

Modification of poly(ethylene terephthalate) by combination of reactive extrusion and followed solid-state polycondensation for melt foaming

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ABSTRACT: A combination of reactive extrusion and followed solid-state polycondensation (SSP) was applied to modify the virgin fiber grade poly(ethylene terephthalate) (v-PET) and recycled bottle-grade PET (r-PET) for melt foaming. Pyromellitic dianhydride (PMDA) and triglycidyl isocyanurate (TGIC) were chosen as the modifiers for the reactive extrusion performed in a twin-screw extruder. For comparison, commercially available chain extender ADR JONCRYL ADR-4370-S was also used. The characterizations of the intrinsic viscosity, i.e., $[\eta]$, and rheological properties whose changes were correlated to the long chain branches introduced in the molecular structure were performed on the modified PET to evaluate their chain extension extent. The results revealed that the $[\eta]$ of 1.37 dL/g was obtained for PMDA modified v-PET while that of 1.15 dL/g for TGIC modified r-PET. Such difference was attributed to the different reactivity of the two chain extenders with the two types of PET. Increases in shear viscosity and storage modulus, and the high pronounced shear thinning behavior were also observed in the modified PET. Finally, the foamability of the certain modified PET was verified by the batch melt foaming experiments. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42708.

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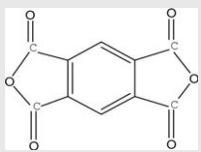
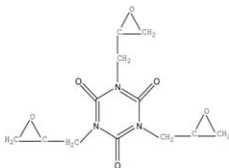
INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used in synthetic fibers, beverage, food, and other liquid containers and also engineering plastics due to its attractive combination of good mechanical properties, high-temperature resistance, good barrier properties toward moisture and oxygen, and recyclable characteristics. The majorities of the world's PET production are PET granules of fiber and bottle grade, which differ in the molecular structure, molecular weight, and performances. Taking advantage of the combination of good performances and lightness, in recent years, low-density PET foams are attracting increasing attention in the food packaging, building/construction, transportation, wind power, marine, and other industries currently utilizing rigid polyurethane (PUR), polystyrene (PS), or poly(vinyl chloride) (PVC) foams. However, melt foaming of PET to produce the low-density PET foams is faced with several challenges, especially the inadequate rheological characteristics, i.e., the low melt strength, due to its linear molecular structure.¹ Neither fiber nor bottle-grade PET is suitable for the melt foaming.

PET bottle recyclates are mainly used for the production of polyester fibers. However, traditional PET recycling markets like fiber applications were hardly in a position to absorb the increasing

amount of recollected and recycled PET bottles.² Moreover, recycling of PET from bottle to fiber is a downgrade process, during which the molecular weight and intrinsic viscosity (IV) reduces, and so does the melt strength. Therefore, some efforts using chain extension^{3–11} have been paid to extend the molecular weight, weight distribution, and degree of branched structures of virgin or recycled PET to improve their melt strength. The chain extension reaction can be carried out in solution or at the molten state in a mixer chamber or by extrusion. The chain extension by using the reactive extrusion process through addition of chemical chain extenders may be the most widely used method for its low cost, superior operability, and high efficiency. The chain extender contains at least two functional groups which can react with the hydroxyls and/or carboxyl end groups of PET. The common available functional groups in the chain extenders can be acid anhydride, epoxy and oxazoline, etc.¹² Akkapeddi and Gervasi¹³ investigated a reactive extrusion system of virgin PET with adding different types of chain extenders and obtained modified PET with lower carboxylic content. Inata and Matsumura^{14–19} conducted many studies about evaluating potential chain extenders for modifying virgin PET. Their results showed that di- or poly-functional chain extenders were the preferred ones due to their higher reaction rates without generating by-products. Pyromellitic dianhydride (PMDA)^{20–23} was one of the most successfully

Table I. Chemical Structures of Chain Extenders Used in This Work

No.	Chemical structures	Chemical names
PMDA		Pyromellitic dianhydride
TGIC		Triglycidyl isocyanurate
ADR	Unknown, but containing six epoxy groups	ADR-4370-S

used chain extenders due to its fast reaction rate with PET, tetra functionality, thermal stability, and low cost. Firas Awaja *et al.*^{20,21} investigated the effects of the PMDA concentration and residence time on the IV of recycled PET in the reactive extrusion process. It was shown that the reactive extrusion process was more dependent on the PMDA concentration rather than the residence time. They pointed out that the IV could reach 1.18 dL/g and the stability of the extrusion process for regular PET was guaranteed with adding 0.3 wt % PMDA. Bis-oxazolines,^{9,14,15,18,19,24} which could react very fast with the carboxylic end groups of PET chains, had been proven effective in achieving linear chain extension of the polymer by formation of stable bis-amide bridging segments. Karayannidis *et al.*²⁴ showed that the IV of recycled bottle-grade PET effectively increased from 0.69 to 0.85 dL/g with bis-oxazolines as the chain extender. Other chain extenders such as pentaerythritol (PENTA)^{25–27} and triglycidyl isocyanurate (TGIC)^{28–30} were also used to improve the IV of PET. Adding different chain extenders together could also effectively achieve the chain extension. The combination of bis-oxazolines and PMDA or organic phosphites^{31,32} had been successfully used as the PET chain extenders. Cai Changeng³³ investigated the modification of recycled PET with initial IV of 0.41 dL/g by using combination of bis(2-oxazoline) and phthalic anhydride (PA). The viscosity was improved significantly to 0.70 dL/g, which could basically meet the requirements of industrial production.

Besides the reactive extrusion, the solid-state polycondensation (SSP)^{34–36} is another effective process to increase the IV of PET with little degradation effect, even though it is considered too slow and expensive for application on an industrial scale. Karayannidis *et al.*³⁵ investigated the effects of SSP reaction temperature and time on the IV of the recycled PET. An increase in the IV from 0.73 to 1.48 dL/g was obtained after SSP at 230°C for 8 h. Recently, Nascimento *et al.*³⁷ investigated the chain extended-modified SSP of recycled PET, in which PET flakes previously impregnated with chain extender were submitted to SSP at different temperatures and for different residence times. The results suggested that such methodology was possible to synthesize linear bimodal or branched ultra-high-molecular-weight polyesters. A comparison between impregnation and

extrusion process for modifying SSP with PMDA was also discussed.

In this work, a combination of the reactive extrusion and followed SSP was applied to modify the virgin fiber-grade PET (v-PET) and recycled bottle-grade PET (r-PET) to improve the melt strength. Two chain extenders pyromellitic dianhydride (PMDA) and triglycidyl isocyanurate (TGIC) with different number of functional groups were chosen as the modifiers for the reactive extrusion performed in a twin-screw extruder. For comparison, commercially available chain extender ADR JONCRYL ADR-4370-S (with high epoxy group content) was also used. The melt strength of the modified PET correlated to the long chain branches introduced in the molecular structure was evaluated through characterizations of the intrinsic viscosity (IV) and rheological properties. The thermal physical properties were also determined using differential scanning calorimetry (DSC). Finally, the foamability of the chain extended PET with different melt strength was characterized using a batch melt foaming process.

EXPERIMENTAL

Materials

Two types of PET raw materials were used in this study. Pellets of virgin fiber-grade PET (v-PET) with an IV of 0.65 dL/g and melting point of 259.7°C were supplied by Xinshan Petrochemical Co. Ltd., China. Flakes of recycled bottle-grade PET (r-PET) (nominal PVC content = 400 ppm) with an IV of 0.7 dL/g and melting point of 255°C were processed from postconsumer bottles without polyethylene caps or polypropylene labels by Beijing Incom Resources Recovery Recycling Co., Ltd., China.

Three chain extenders, namely, TGIC, PMDA, and ADR, were commercially available from Sinopharm Chemical Reagent Co., China, Shanghai Aoke Industrial Co., China, and BASF Co., Germany, respectively. Their chemical structures are shown in Table I. The antioxidant 1010 and triphenyl phosphite (TPP), purchased from Sinopharm Chemical Reagent Co., China, were also adopted to reduce the thermal and oxygen degradation of PET. CO₂ (purity: 99.9%, w/w %) and N₂ (purity: 99.9%, w/w %) were obtained from Air Product Co., Shanghai, China. All chemical agents were used as received.

Reactive Extrusion Process

A twin-screw co-rotating extruder with diameter of 20 mm and L/D = 60 (type SHJ-20, Nanjing Giant Machinery Co., Ltd., China) attached to a pelletizer was used for the reactive extrusion modification process. All PET pellets or flakes used were first predried by blowing desiccated air at 110°C for 12 h in an oven and then dried in a vacuum oven at 140°C for 12 h, to minimize the possibility of hydrolytic degradation. The PET and the chain extender were well mixed together before feeding into the barrel and then jointly fed. The feed rate was maintained at a constant value of 1.2 kg/h, and the extruder barrel temperature profile ranged from 265 to 275°C. The effects of the chain extender concentration and extruder screw rotation speed on modification of the v-PET and r-PET were studied.

Table II. IV of v-PET Modified with Different Concentrations of PMDA and Rotation Speeds via Reactive Extrusion

Sample	PMDA concentration (wt %)	Screw rotation speed (rpm)	$[\eta]$ (dL/g)
1	0.3	120	0.74
2	0.3	240	0.65
3	0.5	120	0.75
4	0.5	240	0.78

SSP Process

The SSP process was carried out in a rotary evaporator (type R203B, Shanghai DAYAN Equipment Co., Ltd., China) equipped with a vacuum pump. Before the SSP, all PET pellets were first predried by blowing desiccated air at 110°C for 6 h in an oven and then vacuum dried at 110°C for 12 h. The SSP was conducted at the rotation speed of 50 rpm and vacuum degree below 50 Pa. The effects of the SSP time and temperature on modification of both the extruded v-PET and r-PET were investigated.

Intrinsic Viscosity

The IV of the PET samples was measured with Ubbelohde viscometer in a constant temperature bath at 25°C according to GB-T1632-1993. A mixture of 50 : 50 (by mass) phenol and 1,1,2,2-tetrachloroethane at 110°C was used to dissolve the samples. The flow-out time of the prepared solution were recorded. The IV was calculated by

$$\eta_{sp} = \frac{t}{t_0} - 1 \quad (1)$$

$$[\eta] = \frac{\sqrt{1+1.4\eta_{sp}} - 1}{0.7c} \quad (2)$$

where η_{sp} is the specific viscosity, t_0 is the flow-out time of the solvent, t is the flow-out time of the solution, c is the solution concentration, and $[\eta]$ is the IV.

Differential Scanning Calorimeter

The thermal behavior of the PET samples was investigated using a differential scanning calorimeter (DSC) of type NETZSCH 204 HP under ambient nitrogen atmosphere. The sample (7–10 mg) predried in a vacuum oven at 110°C for 12 h was heated up to 290°C at a rate of 10°C/min.

Rheological Characterization

The rheological behavior of the PET samples was measured using a HAAKE MARS III Rotational Rheometer (Thermo Fisher Scientific Inc. Co., USA) equipped with the parallel plates of 35 mm diameter under nitrogen. Specimens were discs with 30 mm in diameter and 1 mm in thickness, prepared by compression-molding at 255°C. The complex viscosity η^* , storage modulus G' , and loss modulus G'' as a function of angle frequency ω (0.1–100 rad/s) were determined under a constant stress 10 Pa at 285°C.

Melt Batch Foaming Process

The melt batch foaming process was performed in a high-pressure vessel with an internal volume of 120 mL which was

placed in an electronic temperature controlled oil bath whose temperature was controlled with an accuracy of $\pm 0.5^\circ\text{C}$. The pressure of the vessel was detected by a pressure transducer with an accuracy of ± 0.1 MPa. During the foaming process, about 0.5 g predried PET particles was first loaded in a stainless steel cell sealed in the high-pressure vessel, and the vessel was swept for three times with low-pressure CO_2 . The vessel charged with a given amount of CO_2 was then put into the oil bath with a temperature of 280°C, and was retained at CO_2 pressure of 20 MPa for 20 min to make the PET completely melt and dissolve CO_2 into the molten PET matrix. After the vessel was quenched to the foaming temperature, i.e., 260 or 270°C, recharged into CO_2 and kept at CO_2 pressure of 20 MPa for another 10 min, the valve was rapidly opened to release the CO_2 in the high-pressure vessel to induce cell nucleation and bubble growth. The approximate depressurization rate was between 300 and 400 MPa/s. After a cooling process in an ambient-temperature water bath, the vessel was opened up to take out the foamed sample for subsequent analysis.^{38,39}

Scanning Electron Microscopy

The cell morphology of the foamed PET samples was observed using a NOVA NanoSEM450 (FEI, USA) scanning electron microscope (SEM). The SEM specimens were immersed in liquid nitrogen for 10 min and then fractured. The SEM scanned the fractured surfaces with platinum coating.

RESULTS AND DISCUSSION

Chemical Modification of v-PET with PMDA

Effects of PMDA Concentration and Screw Rotation Speed in Reactive Extrusion. Table II gives the IV of the v-PET modified with PMDA of different concentrations (0, 0.3, and 0.5 wt %) and at various extruder screw rotation speeds (0, 120, and 240 rpm). During the reactive extrusion process, there would be a competition mechanism between the effects of chain extension and degradations including thermal, hydrolytic, and oxidative degradation. Therefore, the IV of the extruded v-PET depends on the bias of the two competition effects. As shown in Table II, the IV of the extruded v-PET at the higher rotation speed is smaller than that at the lower rotation speed when the PMDA concentration is 0.3 wt %. However, at the higher concentration of PMDA (0.5 wt %), the difference of the IV between the extruded v-PET at both rotation speeds is nearly negligible. It can be explained that the extent of both chain extension and degradation reactions at the lower rotation speed is larger than that at the higher rotation speed, and the increase in the extent of degradation is sharper than that of chain extension. These two reasons lead to the higher IV of the extruded v-PET at the higher rotation speed. As a result, the PMDA concentration of 0.5 wt % and extruder screw rotation speed of 240 rpm were chosen as the ideal reactive extrusion modification conditions.

Effects of SSP Reaction Temperature and Time. As the reactive extrusion could not make the chain extend sufficiently, SSP was carried out so that the chain extender could effectively react with the unreacted terminal groups of the v-PET to get further chain extending. The effects of the SSP reaction time and temperature on the IV of the v-PET extruded with 0.5 wt % PMDA at the screw rotation speed of 240 rpm (Sample 4 designated in

Table III. Effect of SSP Reaction Time on IV of Sample 4 (Designated in Table II) at Different Reaction Temperatures

Reaction temperature (°C)	The IV of v-PET with different SSP reaction time (dL/g)				
	1 h	2 h	3 h	4 h	5 h
210	0.80	0.88	1.21	1.26	1.28
220	0.89	1.14	1.23	1.37	Gelled
230	0.99	1.33	Gelled	Gelled	Gelled

Table II) were investigated. Table III shows that the temperature has a great influence on the reaction rate of the SSP. The IV increases to 0.80 dL/g at 210°C, 0.89 dL/g at 220°C, and 0.99 dL/g at 230°C at the reaction time of 1 h. The same tendency can be found at other reaction time, indicating that higher reaction temperature leads to faster reaction rate. As regard the reaction time, it is easily noticed that the IV increases with increasing the reaction time at a given reaction temperature. However, too long reaction time at a certain reaction temperature of SSP would cause gel formation in the modified v-PET, resulting in its indissolubility in the mixture of 50 : 50 (by mass) phenol and 1,1,2,2-tetrachloroethane at 110°C. The higher SSP reaction temperature is, the more easily gel formation occurs. It is attributed to severe branching reactions between PMDA and terminal carboxyl of v-PET resulting in cross-linking reaction.

Rheological Behavior of v-PET Modified with PMDA. The rheological properties play an extremely important role in the polymer melt foaming. Thus, the polymers suitable for melt foaming acquire moderate viscosity and favorable elasticity, i.e., high melt strength. The complex viscosity η^* , storage modulus G' , and loss modulus G'' curves of the extruded v-PET with different PMDA concentrations at the screw rotation speed of 240 rpm are shown, respectively, as a function of frequency in Figure 1(a–c). Those of the raw v-PET are also shown for comparison. The complex viscosity of the raw v-PET does not change with changing frequency and keeps horizontal at a small value throughout the examined frequency range. However, with the addition of PMDA, the modified v-PET samples whose complex viscosity is greatly enhanced at the low frequency and constantly decreases with increasing frequency show flow characteristics of shear thinning. Especially, when the concentration

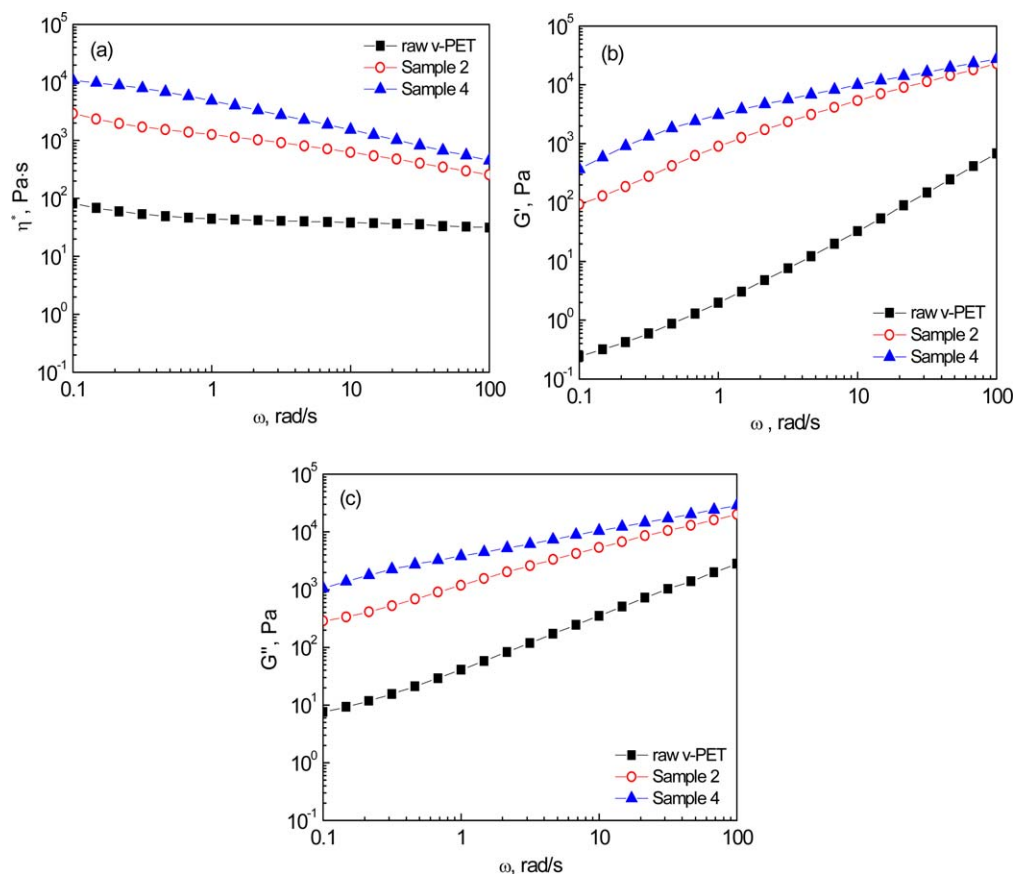


Figure 1. (a) Complex viscosity η^* , (b) storage modulus G' , (c) loss modulus G'' as a function of frequency of raw v-PET, Sample 2, and Sample 4, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

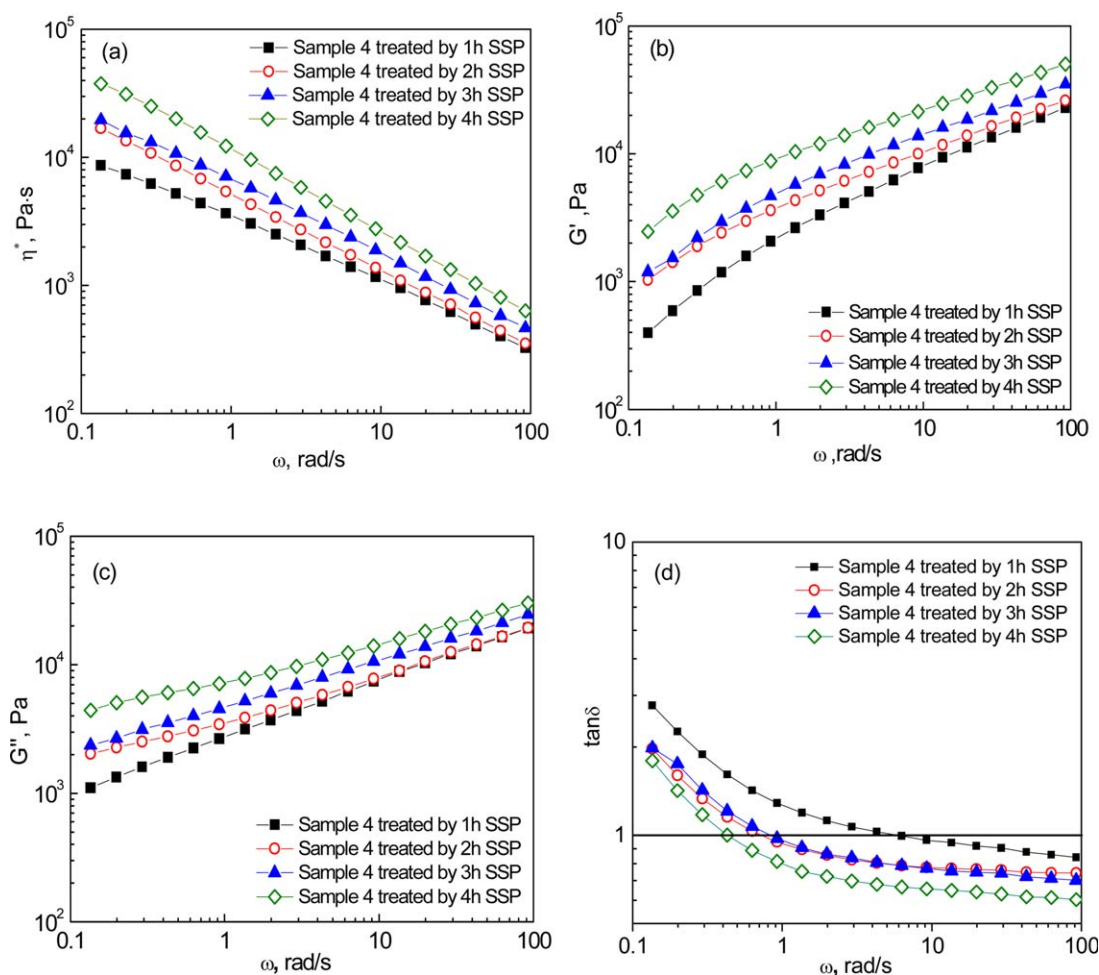


Figure 2. (a) Complex viscosity η^* , (b) storage modulus G' , (c) loss modulus G'' , and (d) loss tangent $\tan \delta$ as a function of frequency of Sample 4 treated by SSP at 220°C for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PMDA is up to 0.5 wt %, quite drastic drop of complex viscosity (from 10,000 to 450 Pa s) can be observed which indicates that modified PET appears obvious shear thinning behavior and turns into non-Newtonian flow as shown in Figure 1(a). The extremely large decrease in the complex viscosity with increasing frequency is also accompanied with a strong increase in the storage modulus and loss modulus of more than an order of magnitude, as shown in Figure 1(b and c). The drastic change in the storage modulus throughout the frequency range is much helpful for the melt foaming process. Such results are attributed to the chain extension/branching during the reactive extrusion process, which coincides with the results of IV measurements.

The effect of SSP reaction time on the rheological properties of the extruded v -PET undergoing followed SSP process was also investigated. Figure 2(a–d), respectively, shows the complex viscosity η^* , storage modulus G' , loss modulus G'' , and loss tangent $\tan \delta$ curves of the v -PET extruded with 0.5 wt % PMDA at the SSP reaction temperature of 220°C and various reaction times as a function of frequency. The longer reaction time is, the bigger complex viscosity, storage modulus, and loss modulus are, especially at low frequency. While for the loss tangent

$\tan \delta$, it decreases with increasing SSP time. Such results suggest that the polymer gets better viscoelasticity with longer SSP time due to chain extension/branching or even formation of moderate cross-linking. Moreover, in comparison with the extruded v -PET, the viscoelasticity of them with followed SSP process is much higher, indicating that the modified v -PET with bigger molecular weight, broader molecular weight distribution and greater degree of long chain branching are obtained through further SSP modification.

Chemical Modification of r -PET with PMDA

Modification of r -PET with different concentrations of PMDA was also investigated. Comparing the raw r -PET with an IV of 0.7 dL/g, the IV of the extruded r -PET decreases to 0.6 dL/g if no chain extender is added, indicating that the molecular weight has a certain loss due to the thermal, hydrolytic, and oxidative degradation during the extrusion. With adding 0.3 wt % PMDA, the IV of the PMDA modified r -PET reaches 0.62 dL/g which is higher than that of the extruded r -PET but still lower than that of the raw r -PET. Even with increasing the concentration of PMDA to 0.5 or 1.0 wt %, the IV still merely changes, i.e., 0.64 dL/g. The results suggest that the effect of degradation offsets that of the chain extension with

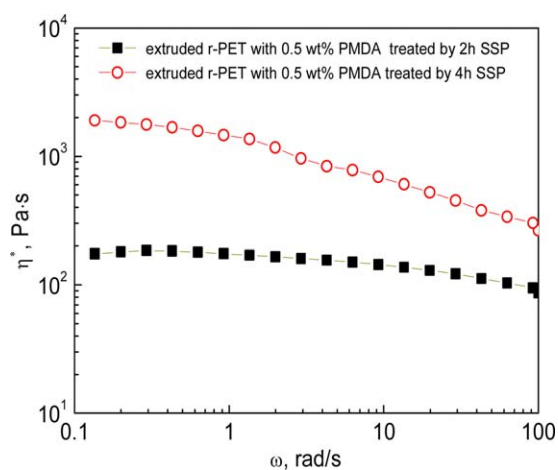


Figure 3. Complex viscosity η^* as a function of frequency of reactive extruded r-PET with 0.5 wt % PMDA and treated by SSP at 220°C for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PMDA as the modifier for the r-PET during the reactive extrusion process.

The IV of r-PET modified with 0.5 wt % PMDA via reactive extrusion at rotation speed of 240 rpm and followed SSP for 2 and 4 h at 220°C was also measured. It is found that at different reaction stages, the effect of modification with PMDA on IV of the r-PET is inferior to that of v-PET. The IV of the r-PET increases to 0.85 dL/g while that of the v-PET increases to 1.14 dL/g after followed SSP for 2 h, and the IV of the r-PET increases to 0.87 dL/g while that of the v-PET increases to 1.37 dL/g after followed SSP for 4 h. As observed, the IV of the r-PET modified with PMDA changes little.

The rheological behavior of r-PET extruded with 0.5 wt % PMDA and treated by followed SSP for different reaction time was also studied. As shown in Figure 3, the complex viscosity curve of the r-PET after SSP for 2 h is almost horizontal at all shear rate range displaying inconspicuous shear thinning phenomenon. With increasing SSP reaction time to 4 h, the complex viscosity also merely changes, which agrees well with the IV results.

Table IV. IV of r-PETs Modified with Different Concentrations of Various Chain Extenders via Reactive Extrusion

Sample	Chain extender	Concentration (wt %)	IV (dL/g)
5	TGIC	0.3	0.63
6		0.4	0.67
7		0.5	0.70
8		0.6	0.72
9		1	0.73
10	ADR	0.3	0.61
11		0.5	0.62
12		1	Gelled

Table V. Effect of SSP Time on IV of Samples 6, 7, and 8 Treated by SSP at 220°C

Raw material	IV of samples 6, 7, and 8 treated by SSP (dL/g)			
	1 h	2 h	3 h	4 h
6	0.71	0.78	0.83	0.87
7	0.76	0.88	0.99	1.07
8	0.81	0.92	1.01	Gelled

The IV values and rheological behavior results both reveal that with the addition of PMDA, chain branching reactions or even some cross-linking reactions between the four functionalities of the PMDA molecular and hydroxyl end groups of PET occur during the modification process. It should be noted that in either the reactive extrusion process or the SSP process, the modification effect of PMDA on the v-PET is much more effective than that on the r-PET. Considering the industrial demand, the bottle-grade PET with higher molecular weight and broader molecular weight distribution than the fiber-grade PET contains fewer potentially reactive hydroxyl end groups, which leads to the difficulty of chain branching with PMDA. Therefore, PMDA which has ideal chain extension effect for the v-PET is not effective for the modification of the r-PET.

Chemical Modification of r-PET with TGIC and ADR

Effects of the Chain Extender Type and Concentration. As PMDA was not that effective for modification of r-PET, two multifunctional epoxides, i.e., TGIC and ADR, as the chain extenders were used to investigate their modification effects on the r-PET. Different from PMDA reacting only with one terminal hydroxyl group of PET, the epoxides can react with both the carboxyl and hydroxyl groups of PET by esterification and etherification, and the secondary hydroxyls formed from these reactions may further react with carboxyl or epoxy groups leading to branching or cross-linking.^{12,28} At the extrusion conditions of main motor's rotation speed of 240 rpm, the IV of the reactive extruded r-PET with the addition of different concentrations of TGIC or ADR is shown in Table IV. With the addition of ADR, the IV of the r-PET after the reactive extrusion does not increase. Moreover, a serious phenomenon of cross-linking reaction exists leading to gel formation when the concentration of ADR increases to 1.0 wt %. The results reveal that ADR is also improper for modification of the r-PET. With regard to TGIC, the IV of the r-PET after the reactive extrusion increases with increasing TGIC concentration. The IV of the r-PET modified with TGIC is higher than that of the r-PET modified with ADR, and even higher than the IV of the raw r-PET at the proper chain extender concentration. Therefore, TGIC as the effective chain extender for modification of the r-PET is confirmed. The effect of TGIC concentration on the IV of r-PET modified by reactive extrusion and followed SSP at 220°C was further investigated. As shown in Table V, the IV increases with increasing TGIC concentration at a given SSP reaction time, and the same trend is observed with increasing SSP reaction time at a given TGIC concentration. However, gel formation occurs at the SSP time of 4 h when the TGIC concentration

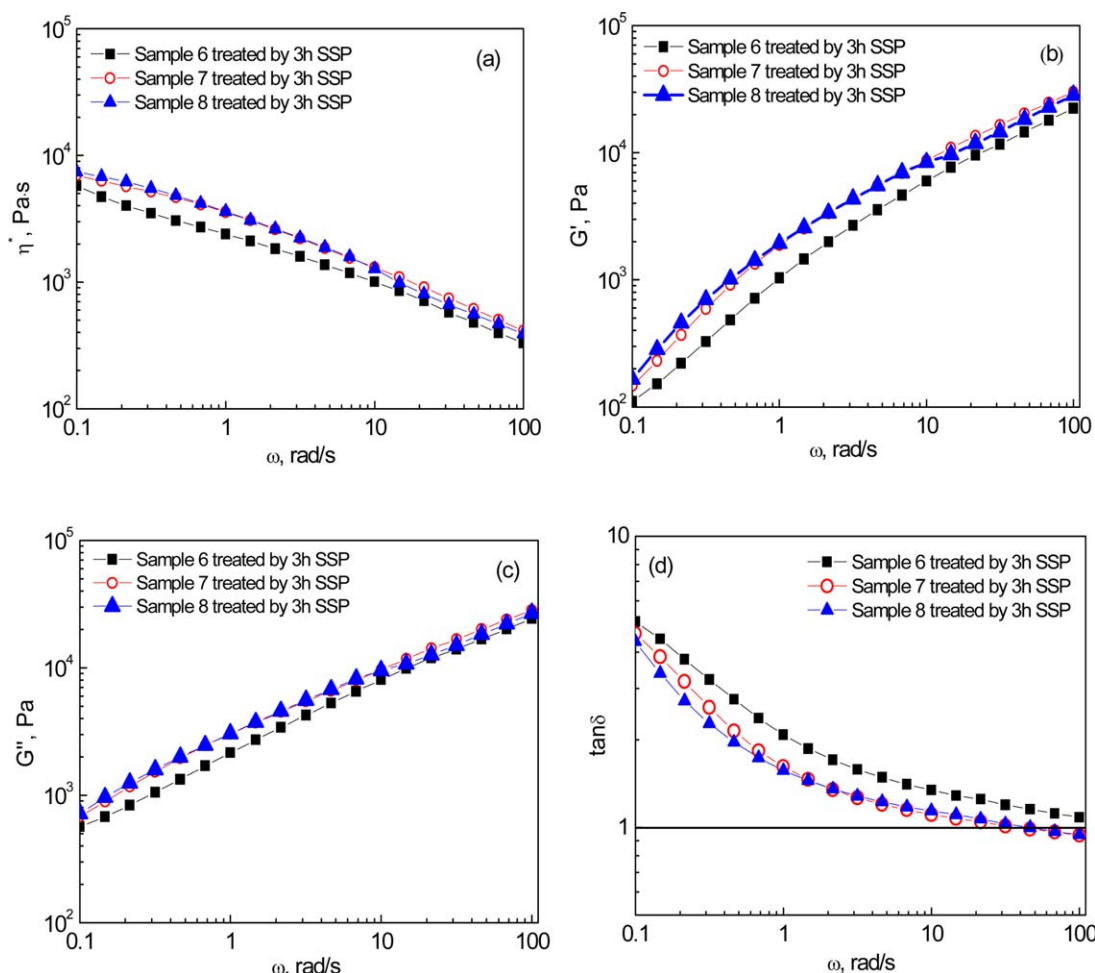


Figure 4. (a) Complex viscosity η^* , (b) storage modulus G' , (c) loss modulus G'' , and (d) loss tangent $\tan \delta$ as a function of frequency of Samples 6, 7, and 8 treated by 3 h SSP at 220°C, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is 0.6 wt %. Therefore, too long reaction time at high TGIC concentration would cause cross-linking reaction.

Rheological Behavior of r-PET Modified with TGIC. The complex viscosity η^* , storage modulus G' , loss modulus G'' , and loss tangent $\tan \delta$ curves of the extruded r-PET with different TGIC concentrations (Samples 6, 7, and 8) and treated with followed SSP for 3 h are shown, respectively, as a function of frequency in Figure 4(a–d). It shows that the modified r-PET performs shear thinning behavior and displays a non-Newtonian behavior in the whole frequency range. Moreover, r-PETs modified with 0.5 and 0.6 wt % TGIC show a higher complex viscosity than that of the r-PET modified with 0.4 wt % TGIC. Similarly, in all the range of test frequency, both the storage modulus and loss modulus of the r-PET modified with 0.5 and 0.6 wt % TGIC are higher than that of the r-PET modified with 0.4 wt % TGIC. Therefore, the r-PET modified with higher TGIC concentration performs more ideal viscoelasticity which is helpful for the melt foaming process.

In Figure 4(d), the loss tangent $\tan \delta$ of the r-PET modified with low concentration of chain extender is always bigger than that of the r-PET modified with higher concentration of TGIC, implying the viscosity is dominant in all the range of test

frequency. Besides, $\tan \delta$ of the r-PET modified with 0.5 or 0.6 wt % TGIC is smaller than 1 at higher frequency, i.e., $G' > G''$, indicating that the modified r-PET has high storage modulus, and more importantly, the elasticity is in a dominant position in viscoelasticity. Such rheological behavior is beneficial to support bubble growth avoiding collapse of bubbles during the melt foaming process.

Effects of Antioxidant and Heat Stabilizer. The oxidative, thermal, and hydrolytic degradation will affect the reactive extrusion and also the process of SSP for PET. Adding some antioxidants and heat stabilizer can suppress the oxidative and thermal degradation. The r-PET mixed with 0.5 wt % TGIC as the chain extender, 0.3 wt % antioxidant 1010, and 0.2 wt % TPP as the heat stabilizer was used for the reactive extrusion and followed SSP process.

Comparison of the IV between 0.5 wt % TGIC modified r-PET with and without antioxidant and heat stabilizer at different reaction stages is shown in Figure 5. The extruded r-PET with 0.5 wt % TGIC, antioxidant, and heat stabilizer is designated as Sample 13. Modification at Stage 1 means the r-PET treated only by reactive extrusion, modification at Stage 2 is the extruded r-PET treated with followed SSP for 2 h, and modification at Stage 3 is

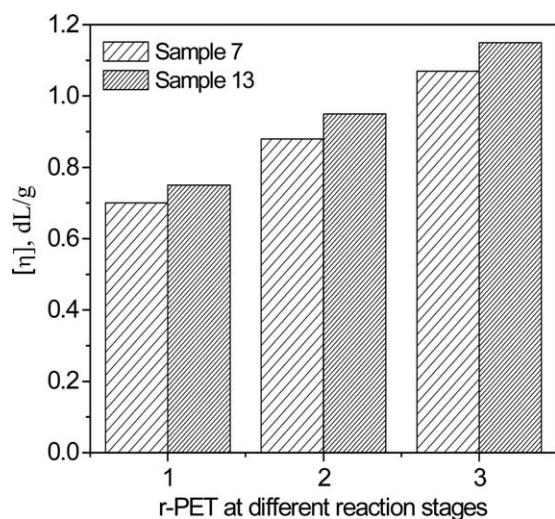


Figure 5. IV of Sample 7 and 13 after various modification process. Stage 1: reactive extruded r-PET; Stage 2: reactive extruded r-PET treated by 2 h SSP at 220°C; Stage 3: reactive extruded r-PET treated by 4 h SSP at 220°C.

the extruded r-PET treated with followed SSP for 4 h. The IV of the modified r-PET added with antioxidant 1010 and TPP at all the reaction stages is increased (the maximum is 1.15 dL/g), indicating the r-PET gets better modification effect through the addition of antioxidant and heat stabilizer.

Figure 6 shows the complex viscosity η^* , storage modulus G' , and loss modulus G'' curves of the raw r-PET, Sample 7 treated by 4 h SSP, and Sample 13 treated by 4 h SSP, respectively. Different from the raw r-PET which has approximate horizontal line of the complex viscosity, the modified r-PET samples display both obvious shear thinning phenomenon and higher complex viscosity. In addition, the modified r-PET with antioxidant and heat stabilizer has the highest viscoelasticity. The results also coincide with those of IV measurements.

Thermophysical Properties of Modified PET

The DSC plots of raw v-PET, 0.5 wt % PMDA extruded v-PET (Sample 4) and that treated by followed SSP, raw r-PET and 0.5 wt % TGIC extruded r-PET (Sample 7) and that treated by followed SSP in the heating round are shown in Figure 7(a and b). As shown in Figure 7(a), the raw v-PET and extruded v-PET

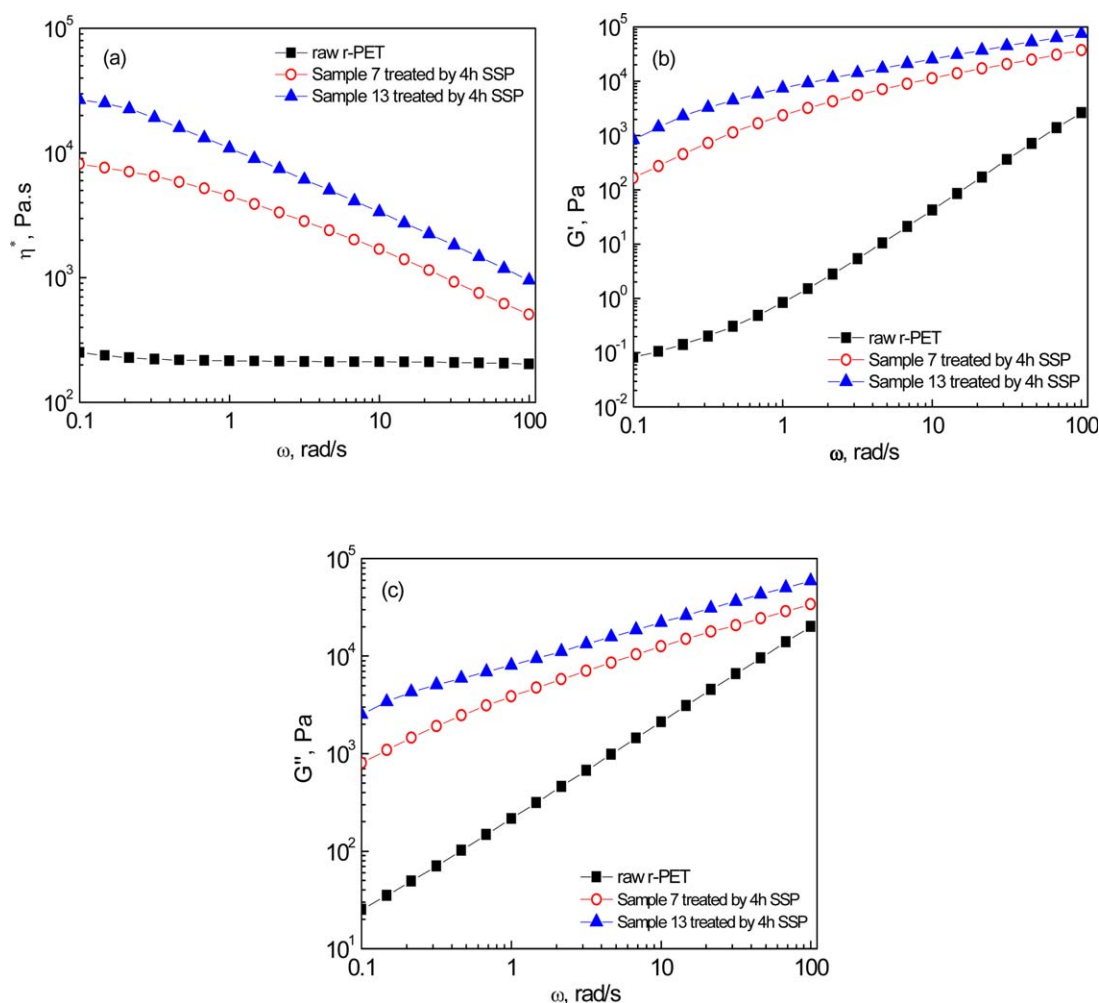


Figure 6. (a) Complex viscosity η^* , (b) storage modulus G' , (c) loss modulus G'' as a function of frequency of raw r-PET, Sample 7 treated by 4 h SSP, and Sample 13 treated by 4 h SSP, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

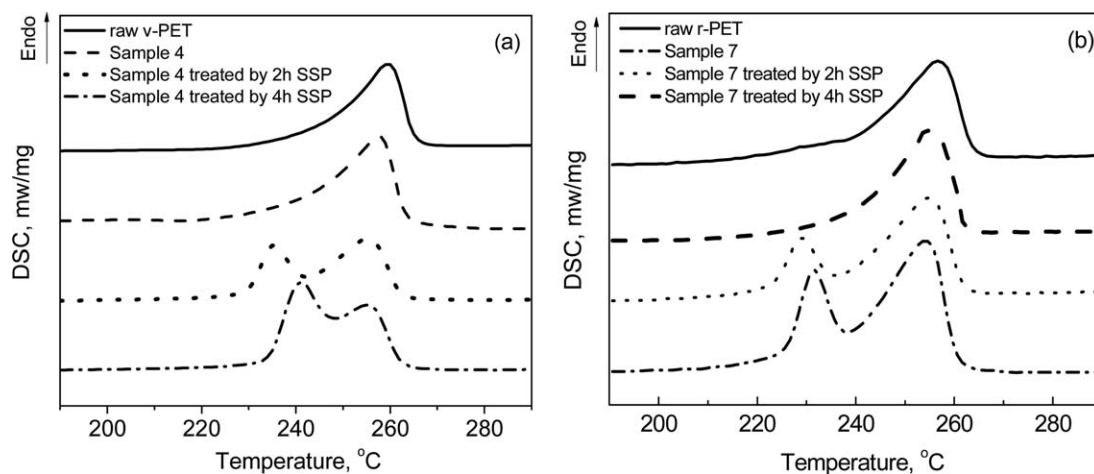


Figure 7. DSC plots in the heating round of raw v-PET, Sample 4, raw r-PET, and Sample 7 at different modification stages.

both show a single melting peak. However, the extruded v-PET treated by followed SSP shows double melting peaks. The peak at the higher temperature is close to the melting peak of the raw v-PET and the temperature of the other peak is close to the SSP reaction temperature. The multiple melting behavior is common for modified PET depending on the crystallization

conditions, which has not been well understood to date.^{40,41} The multiple melting peak behavior of semicrystalline polymers crystallized from the melt has been investigated extensively and it is proposed to link to partial melting, recrystallization, and remelting, to distribution of crystals with different lamellar thickness, and to melting of different crystal structures.⁴² After

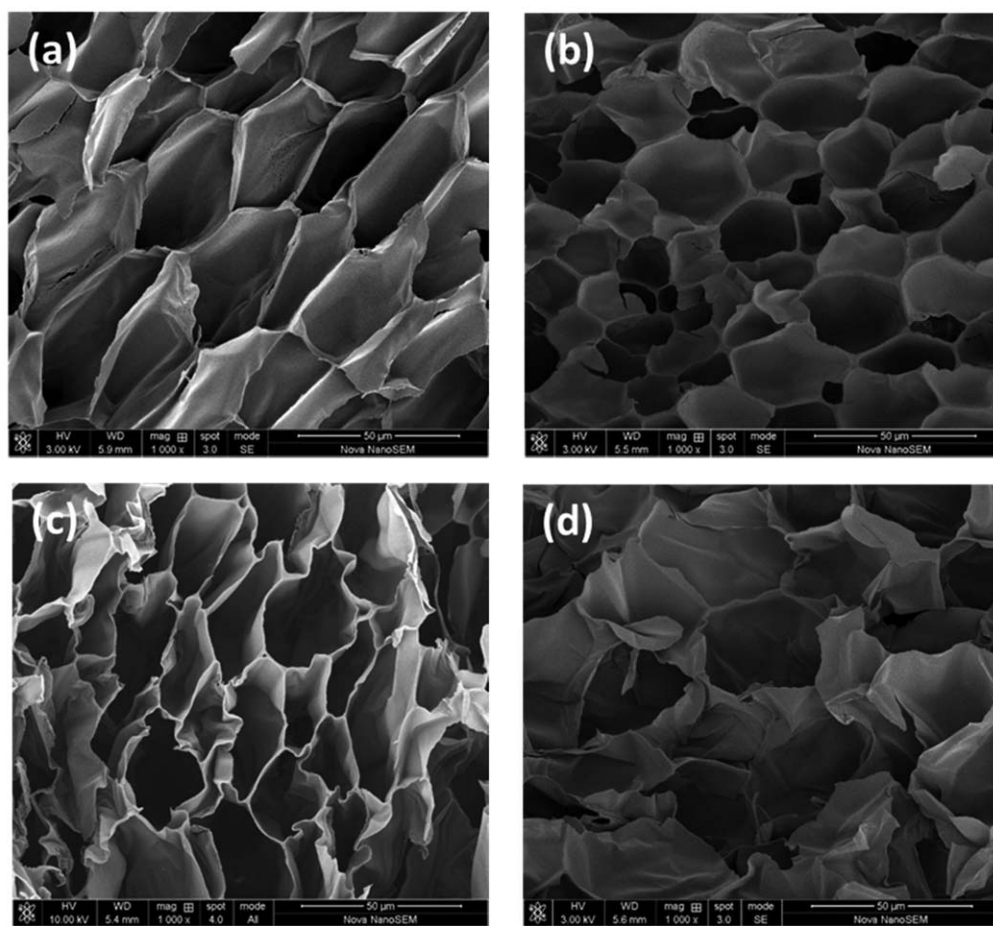


Figure 8. SEM micrographs of Samples 14 and 15 foamed at different temperatures. (a) Sample 14, 260°C; (b) Sample 14, 270°C; (c) Sample 15, 260°C; and (d) Sample 15, 270°C.

the reactive extrusion of v-PET, the formation of long chain branching structure reduces the regularity of molecular chain. For the extruded v-PET treated by followed SSP, the SSP process might promote the development of less imperfect crystallites with lower melting temperature into more perfect ones with higher melting temperature. Then, with deepening of the SSP process, as displayed in Figure 7(a), the distance between the two melting peaks is shortened. Moreover, the area of the peak at lower temperature increases and at higher temperature decreases while the temperature at the higher peak remains unchanged after the SSP. For the modified r-PET, the same tendency is observed in Figure 7(b). In general, long branched chain structure existing in both modified PET changes the crystallization behavior leading to different thermophysical properties eventually.

Melt Foaming of PET

A batch melt foaming process was applied to verify the foamability of the different PET samples. The foaming results of the raw v-PET and r-PET at certain foaming conditions show no formation of foams because of their low melt strength as expected. Samples 4 and 13 both treated by followed 4 h SSP at 220°C are designated as Samples 14 and 15. The SEM micrographs of foamed Samples 14 and 15 are shown in Figure 8. It shows that the modified PET foams with diameter about 30 μm, the cell density higher than 5.4×10^8 cells/cm³, and the expansion ratio higher than 15 times are obtained. In comparison with the raw PET, the modified PET by using reactive extrusion and followed SSP gains good foamability. Under a batch foaming process, it could be melt foamed in a temperature range from 260 to 270°C, indicating that the chain extension reaction greatly improves the melt strength of PET.

CONCLUSIONS

A combination of reactive extrusion and followed SSP was used to modify v-PET and r-PET with chain extenders in order to improve their melt strength and melt foamability as well. Two chain extenders PMDA and TGIC with different number of functional groups were chosen as the modifiers for the reactive extrusion performed in a twin-screw extruder to investigate their modification effects on the molecular structure of PET, i.e., average molecular weight, molecular weight distribution, and branching. A commercially available chain extender ADR JONCRYL ADR-4370-S (with high epoxy group content) was also used for comparison purpose. The reactive extruded PET was then treated using the followed SSP. The IV and rheological behavior characterizations were applied to evaluate the chain extension extent of the PET.

During the reactive extrusion process, the effects of PMDA concentration and screw rotation speed on the modification of the v-PET were investigated. It was revealed that the chain extension depended strongly on chain extender concentration. The effect of reaction temperature and time in the SSP process were also studied. The results suggested that the temperature had a great influence on the SSP reaction rate and too long reaction time of the SSP would cause gel formation of the modified v-PET. At the optimized modification condition, the IV of the resulted

v-PET was increased to 1.37 dL/g. The rheological behavior also showed that the modified v-PET gained higher dynamic complex viscosity, storage modulus, and loss modulus, i.e., higher viscoelasticity and melt strength in comparison with the raw v-PET. The same experiments were also conducted on the r-PET and the results showed that PMDA modification effect on the r-PET was inferred to that on the v-PET, which was attributed to the differences of the polymer initial molecular weight and molecular weight distribution.

Two multifunctional epoxides, i.e., TGIC and ADR, as the chain extenders were then used to investigate their modification effects on the r-PET, in which TGIC was found to be effective. The effects of TGIC concentration and SSP reaction time on the modification of the r-PET were investigated. Chemical modification of the r-PET by TGIC led to an increase in IV from 0.7 to 1.07 dL/g, and the IV could be further increased to 1.15 dL/g with the addition of the antioxidant and heat stabilizer. Rheological characteristics showed the storage modulus, loss modulus, and dynamic complex viscosity of the modified r-PET increased and the loss tangent decreased compared with those of the raw r-PET, indicating that the high melt strength r-PET was obtained by chain extension with TGIC.

Thermal analysis using DSC showed that the chain extension reaction decreased the regularity of PET molecular chains and changed the crystallization behavior of PET. The DSC plots of the both modified PET after SSP in the heating round showed double melting peaks. The foamability of the modified PET was also verified by using a batch melt foaming process. The both modified v-PET and r-PET foams with cell size about 30 μm, the cell density higher than 5.4×10^8 cells/cm³ and the expansion ratio higher than 15 times could be obtained, indicating that the viscoelasticity and melt strength of the modified PET were greatly improved due to the chain extension by using the combination of the reactive extrusion and followed SSP.

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