Chain Extension of PA1010 by Reactive Extrusion by Diepoxide 711 and Diepoxide TDE85 as Chain Extenders

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ABSTRACT: The chain extension behaviors of two diepoxides, epoxide TDE85 and 711, were studied to evaluate their coupling effects on polyamide 1010 (PA1010). The former gave better coupling effects and a faster reaction rate. The torque of PA1010 melt increased dramatically with reaction time. The effect of the diepoxy chain extender on the flowability, thermal properties, and mechanical properties of chain-extended PA1010 was investigated. The melt flow index (MFI) dramatically decreased as the diepoxide was added to PA1010, and the notched Izod impact strength of the chain-extended products also increased. Furthermore, study on the usage of chain extender showed that there exists an approximate platform on the curve of melt torque versus content of chain extender, beyond which crosslinking may occur. Theoretical analysis of the occurrence of crosslinking was carried out by Flory criterion, which demonstrated that the average amount of functional groups in the chain extension system played a significant role in avoiding crosslinking. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2347–2355, 2004

Key words: chain extension; polyamide; diepoxide; crosslinking

INTRODUCTION

The mechanical and chemical properties displayed by Polyamide 1010 (PA1010) have rendered it a useful polymer for significant practical applications. Produced by polycondensing a mixture of diamine and dicarboxyl in the presence of catalysts at a high temperature and in a vacuum,[1] it has a lot of advantages in many ways. The standard industrial polymerization processes, however, are efficient only in producing PA with a limited M_w because the high viscosity makes it very difficult for small molecules, such as water, to escape. To overcome the limitation, a postpolycondensation method in solid phase was developed; however, the very slow reaction rate and the necessity of large special equipment limit its application. For this reason, the chain extension is an attractive option. The chain extenders for PA are generally bifunctional compounds that can react easily with the end groups of PA and link two or more polymer chains together, producing PA with relatively high molecular weight.[2]

Chemicals that can be used as concentrate-type chain extenders, such as phosphate ester and phosphite ester, could generate some high-boiling-point byproducts in chain extension reaction, although they do have some effects on chain extension. An example is shown in Scheme 1. Consequently, addition-type chain extenders generating no byproducts are preferable. Bifunctional compounds, such as diepoxides, diisocyanates, and bis(cyclic carboxylic anhydride), belong to this kind.[3–5] However, some of these bifunctional chain extenders may cause undesirable branching or crosslinking, or introduce less thermally stable linkages in the main chain of PA with immoderate content.

Inata and Matsumura used many types of oxazines, such as biscyclic imino ethers, as chain extenders for both poly(butylene terephthalate) (PBT) and poly (ethylene terephthalate) (PET).[6–11] Both those reacting with carboxyl groups and those reacting with hydroxyl groups can help the chain extension of polyesters.[12–14] Other researchers have also used various kinds of chain extenders for polyesters, most of which stand a good chance of helping to increase the molecular weight of polyamides.

This study aims to lay out the coupling effects of two diepoxides and other properties of the chain-extended products by reactive extrusion. The results indicated epoxide TDE85 showed better coupling effect than did epoxide 711, although both can dramatically increase the melt viscosity within several minutes. There exists an optimal range of content of both chain extenders, respectively, beyond which crosslink-

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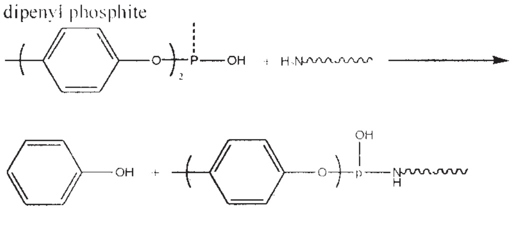


Scheme 1

ing may occur. On the other hand, Flory's criterion, of the occurrence of crosslinking used to analyze the structure of the chain-extended products, predicts what is the most critical in the system and proposes how to avoid immoderate crosslinking theoretically.

EXPERIMENTAL

Materials

PA1010 was supplied by Tianjin Zhonghe Chemical Factory (Tianjin, China). Epoxides TDE85 and 711 were provided by Tianjin Synthesis Material Institute, (Tianjin, China), listed in Scheme 2. Starting materials were used as received without any purification except that PA1010 was dried at 80°C for 12 h prior to use.

Chain extension reaction by haake mixer and extruder

Some well-dried PA1010 pellets were added into the mixing chamber of a Haake rheometer 600 mixer. The rotor speed was set as 40 rpm, and the temperature was 240°C. After complete melting of the pellets, the chain extender was added into the PA melt. The melt torque during mixing was recorded to measure the extent of the reaction. A reactive extrusion was performed on a corotating douple-screw extruder. The screw had a diameter of 30 mm and L/D ratio of 25. A mixture of well-dried PA1010 and the diepoxy was fed to the extruder and extruded at 220–240°C with a screw rotating speed of 30 rpm. The residence time was kept for ≈3–5 min by adjusting the extrusion rate. The extrudate was cooled by water and pelletized.

Tests of properties

The chain-extended PA pellets, which were dried at 75°C for 12 h, were injection-molded by a Zhende XS-Z-80 injection-molding machine to prepare impact and tensile bars. The injection-molding temperature was between 220 and 230°C. Tensile tests were performed on a GT-TS-2000 system with a tensile speed of 50 mm/min. The MFI was measured in a Jida XRZ-400 MFI testing instrument with a 2.160 kg load at 230°C. Isothermal crystallization and melting behavior of various chain-extended samples were measured with a Shimadzu-60 differential scanning calorimeter (DSC). The instrument was calibrated with indium during these measurements. The samples were heated to 250°C at 20°C/min, held at that temperature for 5 min, then cooled to 50°C at 20°C/min, and finally heated to 250°C again at the same rate. Rheologic tests of original PA1010 and chain-extended products by TDE85 and 711 were carried out in a Rh-2000 Rheometer at 240°C, with the shear rates ranging from 50 to 3000 s^{-1}. The apparent viscosity and the non-Newton index were calculated by the computer.

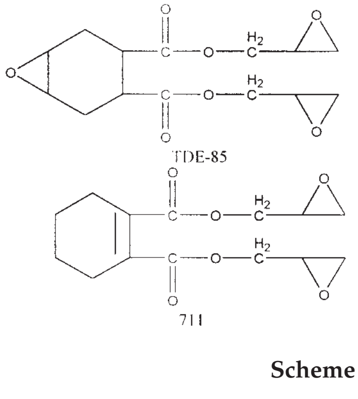
RESULTS AND DISCUSSION

The main reactions of the diepoxy with PA1010 can be categorized into three types, which are shown in Scheme 3.

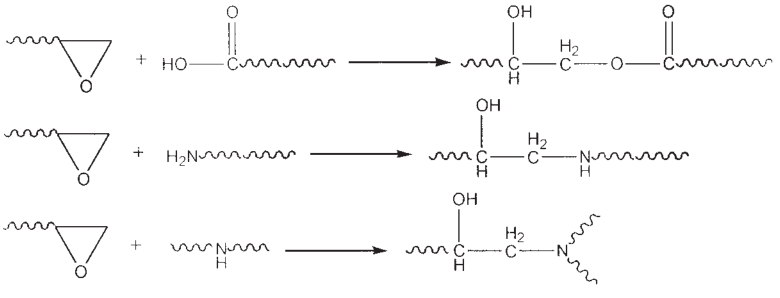
The epoxy group can primarily react with the carboxyl group, amine group, and imide group formed after coupling reaction between the amine and epoxy group. The reactivity of the side hydroxyl group formed during chain-extension reaction is relatively low so as to be ignored if chain extenders are not excessive. The reactivity of acylamino groups in the macromolecular chain is even much lower than that of the former, although their content is several hundred times that of the end groups.

Coupling effect of the diepoxides in Haake mixer

A Haake torque rheometer was used to measure the coupling effect of the chain extenders. It is observed from Figure 1[4–6] that the melt torque reaches its maximum within 3–5 min when a definite amount of diepoxide is used. After the addition of the diepoxide to the nylon melt, the torque immediately increased very fast, which was caused by the chain-extension reaction. The coupling effect of epoxide TDE85 is better than that of epoxide 711. After the chain-extension reaction was completed, the torque was maintained at a stable value for a very long time, showing good thermal stability of the chain-extended products.



Scheme 2



Scheme 3

Mechanical properties of chain-extended PA1010

The results of mechanical tests were summarized in Tables I and II. The value of melt-flow index (MFI) dramatically decreases when a definite amount of TDE85 is used; for example, when 0.5% epoxide TDE85 is added, MFI decreases to as 1/10 as origin. The PA melt with much higher viscosity can even be drawn to tenuous fiber thread in the process of extrusion. Generally speaking, the increase of molecular weight by chain extension causes only small changes in the tensile, yield, and flexural strength in most cases, except for the dry condition. Elongation at break decreases from about 300 to 200% until 0.5% chain-extender TDE85 is added, whereas the Izod impact strength of PA1010 obviously doubles as its origin. In some bars that were prepared by adding more TDE85, brittle fracture can hardly be found. Figure 2 shows the stress–strain curves of the chain-extended PA melts. The stress–strain curves differ from different kinds of chain extenders. The blank bars, extruded without any chain extender, show a little worse tensile strength than the virgin bars. The tensile strength of chain-extended sample by epoxide TDE85 is superior to that of sample by epoxide 711, despite a little decrease of elongation at break in both cases. The necking was obvious and propagated almost through the entire gauge length of the specimen prepared by adding epoxide 711. Nevertheless, the same phenomenon is not obvious in the case of chain extension by epoxide TDE85, especially if more content is used.

Rheological properties of chain-extended products

Figure 3 indicates different "Apparent viscosity versus shear rate" plots of chain-extended products by different amounts of epoxide TDE85. The value of apparent viscosity dramatically increases with the increase of chain extender's dosage, but the decrease caused by stronger shear seems to be more prominent. The non-Newton index showed the same trend which was also summarized in Table III. Figure 4 compared the chain extension effect by 0.5 or 1.0% epoxide 711 with that by epoxide 0.5% TDE85. Not only did the coupling effect of the former become poorer than that of the

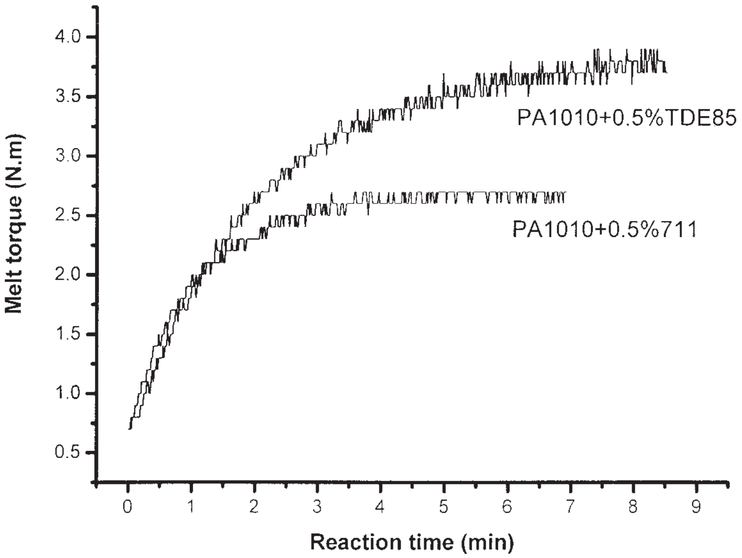


Figure 1 Melt torque changes with 0.5% 711 and 0.5% TDE85 as chain extenders at 240°C and the rotor speed of 400 rpm.

TABLE I
Mechanical Properties of Chain-Extended Products

C.E. content	Dry condition			Normal condition					Wet condition		
	A	D	E	A	B	C	D	E	A	D	E
0% TDE	267%	54.55	22.8	301%	31.06	52.62	44.51	35.9	294%	38.71	127.2
0.1% TDE	260%	54.78	38.3	290%	31.12	53.29	42.73	46.4	270%	39.98	152.7
0.2% TDE	254%	54.9	39.8	284%	32.81	51.89	48.97	57.8	257%	43.4	160.5
0.3% TDE	231%	56.12	49.4	260%	31.89	48.06	48.61	68.9	240%	42.91	179.6
0.4% TDE	210%	54.01	56.9	222%	33.56	52.42	46.97	74.9	214%	41.22	209.6
0.5% TDE	203%	54.43	63.8	223%	33.76	56.71	46.9	80.8	216%	42.15	239.5
0.5% 711	141%	58.36	40.2	250%	34.35	44.74	51.36	61.5	248%	40.10	167.7
1.0% 711	235%	57.31	60.1	189%	30.63	42.50	51.45	71.4	246%	39.29	175.8

A: Elongation at break; B: Yield strength (MPa); C: Tensile strength (MPa); D: Flexural strength (MPa); E: Izod impact strength (J/m).

latter, but also the chain extension effect by different content of epoxide 711 uncommonly showed little obvious distinction; neither did the mechanical properties of them. In fact, even the increase of melt torque by epoxide TDE85 did not accelerate rapidly at once, as a matter of experience. The reasons will be explained in the next section.

EFFECT OF CONTENT OF CHAIN EXTENDERS ON COUPLING

Inata and Matsumura pointed out in their articles[6–11] that the coupling effect reached its maximum with definite content of bisoxazolines (BOZ) as chain extenders. Because if an excess amount of BOZ is added, the blocking reaction would occur predominantly and the polyamide of not-so-much-increased molecular weight but much decreased carboxyl concentration would be produced.

This attributes to the case that the chain extenders can only react with one of both end groups of the polyamide molecule. In our case, both end-amide group or even imide group and end-carboxyl group can react with the diepoxides; the change tendency of coupling effect with content of chain extender is somewhat complicated. This kind of chain extension, accompanied by its crosslinking phenomenon, had been widely tested, but seldom theoretically analyzed. Supposing that A and B are end groups with different reactivities to chain extenders, and the ratio of the less reactive former to the more reactive latter is *n*, the characters of chain extension reaction can be classified into three categories.

If *n* is small, the chain extender reacts mainly with B by coupling effect when the usage of chain extender is equivalent to B. If it exceeds that level, the coupling reaction between chain extender group and A can no longer be ignored; in the mean time, the contribution of A to the coupling reaction can be raised by the blocking reaction of B and chain extenders. Whether the coupling effect goes down or not depends on the competition between the negative blocking effect by B and the positive coupling effect by A. With the small value of *n*, however, an excess amount of chain extenders could do nothing but decrease the coupling effect. It can be given as an extreme example of chain extension of polyamide or polyester by bisoxazolin, where *n* tends to be zero. When a little larger value of *n* is presumed, which can fitly compromise the integrated effect of blocking by B and effect by A, a platform in the curve plotting coupling effect versus content of chain extender can appear. It means that, at this critical value of *n*, the counteraction leads to the

TABLE II
Thermal Properties and MFI of Chain-Extended Products

C.E. content	T_m/°C	H_m/(J/g)	T_c/°C	H_c/(J/g)	T_{mt}/°C	C%	MFI/(g/10 min)
0% TDE	202.31	73.79	174.41	66.95	192.11	30.20%	9.80
0.1% TDE	201.79	63.77	174.02	58.07	191.72	26.10%	6.55
0.2% TDE	200.17	68.06	173.79	53.36	190.09	27.90%	3.10
0.3% TDE	199.63	62.46	172.85	49.7	189.71	25.60%	2.31
0.4% TDE	199.31	65.35	172.89	54.17	189.55	26.80%	1.24
0.5% TDE	199.95	65.24	172.06	58.51	190.49	26.70%	0.94
0.5% 711	201.16	66.82	173.68	59.91	191.43	27.39%	2.64
1.0% 711	200.66	67.36	174.26	60.09	190.92	27.61%	2.31

T_{mt} is the first peak temperature in the DSC melt curve.

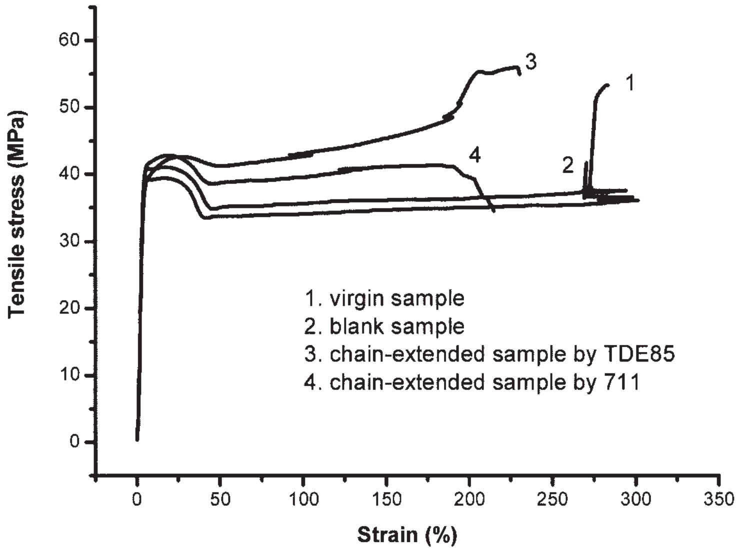


Figure 2 Plots of tensile stress versus strain of different samples.

unchangeable coupling effect within some range of content of chain extender. Beyond the critical value of *n,* the platform becomes more and more acclivitous and the coupling effect keeps rising during the whole range. On the assumption that *n* is 0.02, 0.05, and 0.1, Figure 5(a, b, and c) simulates these three conditions by ideal kinetics model and Runge–Kutta numerical method,[15–16] which is concretely expressed in the Appendix. Despite its difference from actual instance, the model accords well with the analysis above qualitatively.

The experiments in the Haake mixer provided a real relation between the coupling effect and the content of chain extenders. In these experiments, epoxide 711 is preferable because of its relatively lower functional degree. Figure 6 shows that the relation keeps close to the second case; that is, a platform appeared in the content range from about 0.5 to 0.8%. Also, an excess amount of diepoxides would finally lead to crosslinking of polyamide molecules, in fact, so there will exist a sharp steep sooner or later. Hence, the problem as to why there are no obvious mechanical and rheological distinctions between chain-extended products by more chain extenders and those by less chain extenders can be explained. The platform range also helps invariably control the optimal coupling effect in a range of chain extender dosages, the lack of which causes insufficiency of chain extension, but an excess of which leads to severe crosslinking. The platform of chain extension by epoxide TDE85 may also exist, but

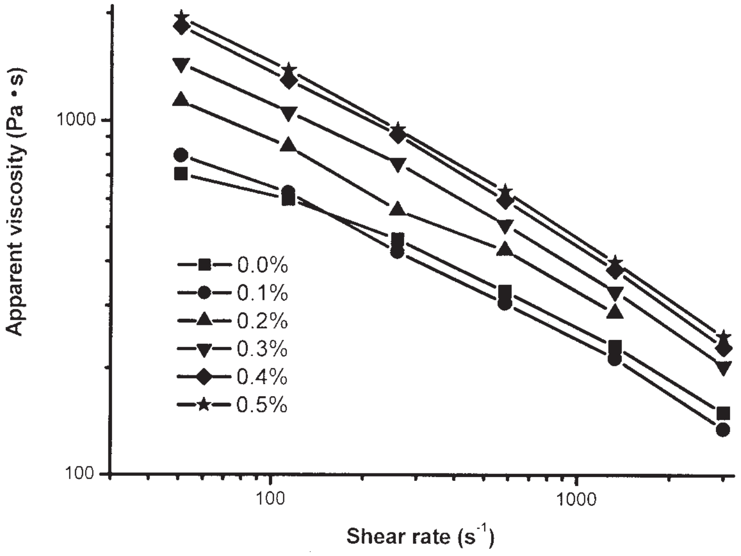


Figure 3 Plots of apparent viscosity versus content of TDE85 at 240°C and different shear rates.

TABLE III
Apparent Viscosity (Pa s) /Non-Newton Index of Chain-Extended Products

Shear rate (s^{-1})	TDE85 content						711 content	
	0%	0.10%	0.20%	0.30%	0.40%	0.50%	0.50%	1.00%
50.63	0.84	0.67	0.62	0.66	0.62	0.61	0.62	0.60
112.72	0.78	0.63	0.60	0.61	0.57	0.56	0.58	0.57
258.07	0.71	0.59	0.58	0.55	0.52	0.52	0.54	0.53
583.2	0.65	0.54	0.57	0.49	0.47	0.43	0.50	0.50
1323.9	0.59	0.50	0.55	0.44	0.37	0.38	0.45	0.47

with a narrower range of chain extender dosages. It should be noticed that the platform range differs in various systems and equipments.

Theoretical analysis of crosslinking control

When the content of chain extenders exceeds a definite level, the undesirable crosslinking will occur to some extent. To the same kind of PA and chain extenders, it is found that crosslinking can sometimes occur, while sometimes it cannot. The radical factor lies in the average degree of functional groups in the chain extension system. Flory's criterion, which is traditionally used to predict the reaction degree of crosslinking formed in small molecular systems, can be shared in the chain extension system of polyamide.

A polyamide molecule with one end-carboxyl group and one end-amide group can be regarded as a three-functional molecule with epoxy groups as chain extenders, because the imide groups, formed by a reaction between amide group and epoxy group, can continue to react with the epoxy group. Hence, assuming the ratio of PA to diepoxy is 2/3, the average degree of functional groups f equals 2.4, and the critical reaction degree P_c is $2/f$, that is, 0.833. Although the high viscosity of the chain extension system could prevent the reaction from being fully carried out; however, the reaction degree beyond 0.833 seems not too difficult to reach; thus normally crosslinking structures may form.

Actually, a polyamide molecule with a higher or lower ratio of carboxyl group to amide group can decrease or increase its average degree of functional groups. In extreme cases, the value of f tends to be 2 to carboxyl-blocked polyamide and tends to be 4 to amide-blocked polyamide. The epoxy number of chain extenders may not always be maintained as 2, or otherwise could be a little more or less than 2. Both factors mentioned above can contribute to the variation of f in the chain extension system. Accordingly, P_c can probably increase to the extent of which the reaction degree can hardly reach because of the system viscosity; thus, no crosslinking will occur, and vice versa.

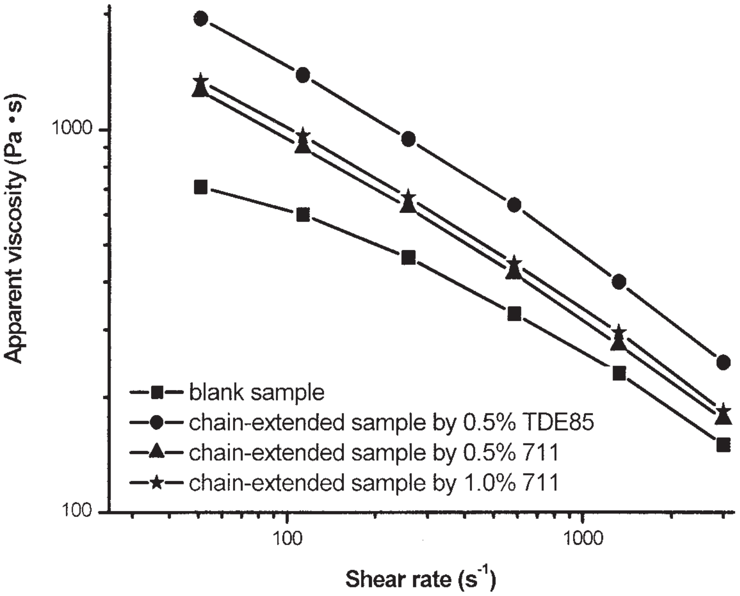


Figure 4 Plots of apparent viscosity versus shear rates at 240°C with different content of 711 and TDE85.

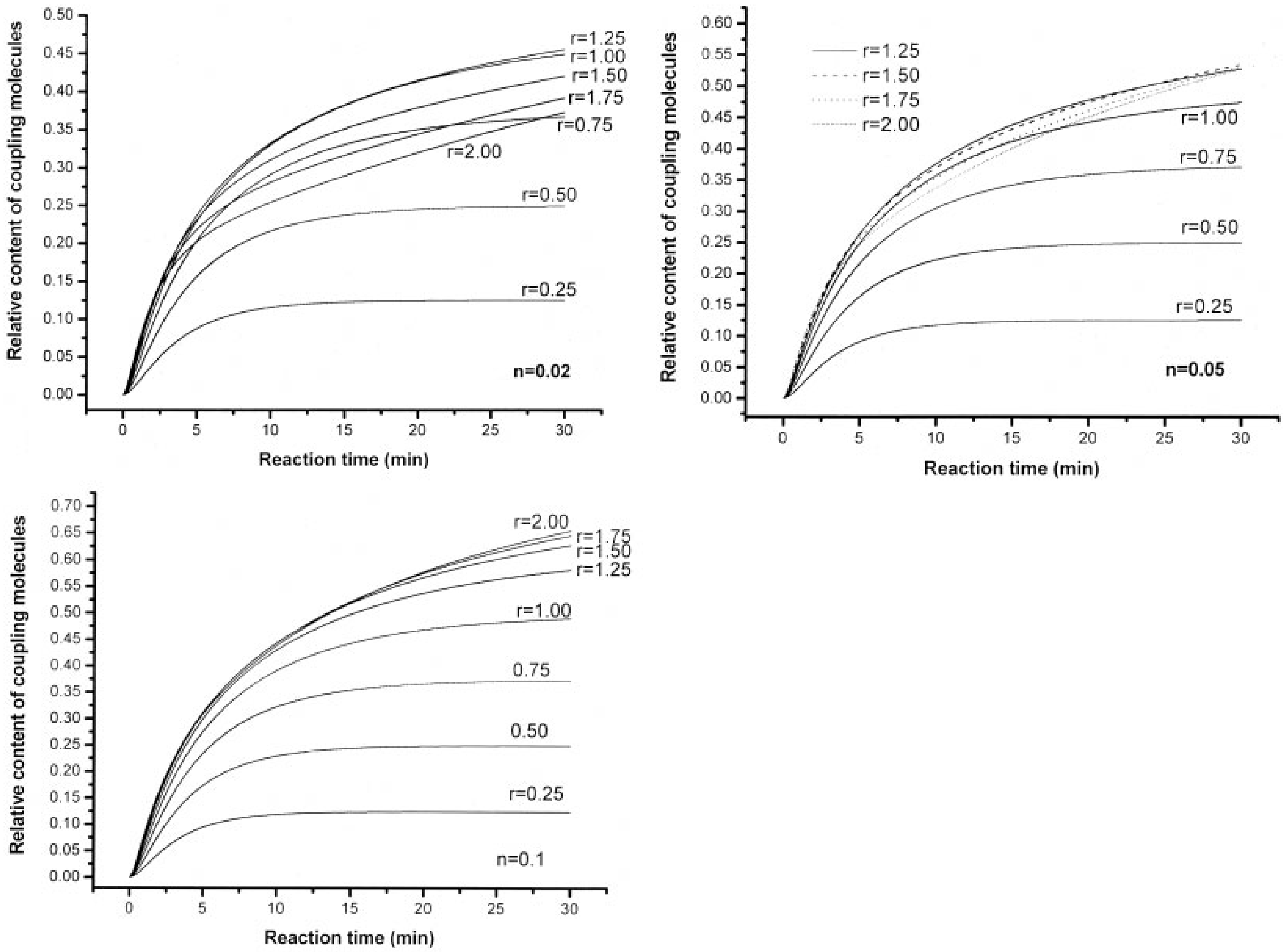


Figure 5 (a) Relative content of coupling molecules versus reacting time (n = 0.02). (b) Relative content of coupling molecules versus reacting time (n = 0.05). (c) Relative content of coupling molecules versus reacting time (n = 0.1).

The aforementioned analysis makes possible the control of crosslinking, and the crucial factor is how to decrease the value of *f*. Traditionally, a deficient amount of chain extenders can surely solve the problems. Another method, by which higher coupling efficiency can be achieved, is to mix a small quantity of monoepoxide into the diepoxide. It can be given a concrete example as follows.

Supposing the reaction degree of the system could reach 0.9, we blend 2 mol PA and $(3 - x)$ mol epoxide 711 in system 1 and blend 2 mol PA, 3 mol epoxide 711 and y mol single-functional epoxide. We aim that both systems will not form crosslinking by Flory's criterion. As a result, x is 0.5 mol and y is 4/9 mol, through simple calculation. Hence, the coupling efficiency of the former is 83.3%, less than that of the latter, which is 92.6%. So, if the single-functional epoxide is available and matches the reactivity of double-functional epoxide, a mixer of chain extenders with controllable functional degree is a preferable way to avoid the crosslinking.

CONCLUSION

1. Both diepoxy TDE85 and diepoxy 711 are effective chain extenders for PA1010; the coupling effect of the former is better than that of the latter.
2. The time needed for this chain-extension reaction can be less than 5 min; so it can be performed in a twin-screw extruder. The MFI dramatically decreased, and the Izod impact strength doubles as its origin without any loss of other mechanical properties when 0.5 wt % TDE85 was used.
3. There exists a platform in the curve plotting coupling effect versus content of chain extender. Excess amount of diepoxides would finally lead to crosslinking. Hence, there may be no obvious mechanical and rheological distinctions between chain-extended products by more chain extenders and those by lesser ones can be explained.
4. The predominant factor that causes whether crosslinking occurs or not is the average degree of functional groups in the chain-extension system. By using a smaller amount of diepoxide and

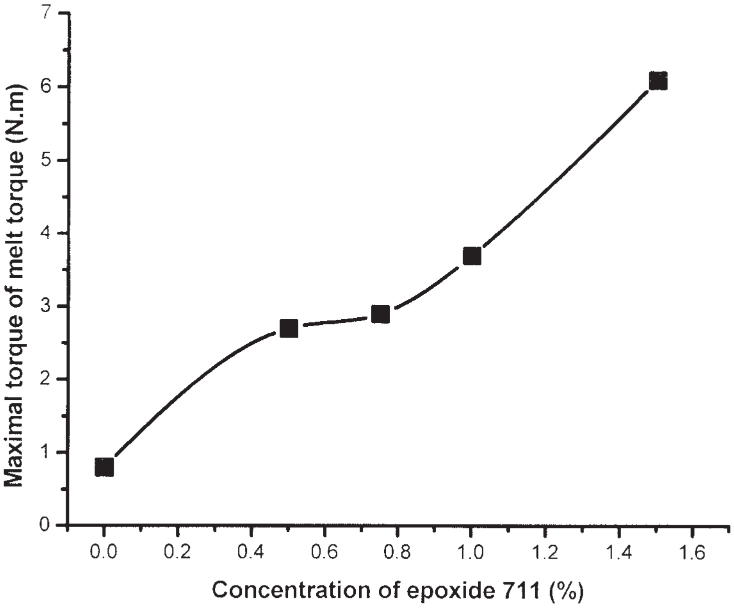


Figure 6 Maximal torque of melt torque with different concentration of epoxide 711 as the chain extenders of PA1010.

mixing it with single-functional epoxide, both can avoid the formation of crosslinking: the latter method owning higher coupling efficiency.

APPENDIX

Simulation of polymer with end groups of different reactivity by reaction kinetic model

$$X \leftarrow M\text{-}Y + Z\text{-}Z \rightarrow Z\text{-}M\text{-}Y \qquad \text{(A1)}$$

$$X \leftarrow M\text{-}Y + Z\text{-}M\text{-}Y \rightarrow Y\text{-}M\text{-}M\text{-}Y \qquad \text{(A2)}$$

$$X\text{-}M\text{-}Y + Z\text{-}M\text{-}Y \rightarrow X\text{-}M\text{-}M\text{-}Y \qquad \text{(A3)}$$

where X is end group of higher reactivity, Y is the one of lower reactivity, M is macromolecular chain, and Z is functional group of chain extender. Supposing $X \rightarrow M\text{-}Y$ is A, $Z\text{-}Z$ is B, $Z\text{-}M\text{-}Y$ is C, $X\text{-}M \rightarrow Y$ is D, $Y\text{-}M\text{-}M\text{-}Y$ is E, $X\text{-}M\text{-}M\text{-}Y$ is F, and omitting the subsidiary products, such as $X\text{-}M\text{-}M\text{-}X$, a set of differential equations can be listed as follows:

$$d[A]/dt = \text{-}2k_1[A][B]\text{-}k_2[A][C]$$

$$d[B]/dt = \text{-}2k_1[A][B]$$

$$d[C]/dt = 2k_1[A][B]\text{-}k_2[A][C]\text{-}k_3[D][C]$$

$$d[D]/dt = k_3[D][C]$$

$$d[E]/dt = k_2[A][C]$$

$$d[F]/dt = k_3[D][C]$$

Defining $A = [A]_1/[A]_0$, $B = [B]_1/[B]_0$, $C = [C]_1/[A]_0$, $D = [D]_1/[D]_0$, $E = [E]_1/[A]_0$, $F = [F]_1/[D]_0$, $K_1 = k_1[A]_0$, $K_2 = KK{=}k_2[A]_0$, $K_3 = k_3[A]_0$, $r = 2[B]_0/[A]_0$, $R = [D]_0/[A]_0$.

The differential equations can be changed into

$$dA/dt = \text{-}rK_1AB\text{-}K_2AC$$

$$dB/dt = \text{-}2K_1AB$$

$$dC/dt = rK_1AB\text{-}K_2AC + K_3DC$$

$$dD/dt = \text{-}K_3DC$$

$$dE/dt\text{-}K_2AC$$

$$dF/dt = K_3DC$$

where E and F are chain-extended products. $E+RF$ can be used to describe the effect of chain extension reaction and the contribution to the increase of melt torque. Here, as a predigestion, assuming $R = 1$, that is, X equals Y.

Defining $k_1 \approx k_2$ and $k_3/k_1 = n$, three different circumstances were simulated by ideal kinetics model and Runge–Kutta numerical method, as shown in Figure 5(a, b, and c). Despite its difference from actual instance, the model accords well with the analysis qualitatively.

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