Supplementary Materials

Delamination of polyamide/polyolefin multilayer films by selective glycolysis of polyurethane adhesive

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Supplementary Text

Materials

Each multilayer film consists of three plastic types, whereby a PO (PE or cPP) is glued with PUR adhesive to OPA. The PUR glue contains blue ink in a PE/OPA multilayer. **Fig. S1.** is an image showing the multilayer roles. The origin of the various chemicals used for the investigation can be found in **table S2.**

ATR FTIR characterization

ATR FTIR analysis was used to identify the different plastic types before and after solvent treatment of the films. **Fig. S2.** and **fig. S3.** illustrate the ATR FTIR spectra of both faces of the cPP/OPA and PE/OPA multilayers, respectively.

The assignment of the vibrational peaks was consistent with literature [1–3]:

Polypropylene (in cm^{-1}): 2952 (s, $\nu_{as}CH_3$), 2917 (s, $\nu_{as}CH_2$), 2869 (s, ν_sCH_3), 2838 (s, ν_sCH_2), 1457 (s, $\delta_{as}CH_3$), 1367, 1159 (w), 998 (w), 973 (w) , 841 (w), 806 (w).

Polyamide 6 (in cm^{-1}): 3301 (s, ν NH with H-bonding), 3075 (w, NH overtone), 2928 (s, $\nu_{as}CH_2$), 2860 (s, ν_sCH_2), 1631 (s, ν C=O, Amide I) , 1534 (s, δNH, Amide II) , 1465 (w), 1366 (w), 1260 (w), 1196 (w), 1165, 673 (s, δ NH).

Polyethylene (in cm^{-1}): 2915 (s, $\nu_{as}CH_2$), 2846 (s, ν_sCH_2), 1467 (s, $\delta_{as}CH_2$), 724 (s, CH_2-rocking).

Fig. S4. ATR-FTIR spectra of the uncured and cured PUR adhesive. By this, the following vibrational peaks were characterized[4]:

Uncured PUR adhesive (in cm^{-1}): 3344 (b, weak, ν NH), 2930 (s, $\nu_{as}CH_2$), 2860 (s, ν_sCH_2), 2255 (s, ν N=C=O), 1728 (s, ν C=O), 1588 (w, δ NH), 1525 (m), 1413 (weak), 1217 – 1016 (m), 812 (m) 756 (w), 564 (m).
Cured Polyurethane adhesive (in cm^{-1}): 3344 (b, weak, ν NH), 2930 (s, $\nu_{as}CH_2$), 2860 (s, ν_sCH_2), 1728 (s, ν C=O), 1588 (w, δ NH), 1525 (m), 1413 (weak), 1217 – 1016 (m), 812 (m) 756 (w), 564 (m).

Fig. S6-S7 ATR-FTIR spectra of residual films after the glycolysis-delamination of OPA/PE and OPA/PP multilayers by ethylene glycol and diethylene glycol.

Screening of additives for delamination

Table S1. Illustrates the various carboxylic acid or basic additives that were screened in order to obtain pure PP films during the delamination process.

Optimal delamination conditions for multilayer films at higher temperature

At first the multilayer films were delaminated by treatment at 150°C, by submerging the film strips in 1 mL of DEG, with KOH or ethanolamine as additives. The mass balance of these obtained films after 1 and 3h, is illustrated in **Fig. S5.**

Complementary to the FTIR analysis, purity of the treated films after treatment was checked by UV-Vis; by this second technique, the absence of aromatic components (no absorbance at 254 nm) gave clear indication that the films were completely purified from the aromatic-containing PUR adhesive. (**Fig. S8**.)

NMR study of outer plastic layers of the multilayers

By liquid ^{1}H-NMR (600 MHz) at elevated temperature, (**Fig. S9-S11**) 10 mg samples of the obtained pure split films (OPA, PE and PP) were characterized.[5] Samples were firstly obtained by treatment of the multilayer films in DEG/EA for 3h at 150°C. By ^{1}H-NMR, no solvent or PUR impurities were detected in the pure films. ^{1}H-NMR shifts of these outer polymer layers of the multilayer films were the following:

Polyamide 6 (trifluororethanol /$CDCl_3$ (40°C, 4/1 v%) = 6.48 ppm (NH, b), 3.17 (CH_2, m), 2.02 (CH_2, t, J = 12 Hz), 1.59 (CH_2, m), 1.50 (CH_2, m), 1.32 (CH_2, m).

Polyethylene (d^8-toluene (80°C), 600 MHz) = 1.36 (CH_2, s), 0.96 (CH_3, s).

Polypropylene (d^8-toluene (80°C), 600 MHz) = 1.65 (CH, m), 1.33 (CH_2, m), 0.91 (CH_3, m).

NMR study of PUR adhesive

According to model compounds the PUR adhesive was characterized. Firstly, commercial polycaprolactone displayed (**Fig. S12**) the same ^{1}H-shifts (400 MHz) as the aliphatic peaks in the PUR adhesive:

Polycaprolactone (d^6-DMSO, 400 MHz) = 3.99 (CH_2, m), 2.28 (CH_2, b), 1.55 (CH_2, b), 1.30 (CH_2, b).

As model components for the aromatic isocyanate derivatives in the PUR adhesive, 4,4’-MDI and 4,4’-methylene dianilines (MDA) were characterized. Additionally, for a representation of the aromatic carbamates in the prepolymer backbone, a model compound of dimethyl (methylenebis(4,1-phenylene))dicarbamate was synthesized by reacting MDI in an excess of methanol. ^{1}H-NMR shifts of the model compounds (**Fig. S13-15)** were as following:

4,4’-methylene diisophenyl diisocyanate (d^6-DMSO, 400 MHz) = 7.41-7.14 (m, CH, 8H), 4.02-3.92 (m, CH2, 2H).

Dimethyl (methylenebis(4,1-phenylene))dicarbamate (d^6-DMSO, 400 MHz) = 9.53 (NH, 2H, s), 7.35 (CH, 4H, d, J=8.5 Hz), 7.10 (CH, 4H, d, J= 8.5 Hz), 3.79 (CH2, 2H, s), 3.65 (CH3, 6H, s).

4,4'-methylenedianiline (d^6-DMSO, 400 MHz) = 6.83 (CH, 2H, d, *J* = 8.5 Hz), 6.48 (CH, 2H, d, *J* = 8.5 Hz), 4.80 (NH2, 4H, s), 3.58 (CH2, 2H, s).

Solvent impurities by delamination process

To investigate the solvent impurities that accumulate after several delamination cycles by the solvent, ^{1}H-NMR was used on solvent aliquots after subsequent cycles (d^6-DMSO, 400 MHz). Firstly, the spectrum of KOH in diethylene glycol (0.2 M) displayed no impurities. However, after one and three reactions with the diethylene glycol, the spectra showed some peaks originating from the PUR adhesive, but in small quantities with DEG as the major peak in the spectra. These ^{1}H-NMR spectra are shown in **Fig. S16**.

Density based method for separation of the split OPA and PP films after delamination

After delamination, by adhesive glycolysis-hydrolysis, a solvent mixture is obtained that contains a pure OPA film and pure PP film, with the adhesive PUR still dissolved in the diethylene glycol. As a conceptual method to separate the physical mixture of these two films in the solvent, the split films were brought into diethylene glycol solvent for density based fractionation. By this it was seen that the PP film, which has a lower density than the solvent, floated to the top of the diethylene glycol, while the OPA film (with higher density) sunk to the bottom of the diethylene glycol. This experiment is illustrated in **Fig. S17**. Hence, this method of solvent based density fractionation can potentially be useful for further physical separation of the split plastic fractions when densities of the various plastic layers are sufficiently different.

Carbon footprint calculations

Table S3. Gives more clarification in the assumptions that were used to calculate the carbon footprint of the delamination process and compare this with incineration processes.

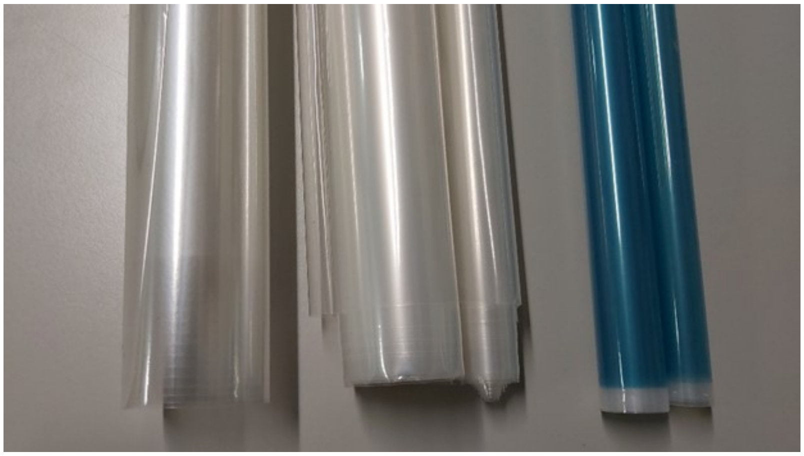

Figure S 1 Picture of roles of multilayer film A (OPA/PUR/PP, left role), film B (OPA/PUR/PE, middle role) and film C (OPA/PUR resin with blue ink/PE, right role).

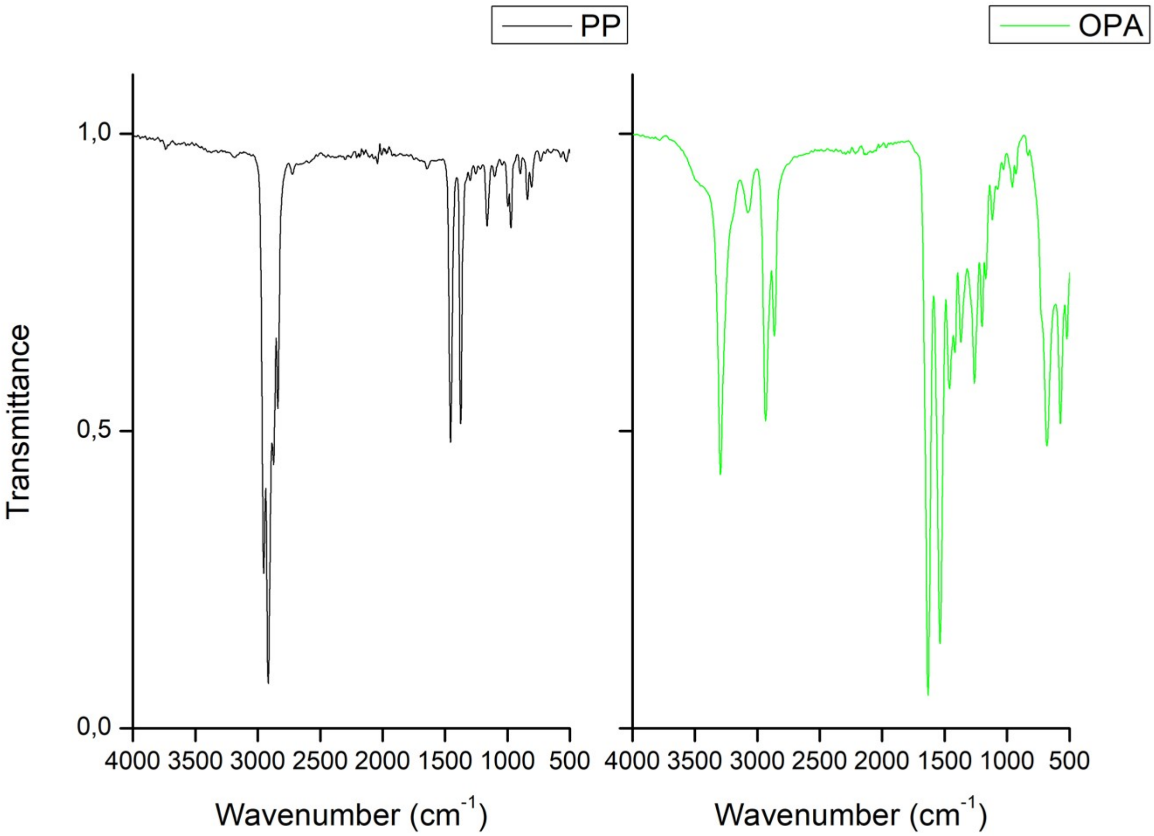

Figure S 2 ATR-FTIR of both faces (sides) of flexible multilayer film A, which consists of polypropylene (PP) and biaxially-oriented polyamide (OPA). A PUR-based glue causes the attachment of the two layers.

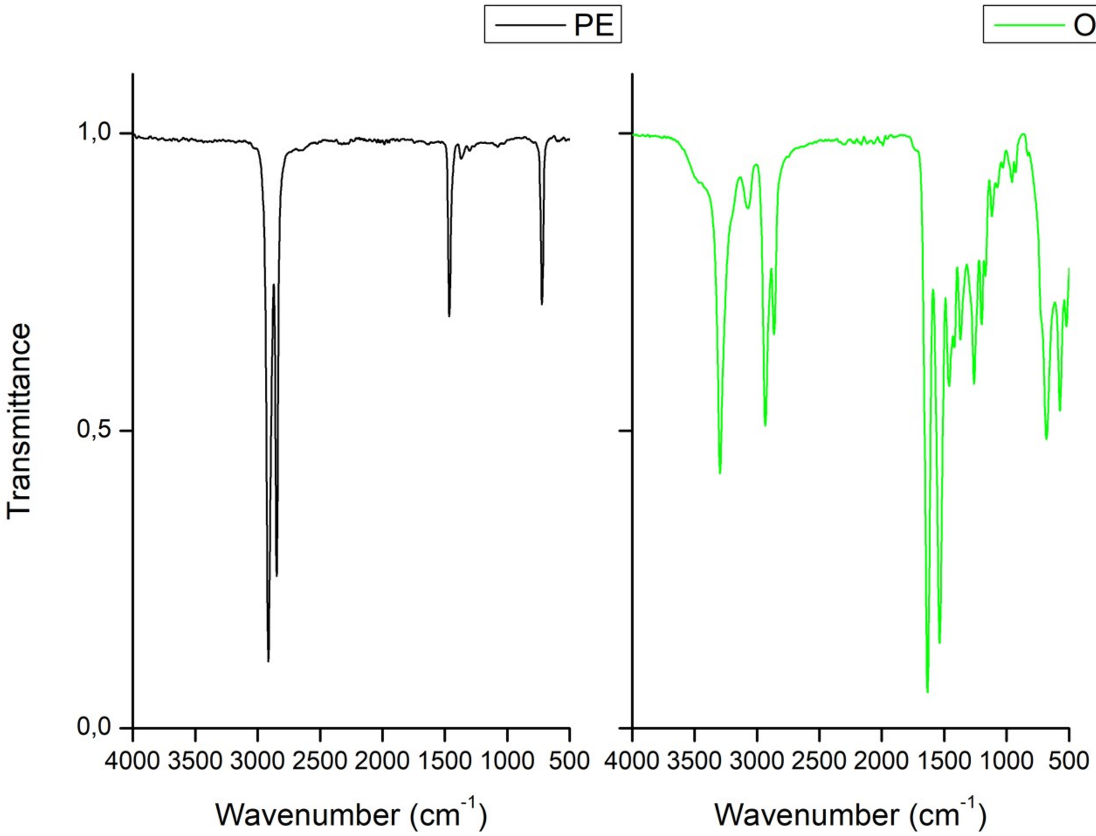

Figure S 3 ATR-FTIR of both faces (sides) of flexible multilayer film B, which consists of polyethylene (PE) and biaxially-oriented polyamide (OPA). A PUR-based glue causes the attachment of the two layers.

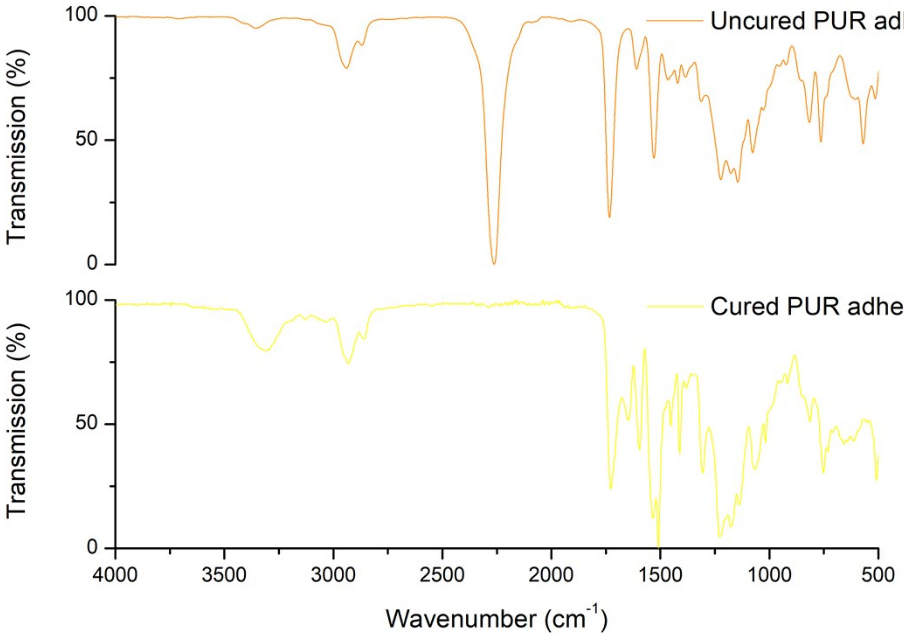

Figure S 4 ATR-FTIR of uncured PUR adhesive (orange) with unreacted –N=C=O groups at (2250 cm-1). Curing of glue was mimicked by heating 100 mg glue in the presence of water at 150°C, for 10 min. ATR FTIR of cured PUR adhesive displays no unreacted isocyanate.

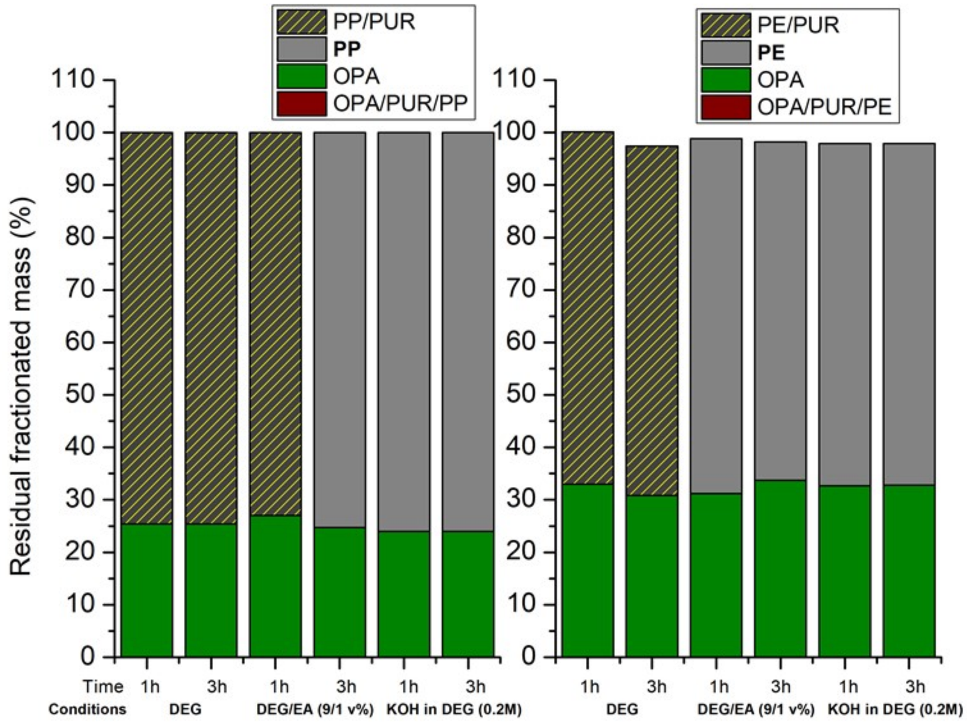

Figure S 5 Delamination of multilayer films at 150°C. Treatment in DEG with ethanolamine (0.9/0.1 mL); DEG with KOH base (0.2M, 1 mL), results in pure PP (right graph) or pure PE (right plot) after 1h. Using pure DEG (1 mL) as the solvent, leads to split films with an impure polyolefin/PUR fraction.

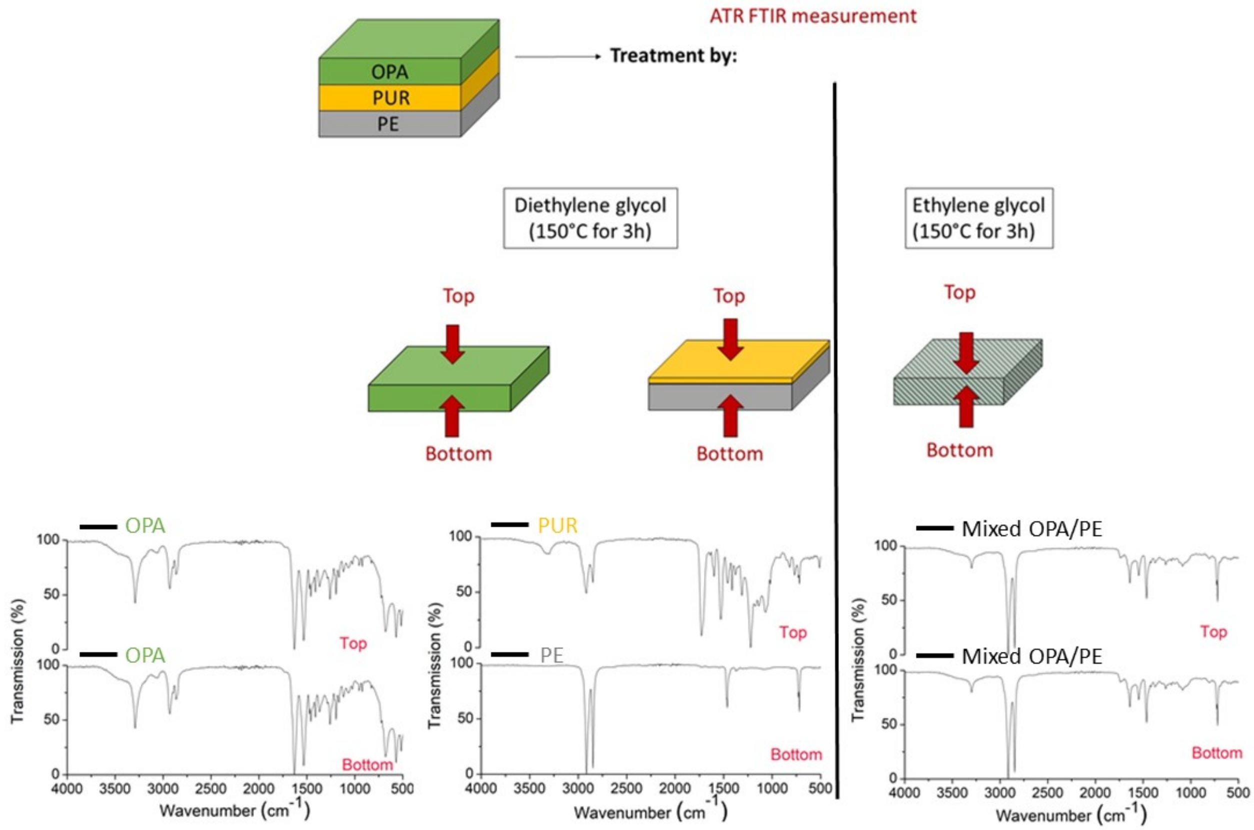

Figure S 6 ATR FTIR spectra of the delaminated OPA/PE film, treated by diethylene glycol or ethylene glycol. Red arrows represent the surfaces of the delaminated films that were analyzed. Diethylene glycol treatment gave two films, of which a pure OPA film (green) and a mixed PE/PUR film (grey and yellow faces). Treatment in ethylene glycol yielded a clump with mixed OPA/PE in the spectrum at both sides (grey shaded green).

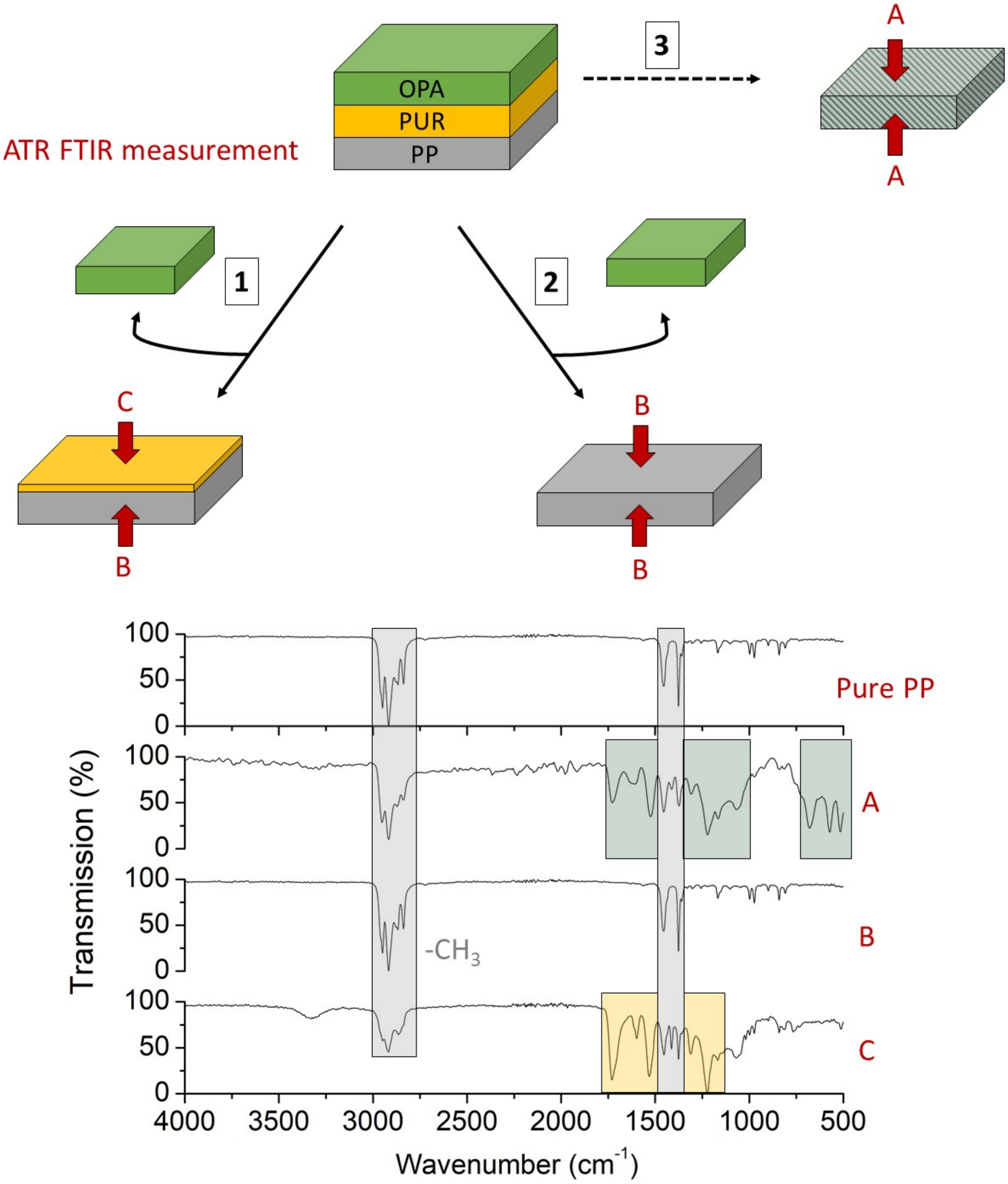

Figure S 7 Comparison of ATR FTIR spectra of the residual PP films, obtained after various conditions for delamination. ATR FTIR was measured on both faces of the films. (1) Delamination with diethylene glycol, without KOH, yielded residual films with pure PP on one side (spectrum B) and mixed PP/PUR on the other (spectrum C). (2) Delamination with diethylene glycol and added KOH or ethanolamine yielded PP films that are pure on both sides (spectrum B). (3) Delamination with ethylene glycol does not give efficient separation, with residual film consisting of mixed PP/OPA on both sides (spectrum C). Colored frames in the spectra represent FTIR peaks from the corresponding plastic types.

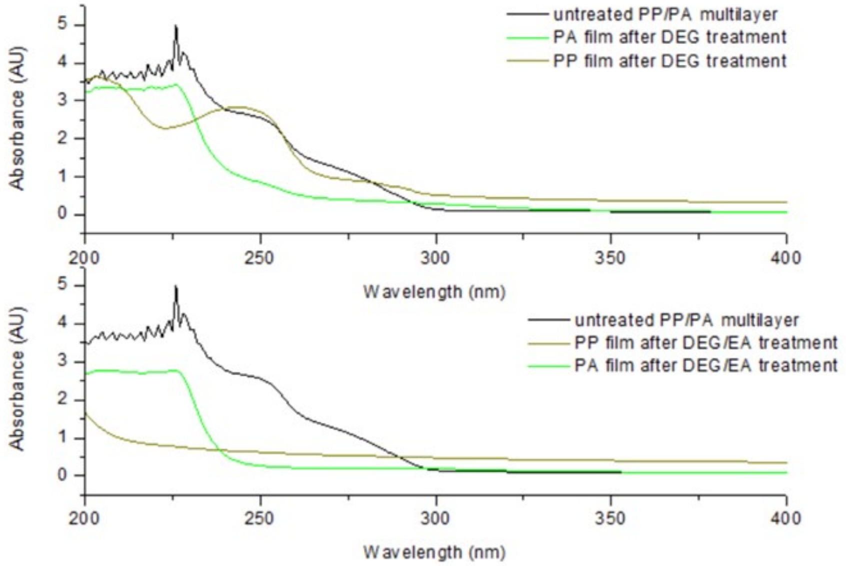

Figure S 8 UV-Vis absorbance spectra of multilayer film of OPA/PUR/PP. Comparison of the split OPA films (green) and PP films (brown) after treatment in pure DEG (top spectra) and by 10v% ethanolamine (EA) in DEG (bottom spectra). Absorbance of aromatic MDI peaks at 254 nm in top spectra indicated residual PUR by treatment with DEG, while films after DEG/EA treatment were found pure.

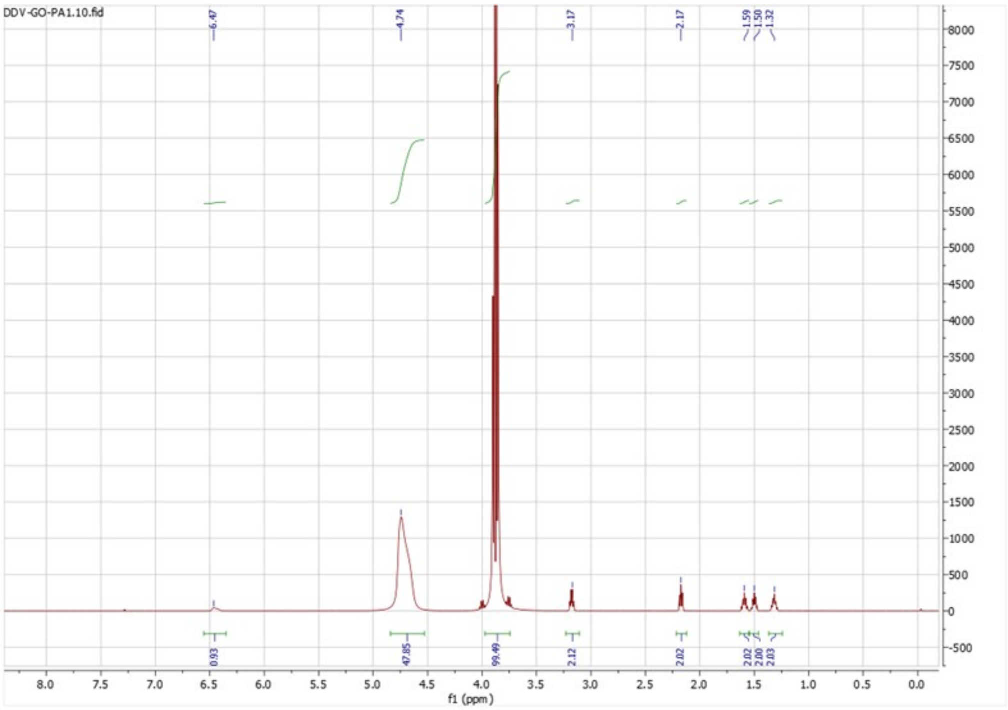

Figure S 9 ^{1}H-NMR spectrum (trifluoroethanol/CDCl$_3$, 40°C,600 MHz) of Polyamide 6-film after treatment with DEG/EA and work-up procedure.

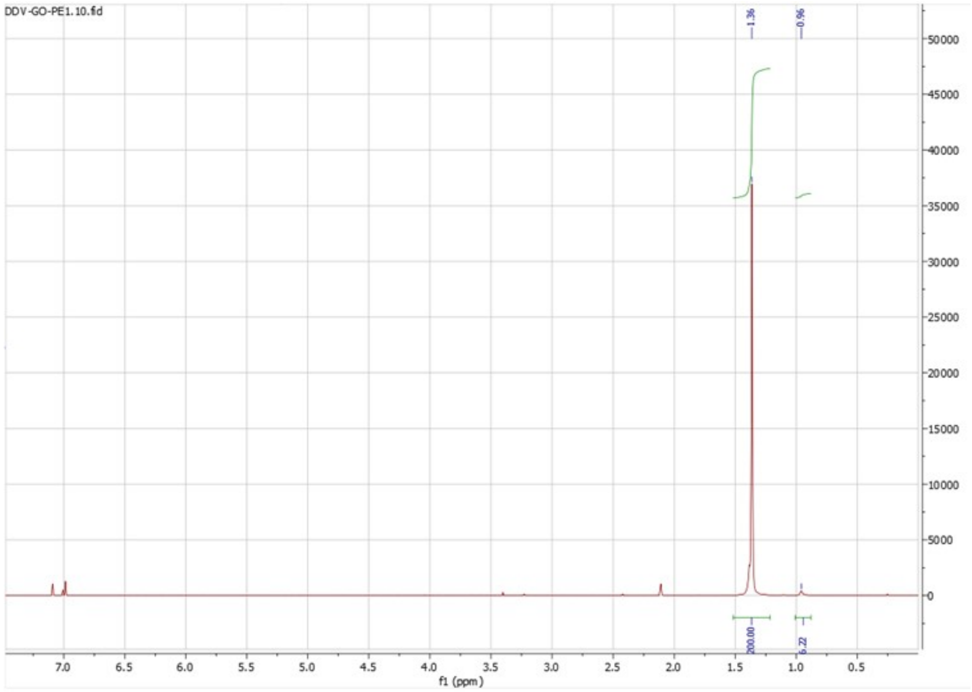

Figure S 10 ^{1}H-NMR spectrum (d^8-toluene, 80°C, 600 MHz) of PE-film after treatment with DEG/EA and work-up procedure.

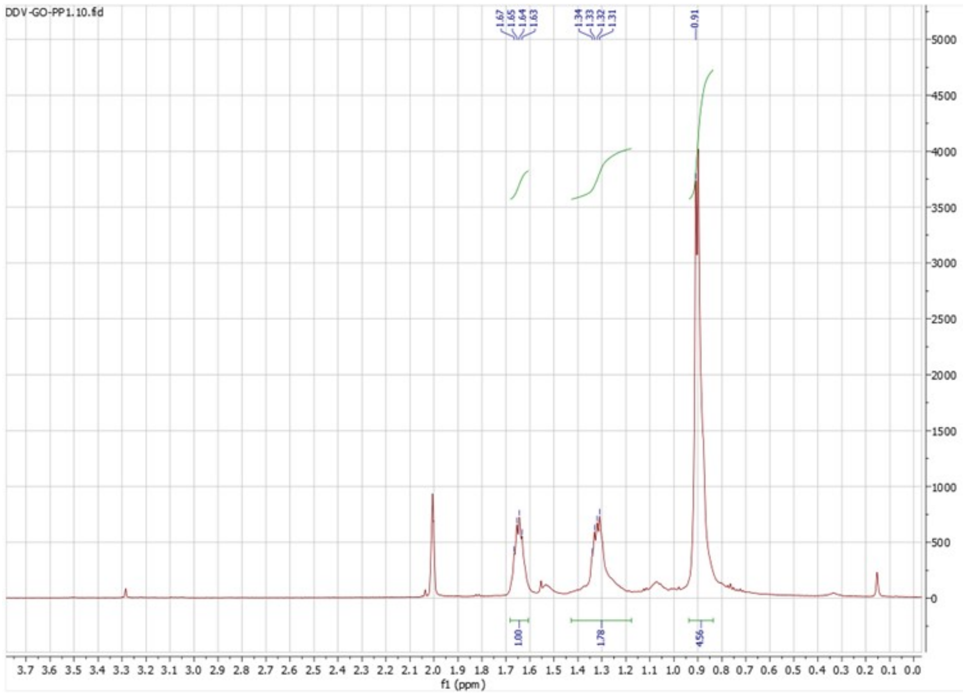

Figure S 11 ^{1}H-NMR spectrum (d^8-toluene, 80°C, 600 MHz) of PP-film after treatment with DEG/EA and work-up procedure.

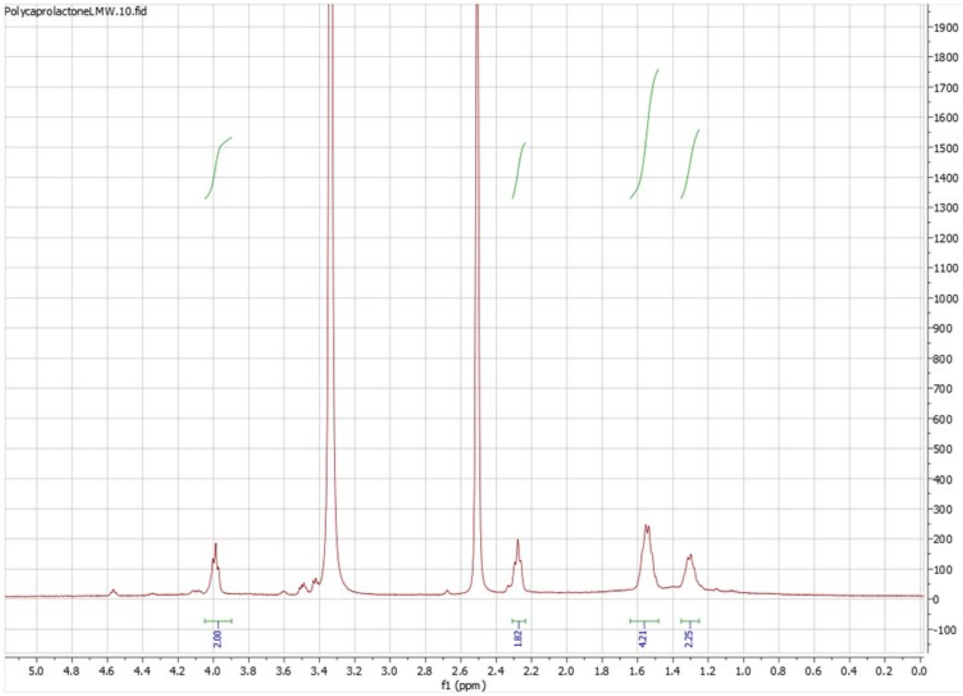

Figure S 12 ^{1}H-NMR spectrum (d^6-DMSO, 400 MHz) of commercial polycaprolactone sample (M_n 10 000).

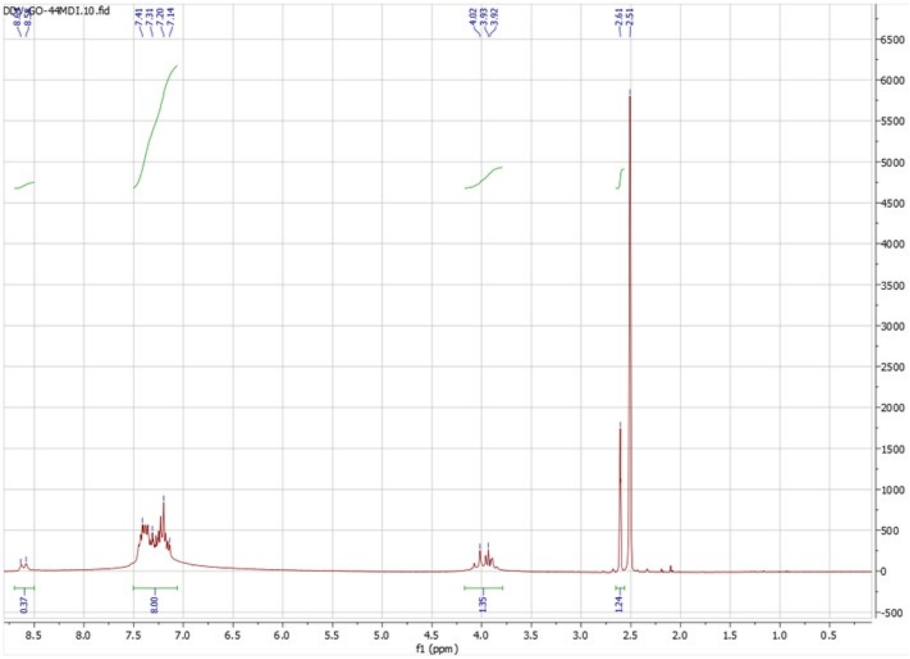

Figure S 13 ^{1}H-NMR spectrum (d^6-DMSO, 400 MHz) of 4,4-methylene diphenyl diisocyanate. (reference compound for uncured PUR adhesive)

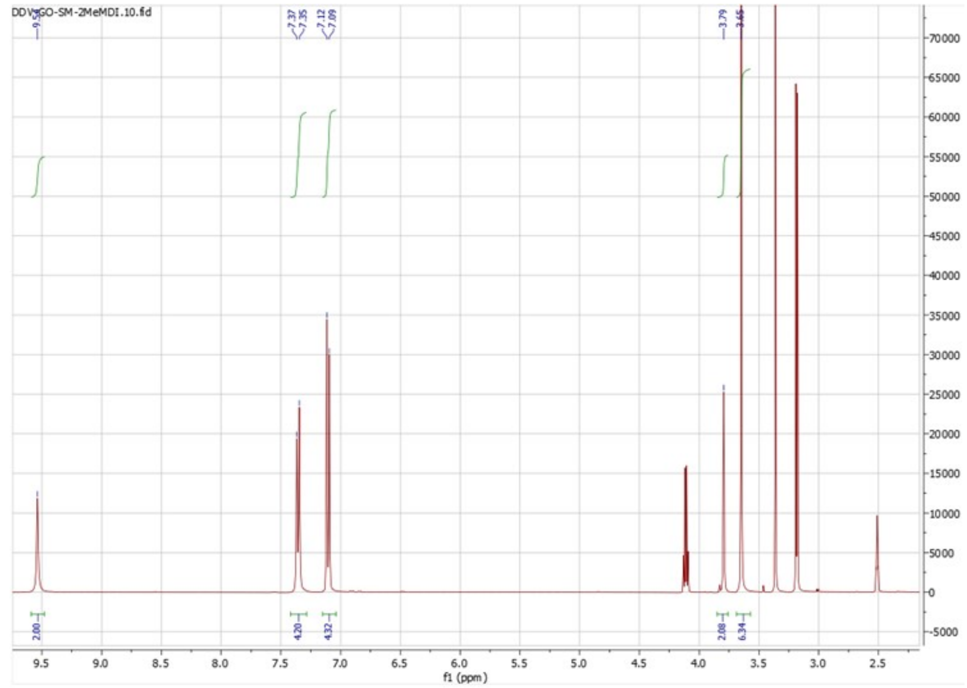

Figure S 14 ^{1}H-NMR spectrum (d^6-DMSO, 400 MHz) of dimethyl (methylenebis(4,1-phenylene))dicarbamate (reference compound for internal carbamates in cured and uncured PUR adhesive).

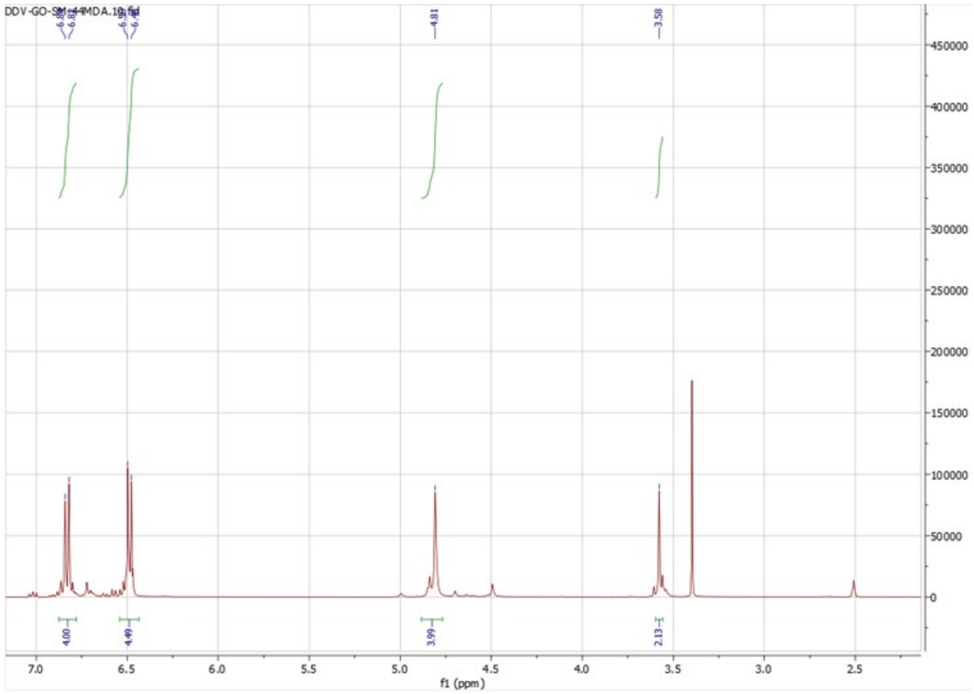

Figure S 15 ^{1}H-NMR spectrum (d^6-DMSO, 400 MHz) of 4,4'-methylenedianiline. (reference compound for glysolysed/hydrolysed PUR adhesive glue)

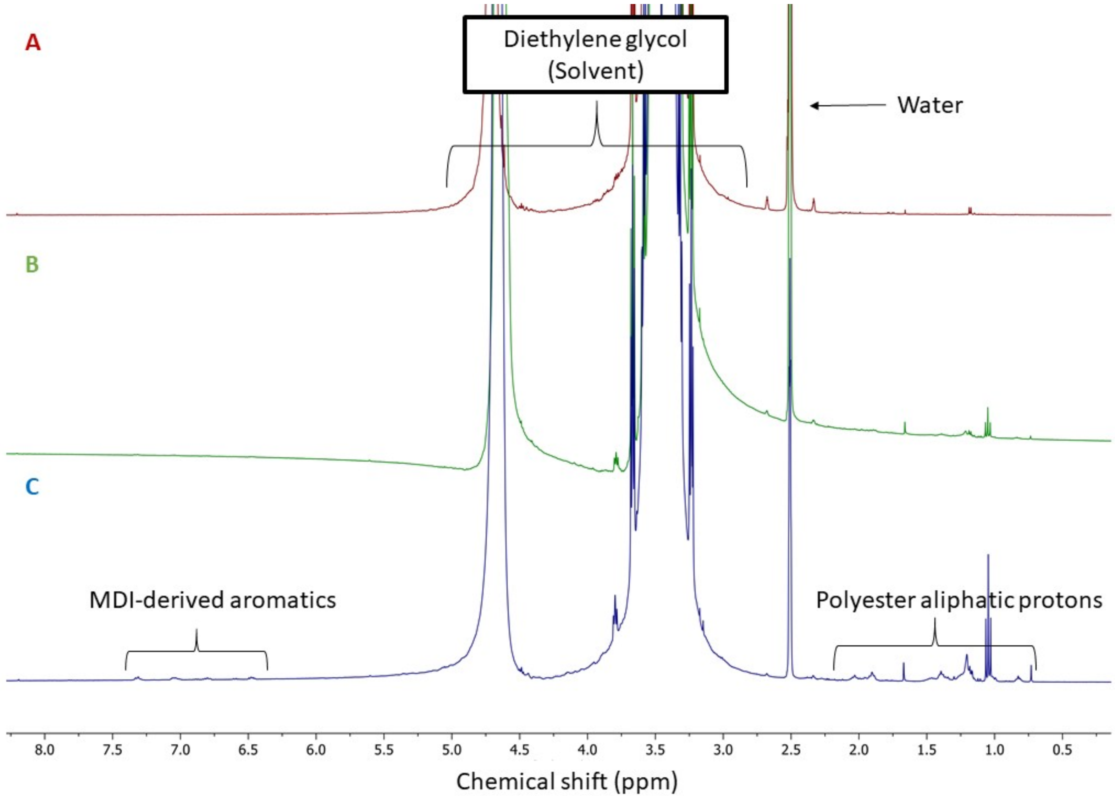

Figure S 16 ^{1}H-NMR of solvent after reaction with multilayer film (OPA/PP film treated at 120°C for 3h). (Spectrum A) KOH in diethylene glycol (0.2 M) solvent, before the reaction, shows only solvent peaks. (Spectrum B) After 1st delamination reaction of multilayer, MDI and polyester peaks originating from PUR adhesive are only present in the noise, with DEG as major peak. (Spectrum C) After 3rd multilayer delamination reaction with same solvent, MDI and polyester peaks are more pronounced but again present in low quantity. Impurities in solvent accumulate only from PUR dissolution.

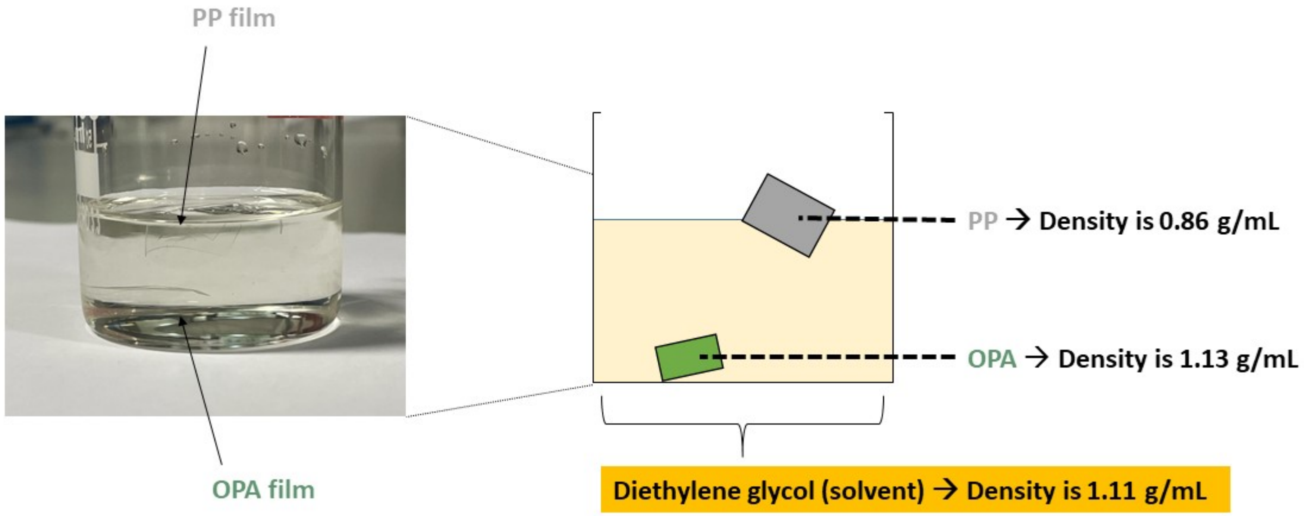

Figure S 17 Schematic illustration and picture of density based fractionation experiment to separate the split OPA and PP film fractions (after delamintion in KOH-diethylene glycol (0.2 M, 1 mL) at 120°C,3h). The split PP film has a lower density than the diethylene glycol solvent, thereby this film floats to the top of the solvent. The oriented polyamide film (OPA) has a higher density than the solvent, causing it to sink to the bottom of the solvent.

Entry	Stirring time (h)	Temperature (°C)	Solvent mixture	Obtained films
1	1	100	DEG	1 film: OPA/PP
2	1	150	DEG	2 films: PP/PUR and PA/PA
3	1	150	DEG/ethanolamine (9/1 v%)	2 films: PP/PP and PA/PA
4	1	150	DEG/ethanolamine (9/1 v%)	2 films: PP/PUR and
5	1	120	DEG /ethanolamine (9/1 v%)	2 films: PP/PUR and PA/PA
6	3	120	DEG/Ethanolamine (9/1 v%)	2 films: PP/PP and PA/PA
7	1	120	DEG/ Acetic acid (9/1 v%)	1 film of PP/PA
8	3	120	DEG/ Acetic acid (9/1 v%)	1 film of PP/PA
9	1	120	DEG/ Propionic acid (9/1 v%)	1 film of PP/PA
10	3	120	DEG/ Propionic acid (9/1 v%)	2 films PP/PP mix PUR and PA/PA
11	1	120	DEG/Hexanoic acid (9/1 v%)	1 film of PP/PA
12	3	120	DEG/ hexanoic acid (9/1 v%)	1 film of PP/PA

Table S 1 OPA/PUR/PP multilayer separation by treatment with diethylene glycol (DEG) with various additives. DEG/co-solvents (0.9/ 0.1 mL) gave no separation for carboxylic acids, while 2-amino-ethanol, as additive did yield pure polymer.

Chemicals	**Supplier**
Toluene	Fisher scientific
p-cymene	Alpha Aesar
xylene	Acros Organics
Acetic acid	Fisher chemical
Propionic acid	Janssen Chimica
Hexanoic acid	Janssen Chimica
Ethylene glycol	Carl Roth
Diethylene glycol	Carl Roth
Triethylene glycol	Carl Roth
Aminoethanol	Janssen Chimica
KOH	Sigma
d^6*-DMSO*	Sigma

Table S 2 Suppliers of the chemicals used for the investigation.

Process	**Assumptions (ref)**	**Name ecoinvent dataset**
Ethylene glycol	Stoichiometric consumption during glycolysis	Ethylene glycol production, alloc. default, U
Polyamide		Nylon 6 production, alloc. default, U
Incineration residue distillation	1% residue via distillation [6]	Treatment of spent solvent mixture, hazardous waste incineration, alloc. default, U
Energy for glycolysis **(at 150 °C)**	Efficiency of heat transfer is 50% [7] Energy needed for the glycolysis is calculated via $Q = mc\Delta T$ Reactor design is not included in the LCA	Market for heat, district or industrial, natural gas, alloc. default, U
Energy for distillation	Based on Aspen simulation [6]	Market for heat, district or industrial, natural gas, alloc. default, U
Polyurethane	PUR is lost during the process, so virgin PUR is needed for laminating new packaging	Polyurethane production, flexible foam, alloc. default, U
Polypropylene	PP can be 100% recovered after the delamination process	Polypropylene production, granulate, alloc. default, U
Polyethylene	PE can be 100% recovered after the delamination process	Polyethylene production, low density, granulate, alloc. default, U
Incineration of multilayer	In the benchmark scenario, multilayer materials are incinerated with energy recovery.	Treatment of waste polyethylene, municipal incineration, alloc. default, U
KOH	0.5 M concentration is used; stoichiometric consumption during glycolysis; residue is fully ending up in bottom fraction and subsequently incinerated.	Potassium hydroxide production, alloc. default, U
Wastewater treatment	The produced wastewater is treated and reused in the process.	Treatment of wastewater, average, capacity 1.1E10l/year, alloc. default, U

Table S 3 Assumptions made for the carbon footprint calculations and the name of used datasets from ecoinvent v3.1.

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