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ORIGINAL PAPER

Enhancement of physical properties of thermoplastic polyether-ester elastomer by reactive extrusion with chain extender

**Tae-young Lee · Chol-han Lee · Sunghwan Cho ·
Dong-ho Lee · Keun-Byoung Yoon**

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Abstract The branched thermoplastic polyether-ester elastomer (TPEE) and diisocyanate compound was melt extruded in an effort to enhance melt viscosity for the blow moulding process. The chain-extended TPEE was prepared with melt condensation of a branched TPEE and 4,4′-diphenylmethane diisocyanate (MDI) for enhancement of the molecular weight of TPEE. The effects of MDI contents as a chain extender on melt, thermal, mechanical and rheological properties of the chain-extended TPEE were investigated. By using a solution and melt viscosity analysis, the chain-extended TPEE was found to be an enhancement of molecular weight and a lightly cross-linked structure. The intrinsic viscosity (IV) increased and melt flow index (MI) decreased with an increasing amount of MDI due to the reaction between the hydroxyl end groups of TPEE and isocyanate groups of MDI. The chain-extended TPEE does not lead to an important drop in elongation at break. The tensile strength and the tear strength are characterized by a significant increase, compared with a branched TPEE. The storage modulus, loss modulus and the complex viscosity of the chain-extended TPEE were also higher. The modified Cole–Cole plots revealed that the chain-extended TPEE shows a higher elasticity than the branched TPEE. The chain-extended TPEE has more suitable melt and rheological properties for the blow moulding processes.

T. Lee · K.-B. Yoon (✉)
Department of Polymer Science and Engineering, Kyungpook National University, Daegu 702-701, Korea
e-mail: kbyoon@knu.ac.kr

T. Lee
R&D Center, Korea Delphi Automotive Systems Co., Daegu 711-712, Korea

C. Lee · S. Cho
Advanced Polymer Material R&D Center, Samyang Corp., Daejeon 305-717, Korea

D. Lee
Dongyang Mirae University, Seoul 152-714, Korea

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Introduction

A thermoplastic elastomer (TPE) is widely used owing to excellent processability and elasticity [1]. TPE has an elastomeric behaviour at room temperature which can be moulded at high temperature like common thermoplastics. Thermoplastic polyether-ester elastomer (TPEE) is one of the TPE which is composed of polybutylene terephthalate (PBT) as the hard segment, and amorphous poly(alkylene glycol), typically polytetramethylene glycol (PTMG), as the soft segment. TPEE has a good elasticity, superior oil and chemical resistance, high heat resistance, as well as excellent low temperature impact strength [1, 2]. The major application is automobiles, electronics and electronic parts. Furthermore, TPEE is replacing the cross-linked rubbers due to its superior lightweight, fatigue-resistance and recyclability [3].

However, with TPEE it is difficult to perform the extrusion process due to its low melt viscosity and melt tension [4, 5]. Although the melt viscosity and melt tension of TPEE could be improved with the addition of a branching agent during melt polymerization. It has insufficient melt viscosity for blowing extrusion processes.

In the case of poly(ethylene terephthalate) (PET), several attempts have been made to increase the melt viscosity and melt tension using reactive ‘chain extenders’ or ‘modifiers’ such as multifunctional epoxy and anhydride compounds [6, 7], which easily reacted with the carboxyl or hydroxyl groups of polymer chain end [8]. The molecular weight of PET significantly increased with the reaction between multifunctional chain extenders and carboxyl end of polymer chains [7].

Recently, Kuramochi et al. [9] reported that the glycidyl compounds had effected reactive extrusion of TPEE as a chain extender. We also reported that the polymerization of a branched TPEE and diiocyanate compound was a useful chain extender for a branched TPEE [10].

In this study, investigations were made on the influence of the molecular weight on the physical properties of the chain-extended TPEE. The chain-extended TPEE was prepared by the reaction of a branched TPEE and 4,4′-diphenylmethane diisocyanate (MDI). The effects of MDI contents on melt, thermal and mechanical properties of the chain-extended TPEE that were produced by reactive extrusion. The structure of the chain-extended TPEE was confirmed by rheological characterization.

Experimental

Materials

A branched TPEE (TRIEL 5400, Samyang Corp., Korea) was used which was then synthesized from PTMG (Mn = 2,000) as a soft segment, dimethyl terephthalate

(DMT) and 1,4-butandiol (1,4-BD) as hard segments. Glycerol and 4,4′-diphenylmethane diisocyanate (MDI, Aldrich Co.) was used as a branching agent (0.3 mol%/1,4-BD) and a chain extender, respectively. The formula of a branched TPEE precursor obtained from polycondensation is shown in Scheme 1.

Preparation of the chain-extended TPEE

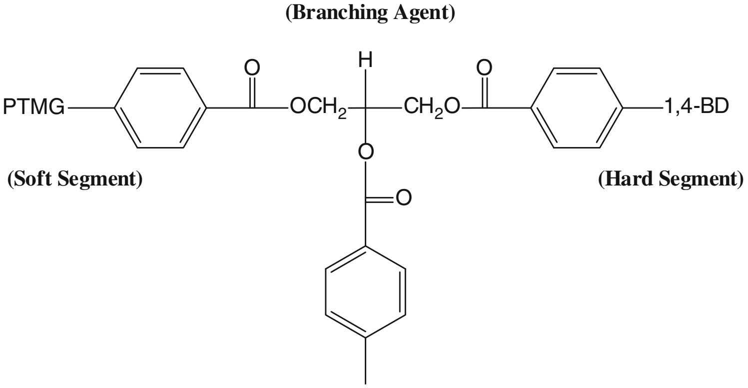
The reactive extrusion of a branched TPEE was carried out by adding 0.5–2.0 wt% of MDI into a pilot-scale twin-screw extruder containing gas bents and a vacuum system (ZSK-25, W&P), together with 96 wt% of TPEE and 4 wt% of thermal-stabilizer, antioxidant and lubricant. During the reactive extrusion, the temperature of the extruder was kept in the range of 170–240 °C with a screw rotational speed of 150 rpm. A feed rate and residence time was kept 12.5 kg/h and 45 s, respectively.

Characterizations

The carboxyl end group content was determined according to Pohl's method. The intrinsic viscosity (IV) of the chain-extended TPEE was determined with a capillary Ubbelohde type viscometer at 35 °C, using a polymer solution with a concentration of 0.08 g/mL in a solution of *o*-chlorophenol.

The melt flow index (MI) was measured by Melt Indexer (MP-MPX62.92, Göttfert, Germany) at 230 °C for 2 min at a constant load (2.16 kg) (ASTM D1238). The melt flow rate ratio (FRR) is the ratio of the throughput under a load of 2.16 kg to that under a load of 10.0 kg. FRR was measured by a Melt Indexer at 230 °C for a period of 10 min.

The measurement of the thermal behaviour was conducted with differential scanning calorimetry (Q400, TA Instruments) operating at a heating and cooling rate of 10 °C/min. All samples were heated to 280 °C and kept isothermal for 3 min to erase the previous thermal history. Then they were cooled to 30 °C at 10 °C/min



Scheme 1 Formula of branched TPEE precursor obtained from polycondensation

and subsequently canned between 30 and 280 °C. The melting temperature (T_m) and heat of fusion (ΔH) was determined in the second scan.

Values of tensile strength, elongation at break and tear strength were determined according to the ASTM D395 and D624. At least five specimens were tested for each sample to get an average value (H10K, Tinius Olsen).

The insoluble content of the chain-extended TPEE was determined from chloroform solutions at 40 °C. The solution was filtered with a 0.5 μm filter and then dried under a vacuum for 24 h at room temperature.

The rheological properties were measured with a rheometrics mechanical spectrometer (Haake Mars Rheometer) using parallel plates (diameter 25 mm) at 220 °C in a nitrogen atmosphere. The rheometer system was programmed to perform frequency sweeps within the range of 0.1–100 rad/s.

Results and discussion

Preparation of the chain-extended TPEE

A branched TPEE was synthesized from PTMG as a soft segment, DMT and 1,4-BD as hard segments and glycerol as a branching agent [10]. However, the melt viscosity of the obtained branched TPEE was too low for the blow moulding processes.

The introduction of hydroxyl groups in the TPEE chain end provides chain extension sites with diisocyanate. The melt reaction of a branched TPEE with MDI is especially an attractive method for the preparation for the high molecular weight of polycondensation polymers. Hydroxyl groups and isocyanate groups can react under mild conditions, and as such, the reaction leads directly to the formation of urethane bonds which are thermally and hydrolytically stable. To enhance the melt viscosity of TPEE, a branched TPEE was reacted with 4,4′-diphenylmethane diisocyanate (MDI) at a twin-screw extruder.

To confirm the formation of a high molecular weight TPEE containing urethane bonds by melt reaction between a branched TPEE and MDI, its FT-IR measurement was studied. The disappearance of the characteristic peaks of –NCO groups at 2280 cm^{-1} was obvious and the urethane bond formed by the reaction between –OH and –NCO groups were observed in the region between 1880 and 1440 cm^{-1}.

A branched TPEE has two kinds of chain ends, one is hydroxyl and the other is carboxyl groups. The carboxyl chain ends and isocyanate can react, and the reaction leads to the formation of amide bonds. However, the reactivity of hydroxyl and isocyanate is much higher than that of carboxyl and isocyanate. Very weak characteristic peaks of amide groups observed in FT-TR spectrum of the chain-extended TPEE. It is considered that a small amount of the carboxyl group reacted with MDI due to the reactivity being much lower than with the hydroxyl groups.

The solution and melt viscosity was an excellent indicator of molecular weight. The extending efficiency was evaluated by the increase of intrinsic viscosity as a function of MDI amounts. The chain-extended TPEE was characterized by the determination of the IV, MI, and FRR, to confirm the reaction of a branched TPEE and MDI. The results are shown in Table 1.

The intrinsic viscosity increased by increasing the amounts of MDI. It is considered that the hydroxyl groups in the chain end of TPEE reacted with isocyanate of MDI, which leads to a chain extension of TPEE. This chain extension of TPEE was also confirmed by melt flow methods. The MI dramatically decreased by increasing MDI contents, in spite of a small amount MDI (0.5 wt%), MI had dropped in 4.58 g/10 min. The IV increased by a linear equation, whereas MI decreased by a log equation. It may be associated with the chain entanglements of a chain-extended main chain and long chain branching which is created by reactive extrusion of TPEE. Because, IV was measured in a diluted solution which could not be included in the influence of chain entanglements [11, 12].

The FRR is defined as the ratio of the melt index at a load of 10.0 kg to that at a load of 2.16 kg. In general, the FRR is commonly used as an indication of the way in which rheological behaviour is influenced by the molecular weight distribution (MWD) [13]. As shown in Table 1, the FRR did not change significantly with a lower content of MDI (1.0 wt%), thereafter it increased rapidly with MDI content above 1.5 wt%. It may be suggested that a large amount of MDI could generate high molecular weight fractions and long-chain branches. From the results of FRR, MWD was broadened by the reaction with MDI and the chain-extended TPEE showed a stronger shear thinning [13, 14].

Dhavalikar et al. [8] reported that the chain-extended PET had not only an improvement of chain extension but a formation of a gel-like structure by the reaction of PET and a chain extender.

The content of the insoluble fraction was investigated to confirm the cross-linked structure of the chain-extended TPEE. The insoluble fraction was investigated with boiling chloroform because the chain-extended TPEE completely solved in *o*-chlorophenol at 35 °C. The insoluble fraction was determined by dissolving in chloroform and then filtering with 0.5 μm pore size filter, the results are shown in Fig. 1.

Unreacted TPEE did not contain any insoluble fraction, whereas the chain-extended TPEE contained insoluble fractions. Insoluble fraction of the chain-extended TPEE increased up to 90 wt% with increasing amount of MDI. This result may suppose to form high molecular weight fractions and/or lightly cross-linked structures [6, 8] by the reaction of the long chain branch of TPEE and MDI.

From the above results, it is considered that the branched TPEE easily reacted with MDI. The molecular weight of the chain-extended TPEE is sufficiently enhanced for blow moulding processes (MI = 0.32 g/10 min). The chain-extended

Table 1 Characteristics of the chain-extended TPEE with various amounts of MDI

MDI content (wt%)	Carboxyl content (eq/10^6 g)	IV (dL/g)^a	MI (g/10 min)	FRR
None	33	3.32	14.00	7.6
0.5	32	5.84	4.58	6.0
1.0	30	7.54	2.00	7.3
1.5	29	10.28	0.81	10.3
2.0	24	13.29	0.32	15.0

[a] Measurement conditions; 35 °C, 0.08 g/mL, *o*-chlorophenol

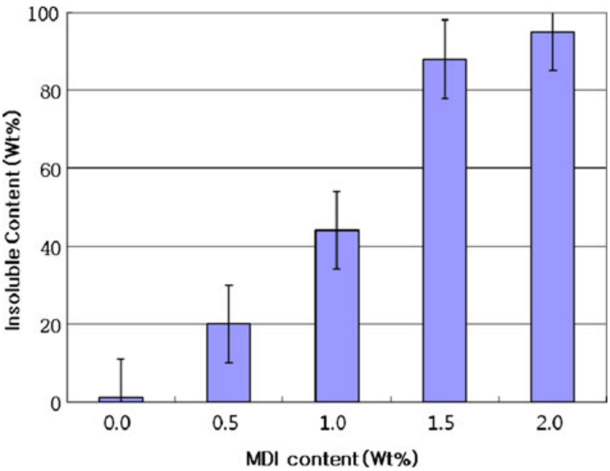


Fig. 1 Insoluble content of chain-extended TPEE (dissolving in boiling chloroform)

TPEE has high molecular weight fractions and/or lightly cross-linked structures which could be formed by the reaction at high content of MDI.

Thermal properties of the chain-extended TPEE

DSC heating curves of a branched TPEE and the chain-extended TPEE are shown in Fig. 2 and the transition temperature and heat of fusion are summarized in Table 2.

Melting temperature (T_m) slightly decreased with an increase of MDI contents by approximately 3 °C. The endothermic (ΔH_m) and exothermic (ΔH_c) heat of fusion of chain-extended TPEE clearly decreased with an increasing amount of MDI. It is considered that reactive extrusion of TPEE and MDI reduced the crystalline ability of chain-extended TPEE. The chain-extended TPEE with a higher MDI content was hard to crystallize due to the formation of long branches and lightly cross-linked structures [15].

Mechanical properties of chain-extended TPEE

The tensile strength, elongation at break and tear strength of the chain-extended TPEE with various amounts of MDI, as well as those of pure components, were tested and the results are summarized at Table 3.

As expected, the addition of MDI significantly changed the tensile behaviour of the chain-extended TPEE. Tensile strength of the chain-extended TPEE was higher than that of unreacted TPEE and the value increased up to 32.7 MPa (with 2.0 wt% MDI). It seems that the higher content of MDI may have caused higher molecular weight and longer branching or lightly cross-linking, which resulted in a significant improvement in tensile strength [16]. On the one hand, tear strength of the chain-extended TPEE dramatically increased in spite of a small amount of MDI (0.5 wt%) because there are more chain entanglements due to either branching or the presence

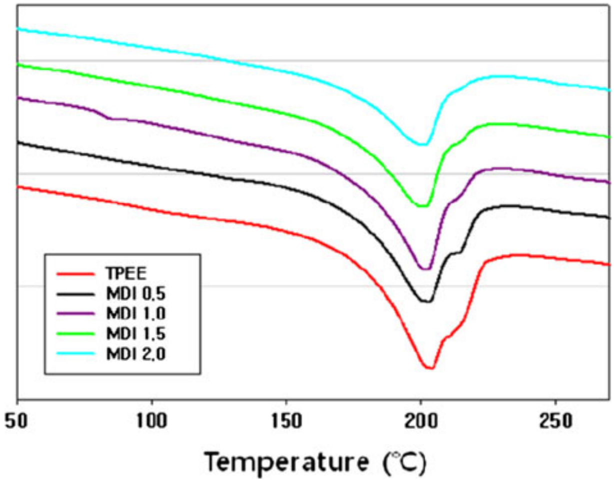


Fig. 2 DSC heating curves of the branched TPEE and chain-extended TPEE

Table 2 Thermal properties of the chain-extended TPEE

MDI content (wt%)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
None	203.8	26.3	162.8	25.6
0.5	202.7	21.8	159.8	22.1
1.0	202.3	19.8	154.2	21.5
1.5	201.2	18.2	161.3	19.7
2.0	201.0	17.1	165.6	18.7

Table 3 Mechanical properties of the chain-extended TPEE

MDI content (wt%)	Hardness (shore D)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kgf/cm)
None	41	18.1	840	117
0.5	39	25.4	620	139
1.0	40	28.8	690	148
1.5	41	27.1	820	146
2.0	40	32.7	800	149

of higher MW fractions. However, hardness and elongation at break were less affected by the addition of MDI.

Rheological properties of the chain-extended TPEE

The reaction of branched TPEE and MDI led to chain extension and a lightly cross-linked structure. The rheological properties of the chain-extended TPEE were investigated to confirm that phenomenon.

Rheological properties such as storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of the chain-extended TPEE was analyzed by rheometric mechanical spectrometer using frequency sweeps within the range of 0.1–100 rad/s. The effect of MDI contents on G', G'' and [η^*] of the chain-extended TPEE and unreacted TPEE was investigated and the results are shown in Figs. 3, 4 and 5, respectively.

The storage modulus (G') and loss modulus (G'') dramatically increased as the MDI content increased. It is mainly attributed to the chemical reaction between the hydroxyl groups of branched TPEE and isocyanate groups of MDI, which result from chain extension and branching. The storage modulus is related to melt elasticity. As seen in Fig. 3, the G' values of the chain-extended TPEEs were

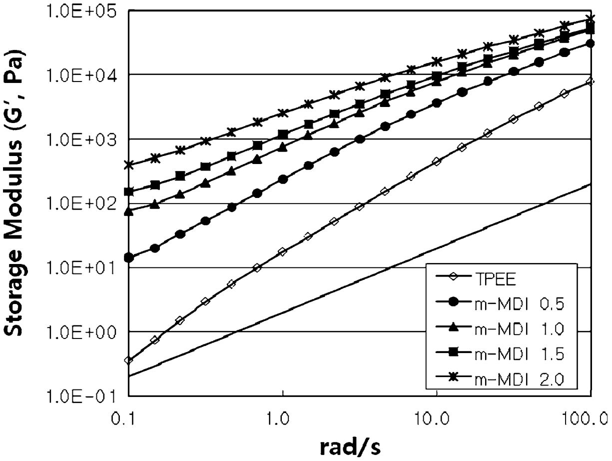


Fig. 3 Effect of the MDI content on the storage modulus (G') of chain-extended TPEE

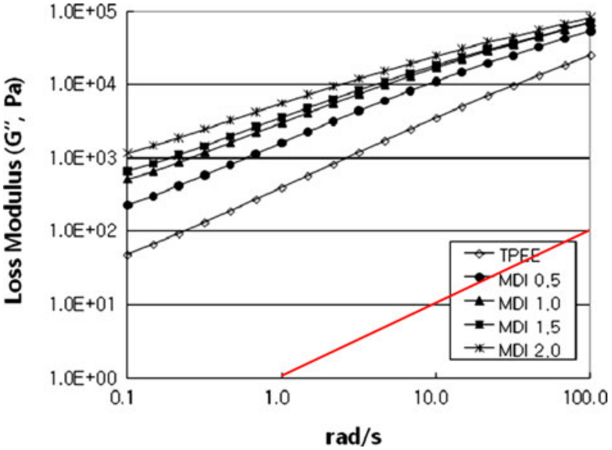


Fig. 4 Effect of the MDI content on the loss modulus (G'') of chain-extended TPEE

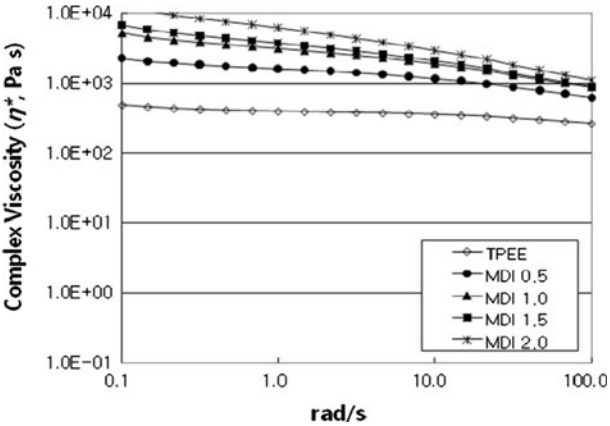


Fig. 5 Effect of the MDI content on the [η*] of chain-extended TPEE

10–100 times higher than that of unreacted TPEE at a low frequency and it gradually converged as the frequency increases. At a low frequency, there are more chain entanglements due to either branching or the presence of higher MW fractions; hence, physical cross-linking play a more important role giving rise to higher storage modulus for the chain-extended TPEE. On the other hand the chain entanglements had less affect on storage modulus at a high frequency [12].

Complex viscosity [η*] of unreacted and the chain-extended TPEE are shown in Fig. 5.

The unreacted TPEE used as a reference showed the lowest zero-shear viscosity, around 5×10^2 Pa s, but the Newtonian plateau could not be observed in the investigated frequency range. Increasing MDI content led to a continuous rise of viscosity and to an accentuation of the shear-thinning behaviour. So, the rheological curves obtained with 2.0 wt% MDI shows the highest complex viscosity at low shear rates and high shear sensitivity as a result of long-chain branching [12, 17]. And this result corresponded with the FRR data of Table 1, higher FRR suggest a stronger shear thinning effect of the chain-extended TPEE.

The chain-extended thermoplastics exhibited enhanced shear thinning behaviours at a lower shear rate region. That is in agreement with the long-time-relaxation mechanism, such as entanglement couplings between the high molecular weight and long chain branches [8].

These rheological behaviours correlate with good processability in blow moulding and extrusion foaming by gas injection [18]. Enhanced shear sensitivity of complex viscosity or rheological behaviours may be correlated with a broad MWD as shown by other researchers [8, 19].

Tan δ is defined as the ratio of G''/G' and is therefore a ratio of viscous to elastic contribution at a given oscillation frequency. Tan δ of the unreacted TPEE was around 22.4 (at 1 rad/s). This value decreased continuously to a value of 2.2 with an increasing MDI concentration from 0 to 2.0%. A decrease in tan δ is indicative of the increase in melt elasticity. And it also means melt behaviours of the chain-extended

TPEE turned from liquid-like into solid-like, which may suggest that the TPEE formed lightly cross-linked structure as well as long-chain branches.

The chain-extended TPEE is having high molecular weights and lightly cross-linked structures enhance the strain hardening behaviour of the elongational viscosity and improved elastic properties. These effects can be related to a higher melt strength and extrudates swell [8, 20, 21].

The melt elasticity of the chain-extended TPEE can be further analyzed through the modified Cole–Cole plot was shown in Fig. 6.

In the modified Cole–Cole plot, the position of the data with respect to the equimodulus line ($G' = G''$) is a measurement of the degree of melt elasticity [22]. The melt behaviour is considered as more elastic, if it is located further right [23]. The data of the chain-extended TPEE with higher content of MDI was located on the right side and approached the 45° line at all frequencies region, whereas the unreacted TPEE approached the 45° line only at a high frequency region. It means that the chain-extended TPEE had more elastic behaviours than unreacted TPEE. And, as mentioned above, melt behaviours of the chain-extended TPEE turned form liquid-like into solid-like by increasing the MDI concentration.

The rheological properties of the chain-extended TPEE had high melt elasticity. The elastic characteristics are affiliated with high molecular weight, broadened MWD and formation of branching as well as lightly cross-linked structures owing to the reaction between a branched TPEE and MDI.

Conclusion

A branched TPEE easily reacted with MDI during the reactive extrusion. The molecular weight (MW) and MWD of the chain-extended TPEE increased by incorporation of MDI. The tensile strength and tear strength of TPEE could be

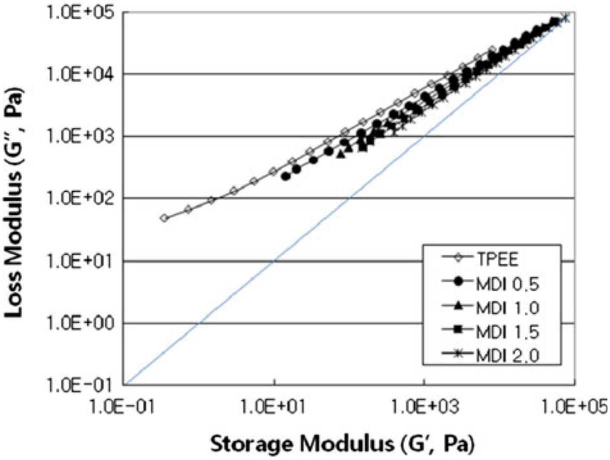


Fig. 6 Modified Cole–Cole plots for unreacted and chain-extended TPEE

greatly improved by the reactive extrusion method. The rheological behaviours of the chain-extended TPEE showed more shear thinning behaviour through the long-chain branching and higher MW and/or broad MWD. The storage and loss moduli and the complex viscosity revealed that the chain-extended TPEE had an overall higher melt viscosity and elasticity than the unreacted TPEE. The chain-extruded TPEE had suitable melt and rheological properties for the blow moulding processes.

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