
Reactive Modification of Poly(ethylene terephthalate) and its Foaming Behavior

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SUMMARY

A methodology for the preparation of chain extended poly (ethylene terephthalate) (PET) and its foams by autoclave batching foaming method was proposed. First, PET was mixed with tetraglycidyl diamino diphenyl methane (TGDDM) as chain extender to generate the branching/crosslinking molecular structure and improve the viscoelasticity of PET. Then, PET foams were prepared using supercritical CO₂ as physical blowing agent. The molecular structures of various PET samples were characterized by the nuclear magnetic resonance, gelation degree and crosslinking density test. The results showed that with the introduction of TGDDM, the branching/crosslinking structure of PET appeared. The influences of various molecular structures on the thermal property and rheology of PET were also studied. The results showed that the crystallization temperature, crystallization rate, and crystallinity of various PET samples decreased with the content of TGDDM, but the modified PET had higher melt elasticity than that of pure PET. PET foam with the addition of 0.4% TGDDM had finer cellular morphology and the highest expansion ratio.

Keywords: Poly(ethylene terephthalate); Chain extender; Foam; Crosslinking

INTRODUCTION

Poly (ethylene terephthalate) (PET) foam exhibits excellent mechanical properties such as high elastic modulus, creep resistance, and thermal stability

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at high temperatures (above 200°C) [1, 2, 3], which made PET foams apply in the fields of construction, aerospace, modern automotive, and food packaging. Carbon dioxide (CO₂), known by its non-flammable, nontoxic, inexpensive, easy to reach a supercritical state, and relatively large solubility in polymer matrix, has been frequently used in polymer foaming as green physical blowing agent. Therefore, preparing PET foam with excellent property using supercritical CO₂ as blowing agent gradually becomes a significant research.

However, common PET is not suitable for preparing PET foam with high expansion ratio, due to its poor melt strength. High melt strength is a vital parameter for controlling cell expansion and stabilization during cell growing [4, 5, 6]. Generally speaking, the poor melt strength is associated with linear molecular structure and low molecular weight. In addition, processing PET is complicated because it's sensitive to heat and shear. PET is easy to hydrolytic degradation if moisture is present during processing. High temperature, pressure, and moisture all result in the loss of molecular weight and the decrease of melt strength. Therefore, in order to solve these problems, many researchers tried to employ chain extender (CE) to modify the molecular structure of PET and prepare PET foams with high performance [7, 8, 9]. Compared with other modified methods, such as radiation crosslinking, blending with other polymer, and nanoparticles filling, chain extension is considered as an effective and convenient way to improve the melt strength of PET. Numerous chemicals could be used as CE, such as, diepoxides diisocyanates, dianhydrides, and pyromellitic dianhydride (PMDA). These chemicals have several reactive groups, which can react with terminal groups of PET to improve the molecular structure and the melt viscoelasticity [10].

Maio et al. used PMDA as CE to modify PET. The results showed that the introduction of PMDA would significantly increase the molecular weight of PET and improve the rheological properties of PET. Foaming study revealed that the fine cellular structure could be obtained by adding proper content of PMDA [11, 12, 13]. Bikiaris et al. used triphenyl phosphate and diimidodiepoxides as CE. They found that these compounds were highly reactive with PET and significant increase the molecular weight and melt strength of PET [14].

The chain extension of PET could not only improve the melt strength, but also affect the crystallization behavior of PET. The crystallization behavior is another important factor for controlling cellular structure. During PET foaming process, the processing temperature was usually close to its crystallization temperature to control cell growth. If the crystallization rate was too fast, the growth of the cells would be hindered. Inversely, if the crystallization rate was too slow, the cellular wall would rupture or collapse. Hence, a proper crystallization property is the key role to prepare PET foams with excellent cellular structure.

In this work, we prepared PET with branch/crosslinking structure (named CEPET) using tetraglycidyl diamino diphenyl methane (TGDDM) as CE. The molecular structure of TGDDM was shown as **Figure 1**. And the CEPET samples were then foamed in the autoclave using supercritical CO₂ as blowing agent. There was seldom work reported the effect of TGDDM as CE on the molecular structure and the foaming behavior of PET. The main aim of this work is to investigate the effect of TGDDM on the molecular structure, rheological, thermal, and foaming properties of PET.

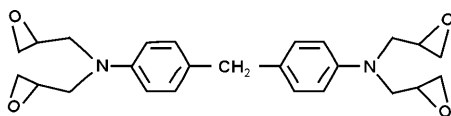


Figure 1. The molecular structure of TGDDM

EXPERIMENTAL

Materials

PET resin (BG-03-80) with an intrinsic viscosity (IV) of 0.8 dl/g and number-average molecular weight (M_n) about 20,000 g/mol was purchased from FSPG HI-TECH Co. Ltd, China. Multifunctional CE, TGDDM (Araldite AG-80), was a tetra-functional monomer with a theoretical epoxy equivalent of 105.5 g/equiv, providing by Shanghai Huayi Com. Ltd.

Preparation of CEPET

The CEPET samples were prepared in a Haake internal mixer at 280°C, with a mixing time of 10 min and mixing speed of 40 rpm. Prior to the melt mixing, PET was dried 160°C for 4 h in a vacuum oven to remove the moisture [15]. The samples formula was shown in **Table 1**. All components used the unit of “parts per hundred resin” (phr) in the formula. After the chain extension, the CEPET samples were dried for further charactering.

Table 1. The weight ratio of each component of the various CEPET

Serials No.	PET/phr	CE/phr
1#	100	0
2#	100	0.2
3#	100	0.4
4#	100	0.6
5#	100	0.8
6#	100	1.0

The PET foams were prepared by batch foaming method in autoclave using supercritical CO₂ as physical blowing agent. In order to investigate the differences of foaming behaviors for CEPET with various TGDDM contents, the samples were prepared and foamed under the same conditions. First, the samples were put into autoclave at a temperature of 270°C and a foaming pressure of 20 MPa for 1 h. After the CO₂ fully diffused and dissolved in the PET melt, the samples experienced an instantaneous pressure drop by release of CO₂ from 20 MPa to 0.1 MPa, which provided a driving force for cell nucleation and growth. The schematic diagram of autoclave batching foaming was shown in **Figure 2**. At last, the foaming samples were prepared for further characterizations.

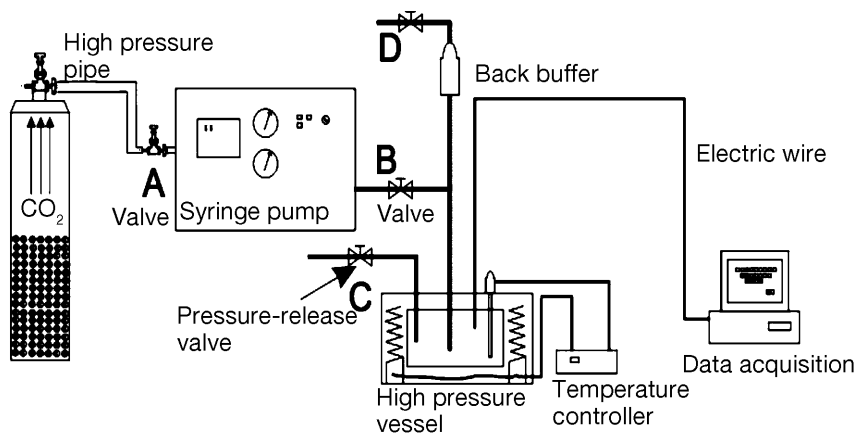


Figure 2. Schematic diagram of autoclave batching foaming, using supercritical CO₂ as physical blowing agent

Characterizations

¹H Nuclear Magnetic Resonance (¹H NMR)

¹H NMR spectra of pure PET and CEPET were obtained using a Bruker spectrometer operating at 600 MHz for proton investigation with tetramethylsilane as the internal standard. Samples were dissolved in a deuterated trifluoroacetic acid solution (CF₃CO₂D). Chemical shifts (δ) were expressed in unit of ppm, and branching points were calculated.

The branching points per 1000 C (BP_{1000C}) on PET chain were calculated using equation (1). The ratio of the integrated peak intensities for the phenyl (-C₆H₄-) of PET and the epoxy methine (-CH₂O-) of TGDDM groups were about 2:1 [16, 17].

$$BP_{1000C} = \frac{1000x}{y} \times 2 \quad (1)$$

Where, y = the area of the phenyl of PET (-C₆H₄-) resonance, x = the area of the epoxy methine of TGDDM (-CH₂O-) resonance.

Crosslinking Structure

The crosslinking structure of CEPET could be described using gelation degree (a) and crosslinking density (V_d). The CEPET samples were firstly swollen in phenol/tetrachloroethane (60/40, m/m) for 24 h. To prepare the swelling samples for weighing, excess solvent on the surfaces of the samples was removed, and then the samples were placed into sealed vials to reduce solvent evaporation during the weighing. At the end of the swelling period, the samples were dried in a vacuum oven at 70°C for 2 days and weighed again to determine the weight of the dry network after extraction of soluble materials, m_d . To calculate the crosslinking density of CEPET, the Flory-Rehner equation was used, as shown in Equations (2)-(4) [18, 19].

The crosslinking degree (a) was calculated from the weight (m) of the sample and the dry weight (m_d) after extraction [20]:

$$a = m_d / m \quad (2)$$

The crosslinking density (V_d) could be calculated by Flory-Rehner equation [21]:

$$V_r = \frac{\frac{m_0 a}{\rho_r}}{\frac{m_0 a}{\rho_r} + \left(\frac{m_1 - m_2}{\rho_s}\right)} \quad (3)$$

where V_r represents the volume fraction of CEPET in the swollen gel, m_0 is the weight of the original samples, m_1 is the weight of the samples after swelling, m_2 is the weight of gelation after drying, ρ_r and ρ_s are the densities of the polymer and solvent, respectively; and a is crosslinking degree.

$$V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s (V_r^{1/3} - V_r / 2)} \quad (4)$$

Where, V_s is the molar volume of the swelling solvent (66.98 cm³/mol for phenol/tetrachloroethane (60/40)), and χ is the Flory-Huggins (rubber-phenol/tetrachloroethane (60/40)) interaction parameter and is taken as 0.36 for the NBR-toluene system in this calculation [22, 23].

Differential Scanning Calorimeter (DSC)

Crystallization and melting behaviors of pure PET and CEPET samples were studied by DSC system purged with nitrogen. The samples were heated to 300°C at rate of 10°C /min, isothermal for 3 minutes, then cooled to 40°C at rate of 10°C /min, the crystallization and melting behaviors were measured [24, 25].

Crystallization rate of pure PET and CEPET samples were analyzed by modified Avrami method. First, samples were heated at 300°C for 3 min to remove the heating history, then cooled to 60°C at 5°C/min, 10°C/min, 20°C/min, and 40°C/min respectively, to study the non-isothermal crystallization of pure PET and CEPET.

Dynamic Shear Rheometer

Shear rheological behavior of various PET samples was observed using a strain-controlled rheometer (MARS Rheometer, TA, USA) at 260°C, with a parallel plates (20 mm in diameter with a gap of 1.0 mm). The frequency range was from 0.1 to 100 rad/s, and the maximum strain was fixed at 5%, to confirm that these conditions were within the linear viscoelastic region under nitrogen. The storage modulus (G'), complex viscosity (η^*), and loss factor ($\tan \delta$) were measured at various frequencies.

Cellular Morphology

The cellular morphology of foaming samples were characterized using a scanning electron microscope (SEM, TESCAN YEGA II, TESCAN s.r.o) at an acceleration voltage of 10 kV. The magnification ratio was 400. Cell density was analyzed by using software image tool and calculated as shown in Equations (5)-(6) [26]:

$$N_c = \left(\frac{n}{A}\right)^{3/2} \cdot \phi \quad (5)$$

$$\phi = \frac{\rho_u}{\rho_f} \quad (6)$$

Where N_c is cell density (cell/cm³), n is cell amount within statistical areas, A is statistical areas in SEM photo (cm²), ϕ is the foaming expansion ratio of polymer, ρ_f is foamed density (g/cm³), ρ_u is unfoamed density (g/cm³).

Density Tester

The density of foaming samples was determined by using density tester (UltraPyc actual density tester, Quanta Chrome, America).

RESULTS AND DISCUSSION

Chemical Reactions and Structural Changes During Chain Extension Process of PET

During the chain extension process, several chemical reactions existed and took place: chain scission induced by degradation, branching and crosslinking induced by chain extension, as illustrated in **Figure 3**. These reactions happened meanwhile and competed with each other. In order to clarify the reaction mechanism, processing torque, branching points, gel fraction, and crosslinking density of various CEPET samples were measured.

The torque curves of PET mixing with CE in the Haake rheometer was illustrated in **Figure 4**. The torque results reflected a function of the mixing time and the reaction efficiency. The torque curve of pure PET showed a decreased trend with increasing time due to the thermal degradation of PET, which was reported in other extrusion process research [27]. After TGDDM was introduced into PET, an increase of the torque was found obviously. When the

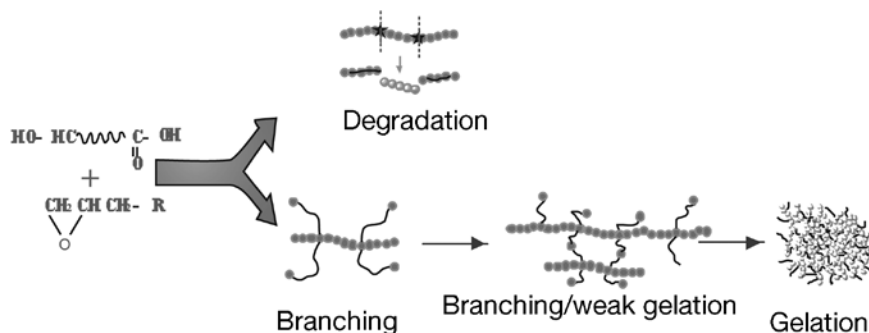


Figure 3. Illustration of possible chemical reactions during the chain extension of PET

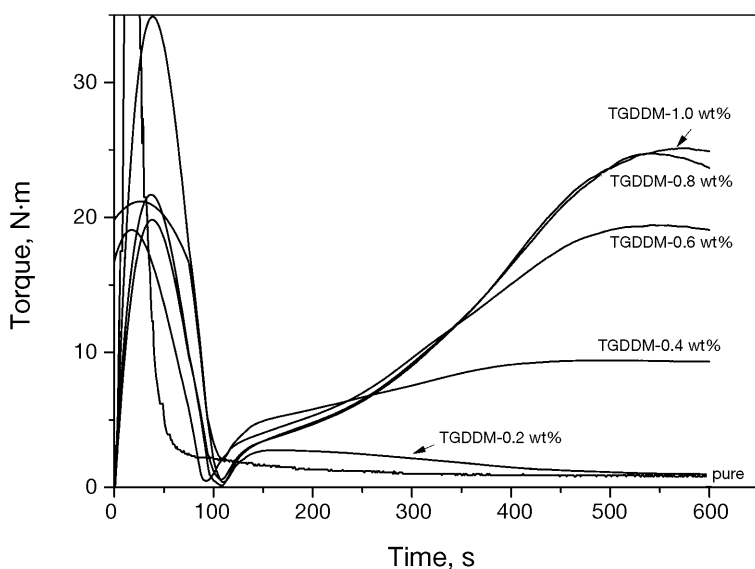


Figure 4. Torque curves of pure PET and CEPET

addition of TGDDM was at 0.4–1.0 wt%, there was an increase in the torque of PET after 2 min of mixing, indicating that the chain extension took place. When the mixing time reached approximately 9 min, the torque curve was at a maximum value. The increase of the torque curves should be attributed to the formation of branching and crosslinking structures. These structures were formed due to the reaction between the epoxy groups on the TGDDM and the carboxyl or hydroxyl groups on the PET chains. The overall torque evolution of the CEPET strongly depended on the CE content. With the CE content, the maximum value of torque increased. The increase of the torque curves of PET were the integrated consequence of above three reactions.

The branching structure of various PET samples could be characterized by ^1H NMR spectra, shown in **Figure 5**. The peaks at the chemical shifts of 9.9 and 6.5 ppm indicated the phenyl ($-\text{C}_6\text{H}_4$) and ethyl ($-\text{CH}_2\text{CH}_2-$) groups

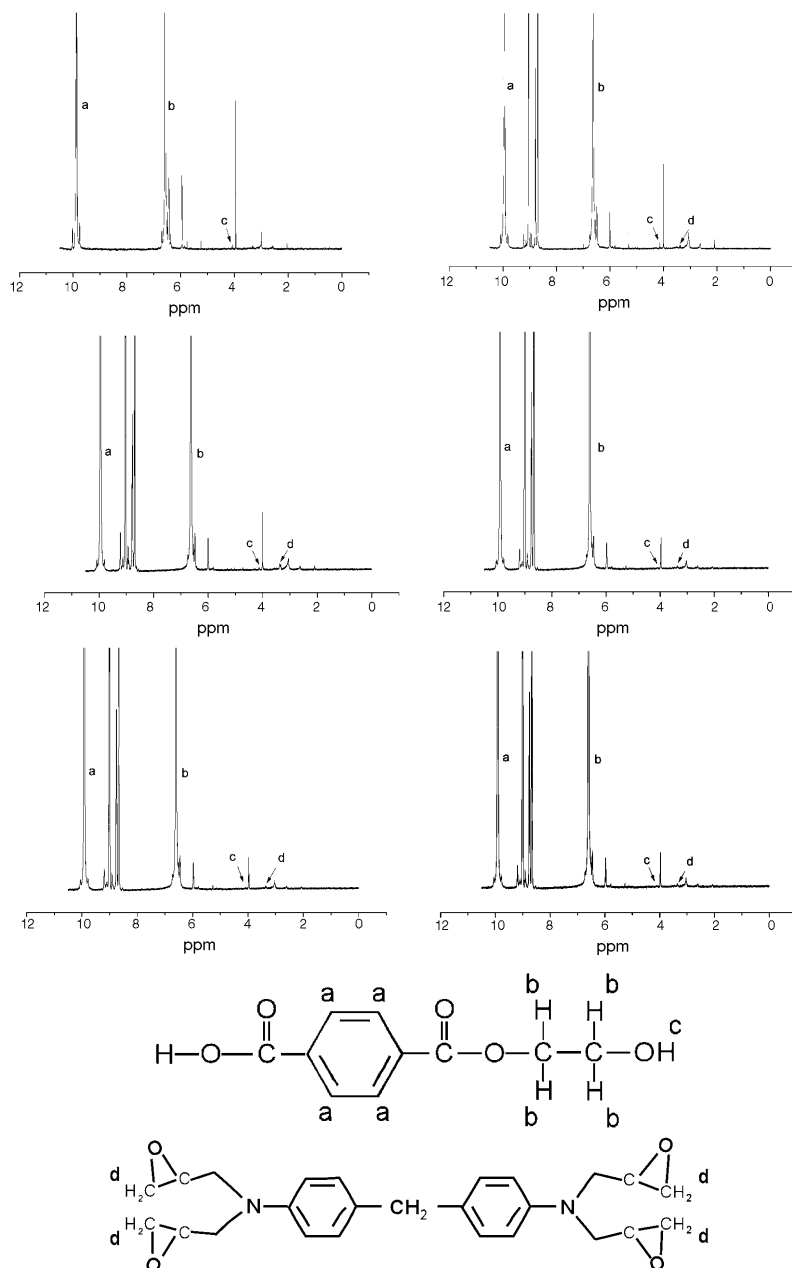


Figure 5. ^1H -NMR spectra of pure PET and CEPET samples; the assignment of the peaks was shown in the above chemical structure

of PET at the (a) and (b) positions, respectively [28]. The resonance peak at 4.1 ppm in the spectra was related to hydroxyl at the (c), the resonance peak at 3.38 ppm in the spectra was ascribed to the presence of methine in the TGDDM at the (d) [29].

The ratio of the integrated peak intensities about the phenyl ($-C_6H_4-$) and ethyl ($-CH_2CH_2-$) groups of PET was about to 1:1. The analysis of the integration ratios of NMR peaks could roughly evaluate the molecular structure of pure PET and CEPET samples. The integration ratio between the (a) and (c) peaks for pure PET was 1000:2.35. After adding TGDDM into PET, the hydroxyl and carboxyl groups on the chain ends of PET were consumed by reacting with TGDDM. For the sample of CEPET with 0.2 wt% of TGDDM, the integration ratio between the (a) and (d) peaks was 1000:2.21. And, for the samples of CEPET with 0.4 wt% , 0.6 wt% , 0.8 wt% , 1.0 wt% of TGDDM, the integration ratio between the (a) and (d) peaks were 1000:3.33, 1000:4.74, 1000:4.95, 1000:6.09, respectively. BP_{1000C} could be calculated by Equation (1) and shown in **Table 2** [30, 31]. Therefore, there were about 4.42, 6.67, 9.48, 9.90, and 12.18 branching points correspond to every 1000 a-type repetitive methane groups for adding 0.2 to 1.0 wt% of TGDDM. As described above, with the increasing content of TGDDM, the BP_{1000C} of CEPET increased gradually, which was expected to improve the foam-ability of PET.

Table 2. The molecular weight of CEPET

Samples	1#	2#	3#	4#	5#	6#
BP_{1000C}	0	4.42	6.67	9.48	9.90	12.18

The gelation degree of CEPET was shown in **Figure 6**. With the increasing content of TGDDM, the gelation degree increased from 5 wt% to 25 wt%. High gelation degree of CEPET was considered as a hinder to prepare foams with high expansion ratio due to the high viscosity preventing the cell growth. Yamaguchi and Miyata found that polymer with weak gel (slightly crosslinking) exhibited an enhanced melt strength, which was beneficial for improving the foam-ability of polymer [32]. Hence, the gelation degree of CEPET should be controlled in a proper level.

In order to further verify the crosslinking structure of CEPET, the crosslinking density of CEPET was calculated and shown in **Figure 7**. Seen from it, the crosslinking density exhibited a similar trend as that of gelation degree. With the increase of TGDDM content, the crosslinking density (V_g) of CEPET gradually increased from 0.004 to 0.023 mol/cm³. The change could be also attributed to the reaction of the epoxy groups on TGDDM and the carboxyl

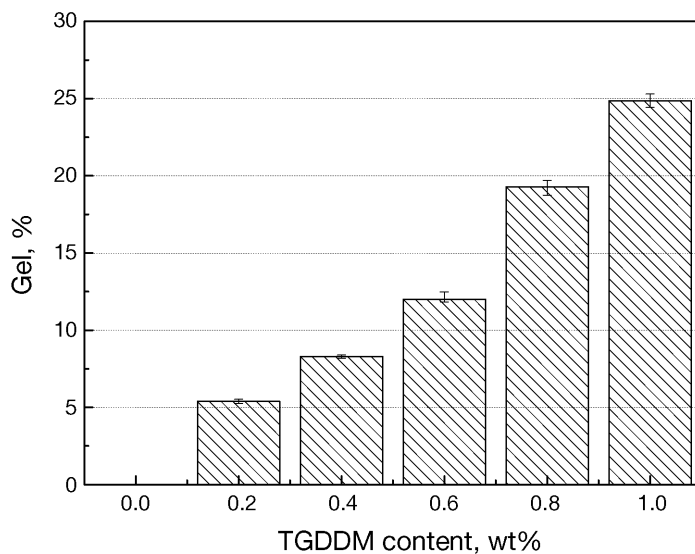


Figure 6. The relationship of gelation degree and various TGDDM contents

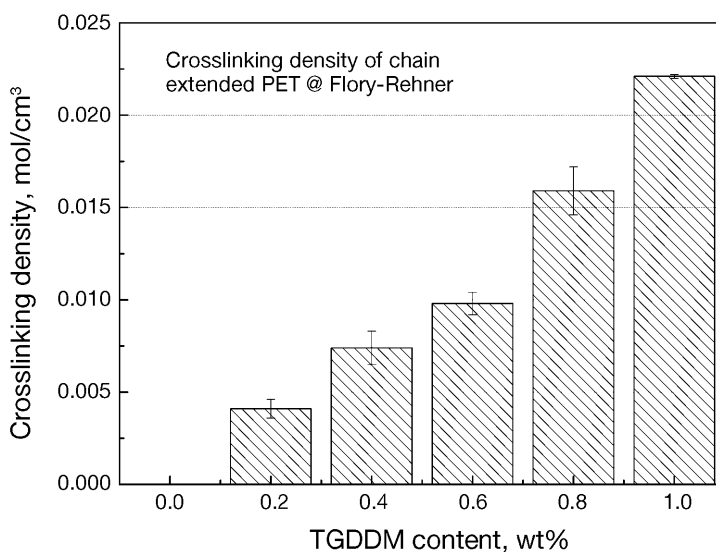


Figure 7. The crosslinking density of CEPET with various CE content

or hydroxyl groups on PET chains. Higher TGDDM content would increase the possibility of crosslinking, which was confirmed by gelation degree and crosslinking density test.

As previously discussed, PET would efficiently react with TGDDM and generate branching and crosslinking structures, which would greatly affect the viscoelasticity and foam-ability of PET. The changes of the molecular structure of PET would affect its thermal behavior and rheology, as discussed in the following sections.

Thermal Behavior of CEPET

Figure 8 and **Figure 9** showed the crystallization and melting thermograms of pure PET and CEPET samples. The corresponding parameters, crystallization temperature (T_c), melting temperature (T_m), and the enthalpy (ΔH), were given in **Table 3**. The crystallinity of PET was computed by Equation (7) [33, 34]:

$$X_c = \Delta H / \Delta H_0 \times 100\% \quad (7)$$

Where, ΔH is the enthalpy for melting, ΔH_0 is the enthalpy of melting for a 100% crystalline PET sample, which is 140 J/g [35].

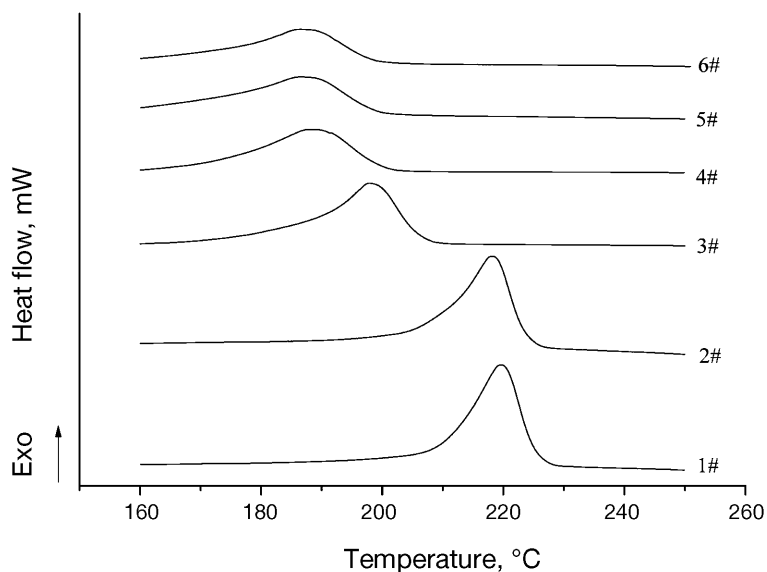


Figure 8. Non-isothermal DSC curves for pure PET and CEPET at cooling rate of 10°C/min

It could be seen from **Table 3** that the T_c of pure PET (1# sample) was at around 220°C. The crystallization peak shifted towards lower temperatures

from 220°C to 187°C with the content of TGDDM. Moreover, the crystallization peak declined and became wide by increasing TGDDM content. The change of crystallization peaks indicated the formation of branching and crosslinking structure of PET, which resulted in the decrease of crystallization rate.

DSC curve of pure PET possessed a melting peak at about 255°C. However, with the content of TGDDM, the melt peak shifted toward lower temperatures from 254°C to 244°C. The change of melting temperature was also associated with the molecular structure of PET. The branching molecular structure of PET would influence the assembly of PET chains into crystal lattices.

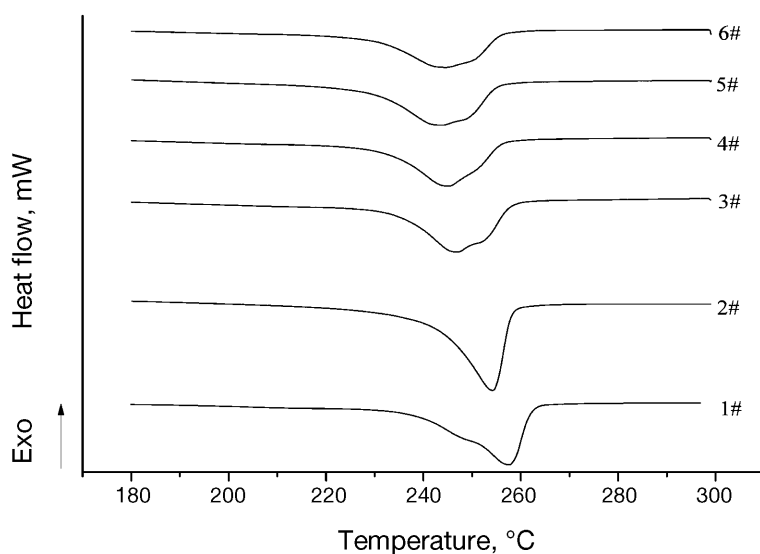


Figure 9. Non-isothermal DSC curves for pure PET and CEPET at heating rate of 10°C/min

Table 3. The crystallization parameters of PET and CEPET samples

Samples	1#	2#	3#	4#	5#	6#
T_c (°C)	220	218	198	188	187	187
T_m (°C)	255	254	247	244	244	245
ΔH (J.g ⁻¹)	36.57	35.07	32.88	30.54	29.64	26.29
X_c (%)	26.12	25.05	23.49	21.81	21.17	18.78

As summarized in **Table 3**, the addition of TGDDM decreased the crystallinity of PET because of the formation of the branching and crosslinking molecular structure of PET, which influenced the crystallization process. The crystallinity decreased from 26.12% to 18.78%, which would influence some physical and mechanical properties of PET foams, such as gas permeability, impact strength, and heat deformation temperature.

The crystallization rate is also other important factor in controlling cellular structure of foams. If crystallization rate of polymer was too high, foaming agent gas could not be diffused into the melt in a limited time, which resulted in low cellular nucleation rate and cell growing rate. On contrast, if crystallization rate was too low, melt strength could not be improved in the cooling period, which led to poor stability of growing cell, cell collapse, eventually poor foaming ratio of foam. PET crystallized slowly during the melt crystallization processes, compared with other semi-crystalline polymers, such as polypropylene and polyethylene. However, according to the classical crystallization theory, the inducing of branching molecular structure could obviously affect the crystallization rate of polymers.

The Avrami equation could be directly used to describe the primary stage of crystallization, which could be expressed as:

$$1 - X(t) = \exp(-Z_t t^n) \quad (8)$$

where Z_t is the rate constant in the crystallization process, n is the mechanism constant depending on the type of nucleation and the growth process parameters, Φ is the cooling rate. For the non-isothermal crystallization, the double-logarithmic form of Equations (9-10) as follows:

$$\lg\{-\ln[1 - X(t)]\} = \lg Z_t + n \lg t \quad (9)$$

$$\ln Z_c = \frac{\ln Z_t}{\Phi} \quad (10)$$

Curves of $\lg\{-\ln[1 - X(t)]\}$ against $\lg t$ are illustrated in **Figure 10**. Each curve shows only the linear portion, and the nonlinear parts that deviate from Avrami equation at high relative crystallinity region are not included. Z_t and n were obtained from the intercept and the slope, respectively. The values of Z_c and n are listed in **Table 4**. A non-integral value of n is often obtained, indicating the overlap of different crystal growth geometries [36].

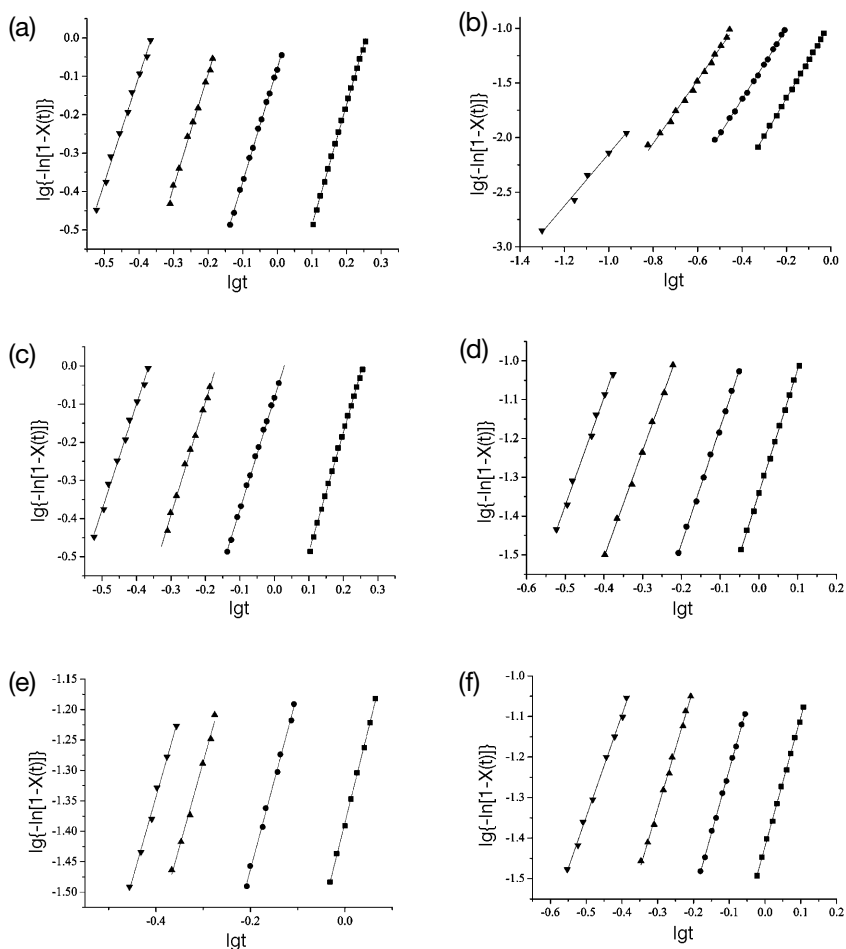


Figure 10. The relationship between $\lg\{-\ln[1-X(t)]\}$ and $\lg t$ for pure PET and CEPET samples. Cooling rate/°C·min⁻¹ ▼-5 ▲-10 ●-20 ■-40 Samples No. (a)1# (b)2# (c)3# (d)4# (e)5# (f)6#

From **Table 4**, it was obvious that the Z_c slightly decreased with the increasing TGDDM content. The n value also decreased, which indicated the crystallization nucleation and growth had been changed. This could be attributed to the existence of branching chains or crosslinking net. On one hand, branching chains were difficult to arrange into crystal lattices, resulting in the decrease of crystallization rate reflected by decreasing Z_c value. On the other hand, the existence of branching points could improve the crystallization nucleation, thus the n value was slightly increased.

Table 4. The crystallization half time and Avrami parameters for non-isothermal crystallization of pure PET and CEPET samples

Samples No.	$\phi/ ^\circ\text{C} \cdot \text{min}^{-1}$	n	Z_c	$t_{1/2}/ \text{min}$
1#	5	3.63	0.85	1.60
	10	2.97	0.99	0.94
	20	2.94	1.03	0.60
	40	2.77	1.03	0.38
2#	5	3.47	0.83	1.70
	10	3.22	0.96	1.12
	20	2.89	1.01	0.64
	40	2.40	1.00	0.41
3#	5	3.13	0.85	1.91
	10	2.93	0.99	1.35
	20	2.86	1.03	0.93
	40	2.77	1.03	0.64
4#	5	3.18	0.76	2.42
	10	3.00	0.92	1.79
	20	2.78	0.98	1.21
	40	2.77	1.00	0.83
5#	5	3.10	0.76	2.59
	10	2.90	0.92	1.91
	20	2.78	0.98	1.25
	40	2.72	0.99	0.92
6#	5	3.19	0.75	2.56
	10	3.13	0.91	1.86
	20	2.97	0.98	1.25
	40	2.52	1.00	0.85

Dynamic Shear Rheology of CEPET

Shear rheological test was employed to study the linear visco-elasticity of polymers. Shear rheological behavior was related and sensitive to the length of molecular chain and topological structure. When adding TGDDM into PET, the segment length and topological structure of PET chains would be changed, and thus the viscoelasticity of PET would be changed, too.

To analyze the rheological behavior of CEPET, three techniques could be used. There were plots of the log complex melt viscosity (η^*), storage modulus (G'), and loss factor ($\tan \delta$) versus various frequency. The improvement of melt elasticity was reflected by the increment of G' . The bigger the G' , the better the

melt elasticity was, thus the higher the melt strength was. **Figure 11** illustrated the relationship of G' and angle frequency for various CEPET samples. At the low frequency zone, four G' - ω curves for 3-6# samples were higher than that of pure PET, which implied that the melt elasticity of CEPET was enhanced by adding TGDDM. This phenomenon also indicated that CEPET had a longer relaxing process due to the formation of branching and crosslinking structure of PET. A plateau zone could be observed for 6# at low frequencies. Hingmann and Marczinke reported similar phenomenon about long chain branching PP [37]. The increment of G' and the decline of the slope of G' at the low frequency region were signatures of branched polymer and the increment of melt elasticity. The shear rheological behaviors of 1-6# suggested that the longer relaxation mechanism existed in the low frequency region by increasing TGDDM content. The melt elasticity of PET was improved by the introduction of branching structure and broadening molecular weight distribution, which could maintain the stability of cell wall during cell growth.

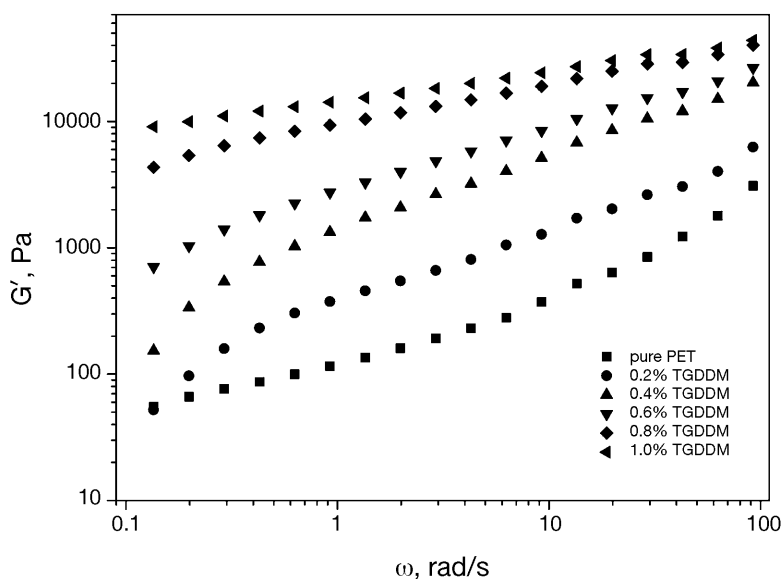


Figure 11. Relationships between storage modulus and angular frequency

Figure 12 illustrated the relationship of complex melt viscosity and angular frequency of PET and CEPET samples. The η^* of CEPET samples were obviously higher than that of pure PET. Compared with other samples, the η^* of 5# and 6# samples had a steep slope and no Newtonian plateau at low frequency. The increase of the η^* of CEPET could be attributed to two reasons: the broad molecular weight and the existence of branching structure. The latter was

thought to be the main reason because of flow restrictions of CEPET chain. High η^* value was expected to prevent cell rupture during cell growing [38].

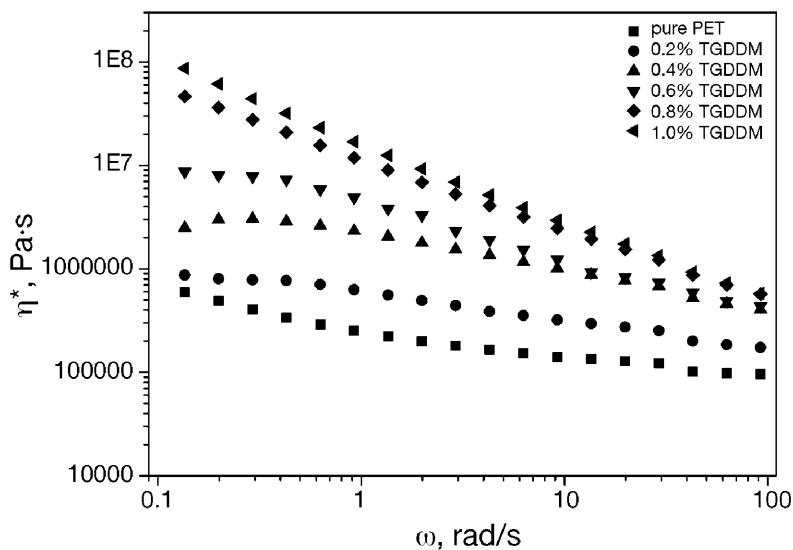


Figure 12. Relationships between complex viscosity and angular frequency

Loss factor ($\tan \delta$) referred to the angle that the strain lagged behind the stress while the PET melt was exposed in an alternating stress field. The smaller the $\tan \delta$ was, the faster the elastic response of the melt was, thus the higher the melt elasticity was. The $\tan \delta$ curves of pure PET and CEPET were depicted in **Figure 13**. It was obvious that the $\tan \delta$ curves of CEPET were much smaller than that of pure PET in low frequency zone, which indicated that the melt elasticity of CEPET samples were superior to that of pure PET.

Foaming Behavior of CEPET

In order to further study the effect of thermal property and rheology of modified PET on its foaming behavior, modified PET foams were prepared by batch foaming technology using supercritical CO_2 as blowing agent. The blowing agent of supercritical CO_2 was firstly dissolved into CEPET melt, and then reduced the pressure of autoclave rapidly to induce the cell nucleation and growth. **Figure 14** presented SEM micrographs of 1-6# foaming samples with various TGDDM contents in magnification ratio of 400. It could be observed that closed cellular morphology was present in CEPET foaming samples.

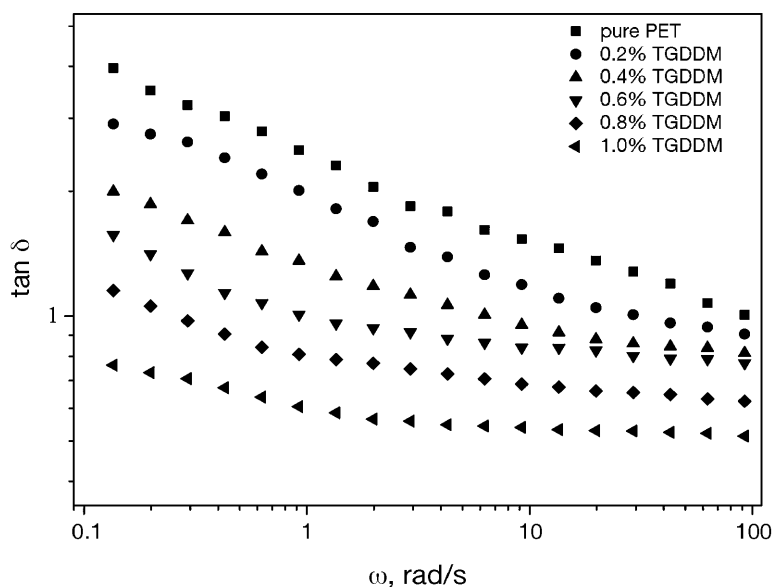


Figure 13. Relationships between loss factor and angular frequency

However, pure PET could not be foamed due to its poor melt elasticity. The SEM photos (3-5#) indicated the dodecahedron cellular morphology of PET foam could be developed with proper TGDDM content (0.4 to 0.8 wt%). The foam with 0.4 wt% of TGDDM had the finest cells size (around 85.59 μm) and the uniform cell dimension distribution. The expansion ratio of 3# was the highest of 20.98 among all the PET foam. For the PET foam samples with TGDDM content of 0.6 wt%, 0.8 wt%, and 1.0 wt%, the cell size were roughly decreased to about 83.42, 61.11, and 38.7 μm , respectively, and the expansion ratio was also decreased. This was because the cell growth of PET was restricted by the high viscosity in the foaming process. The cellular structure for foams (2# and 6#) exhibited irregular oval cellular structure, smaller cell size and non-uniform cell size distribution. This phenomenon should be due to excessive and very low crosslinking degree could not provide enough melt strength for cell growth.

Because the pure PET could not be foamed, thus its density (1#) was close to that of unfoamed PET. The expansion ratio of sample 1# was also slightly lower than that of the CEPET foam (2#) with the TGDDM content of 0.2 wt%. With further increase of the TGDDM content (0.4 wt%) in PET, the foam-ability of PET would be improved greatly, and the expansion ratio of CEPET foams could reach the highest of 20.98 as shown in **Table 5**. But the expansion ratio decreased again when the TGDDM content was more than 0.4 wt%. This

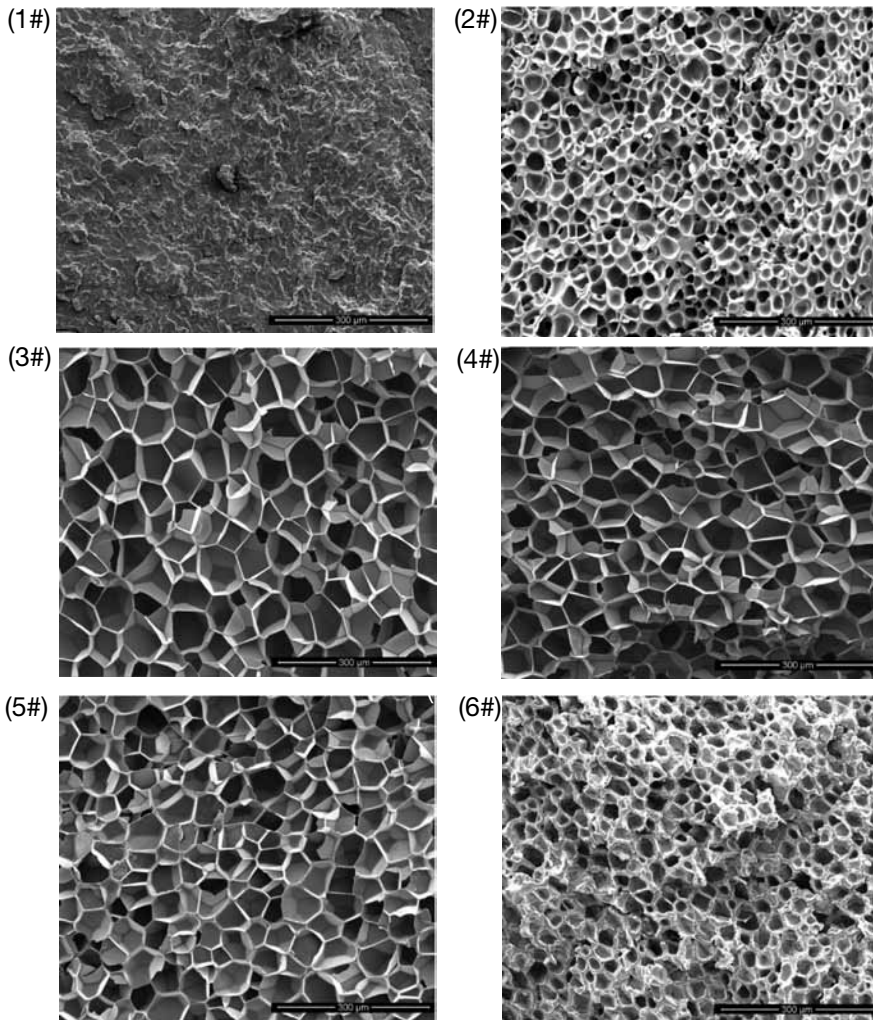


Figure 14. SEM micrographs for pure PET and CEPET

Table 5. Cell morphology data of pure PET and CEPET samples

Foaming samples No.	Cell size (μm)	Density (kg/m^3)	Expansion ratio
1#	-	1.380	1
2#	23.45	0.274	5.17
3#	85.59	0.067	20.98
4#	83.42	0.091	15.56
5#	61.11	0.161	8.91
6#	38.70	0.402	3.55

phenomenon further confirmed that the excessive crosslinking degree would restrict the cell growth of PET.

CONCLUSIONS

In this paper, the effect of the TGDDM as CE on the crosslinking degree, thermal, rheological property, and foaming behavior of PET had been studied. The results showed that CEPET had a branching/crosslinking molecular structure, and the crosslinking degree of PET increased from 0 wt% to 25 wt%, with the content of TGDDM.

The thermal properties of CEPET were affected by the changes of molecular architecture of PET. Compared with pure PET, the crystallization temperature, melting temperature, and crystallinity of CEPET decreased with the content of TGDDM. The introduction of branching and crosslinking structure of CEPET was beneficial to improve the melt viscoelasticity. Compare with pure PET, CEPET melt exhibited an improved storage module and a faster melt elasticity response.

The cellular morphology and expansion ratio of CEPET foams were also improved by the introduction of TGDDM. Pure PET could not be foamed due to its poor foam-ability. The expansion ratio of CEPET with the TGDDM content of 0.4 wt% would reach 20.98. PET foam with the finest cell morphology and the highest expansion ratio could be obtained by adding proper content of TGDDM.

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