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REVIEW ARTICLE

Thermal degradation and hydrolysis depolymerization of printing ink components for plastic packaging in recycling processes: a review

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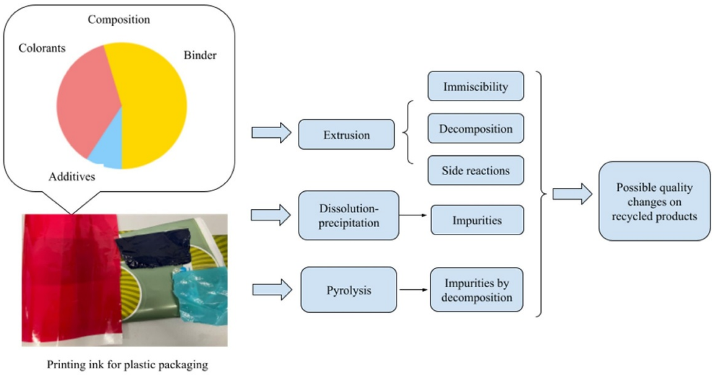
HIGHLIGHTS

- Identifies and elucidates the concurrent thermal degradation and hydrolysis of common binders in flexible plastic packaging during mechanical recycling.
- Reveals that thermal degradation for a variety of binder resins begins between 200–300 °C, with hydrolysis potentially intensified by humidity from cleaning processes.
- Demonstrates how the compatibility between binder resins and polyolefin affects the quality of recycled plastics, emphasizing this issue regarding immiscibility.
- Underscores the influence of binder resins and their degradation products on the efficacy of advanced recycling methods like selective dissolution-precipitation and pyrolysis.

GRAPHIC ABSTRACT



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ABSTRACT

This review covers the decomposition mechanisms of various printing ink binder resins, with a particular focus on their behavior under extrusion conditions in the mechanical recycling process of polyolefin (PO) based plastic packaging. Thermal degradation and hydrolysis of the nitrocellulose (NC) — the most used binder for flexographic surface printing on single-layer flexible plastic packaging, occur concurrently during the mechanical recycling process under 160–210 °C. For other printing ink binders, polyurethane (PU) noticeable degradation takes place between 200 and 300 °C, mostly above 250 °C. However, with the involvement of humidity, degradation by hydrolysis can start from 150 °C. A similar effect is also discovered with the cellulose acetate (CA) derivatives, which are thermally stable until 300 °C and can be hydrolyzed at 100 °C. The thermal stability of polyvinyl butyral (PVB) is not influenced by humidity, with thermal stability ranging from 170 to 260 °C, depending on different types. Ultraviolet (UV)-cured acrylics are thermally stable until 400 °C. The hydrolysis degradation can take place at room temperature. Moreover, this review covers the thermal stability of different colorants used for printing ink application and elaborates on several thermal-stable alternatives of some common colors. This study further reviews how the binder resin affects the quality of recyclates, revealing it to be not only induced by the degradation of the binder resin but also by the immiscibility between the plastic and binder resin. In advanced recycling processes, mainly selective dissolution-precipitation and pyrolysis, the presence of binder resin and its degradation products could still affect the quality of the product. This review accentuates the imperative need for in-depth research to unravel the impact of printing ink constituents on the quality of recycled products.

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1 Introduction

In Europe, plastic packaging accounts for 38% of annual plastic consumption (Plastic Europe, 2022) Common materials in this process include polyethylene terephthalate (PET), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS). This production results in a variety

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of packaging forms, such as rigid packaging (e.g., bottles, boxes, trays, and tubes), and flexible packaging (e.g., bags, films, and sachets) (Plastic Recycler Europe, 2020).

With a short service-life, over 99% of plastic packaging is discarded within a year (Geyer et al., 2017). The common treatment for plastic packaging waste involves mechanical recycling, energy recovery, and landfilling. Recycling, according to the waste hierarchy, should be the preferred treatment route as it reduces greenhouse gas emissions and the use of fossil resources (Volk et al., 2021).

The state-of-the-art recycling process begins with collection and sorting. During sorting, plastic packaging is segregated based on polymer types using near-infrared spectroscopy (NIR) or physical properties, and in some cases, a combination of both. Recently, more detailed sorting processes including color sorting and form sorting (i.e., segregation between PET bottles and trays) are also introduced to some sorting plants (Kuchta et al., 2023). After sorting, the bales of sorted plastic packaging are transported to the recycling plant for mechanical recycling. This process includes bale opening, pre-washing, shredding, friction washing, swim-sink separation, drying, and extrusion (Ragaert et al., 2017; COWI, 2019; Christiani and Beckamp 2020).

The recycling of rigid plastic packaging is relatively well established—with bottle-to-bottle recycling of PET beverage bottles collected through the deposit-return system (DRS) considered successful in countries like Germany, Belgium, and the Netherlands (Picuno et al., 2021). In contrast, the effective recycling rate for post-consumer flexible packaging is just 17% in Europe (Lase et al., 2022). Much of this packaging is down-cycled, with the plastic converted into lower-value products, for instance, waste bags and construction film (Plastic Recycler Europe, 2020; Bashirgonbadi et al., 2022; Lase et al., 2022).

This limitation is primarily due to the complex composition of the flexible plastic packaging stream. Post-consumer flexible plastic waste is usually composed of 70%–80% monolayer films and 20%–30% multilayer films, the latter is necessary for protecting the contents from oxygen, water vapor, UV-radiation, and microorganisms (Kaiser et al., 2018; Lase et al., 2022). Advanced NIR-based sorting technology can separate these multilayer fractions from the monolayer stream, however, the recycling of multilayer packaging is still challenging (Chen et al., 2020; Koinig et al., 2022).

A further challenge is the presence of printing ink on the surface of the packaging. Although printing ink is essential for providing necessary information and marketing appeal, it is a source of contamination in the mechanical recycling process (Gecol et al., 2001; Guo et al., 2022).The ink content in mono-layer flexible packaging can range from 0.5–5 wt.%, and for full-area printing the ink content can take up to 10 wt.% (Guo et al., 2023a). Some components of printing ink are not suited to the extrusion process in plastic recycling due to their low stability under extrusion temperatures and potential side reactions (EuPIA, 2021). These conditions can lead to degradation and side reaction products, altering the thermal and mechanical properties (Gecol et al., 2002; Guo et al., 2022), discoloration, and increasing the volatile organic content of the recycled plastic (Kaedin-Koppers, 2023).

1.1 Composition of printing ink for plastic packaging

Printing inks for plastic packaging consist of three main components: pigments that impart color, binder resins (one or more) that determine physical properties and adhesion, and additives that influence other functionalities (e.g., dispersion in solvent, flexibility, UV-stability) (Kol et al., 2021a). Prior to application, the printing ink is typically suspended in organic solvents or a mixture of different solvents (including alcohols, esters, and water). Solvent-free inks, such as UV-cured acrylics, also exist, but their use is primarily restricted to label applications (Guo et al., 2023b).

Certain printing inks contain an additional layer of varnish, known as the overprint varnish (OPV), on the top of the printing layer to enhance abrasion resistance and optical effects (Flick, 1999; Kol et al., 2021a). The OPV, essentially a pigment-free binder resin, may be identical to or different from the binder that carries the colorants (Guo et al., 2023b; Kol et al., 2023).

Nitrocellulose is the most prevalent binder resin for flexographic printing, holding approximately an 80% share in the EMEA (European, Middle East, and African) market (Guo et al., 2023b). Other binder resins include polyurethane (PU), polyvinyl butyral (PVB), and UV-crosslinked acrylics. However, these binders typically require the use of OPVs (Guo et al., 2023b). Table 1 lists the resins used for printing ink and their respective application fields.

A review of Table 1 reveals that nitrocellulose (NC), polyurethane (PU), and polyvinyl butyral (PVB) are commonly used binder resins for flexible plastic packaging. Polyamide (PA) and cellulose acetate derivatives can serve as co-binders in flexible plastic packaging, while UV-crosslinked acrylate resin is primarily applied to rigid packaging in the form of a label. The chemical structures of the binder resins covered in this review are shown in Fig. 1.

1.2 Degradation mechanisms

Two primary degradation mechanisms come into play during the recycling process (Fig. 2). The first is direct thermal degradation, a known phenomenon concerning nitrocellulose (NC) binder. This pathway is notorious for its gas generation and browning during the extrusion

Table 1 Common binder resins for printing inks according to Guo et al. (2023b) and Ügdüler et al. (2023)

Binder resin	Application	Source
Nitrocellulose (NC)	Printing ink for flexible plastic packaging	Guo et al. (2023b); Ügdüler et al. (2023); Kaedin-Koppers (2023)
Polyurethane (PU)	Printing ink for flexible plastic packaging (currently mainly for multilayer plastic packaging)	Akindoyo et al. (2016); Kaedin-Koppers (2023); Szabo (2002)
Polyvinyl butyral (PVB)	Printing ink for flexible plastic packaging (flexographic and gravure printing)	Rathschlag (2021); Hancock (1993)
Polyamide (PA)	Mainly used as a co-binder or OPV	Hinden and Whyzmuzis (1973); Szabo (2002); Ramadan et al. (2019)
Cellulose acetate (CA) and derivatives	Mainly used as overprint varnish	Yu and Gray (1998); Flick (1999); Yu and Gray (1998); Meng et al. (2017); Robert (2015)
Polymethyl methacrylate (PMMA)	Mainly used for screen printing for textile	Kuo et al. (2022)
Polyvinyl acetate (PVA)	Mainly used for ink jet printing (i.e., paper)	Zhang et al. (2015); Lamminmäki et al. (2011)
Polyacrylic resin	Mainly used label, including in-mold labeling (IML) of rigid packaging material	Duan et al. (2017); Robert (2015)

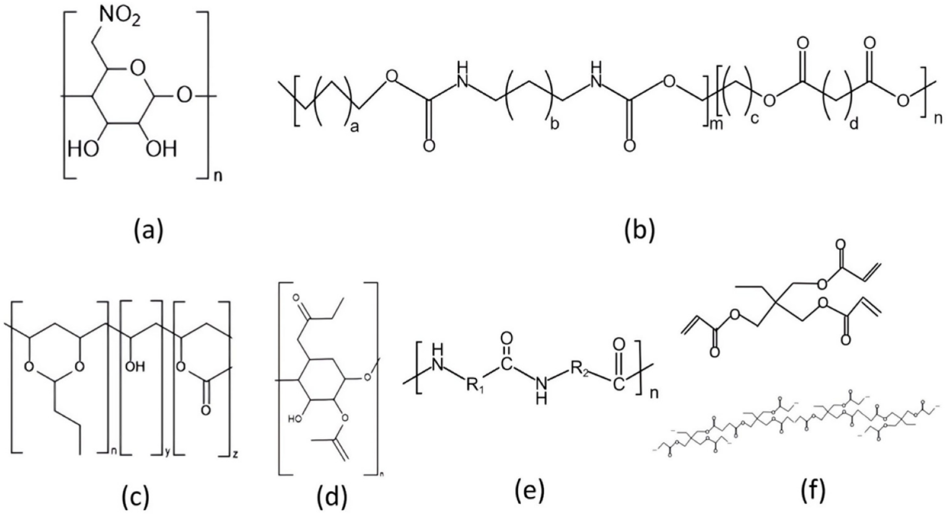
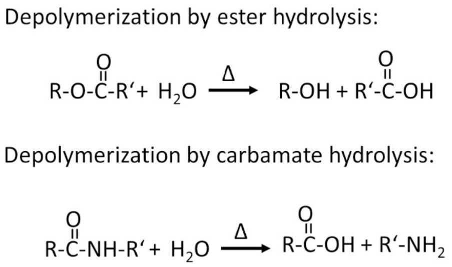


Fig. 1 Chemical structures of common printing ink binders (a) nitrocellulose, (b) polyurethane (aliphatic), (c) polyvinyl butyral, (d) cellulose acetate propionate, (e) polyamide, (f) upper: acrylate monomer, lower: acrylate polymer after UV curing (crosslinking).


Depolymerization by ester hydrolysis:

$$\text{R-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-R}' + \text{H}_2\text{O} \xrightarrow{\Delta} \text{R-OH} + \text{R}'\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OH}$$

Depolymerization by carbamate hydrolysis:

$$\text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-R}' + \text{H}_2\text{O} \xrightarrow{\Delta} \text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OH} + \text{R}'\text{-NH}_2$$

Fig. 2 Depolymerization reactions of polycondensate polymer.

process (Kaedin-Koppers, 2023). However, another often-overlooked mechanism is the hydrolysis degradation of binder resins under extrusion. Under an industrial recycling process, the input material retains 3–5 wt.% water after the mechanical and thermal drying from the upstream cleaning process (COWI, 2019; Berkane et al., 2023). A further reduction of the water content is commercially not feasible due to the energy intensity of the drying process and its role in facilitating bulk density for mass transfer to the extruder by auger conveyors. This level of humidity content is acceptable for polyolefins such as PP and PE. However, for the polycondensate polymers (i.e., PET, PU), the humidity is required to be reduced under 200 ppm or lower, since humidity can induce the hydrolysis degradation of the ester and carbamate bonds under extrusion temperature (Goff and Whelan, 1988).

To mitigate the negative impact of printing ink components on plastic recycling, one strategy involves removing the ink upstream of the extrusion process, a technique known as “de-inking.” De-inking can be achieved mechanically, such as by brushing or chemically, using organic solvents, different acids and NaOH solution (Ügdüler et al., 2023). De-inking with a surfactant-water solution is currently being investigated by different studies since it can potentially enable a simple integration into the plastic recycling process. A cationic surfactant such as centrimonium bromide (CTAB) is the currently most investigated surfactant for the de-inking application (Gecol et al., 2003; Fullana, and Lozano, 2015). Different non-ionic surfactants are also reported to have a de-inking effect (Gecol et al., 2002; Bozzola et al., 2022; Guo et al., 2022). A detailed overview of all the above-mentioned de-inking studies is reviewed in another publication of the authors (Guo et al., 2023b). However, a universally effective de-inking process capable of treating all different printing ink binders does not yet exist (Guo et al., 2023b; Ügdüler et al., 2023). Therefore, it is crucial to understand the influence of the different printing ink binder resins and their potential degradation products under extrusion conditions.

1.3 Objective of the literature review

Based on the comprehensive understanding of the authors, there is an absence of systematic experimental research documenting the influence of printing ink components on the quality of the recyclate (CEFLEX 2020). The objective of this review, therefore, is to consolidate relevant studies concerning the degradation behavior and by-products of key printing ink components—principally the binders and pigments. The aim is to anticipate their potential impact during the mechanical recycling process and thereby provide a theoretical foundation for future experimental investigations.

2 Degradation of binder resins

2.1 Nitrocellulose (NC)

NC is the nitro-derivative of cellulose, which is obtained through a reaction with sulfuric and nitric acids. This reaction replaces the hydroxyl groups (OH–) in cellulose with nitro groups (NO_2^-), as shown in Eq. (1) (McKeen, 2017).

$$(C_6H_{10}O_5)_n \xrightarrow{HNO_3, H_2SO_4} (C_6H_7(ONO_2)_xO_2 + YH_2O \tag{1}$$

It is noteworthy that nitro groups replace not all hydroxyl groups in the cellulose. The specific nitrogen content of the nitrocellulose determines its applications. In the context of printing ink binders, nitrocellulose typically has a nitrogen content ranging from 10.9% to 11.2% and is soluble in ethanol and isopropanol (Heinze et al., 2012).

Nitrocellulose binders are popular due to their low cost and high gloss (Dave, 2020). However, their susceptibility to thermal degradation is a significant disadvantage, with degradation commencing between 160 and 185 °C and complete degradation occurring at 210 °C (Pourmortazavi et al., 2009; Abd El-Wahab et al., 2020; Devra et al., 2022).

The decomposition of nitrocellulose in the solid phase takes place at temperatures between 140 and 190 °C, slightly below the extrusion temperature of LDPE. This thermal degradation largely involves the dissociation of the CO–NO_2 bond. The degradation process begins with the separation of the O–NO_2 bond, leading to the formation of NO_2. Subsequently, nitroxylated groups are formed as oxidation products and concurrently produce peroxyl groups (Dauerman and Taijima, 1968; He et al., 2017).

In the presence of water, concurrent hydrolysis degradation occurs, resulting in the formation of nitric acid. This reaction can initiate at temperatures around 90 °C. The resultant HNO_3 can catalyze further nitrocellulose degradation, leading to uncontrolled self-heating and potential corrosion of recycling plant machinery.

Thus, nitrocellulose decomposition involves a combination of thermal degradation and hydrolysis. This mechanism is thoroughly reviewed by Wei et al. (2019) based on numerous previous studies summarized in Fig. 3.

An overview of the degradation products of nitrocellulose are listed in Table 2.

2.2 Polyurethane (PU)

PU is a diverse polymer family produced by the polycondensation reaction between isocyanate (hard segment) and polyol (soft segment) (Prisacariu, 2011) Depending on the monomer used, polyurethanes can be further classified as aliphatic, featuring C–H chains or branches, and aromatic, which include cyclic, aromatic groups. For coating applications, various chain extenders are integrated into the PU structure, reacting with isocyanates (typically MDI-methylene diphenyl diisocyanate) to form robust, flexible segments (two-component (2K) structure) (Simón et al., 2018; Liu et al., 2020; de Smet et al., 2022). The incorporation of the aromatic component, which hardens the resin film during drying, is essential (Kousaka et al., 1994; Zhang et al., 2017; Ferreira et al., 2021). However, the aromatic functional group has been identified as a potential source of aromatic amines in food packaging materials (Campanella et al., 2015). According to the EU Commission Regulation 10/2011, aromatic polyurethane can be used in food packaging applications without direct contact (European Commission, 2008). The Polyurethanes for printing ink applications have normally a much lower molecular weight (2000–20000 g/mol) (Ji et al., 2020), compare to thermoplastic polyurethane (from around 1×10^5 g/mol up to 6×10^6 g/mol) (Wang et al., 2015; Xiao and Sue, 2019).

Numerous studies have reported that the thermal degradation temperature of different types of polyurethane ranges from 200 to 300 °C (Dyer and Newborn, 1958; Dyer and Wright, 1959; Grassie and Perdomo Mendoza, 1985; Deng et al., 2021). These studies

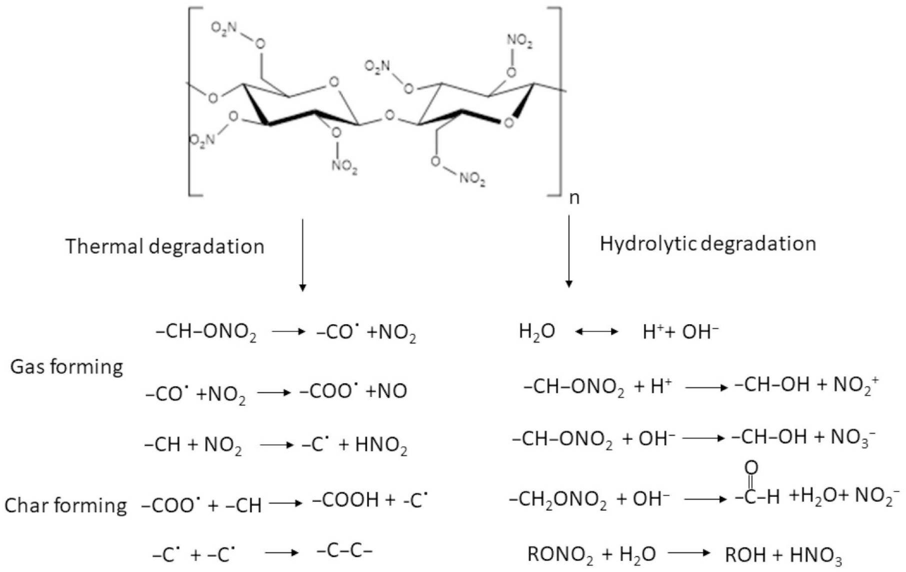


Fig. 3 Thermal decomposition and hydrolysis reactions of nitrocellulose, summarized based on Katoh et al. (2010); Rychlý et al. (2012); Wei et al. (2019).

Table 2 Degradation products of NC, based on Dauerman and Tajima (1968); Wei et al. (2019)

Proportion	Degradation product	Source
Major (> 10%)	NO_2, NO, CO, CO_2, H_2O, char	Klein et al. (1950); MWolfrom et al. (1955); Gelernter et al. (1956); Eyer et al. (2007); Rychlý et al. (2012)
Minor (5%–10%)	HCOOH, HCHO, $(HCO)_2$	Gelernter et al. (1956); Wolfrom and Arsenault (1960)
Trace (less than 10%)	HCN, N_2, N_2O, CH_3CHO, $(H_2C)_2CO$, CH_3=CHCHO, CH_4, H_2C=CH_2, CH_2OH, CH_2CH_2OH, $HCONH_2$	Klein et al. (1950); Wolfrom et al. (1955); Wolfrom and Arsenault (1960); Meyer et al. (2007)

Table 3 Functional groups in polyurethane that possibly degrade under extrusion temperature (Oenema et al., 2022)

Functional groups	Dissociation temperature (°C)
Allophanate	80–120
Biuret	100–125
Urethane	160–200
Urea	140–250

employed the thermal gravity analysis (TGA), only recording the mass loss due to thermal degradation. Other research suggests that weaker C–N bonds (e.g., biuret, allophonic acid begin dissociating at 110 °C, with urethane bond dissociation commencing at 150 °C, leading to random chain scission, and measurable polyether degradation starting from 250 °C (Ravey and Pearce, 1997). The chemical bonds that are unstable under 250 °C are listed in Table 3. Evaluation using chemiluminescence has confirmed the degradation in the 150–250 °C temperature range, which overlaps with the typical extrusion temperatures of PE and PP (Malíková et al., 2010).

In addition to thermal degradation, polyurethane printing ink binders can also undergo hydrolysis, either under acidic or alkaline conditions (Datta and Włoch, 2017). The reaction mechanism is shown in Fig. 4. This hydrolysis is not only an established recycling method for polyurethane but also a potential degradation pathway, so-called "wet-aging" with CO_2 and hydrogen generated as gaseous products (Simón et al., 2018; Barendregt and van den Berg 1980). The ester groups and urethane groups can both be subjected to hydrolysis (Mondal and Martin 2012). There are also polyurethanes using other kinds of polyol without ester groups such as polyether polyol and polycarbonate polyol that are less sensitive to hydrolysis (de Smet et al., 2022). However, the urethane group can still be degraded by the hydrolysis reaction. Typical hydrolysis temperatures range from 150 to 200 °C, with an alkaline environment favoring this degradation. Moreover, carbamate bond hydrolysis represents another polyurethane degradation mechanism. For instance, in a high alkaline concentration of 0.8 mol/L KOH, aliphatic polyurethane can undergo hydrolysis at 40 °C, with alkaline hydrolysis occurring thrice as quickly as acidic hydrolysis (Matuszak et al., 1973).

Previous studies have explored hydrolysis under various conditions. For instance, Gerlock et al. (1980) studied alkaline hydrolysis at 180–260 °C, achieving 87% yield of the monomer toluene diamine (TDA) at 190 °C and 94% yield at 224 °C under 1 atm (Gerlock et al., 1980). In another work carried out by Campbell and Meluch (1976), the degradation also occurred under 1

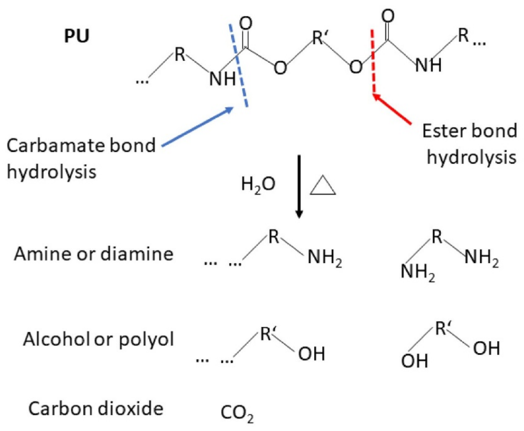


Fig. 4 Hydrolysis mechanism of PU, summarized based on Mondal and Martin (2012); Datta and Włoch (2017).

atm, under temperatures of 232–350 °C. Dai et al. (2002) conducted hydrolysis studies at 150–350 °C. At 250 °C, over 50% TDA yield was obtained in the early reaction stages, while 150 °C required a 30-min retention time to reach the same yield (Dai et al., 2002).

Nonetheless, few studies have examined the hydrolysis of polyurethane during the extrusion process with polyolefin, termed reactive extrusion. At 200 °C, the hydrolysis product from thermoset PU appears powdery. Raising the temperature to 240–280 °C yields a liquid product (Taniguchi et al., 1999a). In a standard extrusion process, barrel pressure fluctuates between 50 and 350 atm, potentially facilitating PU's hydrolysis process (Yang et al., 2012; Motokucho et al., 2018). Residual humidity from 0.5 wt.% can induce PU hydrolysis (Taniguchi et al., 1999b).

Fourier transform infrared spectroscopy (FTIR) is a rapid and relatively low-cost analysis to investigate the degradation of polymer. From different previous studies, we found it is also important to cover the temperature sensitivity of different functional groups in PU under FTIR spectroscopy (Table 4)

2.3 Cellulose acetate derivatives

Derivatives of cellulose acetate, including cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), are typically not utilized alone in the context of printing ink applications. Their principal role is that of co-binders and overprint varnishes (OPVs). To improve their resistance against abrasion and chemicals, cellulose acetate derivatives are occasionally cross-linked (Flick, 1999). For instance, in food packaging, where food contents might contain greasy substances capable of migrating from LDPE or PP packaging and thus softening the printing ink, CAP serves as a base layer between the printing ink constituents and the ink itself (Guo et al., 2023b).

Demonstrating relatively high thermal stability, CAP experiences thermal degradation at temperatures ranging from 300 to 400 °C, as reported by several studies (Carvalho et al., 2010; Huang et al., 2011; Rynkowska et al., 2018). Concerning hydrolytic degradation, the literature lacks direct studies specifically addressing CAP's alkaline hydrolysis. However, as a variant of cellulose ester, hydrolysis reactions can commence at temperatures below 100 °C (Malm et al., 1966; Fischer et al., 2008).

Table 4 Degradation temperature of different functional groups in PU and their accordingly wavelength under FTIR, Summarized by Mondal and Martin (2012); Jiao et al. (2013); Sui et al. (2014); He et al. (2016)

Functional group	Wavelength (cm^{-1})	Degradation temperature (°C)
C–H (benzene ring)	918	280–300
C–N	1220	175
N–H	1531	175
C=C (benzene ring)	1604.4	280–300
C=O	1620	175
C=O	1665	35°C hydrolysis
C=O	1739	175
C=O	1800	175
Isocyanate (–N=C=O)	2274	200 in air, 250 in N_2
Isocyanate (–N=C=O)	2276	RT-200
Isocyanate (–N=C=O)	2280	320–350
CO_2	2340	200 in air, 250 in N_2
Methylene (polyether polyol)	2873	340–360
Methylene (polyether polyol)	2929	340–360
Methyl (polyether polyol)	2979.5	340–360
N–H	3310	175
N–H	3326	100–200
N–H	3389	280–300
Polyol	3600	200 in air, 250 in N_2

2.4 Polyvinyl butyral (PVB)

The thermal oxidative degradation of PVB starts at 70–80 °C and is detected as the accumulation of carbonyl groups and formation of polyenes by infrared (IR) or UV spectroscopy. Noticeable degradation starts at 172–184 °C by mass loss detected by thermogravimetric analysis (TGA) (Ivanov et al., 2014). Another thermogravimetric analysis indicates that PVB's thermal degradation shows a noticeable effect around 260 °C (Dhaliwal and Hay 2002). Notably, PVB is resilient against hydrolytic degradation, primarily attributable to its polymerized carbon-carbon backbone (Herrera et al., 2001; Zhang et al., 2005).

In the realm of coating applications, the PVB used is often cross-linked with isocyanates. This process facilitates the formation of a three-dimensional structure, which enhances resistance against abrasion (Brendgen et al., 2021). The creation of chemical bonds among PVB chains is achieved via the reaction between the isocyanates and the hydroxyl groups (Carrot et al., 2016).

2.5 Polyamide (PA)

PAs have been reported to exhibit thermal stability up to 300 °C. Polyamides such as PA 6, PA 66, or PA 11 are susceptible to hydrolytic degradation under both acidic and alkaline conditions, with degradation primarily occurring through random chain scission (Chaupart et al., 1998).

Although hydrolysis of PA 11 under neutral pH conditions within a temperature range of 90–135 °C has been documented, such reactions necessitate significantly longer experimental durations, exceeding 200 d (Meyer et al., 2002). In contrast, by employing superheated water at 2 MPa, researchers have managed to decrease the average molecular weight of PA by 67%–90% within a 15-min retention time, across a temperature spectrum of 130–210 °C. Substances such as acetic acid, alcohol, and inorganic salts have been found to catalyze this reaction (Wang et al., 2023).

This investigation replicates conditions akin to those experienced during the extrusion process. The outcomes suggest the potential for substantial degradation of polyamide printing ink binders during mechanical recycling processes, a topic warranting further exploration (Hornsby et al., 1996).

2.6 UV-cured acrylate

The main application of UV-cured acrylate is the label for different rigid packaging materials such as bottles or boxes. The structures of the monomer and the cross-linked acrylate induced by UV are shown in Fig. 1 (f).

Similar to the PVB-PA binder resin, cross-linked acrylate also has high thermal stability under typical extrusion temperatures (Czech et al., 2015). The thermal degradation of cross-linked TMPTA polymer starts at around 400 °C (Goswami et al., 2012). However, due to the COOR bond, it can be subjected to hydrolysis degradation, even under room temperature (Suh et al., 2018; Tang and Nozaki, 2022). Introducing the TMPTA-monomer can prompt chain branching and hindering chain scission of polypropylene and increase the melt-flow index (MFI) to up to 10 times (Kim and Kim, 1993; Su and Huang, 2009).

2.7 Colorants

Colorants deliver the desired color of the printing ink, including pigments (solid form) and dye (liquid form). It is possible to apply both variations for plastic printing ink, however, dyes cause bleaching problems due to their water solubility in the recycling process. The pigment is currently the predominant choice for printing ink for plastic packaging. For each color category (i.e., red, yellow, blue), the thermal stability of different colorants is shown in Fig. 5. For the design-for-recycling process of a recycling compatible printing ink, applying thermal-stable pigments is as important as applying thermal-stable binder resin.

Since the pigments are small molecular substances, their thermal degradation can result in the generation of molecules with even smaller substances, these should be considered as contamination for the recycling process. For the thermal stable colorants, a nucleating or anti-nucleating effect is to be expected of the polymers.

Azo-based pigments can be hydrolyzed under either acidic or alkalic conditions (Koh and Kim, 1998; Xie et al., 2023). The upstream recycling process can provide a similar environment for the alkalic hydrolysis, the hydrolysis products have a certain biotoxicity. However, the azo-pigments are currently not in use for the plastic packaging application. For the other kinds of pigments that do not have azo bonds such as PB15:4, PBk 7, or PW:6, lower concerns of their applications in the printing ink should be justified since they are also used for coloring plastics by compounding.

3 The impact of the quality of recycled plastics

The degradation products of printing ink components can potentially affect the quality of recyclates, manifested as discoloration, odor, and polymer degradation, among

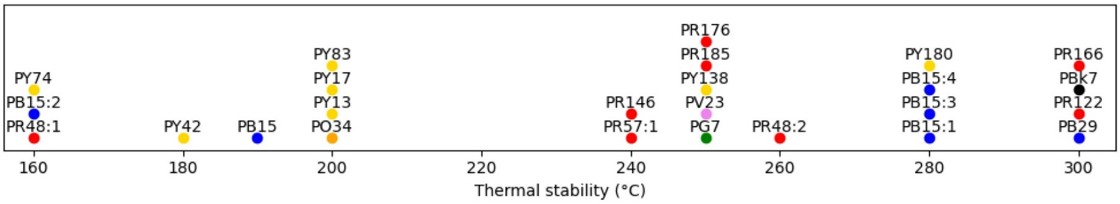


Fig. 5 Thermal stability of different pigments (name demonstrated following the Color Index naming method) applied in printing ink for plastics (P-Pigment, R-Red, Y-Yellow, B-Blue, V-Violet, G-Green, O-Orange, Bk-Black, numbers are the color index (C.I.) numbers), adapted from Guo et al. (2023a).

other effects. It is well known that the degradation of the NC binder system leads to gas formation and results in a brownish hue in the recyclate. Yet, a quantitative assessment of its influence is still to be researched. For other binder systems, potential degradation and its influence on the recyclates' quality are conjectured based on the literature review presented above, focusing on the likely reactions of the binder resin within the process parameters of LDPE film mechanical recycling.

In addition to degradation, the miscibility of these polymers with LDPE introduces another potential complication. Conventionally, different polymers are often immiscible, which alters the properties of the resulting mixture and consequently affects processing parameters such as melting temperature, shear rate, and viscosity-to-volume fraction ratio (Kratofil Krehula et al., 2015; van Puyvelde et al., 2001). Current research on the miscibility of LDPE and other polymers emphasizes polymeric contaminants, such as PP in LDPE. When polyolefin (LDPE, HDPE, and PP) is mixed with non-polyolefin, phase separation is observable even at a 5% non-PO-95% PO blend ratio. This phase separation subsequently modifies the mechanical properties of the blend compared to pure polymers (Demets et al., 2022).

Blend experiments have demonstrated a reduction in the tensile strength of PP by 15% when mixed with 10% cross-linked PU. The reduction in tensile strength exhibited a linear behavior up to 30 wt.%, without the addition of a dedicated compatibilizer like polypropylene grafted maleic anhydride (PP-g-AM) (Taniguchi et al., 1999b). Conversely, the addition of 10% cross-linked PU resulted in a 30% increase in Young's modulus. A 90/10 blend of PP and non-cross-linked polyurethane led to a drop in tensile strength from 35 to 30 MPa, while only a minor decrease in impact strength was reported (Lin et al., 2020).

In a separate study, reactive extrusion was employed to reduce the degree of cross-linking in cross-linked polyurethane. A simple blend of PP/cross-linked PU exhibited lower elongation capacity compared to pure PP. However, blending PP with a cross-linking reduced polymer resulted in a 100% increase in strain at break (Taniguchi et al., 1999a).

In the context of coating and printing ink applications, binder resins are frequently cross-linked, which alters their impact on LDPE recyclates compared to their non-cross-linked counterparts. For example, cross-linked polyurethane coating behaves like a filler when blended with LDPE, increasing LDPE's melt flow index (MFI) by 25%, and reducing tensile and bending strength, while enhancing impact strength. Electron microscopy analysis also revealed poor bending behavior (Kismet et al., 2021).

For cellulose acetate (CA)-based binder systems, various studies have explored blends of cellulose acetate, CAP, and cellulose acetate butyrate (CAB) with LDPE. A 20 wt.% blend of CA, CAP, or CAB with LDPE can increase the tensile strength by around 20%, but these blends demonstrate a significant decrease in elongation at break (Kosaka et al., 2007). It has been reported that CAB is immiscible with LDPE, a characteristic likely shared by CAP due to their similar chemical structures (Wang et al., 2008). However, the blend ratio used in these studies exceeds the typical ratio of printing ink binders to printed substrates.

A research by Gadaleta et al. (2023) investigated the blending of LDPE with low concentrations of plasticized cellulose acetate with triacetin (1–10 wt.%). Their findings indicated a decrease in the melt temperature from 116 to 110 °C, suggesting that cellulose acetate molecules can obstruct the crystallization of LDPE. Mixing cellulose acetate with LDPE can increase the tensile strength of the blend and reduce the elastic modulus, meaning the cellulose acetate derivatives can act as an impact modifier for LDPE (Gadaleta et al., 2023).

Moreover, degradation products could potentially affect the polyolefin polymer itself. These products often contain substances with carboxyl functional groups; potentially initialize further degradation, as illustrated in Eqs. (2) and (3) (Cruz and Zanin, 2003).

$$\mathrm{ROOH} + \mathrm{M}^{2+} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{M}^{3+} + \mathrm{OH}^{-} \tag{2}$$

$$\mathrm{ROOH} + \mathrm{M}^{3+} \rightarrow \mathrm{ROO}^{\cdot} + \mathrm{M}^{2+} + \mathrm{H}^{+} \tag{3}$$

This degradation behavior is relevant for the cross-linked UV-acrylates since the ester bond in the trimethylolpropane triacrylate (TMPTA) can be also subjected to a hydrolysis degradation, releasing the free carboxyl functional groups (Aoi et al., 2023), facilizing the degradation of the PO backbone with the involvement of metal from i.e. processing aggregation, pigment.

To summarize the literatures covered in this chapter, the impacts of different binder resins in the mechanical recycling process on the quality of the recyclates are listed in Table 5.

4 Outlook beyond mechanical recycling

Beyond the scope of mechanical recycling, advanced recycling technologies such as selective dissolution and precipitation, solvolysis, pyrolysis, and gasification emerge as promising supplementary approaches. These technologies offer potential solutions to circumvent existing limitations within the recycling technologies. This section of the review aims to elucidate potential challenges that the chemical structures of printing ink components might face within the reaction environments of various advanced plastic recycling technologies.

4.1 Selective dissolution-precipitation

This technique leverages variating solubility for the

Table 5 Degradation behaviors in extrusion process and potential impact on recyclate quality of common binder resins for plastic printing ink

Binder resin	Degradation behavior	Impact on recyclate quality
NC	Complete degradation	unknown
PU	Partially degradation when humidity involved	Decrease in tensile strength
PVB	No degradation	Slightly decrease the melting temperature and increase the degree of crystallinity Decrease the notch impact strength
UV-acrylics	Partially degradation when humidity involved	Generating more carboxyl groups facilitates the degradation of PO, with an unknown quality impact
CA derivatives	Partially degradation when humidity involved	Decreasing the melt temperature and degree of crystallinity Increasing in tensile strength and decreasing in elastic modulus
PA	Partially degradation when humidity involved	Slightly increase in MFI Slightly decreasing in the degree of crystallinity

different organic solvents to selectively dissolve plastics; subsequently, an anti-solvent is introduced to precipitate plastics (Vollmer et al., 2020; Kol et al., 2021a; 2021b). The primary applications of this method encompass the recycling of polyethylene, polypropylene, and polystyrene. Commonly utilized solvents include toluene, xylene, cyclohexane, and p-cymene, whereas anti-solvents often involve methanol, ethanol, and acetone (Zhao et al., 2018; Walker et al., 2020).

Regarding nitrocellulose, it appears to resist dissolution in solvents like toluene and xylene, although it may be soluble in anti-solvents such as methanol and acetone (Kotter and Groven, 2022). Polyurethane displays solubility in highly polar solvents like water and acetone, but its cross-linked form, produced in the printing process, tends to swell rather than dissolve in organic solvents (Emamikia et al., 2015). Polyvinyl butyral (PVB) demonstrates variable solubility in different organic solvents, both those utilized as solvents and anti-solvents (Carrot et al., 2016). On the other hand, cross-linked acrylics, due to their three-dimensional structure, remain insoluble in organic solvents.

Co-binders based on cellulose derivatives, such as CAP and CAB, exhibit solubility in various alcohols (methanol, ethanol, 1-propanol) and in toluene (Ramanaiah et al., 2011). This suggests that these resins may not be easily separated in the selective dissolution and precipitation process. Nevertheless, it's important to note that binder resins for plastic packaging printing inks are frequently cross-linked, which could reduce their solubility in organic solutions (Ramanaiah et al., 2012). Further experimental investigations are needed to discern the behavior of printing inks in a selective dissolution process.

4.2 Pyrolysis

This advanced recycling method involves the depolymerization of plastics under high temperatures (around 500 °C) in a low-pressure, oxygen-free environment (Ragaert et al., 2017; Vollmer et al., 2020). However, the presence of specific impurities can compromise the quality of the output. For polyolefin, the anticipated pyrolysis products are petrochemical feedstock such as naphtha (Thevenon and Vollmer, 2023). Conversely, other polymers tend to decompose into their monomers (Sun, 1998). It can thus be inferred that printed plastic packaging would likely transform into a mixture of the primary product (e.g., diesel or naphtha) and diverse monomers originating from the printing ink resins. This scenario may necessitate additional purification steps, such as distillation (Thahir et al., 2019; Baena-González et al., 2020; Lee et al., 2021).

An overview of the potential pyrolysis products of different print ink binder resins is presented in Table 6.

5 Printing ink design and industrial recycling process

This review covers the potential degradation and side reactions of the printing ink binder and pigments for

Table 6 Possible reaction conditions and products of binder resins except nitrocellulose (NC) in pyrolysis process

Binder resin	Degradation products	Reaction condition	Source
PU	Gas including H_2, NH_3, H_2O, CO, and CO_2, nitrogen-containing hydrocarbons (i.e., nitrile), high molecular compounds including polyaromatics, polyesters, polyethers, etc.	Various, above 250 °C	Oenema et al. (2022)
PVB	Acetic acid, butanoic acid, furan,butanal, butenal, butanol	360–450 °C	Liau et al. (1996)
PA	Caprolactam, hydrocarbons, and *N*-Containing hydrocarbons,	400–600 °C, 1–1.15 bar with Zeolite catalyst	Bockhorn et al. (2001); Zakharyan and Maksimov (2022)
Acrylics	Different tertiary ether, ketone, alcohols, and acrylate monomers	400 °C	Matsubara et al. (2002); Belbakra et al. (2021)
Cellulose acetate derivatives	CO, CO_2, methyl acetate, butyric acid, methyl butyrate, ketene, acetaldehyde, CAB oligomer	400–600 °C	Gongwer et al. (1997)

plastic packaging. As long as there is no universal de-inking process with a higher technical readiness level (TRL) that can remove all the different kinds of common printing ink for plastic packaging. The input stream for recycling will be with printing ink binders mixed inside as contamination, regardless of with recycling process applied. Currently, the most applied recycling technology is the mechanical recycling by extrusion. Therefore, this study focused on the potential reactions of the printing ink components under the extrusion temperature. The humidity from the washing process is an unignorable part since it facilitates the degradation by hydrolysis. The outcome of this review can assist the synergy between the printing ink producer, packaging developer, and recyclers to avoid contamination from the printing ink on the packaging surface either by applying a thermal-stable ink or applying a de-inkable printing ink with an extra de-inking process.

6 Limitation of this review

This review covers the literature on the degradation behavior of the different printing ink resins, both under the ideally "dry" condition and the "wet" condition with the potential involvement of water (in an industrial recycling process from cleaning). One limitation acknowledged by the author during the review processes is the polymers investigated in the covered literature were not for the printing ink binder application, but for i.e., coatings or serve as blending or impurities. Given the similarity in the chemical structures, the degradation behavior can be derived and serve as a hypothesis for further experimental works, which will be carried out by the authors.

7 Conclusions

Printing ink is an essential component in contemporary packaging design. However, its effect on the recycling process necessitates thoughtful consideration during package conception. The behavior of the widely used nitrocellulose (NC) binder under mechanical recycling conditions is well understood. Nitrocellulose mainly goes under thermal decomposition during the mechanical recycling process (extrusion). Yet, for other alternative binder systems, thermal degradation during polyolefin recycling extrusion temperatures is often negligible. Residual humidity from the cleaning process upstream of extrusion might facilitate hydrolytic degradation of polyurethane, polyamide, or cellulose acetate derivatives. The degradation effect can include depolymerization and reduction of cross-linking rate. However, both undegraded printing ink binders and their degradation products could possibly change the quality of the recyclates. Even when advanced recycling technologies are implemented in the future, the printing ink can remain a source of contamination in the recycled product (recycled plastic or oil from pyrolysis). The findings from this literature review work can serve as a decision-making basis for the design of plastic packaging printing ink for the printing ink producers in order to facilitate the inclusion of printing ink into the "design-for-recycling" principle. Nonetheless, more research is needed to ascertain the rate of degradation of printing ink binder resins and its influence on the overall process also in different chemical recycling processes.

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