecular motion; k_o and h are the intercept and the slope of the reaction rate, respectively [4].

APPENDIX (B)

I-B: Flow in the extruder:

In a twin-screw extruder, the overall flow in a co-rotating intermeshing screw is consisted of two major regions of the intermeshing (I) and translation region (T).

The overall flow is then made of ...IT IT IT... In the intermeshing region, the flow is complex if we assume a steady state, for incompressible Newtonian or non-Newtonian fluid in the screw channel, where H< <W, the equation can be simplified as expressed by a continuum flow in a plane [11, 12]:

$$\frac{\partial p}{\partial x} = \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} \qquad (3)$$

$$\frac{\partial p}{\partial y} = \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} \qquad (4)$$

$$\frac{\partial p}{\partial z} = \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} \qquad (5)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \qquad (6)$$

Where: p is pressure, τ stress tension as $\tau_{ij} = \mu(u_{i,j} + u_{j,i})$, for the generalized Newtonian fluid.

For this case, the energy equation of the flow is given as:

$$-\rho C(u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} + w\frac{\partial T}{\partial z}) + \frac{\partial}{\partial x}(k\frac{\partial T}{\partial x}) +$$
$$\frac{\partial}{\partial y}(k\frac{\partial T}{\partial y}) + \dot{Q} = 0 \qquad (7)$$

Where, in this equation, k is thermal conductivity of fluid, T is temperature, r is the density, C is the specific heat u, v, w are the velocity fields; $\dot{Q}$ is the heat source which arises due viscous dissipation and depends on the viscosity of the system in the inter-meshing region, and the equation for $\dot{Q}$:

$$\dot{Q} = \mu[2(\frac{\partial u}{\partial x})^2 + (\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x})^2 + 2(\frac{\partial v}{\partial y})^2 + (\frac{\partial w}{\partial x})^2 +$$
$$(\frac{\partial w}{\partial y})^2] \qquad (8)$$

Where, the viscosity and shear rates are defined according to the constitutive equation:

$$\mu = \mu_0 (\frac{\dot{\gamma}}{\dot{\gamma}_0})^{n-1} e^{-b(T-T_0)} \qquad (9)$$

$$\dot{\gamma} = [2(\frac{\partial u}{\partial x})^2 + (\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x})^2 + 2(\frac{\partial v}{\partial y})^2 + (\frac{\partial w}{\partial x})^2 +$$
$$(\frac{\partial w}{\partial y})^2]^{\frac{1}{2}} \qquad (10)$$

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