Upcycling of Post-consumer Polyolefin Plastics to Covalent Adaptable Networks

via In-situ Continuous Extrusion Cross-linking

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Experimental Section

Materials. Butanediol (BDO), maleic anhydride (MA), dicumyl peroxide (DCP) were obtained from Aladdin Reagent, China. Toluene, xylene and plastic bags were bought from Sinopharm Chemical Reagent Co., Ltd., China. LDPE N210 with melt index (*MI*) around 2 g 10 min⁻¹ was supplied by Sinopec Group, China. HDPE HMA-025 was purchased from ExxonMooil, Saudi Arabia. All the chemicals or materials were utilized as received.

Preparation of PE CANs. The preparation of PE CANs is carried out on an industrial-scale twin screw extruder with 11 sections for temperature control, which was set at 175 °C for 1-3 sections, at 180 °C for 4-8 sections and 175 °C for 9-11 sections, and the feeding speed and main engine speed of the twin screw extruder were set at 8 rpm/min and 80 rpm/min, respectively. Before the experiment, pure LDPE was used to clean the machine. Then LDPE, maleic anhydride (MA), butanediol (BDO), free radical initiator dicumyl peroxide (DCP) were mixed well with different feeding ratio (Table S1). Subsequently, the mixture was put into the feeding port of the twin-screw extruder. PE and PE CANs can be distinguished by color change, through which the discharge time can be recorded within 2-3 min, and the samples after 5 min is cooled and granulated for subsequent process. Granular samples after drying were molded and post-cured by hot press at 150 °C for 30 min and 180 for 1h in a hollow mold to get film PE CANs with thickness of approximately 500 μm and 1 mm. The same process was also used to prepare PE-MA without BDO added and HDPE-CAN. Before use, PE-MA was extracted in refluxing acetone to remove unreacted MA.

Preparation of plastic bag CAN (PB-CAN). Plastic bags were first hot pressed in a hollow model with thickness around 1 mm at 150 °C for 3 min, and then granulated it in a crusher to

meet the feeding requirements of twin screw extruder. Subsequently, Plastic bag particles (2.94 kg), MA (60 g), BDO (27.6 g) and free radical initiator DCP (6 g) were mixed well and the rest of the preparation process is the same as that of PE CANs.

Recycle process. First set the parameters of the twin-screw extruder, which are consistent with the parameters of the PE CANs preparation process. The inside of the twin screw extruder was cleaned with LDPE, and then 2 kg of samples (PE-CAN1 or PB-CAN) were put into the feeding port of the twin-screw extruder. The samples came out from the extruder was recorded within 2-3 min, and the samples after 5 min were cooled and granulated for subsequent process. Granular samples after drying were molded by hot pressing at 150 °C for 10 min in a hollow mold to get recycled films with thickness of approximately 500 µm and 1 mm. Repeat the above steps to recycle the sample for three cycles.

Titration of the efficiency of MA grafting. 1.0 g of PE-MA was dissolved in 100 mL of xylene at 110 °C. Few drops of water were added, which makes the solution acidic. 1 wt.% bromothymol blue was used as indicator. The solution was then titrated against 0.1 mol L⁻¹ KOH (in ethanol) until the appearance of faint blue color, indicating the completion of titration. The amount of KOH required was recorded through three titrations. The efficiency of MA grafting was calculated by the equation¹ $f = (V_{KOH solution} \times N \times M_m)/(2 \times 10)$, where $V_{KOH solution}$ is the volume (mL) of KOH solution used, N = 0.1 (concentration of KOH solution), and M_m = 100 (the molecular weight of grafted MA residue). The resulting graft ratio was obtained as 0.8 wt.%.

Gel Content and swelling ratio test. For gel content test, all samples (around 300 mg) were separately put into the Soxhlet extractor for extracting with toluene or xylene for 24 h and then

dried in an oven at 100 °C for 12 h. m_0 is the initial mass and m_1 is the final mass after Soxhlet extraction, the gel content is calculated by 100% × m_1/m_0 . For swelling ratio test, the samples were separately immersed in toluene or xylene at reflux temperature for 24 h. m_0 is the initial mass of the samples and m_1 is the mass after swelling; the swelling ratio is calculated by 100% × $(m_1 - m_0)/m_0$.

Rheology studies. Viscoelastic properties of samples we determined using a TA Instruments HR-3 rotational rheometer equipped with parallel plate geometry (25 mm in diameter) under N_2 . During the experiment, the axial force was controlled at around 1 N through the axial force control program.

a. Stress-creep recovery above melting point: Creep-recovery measurements were conducted at 120 °C by imposing a constant stress 1000 Pa for 30 min (creep) and releasing it for 30 min (recovery) while measuring the strain.

b. Stress relaxation: Stress relaxation tests were carried out between 140 °C and 180 °C by applying a constant shear strain of 1%. The relaxation time τ^* calculated from the relaxation modulus relaxes to 1/e. The activation energy of the bond exchange process E_a was calculated from the Arrhenius law with temperature as follows:²

$$\tau^*(T) = \tau_0 \exp(E_a/RT)$$
 eq S1

c. Temperature sweep: Temperature sweeps were carried out from 180 °C and 50 °C with a cooling rate 5 °C min⁻¹ and a constant angular frequency of 1 rad s⁻¹.

d. Frequency sweep: Frequency sweeps were performed from 0.01 to 100 rad s⁻¹ at 180 °C with a constant strain amplitude of 0.5%.

Thermo-mechanical studies.

a. Calorimetry. Melting and crystallization transitions of materials were determined by differential scanning calorimetry (DSC). Sequences of temperature ramps (heating, cooling, heating) in the 25 °C – 200 °C rang were performed at 10 °C min⁻¹ using a NETZSCH Instrument DSC 214. The first heating ramp was performed to reset the sample's thermomechanical history. The degree of crystallinity χ_c was calculated from the specific enthalpy of melting ΔH_m as $\chi_c = \Delta H_m / \Delta H_m^+$, where $\Delta H_m^+ = 288$ J g⁻¹ corresponds to the specific enthalpy of melting of a fully crystalline polyethylene.³

b. Dynamic mechanical analysis. Dynamic mechanical analysis was carried out using a TA Instruments Q800 in tension mode. Temperature ramps were performed at a constant rate of 5 °C min⁻¹ from 0 °C to 200 °C with a maximum strain amplitude of 1% at a fixed frequency of 1 Hz. The tensile creep TTS test was conducted at temperatures between 20 °C and 100 °C in intervals of 10 °C for samples with dimensions of 20 mm × 0.5 mm × 500 μ m. During the measurement of each isotherm, a constant force of 1 MPa was applied for 5 min followed by a 5 min recovery period. For the tensile-creep recovery tests below melting point, the samples with dimensions of 20 mm × 0.5 mm × 500 μ m were stretched by a constant force of 1 MPa at 10 °C for 50 min, followed by a 30 min recovery period.

c. Tensile tests. Tensile tests were carried out on a Z1.0 tensile machine (Zwick, Germany). Samples were cut into dog-bone shapes with the thickness around 0.5 mm and tested at a cross-head speed of 2 mm min⁻¹ before yielding and 20 mm min⁻¹ after yielding.

Characterization

Melt Flow Index (MFI) was measured on an Extrusion Plastometer YK-3651A produced by Dongguan YK Group. According to the Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer (ASTM D-1238), about 3 g of granules were introduced into the cylinder bore via hopper and heated for 300 s at 190 °C with piston, then loading the weight (2.16 kg in total) to extrude melt through the orifice. The extrudate was cut at set intervals for 5 or 7 times, weighted and transform unit to g 10 min⁻¹. ¹H NMR spectra of PE and PE-MA were recorded by an AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) with 1,1,2,2-Tetrachloroethane-d₂ as the solvent, operating at 400 and 75.5 MHz, respectively. Before testing, NMR tubes with sample and solvent were heated at 110 °C for 1 hour to dissolve the samples. The FT-IR spectra of polymers were performed by a Micro-FTIR Cary660 (Agilent, America) and the absorbance mode was used. The molecular weight (MW) and polydispersity index (PDI) of PE-MA were measured on waters1525 & Agilent PL-GPC220. Trichlorobenzene was used as an eluent with a constant flow rate of 1 mL min⁻¹ and the experiments were operated at 150 °C.



Supplemental Figures and Tables

Figure S1. ¹H NMR of LDPE and PE-MA with 1,1,2,2-Tetrachloroethane-d₂ as the solvent.



Figure S2. Molecular weight distribution plots of PE and PE-MA from the GPC tests. The MW of PE and PE-MA are 157451 and 184049, respectively. The polydispersity indexes (PDI) of PE and PE-MA are 4.93 and 7.37, respectively.



Figure S3. Rheological frequency sweep curves of sample with 1 wt.% MA, 0.1 wt.% DCP of LDPE and MA, and BDO with equal molar ratio of MA loading at 180 °C. Where G' is storage modulus and G" is loss modulus.



Figure S4. Rheological frequency sweep curves of different samples at 180 °C. Where G' is storage modulus and G" is loss modulus.



Figure S5. DSC curves of PE, PE-CAN1, PE-CAN2 and PE-MA.



Figure S6. Creep TTS curves of a) PE, b) PE-MA, c) PE-CAN1 and d) PE-CAN2.



Figure S7. Creep curves of PE and PE CANs at 120 °C obtained from rheological test.



Figure S8. Stress relaxation curves of PE-CAN1 at different temperatures.



Figure S9. Stress relaxation curves of PE-CAN2 at different temperatures.



Figure S10. Image of PE-CAN1 extruded in an industrial-scale twin screw extruder.



Figure S11. FT-IR spectra of the original and recycled PE-CAN1.



Figure S12. Representative stress-strain curves of the original and recycled PE-CAN1.



Figure S13. FT-IR spectra of plastic bag (PB) and PB-CAN.



Figure S14. DMA curves of PB and PB-CAN.



Figure S15. DSC curves of PB and PB-CAN.



Figure S16. Representative stress-strain curves of PB and PB-CAN.



Figure S17. Creep TTS curves of (a) PB and (b) PB-CAN.



Figure S18. Creep-recovery curves of PB and PB-CAN at 50 °C obtained from DMA test.



Figure S19. Creep-recovery curves of PB and PB-CAN at 120 °C obtained from rheological

test.



Figure S20. Stress relaxation curves of PB at 180 °C and PB-CAN at different temperatures.



Figure S21. Arrhenius analysis of the characteristic relaxation time, τ^* , versus 1000/T for PB-CAN.



Figure S22. FT-IR spectra of the original and recycled PB-CAN.



Figure S23. DSC curves of the original and recycled PB-CAN.



Figure S24. Storage modulus curves of the original and recycled PB-CAN obtained from rheological temperature sweep tests.



Figure S25. Stress-strain curves of original and three cycles recycled PB-CAN.



Figure S26. FTIR spectra of HDPE and HDPE-CAN.



Figure S27. Rheological frequency sweep curves of HDPE and HDPE-CAN at 180 °C.



Where G' is storage modulus and G" is loss modulus.

Figure S28. Stress relaxation curves of HDPE and HDPE-CAN at 180 °C.

Samples	PE (kg)	PB (kg)	MA (kg)	BPO (kg)	BDO (kg)	MI (g 10 min ⁻¹)
PE	-	-	-	-	-	2
PE-CAN1	2.94	-	0.06	0.006	0.0276	0.06
PE-CAN2	2.88	-	0.12	0.012	0.0552	0.02
PE-MA	2.94	-	0.06	0.006	-	1.424
PB- CAN	-	2.94	0.06	0.006	0.0276	0.085

Table S1. The formulations and melting index (MI) for different samples.

Sample	Swelling rat	e (%)	Gel content (%)		Crystallinity	Melting	Crystallization
	In toluene	In xylene	In toluene	In xylene	(%)	point (°C)	temperature (°C)
PE	-	-	0	0	30	111.8	94.4
PE-CAN1	620	632	64	63	26	111.1	93.7
PE- CAN2	570	591	67	65	24	110.1	92.9
PE-MA	59	62	13	11	27	110.8	94
PB	-	-	0	0	29.2	109.5	94.3
PB- CAN	567	599	61	58	25.9	109	94.3

Table S2. Swelling rate, gel content, crystallinity, melting point and crystallization temperature for different samples.

Table S3. Mechanical Properties of the samples.

Sample	Young's modulus	Ultimate tensile	Elongation	
	(MPa)	strength (MPa)	at break (%)	
PE	265±1.5	16.5±0.3	470±32	
PE-CAN1	271±2.9	19.8 ± 0.8	411±69	
PE- CAN2	267±3.2	17.3±1.2	389±64	
PE-MA	248±2.1	14.5±0.6	282±42	
PB	231±3.6	17.5±0.7	472±26	
PB- CAN	243±5.2	17.3±1.2	298±72	

Table S4. Mechanical properties and recycle rate (R.R.) of the original and recycled samples.

Sample	Young's	R.R. of	Ultimate	R.R. of σ_{m}	Elongation	R.R. of
	modulus	YM (%)	tensile strength	(%)	at break	ε (%)
	(YM, MPa)		(o _m , MPa)		(ε,%)	
PE-CAN1	271±2.9	-	19.8±0.8	-	411±69	-
1 st recycled	269±7.9	99.3%	18.3±0.7	92.4%	388±54	94.4%
PE-CAN1						
2 ^{ed} recycled	254±6.5	93.7%	16.9±1.3	85.4%	349±38	84.9%
PE-CAN1						
3 rd recycled	258±4.9	95.2%	15.3±1.1	77.3%	325±59	79.1%
PE-CAN1						
PB-CAN	243±5.2	-	17.3±1.2	-	298±72	-
1 st recycled	239±3.9	98.4	16.9±0.7	97.7	273±46	91.6
PB-CAN						
2 ^{ed} recycled	235±6.6	96.7	16.5±1.3	95.4	253±69	84.9
PB-CAN						
3 rd recycled	212±5.4	87.2	15.5±0.9	89.6	239±58	80.2
PB-CAN						

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