Effect of the Trifunctional Chain Extender on Intrinsic Viscosity, Crystallization Behavior, and Mechanical Properties of Poly(Ethylene Terephthalate)

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ABSTRACT: In this work, poly(ethylene terephthalate) (PET) chain-extending products with different molecular weights were prepared by reactive extrusion using isocyanate trimer (C-HK) as the trifunctional chain extender. The effect of the chain extender C-HK on the intrinsic viscosity, melt flow property, crystallization behavior, crystallization morphology, and mechanical property of PET was investigated. The results showed that when the content of the chain extender was increased from 0.6 to 1.4 wt%, the viscosity average molecular weight of PET was effectively increased from $2.36 \times 10^4$ to $5.46 \times 10^4$ g·mol$^{-1}$. After the chain extending, the crystallinity and the time of semicrystallization of PET were significantly decreased. After the isothermal crystallization at 220 °C for 5 min, the spherulites formed by pure PET became larger. With the increase in molecular weight of PET after chain extension, its spherulite size was significantly decreased without changing the crystalline structure. The chain-extended PET also exhibited more excellent bending-resistant and impact-resistant properties. While the tensile strength of PET after chain extension was slightly decreased, the bending strength was increased by a maximum value of 56.8%, and the impact strength was increased by a maximum value of five times.

1. INTRODUCTION

As a kind of thermoplastic resin with excellent performance, poly(ethylene terephthalate) (PET) has been widely used in the production of textile fibers,1−3 packaging films,4,5 and beverage bottles.6—9 However, it still has disadvantages such as a low crystallization rate and difficult molding process, which have always limited its application prospect in other fields.10−16 In addition, the viscosity, melt strength, and mechanical properties of PET are closely related to its molecular weight. Lowering the molecular weight of PET during the thermal, chemical, and oxidative degradation limits its use in other fields such as recycling and reprocessing.17−20

In recent years, the increase in the crystallization rate of PET has been mainly achieved by adding various nucleating agents. Lee et al.21 synthesized a new nanoparticle-nucleating agent of aminopropyl-functionalized polyhedral oligomeric silsesquioxanes (A-POSS). It was found that the crystallization temperature and the crystallization rate of PET were increased by 1.2 and 2.7 times, respectively, by this nucleating agent. The chain extending and branching have been generally carried out for increasing the molecular chain of PET, and the fluidity of the product is decreased. Thus, the improvement of molding processability of PET has been achieved.22 Li et al.23 studied the effect of different chain extenders on the branching and cross-linking of PET. It was found that the intrinsic viscosity and rheological property of PET were significantly improved when poly(butylene terephthalate)-glycidyl methacrylate-styrene copolymer (PBT-GS) was used for chain extending.

The chemical chain-extending method is widely used in chain extending and tackifying modification of PET because the reaction condition that it needs is relatively low, and it has the advantages of low energy consumption and high efficiency compared with solid-state polycondensation and melt polycondensation. Chain extenders are normally small compounds with at least two functional groups, which are able to react with the end groups of polymers.24 The chemically covalent bonds can be formed between polymers, leading to the chain extension and increased molecular weight of polymers. At the same time, the addition type of the chain extender is mostly used in the choice of the chain extender in order to...
avoid the fact that too many small molecule byproducts are produced and the chain-extending reaction is inhibited in the process of chain extending.\textsuperscript{3,25} The chain extenders including pyromellitic dianhydride (PMDA), diisocyanates, and diepoxides have been extensively studied for the chain extension of polymers like PET.\textsuperscript{26−31} Raffa et al.\textsuperscript{32} studied the PET extension and branching using two difunctional chain extenders, 1,6-disocyanatothexane and 1,4-butanediol diglycidyl ether (EPOX). It was found that compared to diepoxide, the addition of diisocyanate led to an increase in viscosity of PET. Can et al.\textsuperscript{33} investigated the effect of three different chain extenders including 1,4-phenylene-bis-oxazoline (PBO), 1,4-phenylene-diisocyanate (PDI), and triphenyl phosphate (TPP) on the mechanical property of the PET/PEN blend. It was found that the tensile strength could reach the optimum value after a certain amount of isocyanate was added. It has been proven that diisocyanates could act as effective chain extenders and be reactive toward the hydroxyl groups of PET, leading to the formation of stable covalent bonds.\textsuperscript{34} So far, there have been many studies carried out on the chain extension of PET with bifunctional chain extenders. A simple and facile method to produce high molecular weight and increased viscosity PET materials is urgently needed.

The efficiency and possibility of the chain extension reaction of polyesters were effectively improved since the −NCO group of the isocyanate-based molecules had relatively high chemical activity. It can be assumed that trifunctional isocyanates containing three reactive isocyanate groups, which are able to react with three hydroxyl end groups of PET polymers, would have a great impact on the molecular weight, crystallization, and mechanical properties of PET. Note that C-HK is a highly toxic chemical. However, because it is the most important commercially and widely used chemical with highly reactive functional −NCO groups, it is still selected for our research work. In addition, there are a few related studies on the effect of the increased molecular weight with trifunctional chain extenders on the crystallization, flow, and mechanical property of PET.\textsuperscript{35,36} Therefore, in this study, the chain-extending products of PET with different molecular weights were prepared by the chemical chain-extending method using isocyanate trimer as a chain extender. The effect of chain-extending PET with different molecular weights on the crystallization and mechanical properties was studied by using a differential scanning calorimeter, X-ray diffractometer, polarizing microscope, and universal testing machine.

2. RESULTS AND DISCUSSION

2.1. Influence of the Amount of C-HK on the Chain-Extending Effect. Figure 1 shows the change trend of intrinsic viscosity and viscosity average molecular weight of chain-extended PET with different contents of C-HK. After increasing the content of the chain extender CH-K, the influence of the Amount of C-HK on the Flow Property of PET. The parameter of the MFR is directly corresponding to the melt viscosity and the molecular weight of polymers. Figure 3 shows the MFR curve of the chain-extended PET after C-HK modification. It can be seen from Figure 3 that at a lower C-HK content of 0.6%, the chain extension effect of PET is not obvious, the MFR of the chain extended PET is about 77.4 g/10 min, and it is basically no different from the MFR value 81.3 g/10 min of pure PET. After increasing the content of the chain extender CH-K, the chain extension effect of PET was gradually increased. Especially when the content of the chain extender in PET was greater than 0.6 wt % and less than 1.2 wt%, the effect of reducing the MFR value was more prominent. The MFR of the chain-extended PET was reduced from 77.4 to 34.8 g/10 min.
When the amount of the chain extender is increased to 1.4 and 1.6 wt %, the molecular chain extension effect reaches the maximum value. In addition, it was most likely that the branching reaction of trifunctional chain extenders with the hydroxyl end groups of PET took place at a high concentration of C-HK. The increase in molecular weight and chain branching also causes the melt viscosity to reach a new height again, and the MFR further shows a small decrease. At the same time, the excessive physical entanglement between the longer molecular chains leads to the generation of gels. The melt gels are more difficult to pass through the dye. Therefore, under the same pressure and same time, the chain-extended PET containing the gel is passing through the dye with less melt mass, and the melt flow rate is lower. The MFR of the final partially cross-linked chain-extended PET reached 30.3 g/10 min.

2.3. Influence of the Amount of C-HK on Crystallization Capacity. Figure 4 shows the melting curve and crystallization curve for chain-extending PET with different contents of C-HK. Table 1 displays the corresponding characteristic value of pure PET and chain-extending PET samples during the melting and cooling process. As can be seen from Figure 4, the melting peak of pure PET appears at 250.4 °C, and the crystallization peak appears at 191.6 °C. The corresponding melting enthalpy and crystalline enthalpy are 43 and 48.3 J·g⁻¹, respectively. After the addition of C-HK, the melting curve of chain-extending PET appears at the melting double peaks around 250 and 240 °C, respectively, and the melting peak gradually shifts to the low temperature. The literature points out that there are two main reasons for the emergence of multiple melting peaks: first, the samples contain a variety of the crystallization of the crystalline polymer. Second, the chain segment with original nonregular arrangement rearranges again after endothermicity in the...
Figure 5. POM image of (a) pure PET and PET after the chain extending with the addition of C-HK: (b) 0.6, (c) 0.8, (d) 1.0, (e) 1.2, (f) 1.4, and (g) 1.6%.

Table 1. Melting Curve and Crystallization Curve Characteristic Value of Pure PET and Chain-Extending PET Samples

| C-HK content (%) | \( T_{m1}/\degree C \) | \( T_{m2}/\degree C \) | \( \Delta H_{m1}/J \cdot g^{-1} \) | \( \chi_c/\% \) | \( T_c/\degree C \) | \( \Delta H_c/J \cdot g^{-1} \) | \( t_{1/2}/\text{min} \) |
|------------------|-----------------|-----------------|----------------------|-------------|-----------------|----------------------|--------------|
| 0                | 250.4           | 43.0            | 30.7                 | 191.6       | −48.3           | 3.2                  |              |
| 0.6              | 251.3           | 43.3            | 30.9                 | 206.8       | −47.0           | 1.4                  |              |
| 0.8              | 252.3           | 40.9            | 29.2                 | 203.8       | −46.6           | 1.8                  |              |
| 1.0              | 250.9           | 39.8            | 28.4                 | 202.1       | −43.0           | 1.7                  |              |
| 1.2              | 251.2           | 39.6            | 28.3                 | 200.5       | −42.4           | 1.7                  |              |
| 1.4              | 248.5           | 36.5            | 26.0                 | 191.9       | −42.1           | 1.8                  |              |
| 1.6              | 246.8           | 34.2            | 24.4                 | 200.3       | −35.4           | 1.5                  |              |

Note: \( T_{m1} \) and \( T_{m2} \) are the melting peak temperatures, \( \Delta H_{m1} \) is the melting enthalpy, \( \chi_c \) is the crystallinity, \( T_c \) is the crystallization peak temperature, \( \Delta H_c \) is the crystallization enthalpy, and \( t_{1/2} \) is the semicrystallization time.

melting process, carries out endothermicity in the vicinity of melting point, and melts again. The latter is more likely to be due to the finding that the increase in molecular weight does not change the crystallinity of PET in the subsequent analysis. It shows that the molecular weight is greatly improved. Meanwhile, the level of difficulty of regular arrangement for molecular chains is significantly affected. It is difficult for the longer molecular chain to achieve the rearrangement completely within the limited crystallization time.

It can also be found in the cooling curve that PET with chain-extending shows a higher crystallization temperature and lower semicrystallization time compared to pure PET. The results show that the initial condition that the crystallization of PET with chain extending requires is lower, and the time that the crystallization process consumes is shorter. Furthermore, it is found in the heating curve, with the increase in the molecular weight, the crystallinity of chain-extending PET gradually decreases. This is because the molecular weight is higher, and the melt viscosity is greater under the same crystallization condition. The movement of the chain segment is limited. Thus, it is even more difficult to regularly align to form a highly ordered lattice. At the same time, the decrease in crystallinity leads to lower energy absorption that is needed to break the lattice upon melting, which is the reason why the melting peak shifts to the left.

2.4. Influence of the Amount of C-HK on Crystallization Morphology. For the crystalline polymer, the molecular structure and crystallization condition greatly affect the crystallization rate, and the crystallization rate has a significant impact on the crystallinity and crystalline morphology of the polymer. For PET as a crystalline polyester, especially after the chain extending and branching, the influence of the molecular structure on crystalline morphology of the polymer is more significant. Figure 5 below shows POM images of pure PET and PET with chain extending with different molecular weights.

Since the spherulites are the main crystalline form of the polymer, it can be observed from Figure 5a that significant spherulites are produced in pure PET at 220 °C after isothermal crystallization for 5 min, and the crystal size is relatively large. From Section 2.1, we can see that the molecular weight of PET significantly decreases with the addition of a 0.6 wt % chain extender. In Figure 5b, it is found that the decrease in molecular weight significantly makes the crystallization rate of PET increase, resulting in the highest number of spherulites and the most obvious refinement phenomenon of spherulites. With the gradual increase in molecular weight, smaller spherulites with obvious black-cross extinction appear on the POM images, the number of spherulites gradually decreases, and the phenomenon of grain refinement still exists. It is also found in Figure 5g that the distribution of spherulites apparently becomes non-uniform when the cross-linking occurs inside the polymer. It can be seen that after the molecular weight is increased, the longer molecular chain limits the movement of the chain segment, and the crystallization rate is gradually decreased. In particular, after the physical cross-linking, the generated spherulites are unevenly distributed, and the growth rate of spherulites varies for each region.

2.5. Influence of the Amount of C-HK on the Crystal Structure. Figure 6 shows XRD patterns of PET extended with different contents of C-HK after annealing under the same condition. It can be seen from Figure 6 that the diffraction peaks of pure PET appear at 16.1, 17.5, 21.4, 22.6,
Mechanical Property. From Section 2.4, it can be seen that the increase in molecular weight plays an important role in the mechanical property of the polymer. PET with a single crystal structure is unchanged by the chain extending. It is indicated that PET with a single crystal structure is unchanged by the chain extending. Figure 7 shows the curves of the mechanical property of pure PET, where the tensile strength generally decreases and fluctuates in the range of 50–55 N/mm² after the modification of C-HK. However, the impact strength and bending strength have relatively large change. The bending strength of pure PET is 73.8 MPa. When the addition amount of C-HK is 1.6 wt %, the bending strength of chain-extending PET reaches a maximum value of 115.8 MPa. The impact strength of PET is 18.9 kJ/m². When the addition amount of C-HK is 1.4 wt %, the impact strength of chain-extending PET reaches a maximum value of 98.8 kJ/m². After the content of the chain extender is continuously increased, the impact strength significantly decreased.

From Section 2.4, it is found that the increase in molecular weight accelerates the crystallization rate of PET and results in more and smaller spherulites, which indicates that after being subjected to external force, the grain with more compact arrangement is better able to be subjected to the stress and disperses to the surrounding, thereby reducing the phenomenon of local stress concentration. At the same time, after the molecular weight has been increased, the lower crystallinity provides more space for slippage among the molecular chain within the amorphous region, resulting in the fact that more energy can be absorbed. Under the co-effect of two kinds of factors, the ultimate performance is a significant improvement in bending strength and impact strength. However, after the chain extending and branching, the distance of the molecule increases, and the interaction force decreases for the molecule chain. As a result, the tensile strength significantly decreases. However, with the increase in the degree of chain extending, the tensile strength can still show the trend of gradual increase. At the same time, when the addition amount of C-HK is 1.6 wt %, the slight physical cross-linking in the products has a great influence on impact strength and has no obvious effect on tensile strength and bending strength.

3. CONCLUSIONS
The products of chain-extending PET with different viscosity average molecular weights were prepared by C-HK chain extending, wherein, the viscosity average molecular weight of chain-extending products was the lowest at 17,700 g mol⁻¹ and the highest at 54,600 g mol⁻¹. It is subsequently found that the melting double peak appears in chain-extending products without changing the crystal structure by the chain-extending effect. The melting and crystallization peaks tend to shift to a lower temperature with the increase in molecular weight. At the same time, the chain-extending products with high molecular weight have lower crystallinity and shorter semi-crystallization time. When the content of C-HK is 1.6 wt %, the crystallinity and semicrystallization time reach the lowest values at 24.4% and 1.5 min, respectively. Compared with the large-size spherulites of pure PET, the grain size of chain-extending PET still appears to have a dispersed distribution, and the interaction force decreases for the molecule chain. As a result, the tensile strength significantly decreases. However, with the increase in the degree of chain extending, the tensile strength can still show the trend of gradual increase. At the same time, when the addition amount of C-HK is 1.6 wt %, the slight physical cross-linking in the products has a great influence on impact strength and has no obvious effect on tensile strength and bending strength.
4. MATERIALS AND METHODS

4.1. Materials. WB-8816 PET was purchased from Changzhou Huarun Polyester Co., Ltd. and its intrinsic viscosity was \([\eta] = 0.81 \text{ dL/g.} The trifunctional chain extender of isocyanate trimer CORONATE HK (C-HK) was purchased from Tosoh Corporation, Japan, and the content of NCO (%) in it was 19.3–20.7. The 1010 antioxidant, phenol with analytical purity, and tetrachloroethane with analytical purity were purchased from BASF China Limited Company, Shanghai Lingfeng Chemical Reagent Co., Ltd. and Shanghai Lingfeng Chemical Reagent Co., Ltd., respectively.

4.2. Preparation of Chain-Extending PET. Pure PET pellets were dried in a blast oven at 120 °C for 12 h to avoid the degradation reactions caused by moisture. The dried pellets were mixed with a certain amount of antioxidant, and 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 wt% chain extenders of C-HK were added respectively. After the even mixing, the mixture was added into a twin-screw extruder to carry out reactive extrusion. The temperature of the twin-screw extruder was set to 210, 230, 240, 250, 260, 265, 265, 265, and 260 °C. After even mixing, the mixture was added into a twin-screw extruder to carry out reactive extrusion. The resulting pellets were placed into a blast oven at 120 °C and dried for 10 h to obtain the final chain-extending products.

4.3. Determination of Intrinsic Viscosity. A small amount of the PET sample was taken and dissolved in the mixed solution of phenol/tetrachloroethane \(\text{w}_{\text{phenol}}/\text{w}_{\text{tetrachloroethane}} = 50/50\). The test was carried out by using an Ubbelohde viscometer at 25 °C. The intrinsic viscosity of the product was calculated by eqs 1–3.

\[
n_i = \frac{t}{t_0}
\]

(1)

\[
n_\infty = n_i - 1
\]

(2)

\[
[\eta] = \frac{1}{c} \sqrt{\frac{2(n_\infty - \ln n_i)}{\alpha}}
\]

(3)

wherein \(t_0\) is the time that the solvent flowed through the capillary, \(t\) is the time that the solution flowed through the capillary; \(n_i\) is relative viscosity, \(n_\infty\) is specific viscosity, \(c\) is the concentration of solution, and \([\eta]\) is intrinsic viscosity.

4.4. Determination of Molecular Weight. The viscosity average molecular weight of \(M_v\) of the chain-extending product was obtained by the Mark–Houwink nonlinear equation (eq 4).

\[
[\eta] = K\bar{M}_v^a
\]

(4)

wherein \([\eta]\) is intrinsic viscosity, \(\bar{M}_v\) is viscosity average molecular weight, and \(K\) and \(a\) are the Mark–Houwink constants that are 0.021 and 0.82, respectively, which could be found and obtained according to the solvent system.

4.5. DSC Test. The crystallization property of PET was tested using a DSC 214 Polyma differential scanning calorimeter from Netzsch, Germany. After 5–10 mg of samples was taken and rapidly heated to 280 °C at a rate of 50 °C/min in a N₂ atmosphere for 5 min to eliminate thermal history, these samples were cooled to 20 °C at a rate of 10 °C/min to obtain the crystallization curve. Then, these samples were heated to 280 °C at a rate of 10 °C/min to obtain the melting curve.

4.6. POM Test. The crystallization morphology of PET was observed by using a NIKON 50I Nikon polarizing microscope with a cooling/heating system from Nikon Instruments (Shanghai) Co., Ltd. A small amount of samples was placed in the cooling/heating system that was preheated to 270 °C. After the samples were completely melted, a layer of cover glass was added on the surface of samples, and the samples were pressed into thin sheets. Then, after the resulting samples were rapidly cooled to 220 °C at a rate of 150 °C/min for 5 min to crystallize, the crystallization morphology of samples was observed.

4.7. XRD Test. The crystal structure of PET was analyzed by using a D/max 2500 PC X-ray diffractionometer from Japan. The Cu target operating at 60 kV and 300 mA was used. The scanning speed was 2 °C/min. The scanning range was 5–50°. PET was needed to anneal in an oven at 180 °C for 2 h before testing.

4.8. Test of Mechanical Property. Mechanical property of PET was tested by using an AGS-10KND universal testing machine from Shenzhen Kaiqiangli Test Instrument Co., Ltd. The tensile strength test is performed according to GB/T 1447-2005, the bending test is carried out according to GB/T 1449-2005, and the Izod unnotched impact strength test is achieved according to GB/T 1843-2008.

4.9. Melt Flow Rate (MFR) Test. A melt flow rate meter (ZRZ1452, Shenzhen Xinsansi Materials Testing Co., Ltd., Shenzhen, China) was used to test the flow performance of PET. The test temperature is 260 °C, a constant force was applied, the total weight of the pressing rod is 2160 g, and the final MFR value is the total weight of the polymer flowing out of the dye within 10 min.

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Z.Z. designed and performed the preparation, characterization, data collection, and wrote the paper. Y.W. and K.W. provided help with the sample tests and analysis. Y.X. carried out the DSC characterization and assisted with analysis. H.G. and K.L. provided guidance and suggestions to the research and contributed to the revision of the manuscript. Z.C. designed and supervised the majority of the experiments and revised the paper. J.Q. reviewed the paper.

Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Tamizifar, M.; Sun, G. Controlled surface functionalization of poly(ethylene terephthalate) fibers with varied vinyl monomers via radical graft copolymerization. Mater. Today Commun. 2018, 17, 124–132.
(2) Liu, Y.; Yin, L.; Zhao, H.; Song, G.; Tang, F.; Wang, L.; Shao, H.; Zhang, Y. Strain-induced structural evolution during drawing of poly(ethylene terephthalate) fiber at different temperatures by in situ synchrotron SAXS and WAXD. Polymer 2017, 119, 185–194.
(3) Liu, Y.; Yin, L.; Zhao, H.; Song, G.; Tang, F.; Wang, L.; Shao, H.; Zhang, Y. Lamellar and fibrillar structure evolution of poly(ethylene terephthalate) fiber in thermal annealing. Polymer 2016, 105, 157–166.
(4) Essabti, F.; Guinauld, A.; Roland, S.; Régnier, G.; Ettaqui, S.; Gervais, M. Preparation and characterization of poly(ethylene terephthalate) films coated by chitosan and vermiculite nanoclay. Carbohydr. Polym. 2018, 201, 392–401.
(5) Dziwiński, E. J.; Iłowska, J.; Gniazda, J. Py-GC/MS analyses of poly(ethylene terephthalate) film without and with the presence of tetramethylammonium acetate reagent. Comparative study. Polym. Test. 2018, 65, 111–115.
(6) Welle, F.; Franz, R. Diffusion coefficients and activation energies of diffusion of low molecular weight migrants in Poly(ethylene terephthalate) bottles. Polym. Test. 2012, 31, 93–101.
(7) Pingale, N. D.; Shukla, S. R. Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste. Eur. Polym. J. 2008, 44, 4151–4156.
(8) La Mantia, F. P.; Botta, L.; Morreale, M.; Scaffaro, R. Effect of small amounts of poly(lactic acid) on the recycling of poly(ethylene terephthalate) bottles. Polym. Degrad. Stab. 2012, 97, 21–24.
(9) Jagtap, R. N.; Wadaonkar, K. K.; Mehta, L. B. Influence of Ethylene-Methacrylic Acid Copolymer on Thermo-mechanical, Morphological and Rheological Properties of Recycled PET/SEBS Blend. Fibers Polym. 2019, 20, 1323–1332.
(10) Morrison, E. D.; Malvey, M. W.; Johnson, R. D.; Anacker, J. L.; Brown, K. A. Effect of chemical environments on stress cracking of poly(ethylene terephthalate) beverage bottles. Polym. Test. 2008, 27, 660–666.
(11) Larciprete, M. C.; Paoloni, S.; Ozari, N.; Mercuri, F.; Orth, M.; Gloy, Y.; Centini, M.; Li Voti, R.; Sibilia, C. Infrared emissivity characterization of carbon nanotubes dispersed poly(ethylene terephthalate) fibers. Int. J. Therm. Sci. 2019, 146, 106109.
(12) Tavares, A. A.; Silva, D. F. A.; Lima, P. S.; Andrade, D. L. A. C. S.; Silva, S. M. L.; Canedo, E. L. Chain extension of virgin and recycled polyethylene terephthalate. Polym. Test. 2016, 50, 26–32.
(13) Duarte, I. S.; Tavares, A. A.; Lima, P. S.; Andrade, D. L. A. C. S.; Carvalho, L. H.; Canedo, E. L.; Silva, S. M. L. Chain extension of virgin and recycled poly(ethylene terephthalate): Effect of processing conditions and reprocessing. Polym. Degrad. Stab. 2016, 124, 26–34.
(14) Zdorovets, M. V.; Korkolov, I. V.; Yeszhanov, A. B.; Gorin, Y. G. Functionalization of PET Track-Etched Membranes by UV-Induced Graft (co)Polymerization for Detection of Heavy Metal Ions in Water. Polymer 2019, 11, 1876.
(15) Xue, B.; Qin, R.; Wang, J.; Niu, M.; Yang, Y.; Liu, X. Construction of Carbon Microspheres-Based Silane Melamine Phosphate Hybrids for Flame Retardant Poly(ethylene Terephthalate). Polymer 2019, 11, 545.
(16) Hu, S. W.; Myung, H. S.; Bae, J. S.; Yoo, E. S.; Im, S. S. Synthesis and crystallization behaviors of modified PET copolymers. Fibers Polym. 2000, 1, 76–82.
(17) Awaja, F.; Daver, F.; Kosior, E. Recycled poly(ethylene terephthalate) chain extension by a reactive extrusion process. Polym. Eng. Sci. 2004, 44, 1579–1587.
(18) Di Maio, L.; Coccolullo, L.; Montesano, S.; Incarnato, L. Chain Extension and Foaming of Recycled PET in Extrusion Equipment. Macromol. Symp. 2005, 228, 185–200.
(19) Aoyama, S.; Ismail, I.; Park, Y. T.; Macosko, C. W.; Ougiwa, T. Higher-Order Structure in Amorphous Poly(ethylene terephthalate)/Graphene Nanocomposites and Its Correlation with Bulk Mechanical Properties. ACS Omega 2019, 4, 1228–1237.
(20) You, X.; Snowden, M. R.; Misra, M.; Mohanty, A. K. Biobased Poly(ethylene terephthalate)/Poly(lactic acid) Blends Tailored with Epoxide Compatabilizers. ACS Omega 2018, 3, 11759–11769.
(21) Lee, A. S.; Jeon, H.; Choi, S.-S.; Park, J.; Hwang, S. Y.; Jegal, J.; Oh, D. X.; Kim, B. C.; Hwang, S. S. Crystallization derivation of amine functionalized T12 polyhedral oligomeric silsesquioxane-
conjugated poly(ethylene terephthalate). Compos. Sci. Technol. 2017, 146, 42–48.
(22) Karayannidis, G. P.; Psalida, E. A. Chain extension of recycled poly(ethylene terephthalate) with 2,2′-(1,4-phenylene)bis(2-oxazoline). J. Appl. Polym. Sci. 2000, 77, 2206–2211.
(23) Li, J.; Tang, S.; Wu, Z.; Zheng, A.; Guan, Y.; Wei, D. Branching and cross-linking of poly(ethylene terephthalate) and its foaming properties. Polym. Sci., Ser. B 2017, 59, 164–172.
(24) Liu, B.; Xu, Q. Effects of Bifunctional Chain Extender on the Crystallinity and Thermal Stability of PET. J. Mater. Sci. Chem. Eng. 2013, 01, 9–15.
(25) Paci, M.; La Mantia, F. P. Competition between degradation and chain extension during processing of reclaimed poly(ethylene terephthalate). Polym. Degrad. Stab. 1998, 61, 417–420.
(26) Bikiaris, D. N.; Karayannidis, G. P. Calorimetric study of Diepoxide Chain-Extended Poly(Ethylene Terephthalate). J. Therm. Anal. Calorim. 1998, 54, 721–729.
(27) Agabekov, V.; Golubovich, V.; Pesetskii, S. Effect of nanodisperse carbon fillers and isocyanate chain extender on structure and properties of poly(ethylene terephthalate). J. Nanomater. 2012, 2012, 7.
(28) Bikiaris, D. N.; Karayannidis, G. P. Chain extension of polyesters PET and PBT with two new diimidodiepoxides. II. J. Polym. Sci., Part A: Polym. Chem. 1996, 34, 1337–1342.
(29) Bimestre, B. H.; Saron, C. Chain extension of poly (ethylene terephthalate) by reactive extrusion with secondary stabilizer. Mater. Res. 2012, 15, 467–472.
(30) Pesetskii, S. S.; Shevchenko, V. V.; Koval, V. N. Effect of isocyanate chain extender on the structure and properties of the blends of poly(butylene terephthalate) and thermoplastic polyester elastomer. J. Thermoplast. Compos. Mater. 2016, 30, 1581–1602.
(31) Jahani, Y.; Ghetmiri, M.; Vaseghi, M. R. The effects of long chain branching of polypropylene and chain extension of poly(ethylene terephthalate) on the thermal behavior, rheology and morphology of their blends. RSC Adv. 2015, 5, 21620–21628.
(32) Raffa, P.; Coltellii, M.-B.; Savi, S.; Bianchi, S.; Castelvetro, V. Chain extension and branching of poly(ethylene terephthalate) (PET) with dir- and multifunctional epoxy or isocyanate additives: An experimental and modelling study. React. Funct. Polym. 2012, 72, 50–60.
(33) Can, S.; Karsli, N. G.; Yesil, S.; Aytac, A. Improving the properties of recycled PET/PEN blends by using different chain extenders. J. Polym. Eng. 2016, 36, 615–624.
(34) Zhang, Y.; Guo, W.; Zhang, H.; Wu, C. Influence of chain extension on the compatibilization and properties of recycled poly(ethylene terephthalate)/linear low density polyethylene blends. Polym. Degrad. Stab. 2009, 94, 1135–1141.
(35) Zendehzaban, M.; Shamsipour, M. Isothermal crystallization kinetics of poly(ethylene terephthalate)s of different molecular weights. J. Iran. Chem. Soc. 2013, 10, 77–84.
(36) Rastin, H.; Ahmadi, Z.; Pakdel, A. S.; Saeb, M. R.; Abbassian, Y.; Liravi, M.; Eslahi, A. A physicochemical route for compensation of molecular weight loss during recycling of poly(ethylene terephthalate). J. Vinyl Addit. Technol. 2016, 22, 387–395.
(37) Jie, Z.; Fa-xue, L.; Jiang-yong, Y. Multiple melting behavior of biodegradable poly(butylene succinate-co-terephthalate) (PBST) copolyester. J. Therm. Anal. Calorim. 2013, 111, 711–715.
(38) Yan, H.; Yuan, H.; Gao, F.; Zhao, L.; Liu, T. Modification of poly(ethylene terephthalate) by combination of reactive extrusion and followed solid-state polycondensation for melt foaming. J. Appl. Polym. Sci. 2015, 132, 132.
(39) Ogasahara, M.; Shidou, M.; Nagata, S.; Yamada, K.; Leong, Y. W.; Hamada, H. Effectiveness of high frequency heating on drying and intrinsic viscosity enhancement of recycled poly(ethylene terephthalate). J. Appl. Polym. Sci. 2012, 126, E166–E171.
(40) He Manjun, Z. H., Chen, W.; Dong, X. Polymer Physics; 3rd ed., Shanghai: Fudan University Press, 2007.