Proceedings of the 19th Plastic Pipes Conference

PPXIX

September 24-26, 2018, Las Vegas, Nevada

PREPARATION AND STUDYING OF THERMOPLASTIC CROSS-LINKED POLYETHYLENE

Cheng Zhi
Menred Group Co., Ltd
Wenzhou, Zhejiang, China

Mingyuan Hu
Menred Group Co., Ltd
Wenzhou, Zhejiang, China

Kaige Duan
Menred Group Co., Ltd
Wenzhou, Zhejiang, China

Chaoxi Zhou
Menred Group Co., Ltd
Wenzhou, Zhejiang, China

Dongming Yu
Menred Group Co., Ltd
Wenzhou, Zhejiang, China

SHORT SUMMARY

The PE properties are obviously improved by crosslinking modified to TPEX, which can approach to that of PEX, while still remaining thermoplastic. It can be processed by the common forming method of thermoplastic; the products can be hot-melted and the scrap can be processed to be reused. The two-layer structure oxygen-resistant PERT pipe prepared by co-extrusion with EVOH/PERT alloy barrier material does not require adhesive and does not delaminate. The scrap material can be reclaimed by hot melt, the crosslinking modification of PE has made a great breakthrough.

KEYWORDS

polyethylene; crosslinking; thermoplastic crosslinked polyethylene; TPEX; dynamic crosslinking; tensile creep; constant heat elongation

ABSTRACT

Cross-linked polyethylene pipe has excellent heat resistance and creep resistance, while it can't be welded by hot melt (fusion) and the scrap can't be recycled for its property of non-thermoplastic; Polyethylene of raised temperature resistance pipe

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

(PERT) can be melted and the scrap can be processed to be reused, but its temperature resistance and creep resistance is not as high as PEX. In this subject, peroxide and silane methods were used to make low cross-linked modified PERT, which temperature resistance and creep resistance can approach to that of PEX, while still remaining thermoplastic. The performance of thermoplastic crosslinked polyethylene (TPEX) pipe is ideal when the cross-linking degree is about 1% to 3%, which timeout passed the test of 95℃, 1h, 22h, 165h, 1000h hydrostatic pressure, and thermal stability test at 110℃ for 8760h is still under way according to the China PEX pipe standard GB/T18252-2008. The creep test has also achieved satisfactory result by Dynamic thermomechanical analysis (DMA). It is indicated that obtained TPEX is thermoplastic material by testing the melt mass flow rate and the hot-melt welding test of TPEX sheet. The result of 95 degrees centigrade MFR test is 0.057g/10min for 5Kg and 1.441g/10min for 21.6Kg, which still remains thermoplastic; The vicat softening temperature increased about 3℃, which has good heat resistance. At present, TPEX has entered the stage of pilot-scale preparation, which can be made into pipes, bars, monofilaments, films and various injection molding products, even calendering (to be tested) by the common process of PE, its scrap can be hot-melt recycled, its products can be hot-melt welded (fused), it can be widely used in the application field of HDPE (including PERT).

INTRODUCTION

As the top of the five general plastics, polyethylene (PE) is widely used because of its excellent comprehensive properties, while the poor temperature resistance and creep resistance limit its application in high-temperature uses. In the past 70 years, in order to improve the deficiency of PE, the science and engineering circles have made strenuous efforts and made many remarkable achievements. The crosslinking of PE is a successful modification method (The product is PEX), which not only improves the heat resistance and creep resistance of PE, but also improves its wear resistance. As a kind of PE pipe material, crosslinking may be an important method to achieve higher grade performance.

There are also a serious drawback of PEX, it loses the thermoplasticity as the linear macromolecules are crosslinked into net structures, the scrap can't be processed to be re-used, which is not only a waste of resources, but also increases the pressure on environmental protection, and the plastic pipes made by PEX also can't be welded by hot melt (fusion), for which plastic men have the thought of changing for a long time. The polyethylene of raised temperature (PERT) pipe has good heat resistance and creep resistance, the pipe can be joined by hot melt welding and the scrap can be recovered by hot melt, for which it is favored in plastic industry and develops rapidly. The original thought of developing thermoplastic crosslinked polyethylene (TPEX) is to obtain a new material with properties close to PEX and still has thermoplasticity, which can be processed like thermoplastic, scrap can be recovered by hot melt and pipe or sheet metal can be welded by hot melt.

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

NOMENCLATURE

PEX: Crosslinked polyethylene, so that polyethylene molecules from linear molecular structure to three-dimensional network structure, from thermoplastic materials to thermosetting materials.

PERT: Polyethylene of raised temperature resistance, it is a kind of non-crosslinked polyethylene pipe, some people have highlighted its non-crosslinked characteristics, called it "high temperature resistant non-crosslinked polyethylene pipe."

TPEX: Thermoplastic crosslinked polyethylene, Polyethylene is also thermoplastic after crosslinking.

DMA: Dynamic thermomechanical analysis.

Heat elongation: According to the mechanical tensile test, the tensile length of the fixed spline, the performance parameters reflected at the moment.

MFR: Determination of the melt-flow rate.

1.0 EXPERIMENTAL

1.1 TPEX manufacturing process using "dynamic crosslinking of polyethylene" method

In TPEX system, there exists at least two phases of cross-linked and non-crosslinked, the former is uniformly dispersed in the non-crosslinked phase in the state of particles, which endows the system with excellent heat resistance and creep resistance, while the latter gives the thermal plasticity of the system.

1.2 The heat resistance of TPEX is close to that of PE-Xa and is higher than that of a certain PERT Ⅱ

Table1: Test of Vicat softening temperature（GB/T1043.1-2008, Method of A120）

Material	Vicat softening temperature /℃
PERTⅡ	121.9
PE-Xa	127.3
TPEX	126.1

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

It can be seen from Table 1 that the heat resistance of the obtained TPEX samples is very close to that of PE-Xa. The heat resistance is basically achieved which is one of the main objectives of this project.

1.3 The thermal strength of TPEX is higher than that of PE-Xa and a certain PERT Ⅱ

Table2: 100% heat elongation of TPEX

（GB/T1040.2-2006, ISO527-2: 19931, B-type spline, stretching speed:50mm/min）

	Material Stretching strength /MPa		
Temperature/℃	PERT Ⅱ	TPEX	PE-Xa
30	14.58	17.74	17.74
60	9.39	12.00	10.21
70	8.29	10.96	9.05
95	5.72	8.03	6.34
110	4.18	5.35	5.07

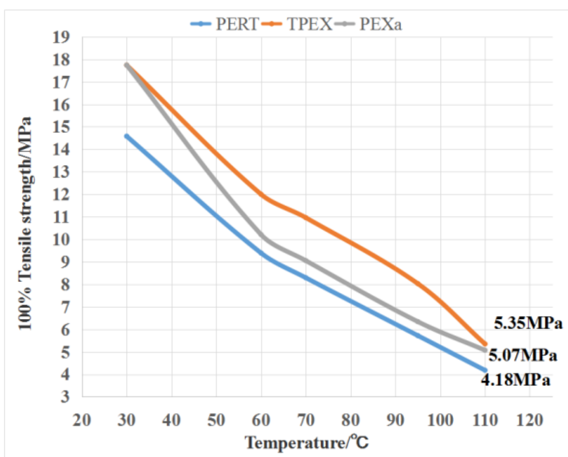


Figure1: 100% heat elongation of TPEX

It can be seen from Table 2 and Figure 1 that the tensile strength of TPEX is always higher than that of PE-Xa and PERT Ⅱ when the elongation is 100% between 30℃ to 110℃, and is 28% higher than PERT Ⅱ at 110 ℃, which exceeds the expectation.

1.4 Mechanical Property

Copyright © 2018 by (*ChengZhi, Chengzhi@menred.com)*

1.4.1 Tensile Property

Table 3: Tensile property of TPEX（GB/T1040.2-2006, ISO527-2: 19931, B-type spline ）

Material	Yield stress/MPa	Yield elongation /%	tensile strength /MPa	elongation at break /%
PERTⅡ	16.21	13.19	19.61	581
PE-Xa	18.88	13.31	19.54	504.67
TPEX	19.39	11.97	24.35	521.17

As can be seen from Table 3, the yield strength and tensile strength of the TPEX are higher than that of the PE-Xa and PERTⅡ, while the yield elongation is slightly lower than that of the PE-Xa and PERTⅡ.

1.4.2 Impact Property

Table 4: Impact property（GB/T1043.1-2008, ISO179-1: 2000 charpy impact property test）

Material	Impact strength/kJ/m^2	Failure mode
PERTⅡ	88.08	P
PE-Xa	105.12	P
TPEX	89.89	P

Table 4 shows that the impact property of TPEX is between PERTⅡ and PE-Xa, and the toughness of the three materials is at the same level.

1.4.3 Bending Property

Table 5: Bending property（GB/T9341-2008）

Material	Bending strength/MPa	Bending modulus/MPa

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

PERTⅡ	10.54	415
PE-Xa	12.72	527
TPEX	13.03	424

Table 5 shows that the flexural strength of TPEX is slightly higher than that of PE-Xa and PERTⅡ, and the flexural modulus is lower than that of PE-Xa. Which indicates that the flexibility of TPEX pipe is higher than that of PE-Xa pipe, the bending construction for small diameter TPEX pipe is easier to be carried out, and the pipe system is more conducive to saving elbows and other connectors.

1.4.4 Hydrostatic Test

Table 6: Hydrostatic test - TPEX（GB/T18992.2-2003）

Temperature/℃	Hoop stress/MPa	Time/h	Elapsed time/h
20	12	1	﹥3
95	4.8	1	﹥22
95	4.7	22	﹥48
95	4.6	165	﹥500h
95	4.4	1000	﹥1000h
110	2.5	8760	under test

Creep data is an important basis for material research, material selection and engineering life evaluation. Creep occurs in all materials when ambient temperature approaches its melting point, however, the macromolecular structure of polymer materials is relatively loose, which shows plasticity at room temperature, and has a strong dependence on temperature. The derivation life of TPEX pipe can only depend on creep data at present. The hydrostatic test data of TPEX is as shown in Table 6 according to the standard of GB/T18252-2000: plastic pipe system for the determination of the long-term hydrostatic strength of thermoplastic pipes. However, the disadvantage of this method is it takes too long time, so the tensile creep test of TPEX, PE-Xa and PERT was carried out at 20 ℃, 70 ℃, 95 ℃ and 110 ℃ by dynamic thermomechanical analyzer (DMA) to accelerate the development.

Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

1.4.5 Tensile Creep Test

Table 7: Tensile creep test

Material / Temperature（℃）	Horizontal step		
	PERTⅡ	TPEX	PEXa
20	13.83e-03%	7.93e-03%	10.28e-03%
70	5.73e-03%	4.46e-03%	32.13e-03%
95	24.56e-03%	5.60e-03%	12.02e-03%
110	28.79e-03%	17.33e-03%	18.76e-03%

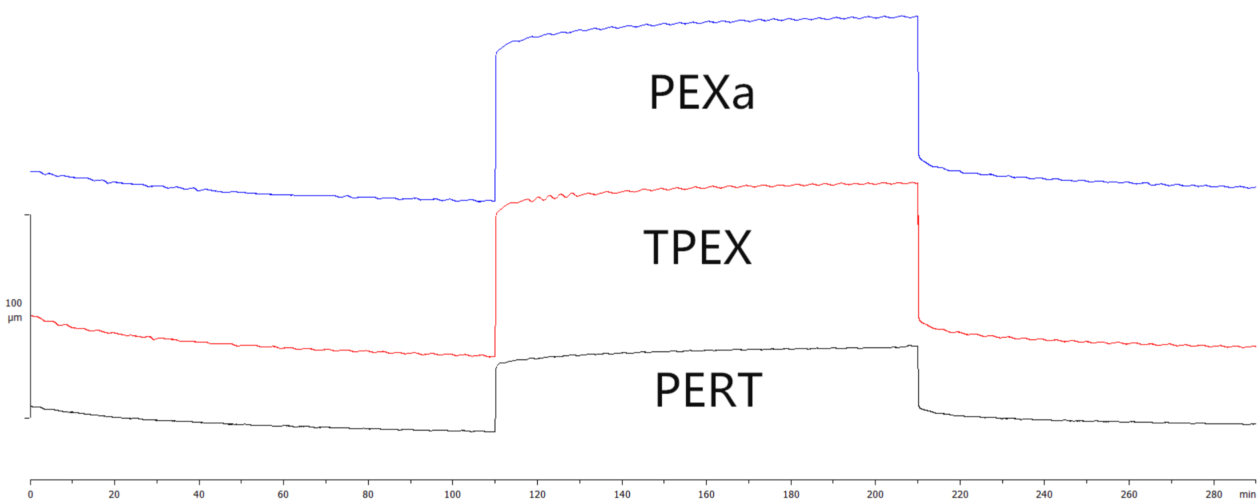


Figure 2: Tensile creep of PERT, PE-Xa and TPEX at 110℃

According to the data analysis in Table 7, figure 2, the variation of tensile creep horizontal step of TPEX measured at 110 ℃ is similar to that of PE-Xa but smaller than that of PERTⅡ, which shows that the dependence of creep on temperature of TPEX is smaller than that of PERTⅡ. This is also one of the goals that want to be pursued by this subject.

1.4.6 TPEX Welding Experiment

Table 8: Test of welding property

Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

Material	Yield stress/MPa	Yield elongation /%	Tensile strength/MPa	elongation at break /%
TPEX Unwelded sheet	18.53	14.88	38.4	722
TPEX Butt welding	20.31	9.94	26.72	530
TPEX Lap welding	19.48	9.67	31.51	652

Experiments on butt welding and lap welding of TPEX sheet were carried out. The results are as shown in Table 8. For butt welding the strength retention rate is 69.6% and the break elongation retention rate is 73.4%, for lap welding the strength retention rate is 82% and the break elongation retention rate is 90.3%. It can be inferred that brace insertion welding has higher reliability for pipe.

1.4.7 Glass Transition Temperature (T_g)

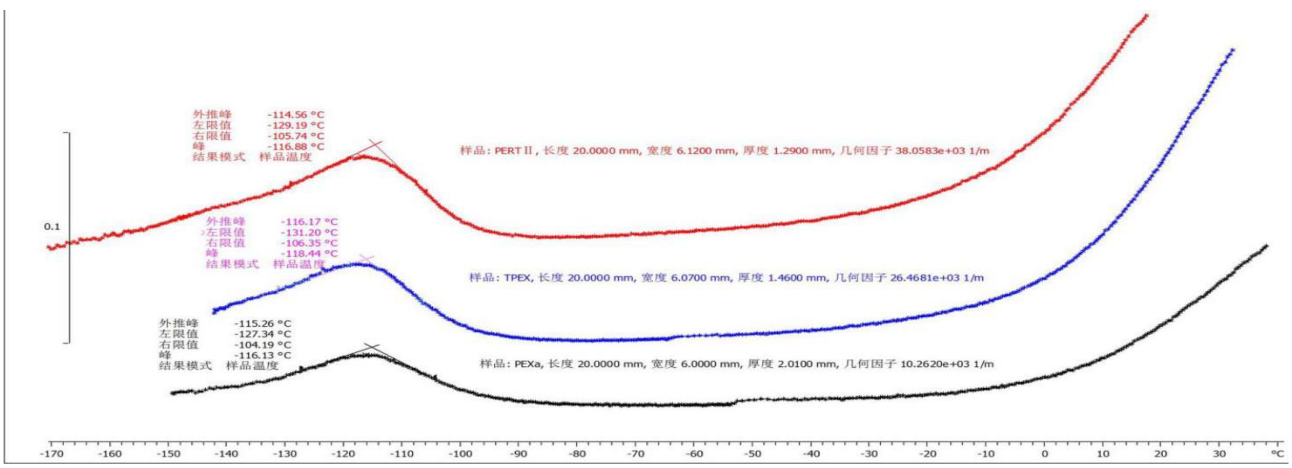


Figure 3: Glass transition temperature

Fig. 3 shows the glass transition temperature of PERT ll, TPEX and PE-Xa, the data respectively are -116.88℃, -118.44℃ and -116.33℃. According to the test results, the glass transition temperature of the three materials is close.

1.4.8 Crystallinity Test

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

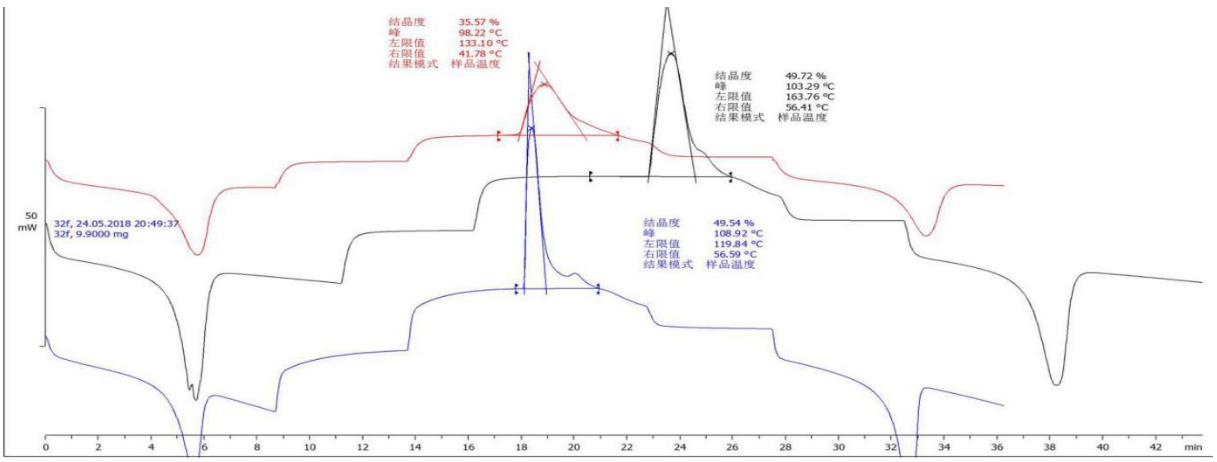


Figure 4: Crystallinity test（GB/T19466.3—2004）

Figure 4 shows the crystallinity of PERT, TPEX and PE-Xa, which respectively are 49.54%, 35.57% and 49.72%, the crystallinity of TPEX is 15% lower than that of PERT and PE-Xa, while the crystallinity of PERT is almost the same as that of PE-Xa.

1.4.9 Test of TPEX Oxidation Induction Time (OIT)

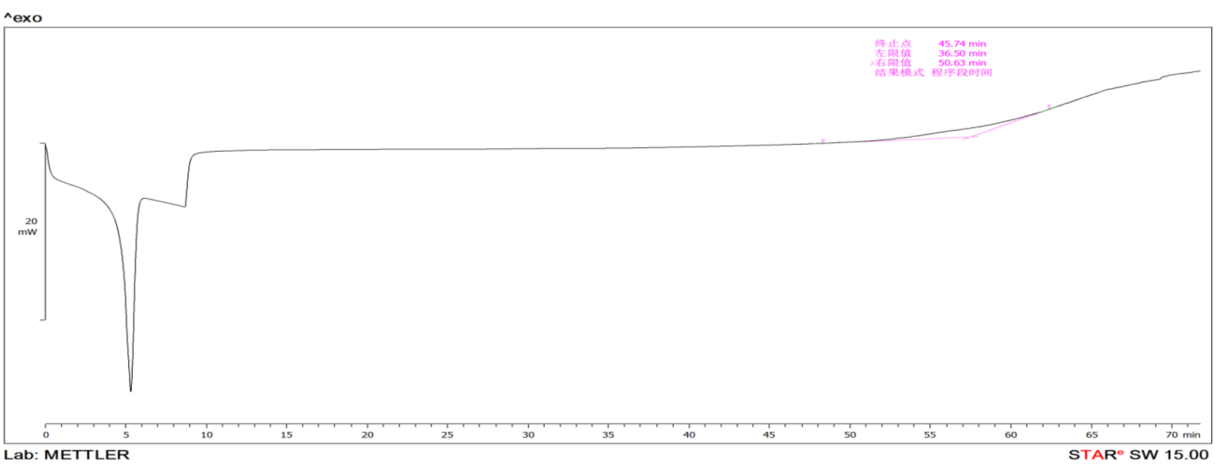


Figure 5: Test of TPEX Oxidation Induction Time（GB/T 19466.6—2009, 200℃, Aluminum crucible）

Figure 5 shows the oxidation induction time of TPEX, which is 45.74 minutes.

2.0 DISCUSSION

2.1 Manufacture of TPEX Raw Material

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

Dynamic crosslinking technology was used for TPEX which is under the progress of patent and omitted in this article.

2.2 Manufacture of TPEX Pipe

TPEX can be extruded like ordinary MDPE, HDPE and PERT. The heat and creep resistance of TPEX pipe is between that of PERT Ⅱ pipe and PEX pipe, while TPEX pipe can be hot-melt welded and the scrap can be remade by hot melt plasticizing for it is thermoplastic crosslinked polyethylene. The pipe manufacturing equipment and pipe hot-melt welding joint tools are the same as ordinary HDPE pipe, and the process flow is shown in figure 6, the equipment schematic diagram is shown in figure 7, the actual situation in the manufacture of TPEX pipe is shown in figure 8:

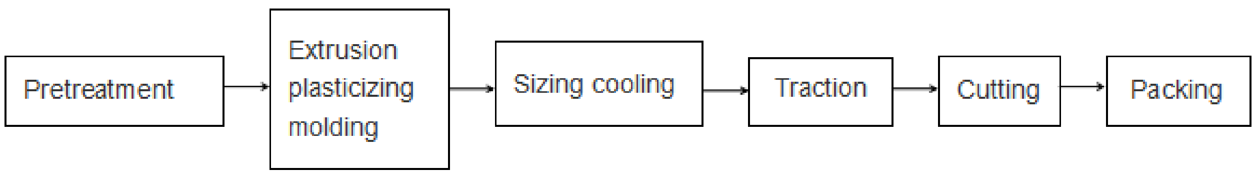


Figure 6: Flow chart of TPEX pipe manufacturing process

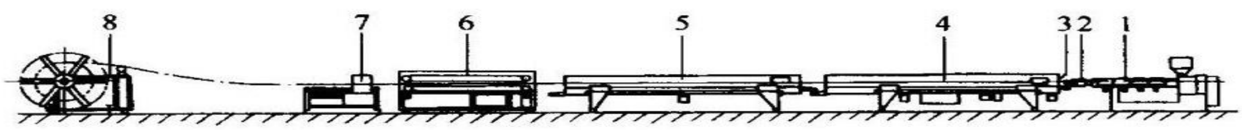


Figure 7: Schematic diagram of equipment for the manufacture of TPEX pipe

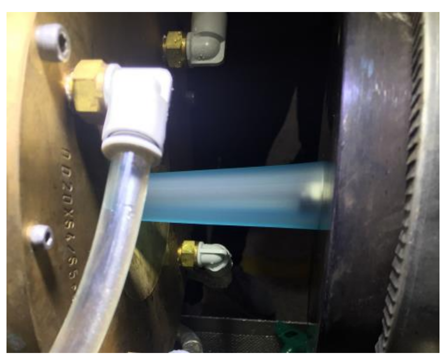
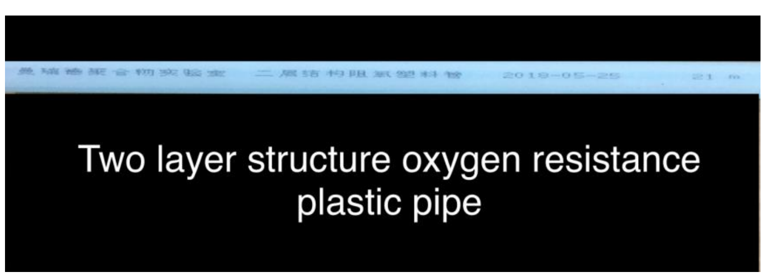


Figure 8: The actual situation in the manufacture of TPEX pipe



 Copyright © 2018 by (*ChengZhi, Chengzhi@menred.com)*

Figure 9: Two layer structure oxygen barrier plastic pipe

TPEX and EVOH/PERT alloy barrier materials developed in the laboratory have been fabricated together to obtain a two-layer oxygen barrier PERT tube as shown in figure 9, although without adhesive, the two layers are not easy to be delaminated and the scrap can be recovered by hot melt.

2.3 TPEX Injection Molding Products

Figure10: The injection molding products of HDPE and TPEX

TPEX can be molded by injection molding process, the injection molding products of HDPE and TPEX are as shown in figure 10, most of the injection molding products of HDPE can be injected with TPEX in addition to thin-walled products, when the heat resistance, creep resistance and wear resistance of the parts are needed, the advantages of TPEX are even greater.

2.4 Molding Processing of other TPEX Products

2.4.1 The melt strength of TPEX is high, which is propitious to blow molding of large hollow products, no need for cross-linking during foaming processing, which is favorable for extrusion of sheet metal, bar and so on.

2.4.2 It is difficult for TPEX in the molding of film, fiber, coating and roll cause the poor liquidity.

2.5 Main Uses of TPEX

TPEX is short for thermoplastic cross-linked polyethylene, a new invention. Its comprehensive properties are close to PEX, and can be processed by the technology of common PE as a thermoplastic, the production of TPEX can be as fast as PERT, and can be made into pipes, bars, plates, hollow products and various injection molding products, even calendaring products (to be tested) and so on.

The scrap of TPEX can be recovered by hot melt, the products can be welded by hot-melted, it can be widely used in most fields of HDPE, PERT and PEX. In 2017, the total output had reached 15 million tons for plastic pipe alone, of which PE pipe accounted for about 35% (5 million tons) including water supply pipe, drainage pipe,

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***

agricultural pipe, mine pipe, gas pipe and so on. If 20% of them are replaced by TPEX in the future, it will need more than 1 million tons of TPEX per year, which will have a bright future.

CONCLUSIONS

The properties of TPEX have been improved obviously according to modification of PE by crosslinking. While remaining thermoplastic, which can be processed by the common forming method of thermoplastic and the products can be hot-melted. By co-extrusion with the EVOH/PERT alloy barrier material developed in a laboratory, a two-layer PERT tube that doesn't need adhesive and doesn't delaminate has been obtained, the scrap can be recovered by hot melt, which is a great breakthrough in PE modification.

The TPEX extrusion products obtained at present are more smooth and delicate than expected, but the TPEX multi-layer coextrusion in the preliminary design is still needed. The hot melt welding process is completed under high pressure, but it is very difficult to obtain high pressure for lap welding in engineering, which is also one of the key points in the future research.

ACKNOWLEDGMENTS

The author thanks tianjin junxing co., LTD for providing abundant experimental data

REFERENCES

[1] Shengpeng Liu, Zhang Miao, Haoze Hu, etc. Research progress of polyethylene modification[J]. J. Wuhan Inst. Tech. 2010, 32(3): 31-36

[2] Qingyun Hu, Mei Li, Guangsheng Ma. Development of a special resin for heat resistant polyethylene (PE-RT) pipe[J]. Guangzhou Chemical Industry. 2014, 41(21): 55-56

[3] Jiang Ping. Study on the performance and processing technology of PE-RT Pipe[J]. Chemical Building Material.2007, 23(5): 29-30

[4] Xiaoping Zhao, Fan Zhen. Peroxide crosslinker and allyl co-crosslinking agent[J]. Plastic Additive. 2003(2): 32-36

[5] S M Tamboli, S T Mhaske&D D Kale. Crosslinked polyethylene e[J]. Indian Journal of Chemical Technology. 2004(11): 853-864

 Copyright © 2018 by (***ChengZhi, Chengzhi@menred.com)***