Waste Polymethyl Methacrylate (PMMA): Recycling and High-Yield Monomer Recovery

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Contents

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Abstract

In recent years, the production and consumption of polymethyl methacrylate (PMMA), an expensive versatile polymer, are widely increased for its superior properties. The extensive use of this material leads to the major concern on management of the waste PMMA and how to recycle it. Approaches to PMMA recycling mainly include different methods for depolymerization of the polymer to recover MMA monomer and then either re-polymerization of the recycled monomer or other utilization of the recycled products. In this chapter, a general background on different processes used for PMMA recycling and the employed apparatus for recycling is presented. Chemical recycling of PMMA with different methods such as gasification, thermal cracking, and catalytic cracking is discussed. Solvent recycling of PMMA is illustrated as well. The features of the main apparatuses of waste PMMA recycling are explained in detail including molten media bath reactor, fluidized bed reactor, conical spouted bed reactor, and extruder. Thermal and mechanical analyses on recycled products are provided in order to enlighten the properties of the recovered material produced through different recycling processes. The effect of fillers as reinforcing agent on recycle process of waste PMMA and also the process of filled PMMA recovery is illustrated. In the end some applications of recycled PMMA in fabrication of nanocomposites and polymeric blends are given. Thus this study paves way to new advances for PMMA waste generation and management while solving many environmental problems.

Introduction

In last decades, the growing production of plastics has resulted in increasing the amounts of waste streams attributing myriad environmental problems. Several feedstock recycling technologies such as degradation, gasification, and pyrolysis processes have been successfully employed for plastics on semicommercial scale. Feedstock recycling is one of the greatest challenges for the recycling of plastics, and various technologies have been successfully introduced and continue to be developed. Poly methyl methacrylate (PMMA) is a versatile transparent thermoplastic due to its excellent properties (transparency, lightness, and safety) that is used in a wide range of applications, such as in the lenses of exterior lights of automobiles, electronics, food containers, and artificial marble [1]. In recent years, the production and consumption of PMMA have increased significantly, for example, annually in Europe 300 Mkg of PMMA is produced. The market size of PMMA is projected to reach USD 8.16 billion by 2025 according to Grand View Research, Inc., registering compound annual growth rate (CAGR) of 7.5% during the forecast period (2016–2025) [2]. PMMA is a relatively expensive polymer compared to standard plastics. Its average price in the world market is about 3 €/liter in accordance with BASF data [3]. As mentioned, there are many applications for PMMA in the course

of which considerable amount of waste polymer may be obtained. Therefore how to recycle PMMA with high efficiency is still a controversial issue demanding profound investigation.

Recycling Methodologies of Waste PMMA

Today the main negative consequence associated with the wide use of polymer materials, reflecting changes in production methods and consumption opportunities, is how to treat with plastic waste in order to minimize their environmentally destructive effects. The solution of this problem indeed includes a large-scale use of the various recycling techniques illustrated in Scheme 1 [4].

From the diagram, it could be noted that the main approaches having been proposed for recycling of waste polymers are categorized as follows:

Primary recycling or reuse: This process, mentioning the "in-plant" recycle of scrap material, remains the most popular as it provides simple and low-priced method. It associates however only with the recycling of clean uncontaminated single-type waste polymer.

Mechanical recycling: This process accomplished whenever the polymer is separable from its related contaminants. Here the polymer can be readily reprocessed into granules by conventional melt extrusion. Mechanical recycling involves an array of stages including separating and seizing of the wastes, decreasing the size of the particles, and filtering the obtained melt. As the main drawback of this type of recycling, the deterioration of product properties after every cycle is inevitable.

Chemical or feedstock recycling: This approach encompasses the transformation of polymeric materials into a diverse range of products including initial monomers,
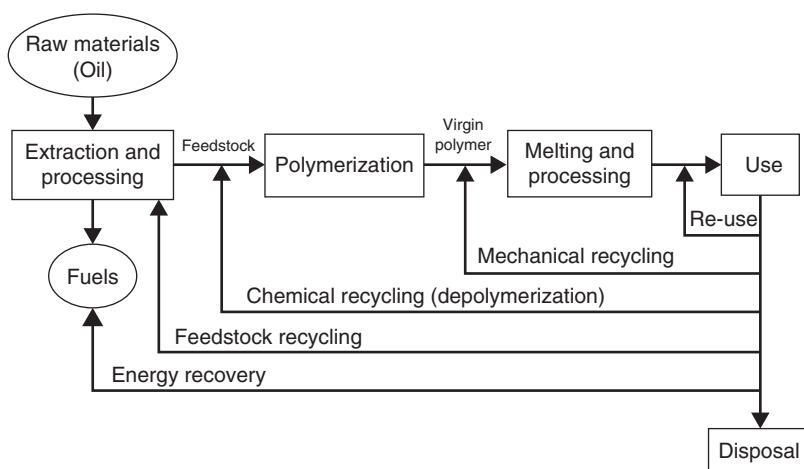
Scheme 1 Industrial ecology of polymeric materials [4]

oligomers, or mixtures of other hydrocarbon compounds employing heat or chemical agents.

Energy recovery: This method utilized ignition of polymers to decrease the volume of organic materials. Despite the fact that polymers are actually high-yielding energy sources, this method has been utterly accused as ecologically unacceptable approach due to the high health risk from air polluted by toxic substances, e. g., dioxins (in the case of the polymers containing chlorine in their structure) [5]. In the following section, the main methodologies to recycle PMMA waste will be discussed.

Chemical Recycling

PMMA recycling based on the laws of recycling and regulations was being investigated through processes on a plant for collecting, sorting, and processing of electronic devices containing PMMA. It is necessary to be mentioned that the so-called recycling systems involves collection, logistics, and other processes as well as recycling process [6, 7]. Among all methods of recycling, chemical recycling is of a great interest due to its ability to the basic monomer of the solid wastes of different polymers. The most important processes for the chemical recycling of waste PMMA material are categorized to gasification processes, pyrolysis, and blast furnace process of Bremer Stahlwerke [8].
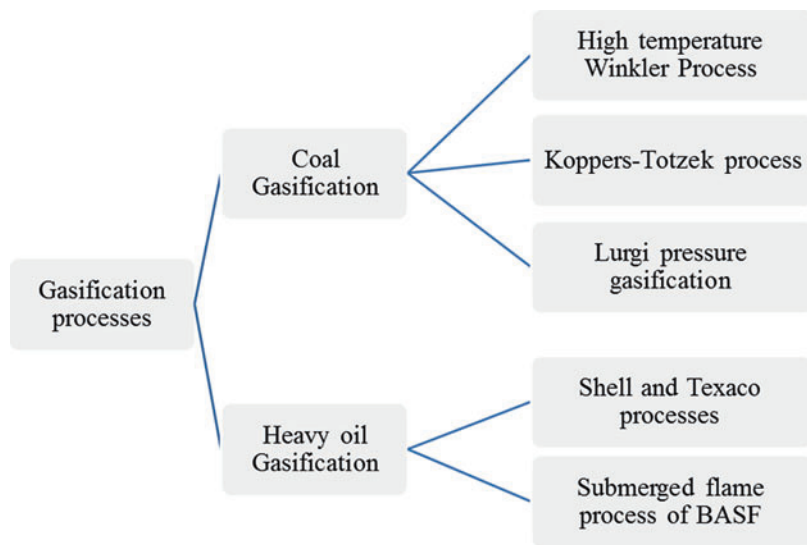
Gasification Process

Gasification is a partial oxidation of hydrocarbons with an oxygen quantity which is understoichiometrical with respect to total combustion. The main object of this process is to obtain synthesis gases including H_2, CO as product, and some by-products like CO_2, H_2O, CH_4, and soot. Depending on the process applied, the gasification agents (oxygen, air, flue gas, steam, and carbon dioxide) can be used separately or in combination. The reaction is mostly conducted at elevated temperatures and pressures, i.e., 1500 °C and 150 bar, respectively [8]. Various types of gasification processes are categorized in Scheme 2.

Alibert et al. studied the effect of oxygen concentration in the range of [18.0–21.0%] during gasification process of horizontally oriented slabs of PMMA. According to Fig. 1, they observed that time-averaged quantities including mass loss rate (Fig. 1a) and heat fluxes (Fig. 1b), and at a lesser extent gas temperature (Fig. 1c), remarkably decrease with oxygen concentration. Physically speaking, the decrease in oxygen concentration results in a decrease in soot production and gas temperature, which, in turn, affects the heat feedback from the flame to the fuel surface, thereby reducing the mass loss rate and heat flux amount [9].

Thermal Cracking (Pyrolysis)

Pyrolysis is very well-known process to obtain a high-quality product for recycling process of polymer wastes. Pyrolysis, also known as thermal cracking, involves the degradation of the polymeric wastes using heat in the inert environment in the

Scheme 2 Various types of gasification process [8]

absence of oxygen (commonly in a nitrogen atmosphere). The products of pyrolysis range from the monomer in a large amount or other secondary products; products similar to crude oil, depending on polymer type, either end-chain or random scission of the macromolecules occur when the waste polymer undergoes high temperature. The process temperature (usually in low-temperature pyrolysis) is 350–600 °C, and above all, the type of the reactor is decisive for the product selectivity leading to obtaining a high-quality material. Thermal decomposition of poly methyl methacrylate to methyl methacrylate monomers was proved to occur at high temperatures about 220–230 °C, while at lower temperatures polymerization reaction outweighs. The flow diagram of the pyrolysis process in the presence and absence of circulated cooling water is illustrated in Scheme 3 [7].

The depolymerization reaction of PMMA is a radical depolymerization where the chain backbone is decomposed by a radical reaction mechanism. The main reaction product is the monomer, followed by other gaseous and liquid fragments which will be discussed in the following sections in detail [10].

Mechanism of the Thermal Decomposition of PMMA

The pyrolytic conversion of PMMA into its monomer occurs according to radical process mechanism. Unzipping mechanism, including propagation reaction, monomer release, and termination reaction, forms primary radical which generates unsaturated polymer chains. These less stable chains further decompose at lower temperatures. Two radicals, the isobutyryl macromolecule radical and the primary macromolecule radical, are formed with random chain session of polymer by means of heat [8]. Consequently, each radical is then degraded by the repeated elimination of monomeric units. MMA monomer is then yielded from degradation of isobutyryl
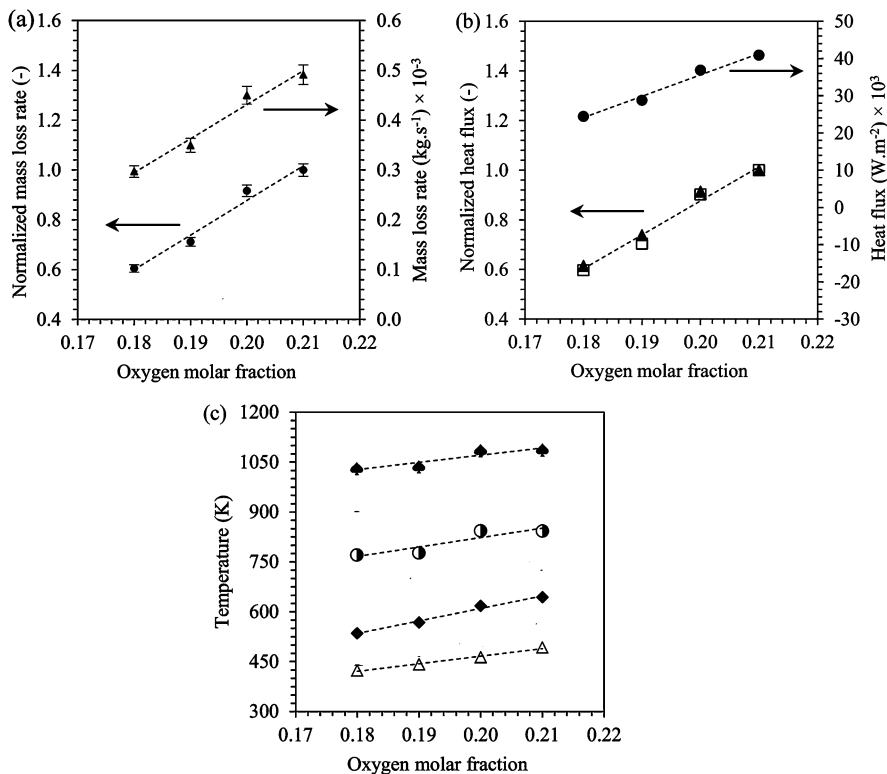
Fig. 1 (**a**) Right-averaged mass loss rate (MLR) (▲ experimental results, - - - linear fit) and left-normalized MLR by $\frac{\text{MLR}_{X_{O_2}}}{\text{MLR}_{21}} = 13.9 X_{O_2} - 1.9$ (● experimental results, - - - linear fit vs. oxygen molar fraction). (**b**) Right-average heat fluxes (• total, ◇ radiative, - - - linear fit) and left-normalized average heat fluxes (□ total, ▲ radiative, - - - linear fit vs. oxygen molar fraction). (**c**) Averaged gas temperature versus the oxygen molar fraction at different heights (♠ 0.05 m, ◑ 0.15 m, ♦ 0.3 m, △ 0.5 m, - - - linear fit) [9]

macromolecule radical. Also, the primary macromolecule radical becomes iso-butyryl macromolecule radical via a PMMA molecule with a methallyl end group and is then degraded to produce an MMA unit [8]. Thus, the degradation of PMMA is claimed to result in a high yield of MMA. Briefly, an endothermic radical chain reaction, unsaturated chain ends, or completely saturated chains are the results from the radical depolymerization of PMMA (Fig. 2 according to [11, 12]). The activation energy of the depolymerization was found to be 105 J mol^{-1} [13]. Lower MMA yield in waste PMMA degradation in comparison with pure PMMA can be due to lower stability of secondary radicals formed during waste PMMA degradation than tertiary radicals formed in pure PMMA degradation [14].

During the depolymerization process, addition of mercaptans is an effective approach to thermally stabilize the product by saturation of unstable double bonds. Moreover, some suitable comonomers such as methyl acrylate (MA) can act as
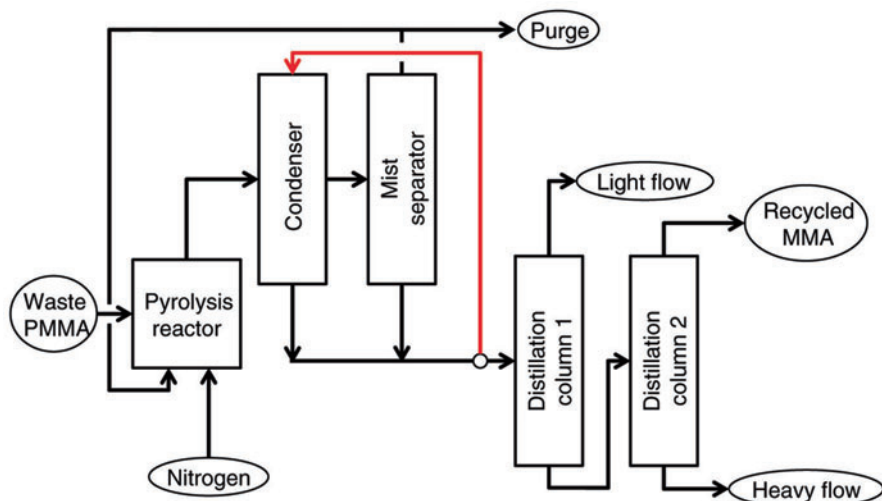
(a) Without circulated cooling water
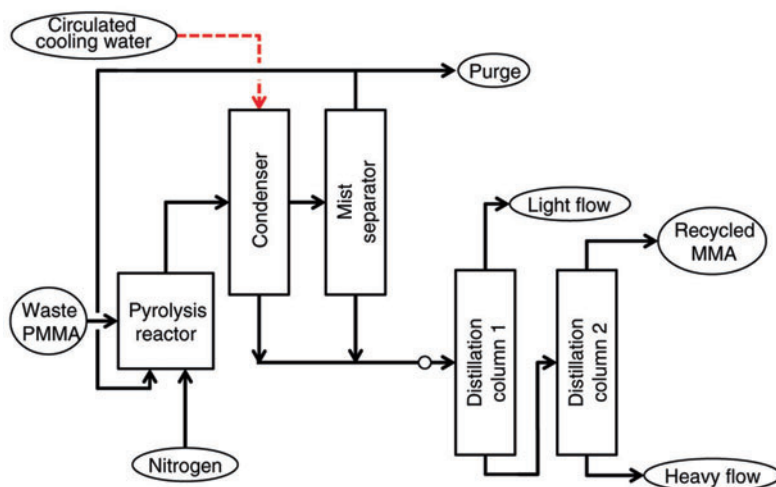
(b) With circulated cooling water

Scheme 3 Recycle of PMMA via pyrolysis method [7]

stabilizer in depolymerization behavior of acrylic polymers. An increasing portion of MA in the polymer diminishes the portion of MMA released by reaction on terminal double bonds. Additionally, a blocking effect of the MA units on the depolymerization reaction in the chain backbone is postulated. The portion and type of the comonomer, the addition of mercaptan, and the molecular weight of the polymer are the main factors which affect thermal depolymerization. Other influencing factors are cross-linking, pigments, and dyeing of the polymer [8].
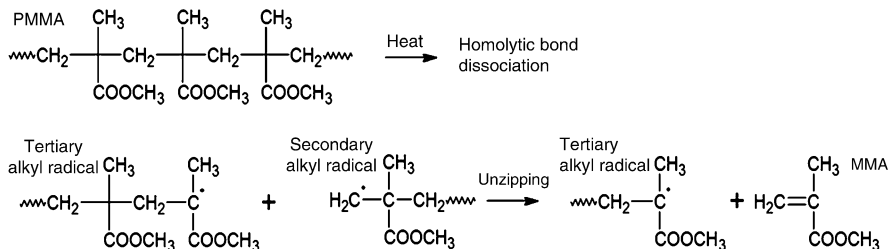
Fig. 2 Thermal depolymerization mechanism of PMMA [11, 12]

Kinetics of the PMMA Thermal Depolymerization Reaction

Thermal degradation of waste plastics is an efficient replacement to traditional methods of recycling. Vessels, autoclaves, rotary kilns and fluidized bed are some reactors that are used in the thermal degradation of wastes. Therefore PMMA thermal degradation can be considered as an economical recycling process due to its behavior on yielding the MMA monomer. Molten metal baths, extruders, and fluidized bed reactors are the ones used in the process of PMMA degradation. PMMA decomposes to MMA at temperatures 220–230 °C, whereas at lower temperatures polymerization process occurs predominantly. Gas and monomers are the main products for this decomposition which is a heterogeneous reaction. Table 1 shows different mechanisms depending on the molecular weight and temperature. These mechanisms were presented by Barlow et al. (1967) [15]. By assumption of no mass or heat transfer restrictions, reaction rate can be measured by the following equations [16].

The intrinsic reaction constant k_m is a function of the temperature according to the Arrhenius Eq. 1:

$$k_m = A\exp\left(-\frac{E_a}{\mathrm{RT}}\right) \tag{1}$$

with A, the Arrhenius factor ($1/s \cdot (m^3/mol)^{ni-1}$), and E_a, activation energy (J/mol). Table 2 shows the activation energy of the overall depolymerization reaction which obtains from the activation energy of the elementary reaction steps [16].

Kang et al. investigated thermal degradation of PMMA using thermal gravimetric analysis (TGA). The TGA curve for the thermal degradation of the two categories of waste PMMA, the automobile taillight lens and the light guide plate, is given in Fig. 3. The fractional conversion is as follows:

$$x = \frac{(m_0 - m)}{(m_0 - m_\infty)} \tag{2}$$

in which m_0, m_∞, and m are the initial sample weight, the residual weight at infinite time, and the residual sample weight at time t. It was shown that in both waste PMMA samples the temperature range where weight loss occurred moved to a

Table 1 Mechanisms for the depolymerization steps of PMMA [16]

Elementary reaction steps	Intrinsic reaction rate equations	Conditions
Mechanism 1		
Random initiation, followed by complete depropagation	$R_P = -2k_{ir}x_0C_P$ $R_M = 2k_{ir}x_0^2C_P = k_mx_0^2C_P$	High temperatures (430–460 °C) and small chain length (D_p, 105–570)
Mechanism 2		
Random initiation, depropagation, and termination by disproportionation	$R_P = 2k_{ir}xC_P$ $R_M = 2k_d\sqrt{\frac{k_{ir}x}{k_{td}}}C_P^{1/2} = k_mC_P^{1/2}$	High temperatures (430–460 °C) and small chain length (D_p, 570–2970)
		Moderate temperature (400–430 °C)
Mechanism 3		
End initiation, depropagation, and termination by disproportionation	$R_P = 0$ $R_M = k_d\sqrt{\frac{2k_{ie}}{k_{td}}}C_{P0}^{1/2} = k_mC_{P0}^{1/2}$	Low temperatures (330–400 °C)

Table 2 Activation energies of depolymerization steps of PMMA from theoretical equations [16]

	K	E_a (activation energy)
Mechanism 1	k_{ir}	$E_{ir} = 287$kJ/mol
Mechanism 2	$k_d\sqrt{\frac{k_{ir}}{k_{td}}}$	$E_d + 0.5(E_{ir} - E_{td}) = 190$kJ/mol
Mechanism 3	$k_d\sqrt{\frac{k_{ie}}{k_{td}}}$	$75E_d + 0.5(E_{ie} - E_{td}) = 75$kJ/mol
With $E_{td} = 12$kJ/mol, $D_R = 275$kJ/mol, $E_d = E_{ie} = 54$kJ/mol		
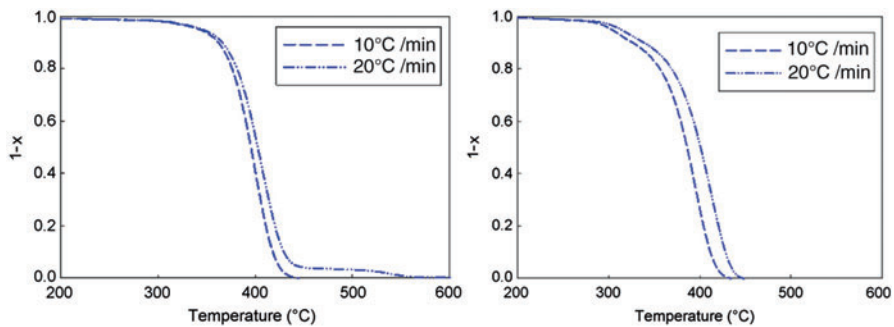
Fig. 3 The TGA curve for the thermal degradation of the waste PMMA: (right) the automobile taillight lens, (left) the light guide plate [14]

higher-temperature region as the heating rate increased. The main thermal degradation was observed at the temperature range of 350–450 °C [14].

Differential thermal gravimetry (DTG) curves were used for analysis of weight losses. They applied two models, the Chatterjee-Conrad (CC) and Freeman-Caroll (FC) to determine the pyrolysis kinetic parameters. The differential method (CC) and the difference method (FC) were used to obtain the kinetic parameters as follow [14]:

$$\frac{dx}{dt} = \beta \frac{dx}{dT} = Ae^{-E_a/RT} f(x) \tag{3}$$

R is the gas constant, T is the temperature, t is the time, and f(x) is the model function. $dT = \beta dt$, if β is the constant rate of heating. FC method was used to analyze the DTG curves, because this method is providing parameters such as (n, E, and A). So it is required to integrate the equation below [14]:

$$\int_0^x \frac{dx}{(1-x)^n} = \int_0^T \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT \tag{4}$$

T_0 is assumed zero, due to the fact that is it very low compared to pyrolysis process temperature. For convenience, $u = -E_a/RT$, therefore Eq. 2 becomes:

$$\frac{1}{1-n}(1-x)^{1-n} = \frac{AE}{\beta R} p(u) \tag{5}$$

in which $p(u) = \int (e^u/u^2) du$. To calculate $p(u)$, for which there was no analytical solution, Lyon's approximation, $p(u) = e^u/(u(u-2))$, was applied. Since $T_0 = 0$, the $p(u)$ at low temperatures can be neglected. Lyon's approximation shows the fractional conversion, x [14]:

$$x = 1 - \left(\frac{AE_a}{\beta R} \frac{e^u}{u(u-2)}(n-1) + 1\right)^{1/1-n} \tag{6}$$

Statistical studies showed that both models simulated the experimental DTG curves fairly well. For instance, theoretical and experimental DTG results of waste PMMA depolymerization at heating rate of 10 °C/min are given in Fig. 4 [14].

Table 3 shows the parameter which is obtained from CC and FC methods according to the above equations [14].

The mass balance of depolymerization of three grades of PMMA (virgin, waste automobile taillight lens, waste light guide plate) via pyrolysis showed that the main product was oil with the yield amounted of up to 99 wt%. Also, data revealed that increasing the reaction temperature caused the oil production to reduce slightly. At 440 °C, the gas production was about 3% wt, whereas at higher temperatures (more than 500 °C) the pyrolysis reaction resulted in higher gas production. The product predominantly composed of CO, CO_2, CH_4, and other hydrocarbons where CO

Fig. 4 Theoretical and experimental DTG results of waste PMMA depolymerization with CC model at heating rate of 10 °C/min [14]
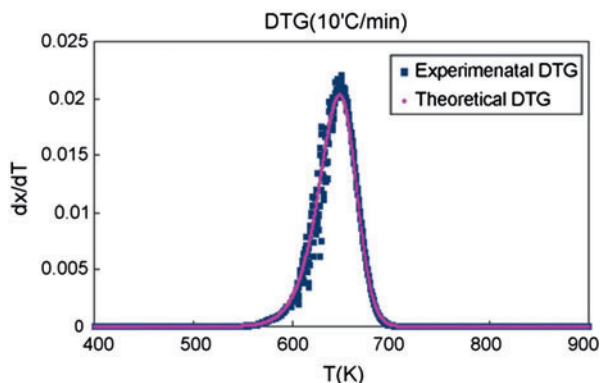
Table 3 Apparent kinetic parameters for the thermal degradation of PMMA using CC and FC models [14]

Method	Heating rate (°C/min)	Activation energy (J/mol)	ln A (min^{-1})	Reaction order, n
Chatterjee-Conrad method	5	102,461	18.11	1
	10	118,494	21.34	1
	15	103,822	18.91	1
	20	139,502	25.36	1
Freeman-Caroll methods	5	331,594	61.73	1.67
	10	206,334	37.75	1.25
	15	263,484	48.40	1.42
	20	256,948	47.00	1.39

and CO_2 stemmed from the oxygen constituent in PMMA. Quantitative and qualitative analysis presented in Table 4 shows the amount of each component of the produced oil. This data was obtained from the GC-MS (gas chromatography-mass spectrometry). The main component, which amounted to up to 98 wt%, was MMA [14].

Catalytic Cracking

Thermal cracking of the polymers usually requires time and high temperatures which reduce the economic efficiency of the process. Catalytic cracking employs catalysts in the pyrolysis reactor to overcome these drawbacks by effectively decreasing the temperature required for cracking and for modifying product distribution as well [17]. While thermal cracking is governed by free radicals, catalytic cracking proceeds through the formation of ionic species on the surface of catalyst resulting in formation of shorter and branched-chain products. The leading advantage of catalytic cracking is to yield of more useful fractions in comparison with conventional thermal cracking [18]. The only difference of catalytic cracking with thermal cracking is the presences of catalyst during recycle process. Thus, various types of catalysts have been applied for the cracking process to achieve fast cracking

Table 4 GC analysis of depolymerization products of PMMA via pyrolysis [14]

wt (%)	Virgin PMMA				Waste PMMA (automobile taillight lens)			Waste PMMA (light guide plate)			
	440 °C	450 °C	460 °C	470 °C	450 °C	470 °C	500 °C	450 °C	470 °C	480 °C	500 °C
MA	1.76	1.41	1.83	1.69	1.39	1.31	1.67	0.96	1.27	1.07	1.05
MMA	97.3	96.78	97.23	96.30	96.59	95.65	96.53	97.29	96.38	96.96	96.76
Methyl isobutyrate	0.20	0.18	0.23	0.20	0.24	0.25	0.36	0.17	0.18	0.16	0.22
Ethyl acrylate	–	–	–	–	0.57	0.77	0.16	–	–	–	–
Butyl acrylate	–	–	–	–	–	–	–	0.18	0.24	0.23	0.25
2-Butenoic acid methyl ester	–	–	–	–	–	0.20	–	–	–	–	–
Methylene-butanedioic acid dimethyl ester	–	–	–	–	0.18	0.33	–	–	–	–	–
1,2-Cyclopentanedicarboxylic acid dimethyl ester	0.30	0.27	0.31	–	0.29	0.40	0.37	–	0.30	0.20	0.22
2-Methyl-3-furancarboxylic acid methyl ester	0.22	0.30	–	–	0.22	–	–	–	–	–	–
2,5-Diethylthiophene	–	–	–	–	0.14	–	–	–	–	–	–
Methacrylic acid ethyl ester	–	0.19	–	0.21	–	–	–	0.18	0.19	0.17	–
Diethyl phthalate	–	0.27	–	0.30	–	0.33	–	–	–	–	–
1-Naphthalenecarboxylic acid methyl ester	–	–	–	–	–	–	–	0.26	–	–	–
Cyclopropanecarboxylic acid methyl ester	–	–	–	–	–	–	–	–	0.29	–	0.20
2-Naphthalenecarboxylic acid methyl ester	–	–	–	–	–	–	–	–	–	0.22	–
Benzene	–	–	–	–	–	–	–	–	–	–	0.15

reactions with improved quality products at low reaction temperatures. Also using shape selective catalyst can control product's distribution which results in a narrow product range. The optimal process optimizes the quantity of the required catalyst and thereby minimizing the costs of the process [19].

In catalytic cracking, simultaneous reactions such as dealkylation, isomerization, condensation, etc. occur via carbocations. One classical carbenium ion which can be described as a protonated cyclopropane structure is transformed into the key intermediate which was been formed by acid catalyzed activation reactions. Two groups of different catalysts, homogeneous catalyst and heterogeneous catalyst, are used in this reactions that among those, heterogeneous catalysts are more popular due to their easy separation and recovery from the system. Some of these catalysts are listed below:
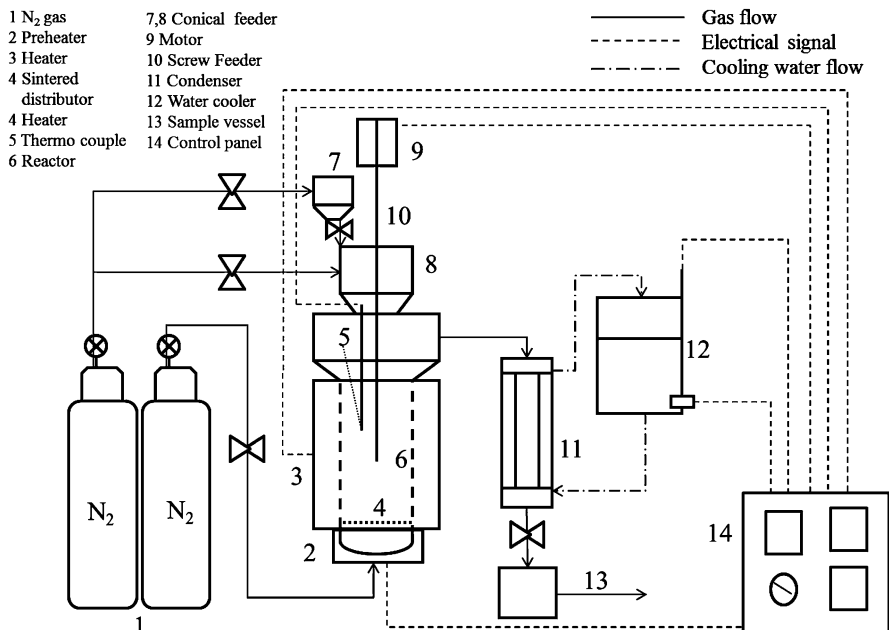
– Acid solids: zeolite, silica-alumina, alumina, fresh, and spent FCC catalysts.
– Mesoporous structured catalysts: MCM-41, FSM-16, and Al-SBA-15.
– Aluminum pillared clays.
– Nanocrystalline zeolite: n-HZSM-5.
– Super acid solids: ZrO_2/SO_4^{2-}.
– Gallosilicates.
– Metals supported on carbon.
– Basic oxides: BaO, K_2O, etc.
– The list is copied and pasted [19].

Khangkham et al. used zeolites, the most frequently used catalysts for degradation, for catalytic cracking of PMMA. The schematic diagram of continuous catalytic degradation unit is given in Fig. 5.

GC-MS data (Table 5) analyzing the chemical composition of the products from degradation of PMMA in the batch experiment showed that the MMA content in the liquid product is over 93% wt. and also the gas product is mainly MMA monomer. Temperature was also proved to be one of the influencing factors in every cracking process. Thermal degradation of PMMA at 320 °C only produces non-condensed gases and jellylike solid residue. By reducing the time and reaction temperature, zeolites as catalyst can enhance the degradation of PMMA where acid sites and acid strength of catalyst mainly control the product yield. For PMMA degradation using zeolite catalyst, the highest product yield was at 270 °C which appeared to be the most convenient reaction temperature. Moreover, the observations showed that product yield isn't significantly affected by the feed rate of PMMA [19].

Solvent Recycling or Dissolution/Reprecipitation

In 1994, solvent recycling is suggested by Papaspyrides [20] as an effective measure in order to achieve desired mobility to separate the additive contained in the waste polymer. The model process presented there belonged to the category of direct recovery of polymer keeping its structure intact. It was involved an array of steps

1 N$_2$ gas   7,8 Conical feeder
2 Preheater   9 Motor
3 Heater   10 Screw Feeder
4 Sintered   11 Condenser
   distributor   12 Water cooler
4 Heater   13 Sample vessel
5 Thermo couple   14 Control panel
6 Reactor

—————— Gas flow
- - - - - - Electrical signal
—·—·—· Cooling water flow

Fig. 5 Schematic diagram of continuous catalytic degradation unit used for PMMA recycling [19]

Table 5 Composition of products from continuous catalytic PMMA with zeolite analyzed by GC-MS [19]

	Temperature (°C)	Yield (wt.%)	MMA content (%)
Liquid	270	23.5	93.7
	280	9.4	93.4
	290	4.8	93.3
	300	6.2	93.7
Gas	270	N/A	60.7

including dissolution of the starting waste material, reprecipitation, washing of the product of reprecipitation, and finally drying. As mentioned, the optimal dissolution/reprecipitation process keeps the polymer structure intact and removes all the impurities and defective materials such as degradation sites and contaminations. Not deniable is the necessity of investigation on many factors as prerequisite for the technical optimization of the solvent recycling process needed to be applied to get high-quality end products such as the rheology of the polymer solutions involved and the characteristic properties of the recycled material including solvent and additives residual trace, maintenance of melt flow rate, and mechanical performance. Various combination of solvent/nonsolvent was applied to recycle PMMA molding

compound via the proposed method to develop a "selective dissolution" approach. They proved that toluene/n-hexane is the most satisfactory solvent/nonsolvent system considering the following four criteria: (a) appropriate precipitation of the polymer, (b) high concentration of "waste," (c) high volume ratio of maximum solution/nonsolvent, and (d) high recovery extent of PMMA, solvent, and non-solvent [20].

They tested various kinds of solvents for the recycling of PMMA including toluene, xylene, and acetone, as well as some nonsolvents such as water, methanol, and n-hexane proceeding two different experimental procedures, miscible solvent/nonsolvent system (procedure I) and two-phase solvent/nonsolvent system (procedure II). In the former, the vessel was charged with the PMMA solution, and then nonsolvent was added gradually during stirring (represented by Add-A) while the reverse, i.e., addition of the solution to the nonsolvent (represented by Add-B). After the precipitation, the polymer was obtained by filtering under vacuum and then dried overnight. The solvent and the nonsolvent were recovered by separation of their mixtures in a distillation column. In the latter, the reaction vessel contained the nonsolvent which now is water plus 0.1% of two different dispersion agents (PVA 4–98 and gum tragacanth). In procedure II the solvent/water systems tested provided a minimum boiling azeotrope. The solution was dispersed into the nonsolvent phase while stirring, and then the system was heated for distillation of the two-phase azeotrope mixture. Two-phase distillate product was collected, and polymer was precipitated in the phase of almost pure water. The organic solvent was recovered from the distillate product by simple decantation. The results of solvent recovery via the aforementioned procedures are tabulated in Table 6. Miscible solvent/nonsolvent systems' results quote that precipitation of the polymer in the form of granule occurs when solution of PMMA in toluene or xylene is added to n-hexane as nonsolvent using Add-B mode, at either 20 °C or 50 °C, while polymer was always precipitated in an agglomeration form using two-phase solvent/nonsolvent systems [20]. Miscible solvent/nonsolvent system of toluene/n-hexane was also successfully employed by Gouli group for solvent recycling of PMMA decorative sheets and reported that the PMMA polymer was completely recovered in the form of granules with acceptable solvents yields [21].

Recycling Apparatuses of Waste PPMA

Monetary saving from recycling polymers typically fall in the in the ~40 to 90% range depending on the grade and type of polymer as well as the recycling methodology [22]. Appropriate recycle apparatus should result in a material significantly cheaper than virgin one minimizing property deterioration during recycle process. In this section, technologies available for recycling PMMA plastic solid waste into products, as well as state-of-the-art apparatus with their designs, will be discussed.

Table 6 Solvent recovery of PMMA via two procedures: miscible solvent/nonsolvent system (procedure I) and two-phase solvent/nonsolvent system (procedure II) [20]

Nonsolvent	Miscible solvent/nonsolvent system (procedure I)				Miscible solvent/nonsolvent system (procedure I) miscible solvent/nonsolvent system (procedure I)			
	Solvent							
	Toluene				Xylene			
	20 °C		50 °C		20 °C		50 °C	
	Add-A	Add-B	Add-A	Add-B	Add-A	Add-B	Add-A	Add-B
Methanol	JL	JL	–	–	E	JL	E	–
n-Hexane	JL	G	JL	G	JL	G	A	G

Nonsolvent	Miscible solvent/nonsolvent system (procedure I)				Two-phase solvent/nonsolvent system (procedure II)		
	Solvent				Nonsolvent	Solvent	
	Acetone					Toluene	
	20 °C		40 °C			20 °C	
	Add-A	Add-B	Add-A	Add-B		Add-B	
Methanol	JL	JL	JL	–	Water	A	
n-Hexane	EA	GA	EA	–			
Water-PVA 498	JL	GA	JL	–	Water-PVA 498	A	
Water-gum tragacanth	JL				Water-gum tragacanth	A	

A Agglomeration of the polymer, *E* Formation of an emulsion, *EA* Formation of emulsion with tendency for agglomeration, *G* Precipitation of the polymer in the form of granules, *GA* Formation of granules that agglomerated on account of their withholding a large amount of solvent, *JL* Formation of jelly polymer lumps

Molten Media Bath Reactor (e.g., Metal, Salt, or Slag)

The molten media process has been proposed to use molten iron or slag as a promising heat source of the process for depolymerization of waste polymer due to its high heat capacity (i.e., it heats relatively slowly, retains heat longer, and cools slowly) [23]. Degussa (chemical industry company, Germany) recycles acrylic polymers using the metal bath process. Depolymerization reactor contains a heated metal bath with a stirring device [8]. Tin and lead (with melting points of 232 °C and 327 °C, respectively) are metals commonly used in this reactor. The ground PMMA is fed from the storage silos onto the stirred metal bath. The stirrer in the reactor provides a thorough mixing and so causes the transferring of the heat from metals to polymer to be satisfactory. Under these conditions PMMA depolymerizes and the gaseous product leaves the reactor. Temperature of the reaction is decisive on yielding a monomer. Best condition is dependent on the reaction conditions – mostly
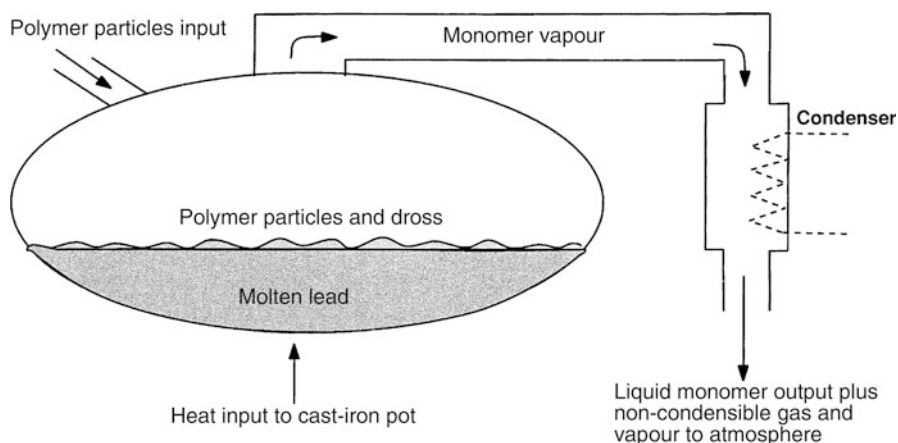
Fig. 6 Schematic representation of the conventional molten media bath reactor (lead-pot) depolymerization process for PMMA [24]

time and temperature – therefore can operator controls temperature to achieve acceptable line of operation. Yellowish product that contains undesired by-products needs further separation and purification process; otherwise, the quality of the product will be low [13].

Depolymerization industry in the UK commonly recycles PMMA by floating it in a molten lead bath (Fig. 6). Newborough et al. reported several serious disadvantages of molten metal bath process:

– Metal-contaminated waste produced by the process.
– Significant contamination of recovered MMA monomers by metals particles.
– The process is extremely energy-consuming since the resulting monomer is required to be further distilled to ensure acceptable commercial purity [24].

The composition of the contaminants in the MMA-condense was also proved by Smolder et al. They obtained MMA yield of about 87% in a lead bath reactor which the yield seemed to be independent of temperature [16].

The influence of using melted tin bath was investigated for thermal degradation of PMMA waste by Popescu group. As expected the huge amount of heat accumulated in melted tin was rapidly transferred to PMMA waste. It leads to the yield of liquids formed from depolymerization reduced from 97% (in the absence of tin bath) to 95% (in the presence of tin bath). Moreover, the amount of remnant carbonaceous mass in the reactor was higher when using molten tin bath [25]. The pyrolysis of PMMA in a molten salt bath of KCl and $MgCl_2$ by Kaminsky group showed that MMA yield varied from 80% at 500 °C to 30% at 700 °C [26].
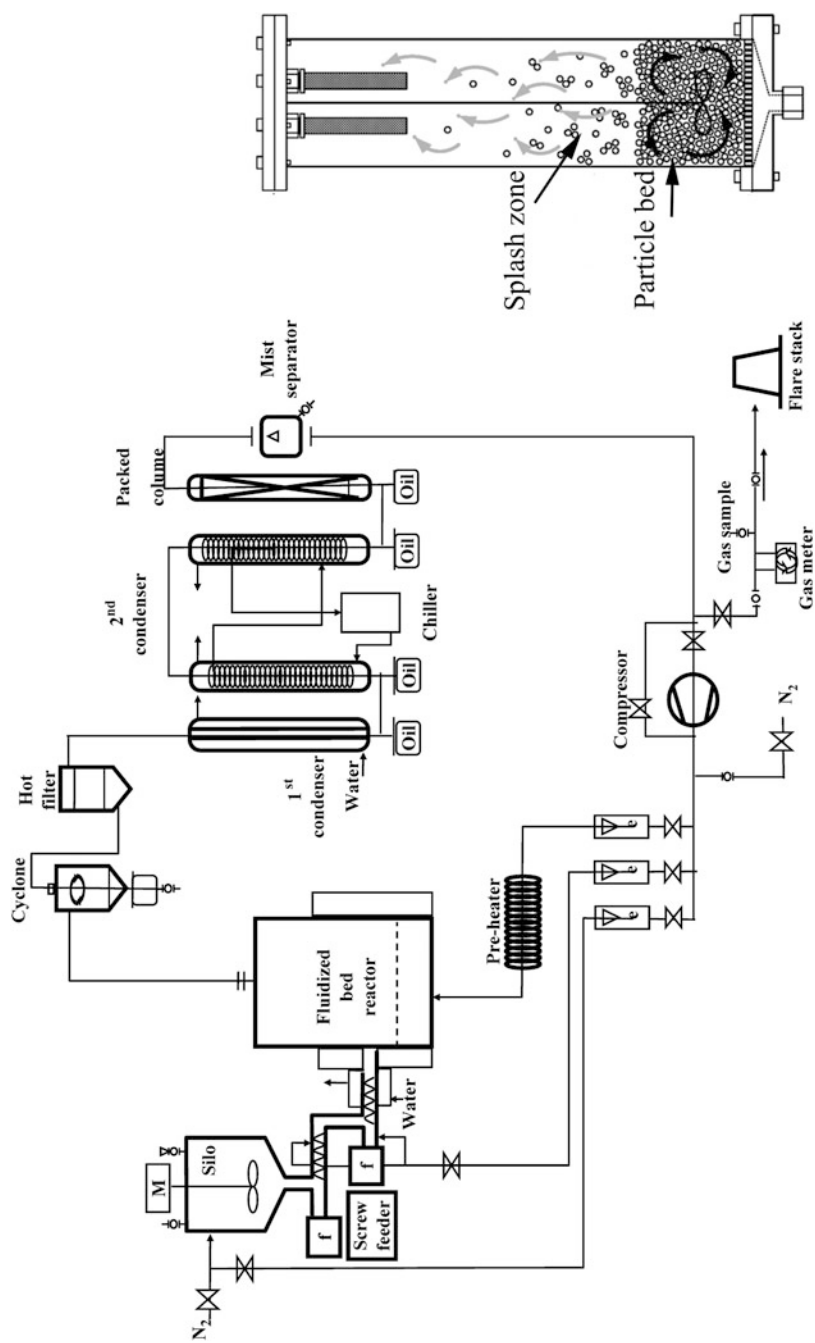
Fluidized Bed Reactor

Quite a number of proposal have now been made to reutilize waste materials by depolymerization wherein, up to now, pyrolysis in a mechanically fluidized heat transfer medium [27] is the method with the highest-MMA monomer yield. It is proven to particularly be suitable for pyrolysis providing appropriate heat and material transfer rates and thus constant temperatures. The key features of this method are largely uniform products, no moving parts in the hot region, no contamination of organometallic compounds in the products, less environmental problems, and no leakage due to the complete sealing which provides wholly closed system [13, 28]. Furthermore, the presence of filler contaminates the molten metal bath, while in a fluidized bed reactor it is possible to recover often expensive fillers [13]. Smolder stated that the MMA yield is mainly dependent on the residence time of the gas in the reactor and to a lesser extent on the operating temperature. The outlined and illustrated procedure for a fluidized bed PMMA depolymerization reactor is applicable for a process of 1 tpd (tons per day) PMMA [16]. The schematic of a bench scale plant for PMMA recycling using fluidized bed reactor is illustrated in Scheme 4. The particle bed is fluidized utilizing either the inert purge gas such as nitrogen or the reactive precursor itself splashing particles into the splash zone leading to soft agglomeration. The purging velocity in operation is controlled to minimize particle elutriation to the filters [29].

This method has intrinsic disadvantages particularly relative to high temperature needed for the depolymerization process (~700 °C) which takes up a significant part of the overall energy consumption [14, 25]. Moreover, the fluidized bed is very sensitive to the presence of filler in polymer such as fibers and high amounts of metals and other fillers [28]. Taking into account these drawbacks, efforts have been devoted to explore a new procedure with the aim to find the best route to reduce the energy consumption and to improve the life cycle energy efficiency.

Conical Spouted Bed Reactor (CSBR)

Conical spouted bed reactor (CSBR) has excellent hydrodynamic behavior, high heat transfers, and versatility which are the key factors which make this process a useful method on recycling PMMA. In CSBR, the operating pressure drop is low and can handle particles with a wide size or density distribution without segregation. The conical spouted bed is very versatile in gas residence time, with values ranging from 1 s to 20 ms in minimum spouting conditions to jet spouted bed, respectively. This characteristic is essential for minimizing secondary reactions. Simple and smaller design due to the absence of distribution plates in this reactor is one of the advantages of this device (Scheme 5) [30]. At the process site, three differentiated zones are created due to the entering the fluid flow into the spouted bed through a single central inlet orifice: (1) spout zone, the central core of the reactor which air flows; (2) annular zone, the surrounding annular area in annulus; and (3) fountain zone where the particles in the fountain continue to move upward due to inertia. The turbulence of the central gas inlet creates a very strong thorough circulation of solids.

Scheme 4 (Left) diagram of pyrolysis bench scale plant for recycle of PMMA using fluidized bed reactor; (right) schematic of the fluidized bed reactor configuration [14, 29]
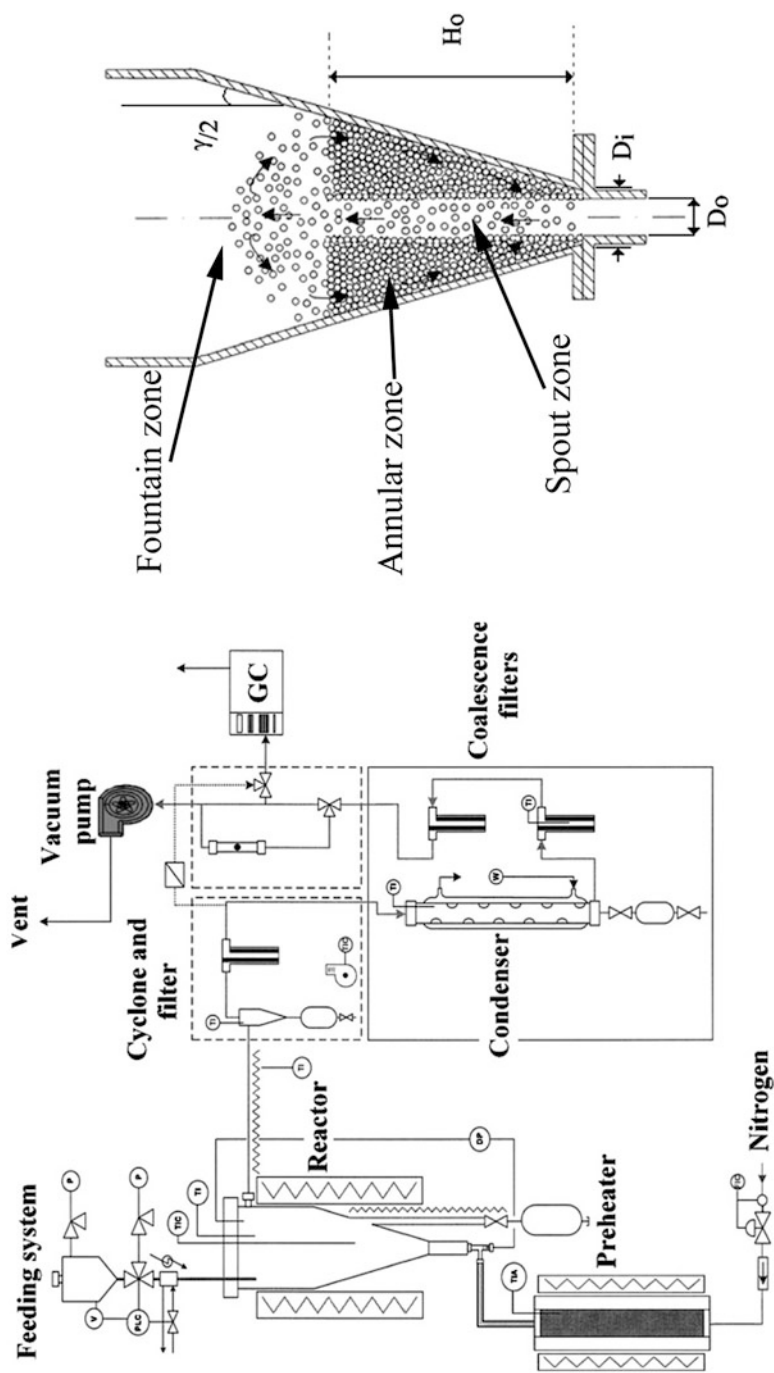
Scheme 5 (Left) diagram of pyrolysis bench scale plant for recycle of PMMA using conical spouted bed reactor (CSBR); (right) dimensions of employed CSBR and solid movement inside [30]

An important feature of CSBR is the absence of any significant dead zones, and thus no solids can become trapped [31]. The vigorous interaction between the gas and solid phases and the cyclic movement of the solid in spouted beds avoids the defluidization problems that occur in plastics pyrolysis in fluidized beds [30]. A composite of a dilute phase along with more suitable system for certain applications rather than conventional fluidization techniques is established due to the particular configuration of CSBRs [32].

According to the calculations, larger particle diameters of the solids improve the performance of CSBR reactor and reduce defluidization problems. Furthermore, by increasing the gas velocity in fluidized beds, particle velocity hardly changes. This happens because most of the excess gases in the bubble phase rise through the bed. The gases must be controlled by mass flow meters and heated to the reaction temperature by a preheater with an internal cartridge. Separating fines from the product stream is done by the system consists of a high-efficiency cyclone and a sintered steel filter. These two components of the reactor are placed at the outlet of the device inside an oven maintained at 543 K to avoid the condensation of pyrolysis oil in either component. By these definitions PMMA is easily handled in a CSBR compared to other plastics due to its lower stickiness, higher reaction rate, and the lack of solid residue. The analysis of PMMA thermal degradation shows that the degradation temperature 553 K is lower compared to other plastics. Due to the great performance of the CSBR, the quantity of inert material required for a given plastic flow rate is one third of that required in fluidized beds [30].

The kinetic parameters obtained at the different heating rates showed that the activation energy is around 165 kJ mol at different heating rates (ranging from 2.5 to 20 $K.min^{-1}$). It is somehow impossible to compare the results obtained here with those of other recycling procedures due to a major dependence of thermal degradation on the molecular weight and grade of the initial waste PMMA. Lopez et al. reported successful pyrolysis of PMMA carried out in CSBR reactor at temperature range of 673–823 K (Table 7), while the literature confirmed that no PMMA pyrolysis occurs in fluidized bed reactors below 713 K [30].
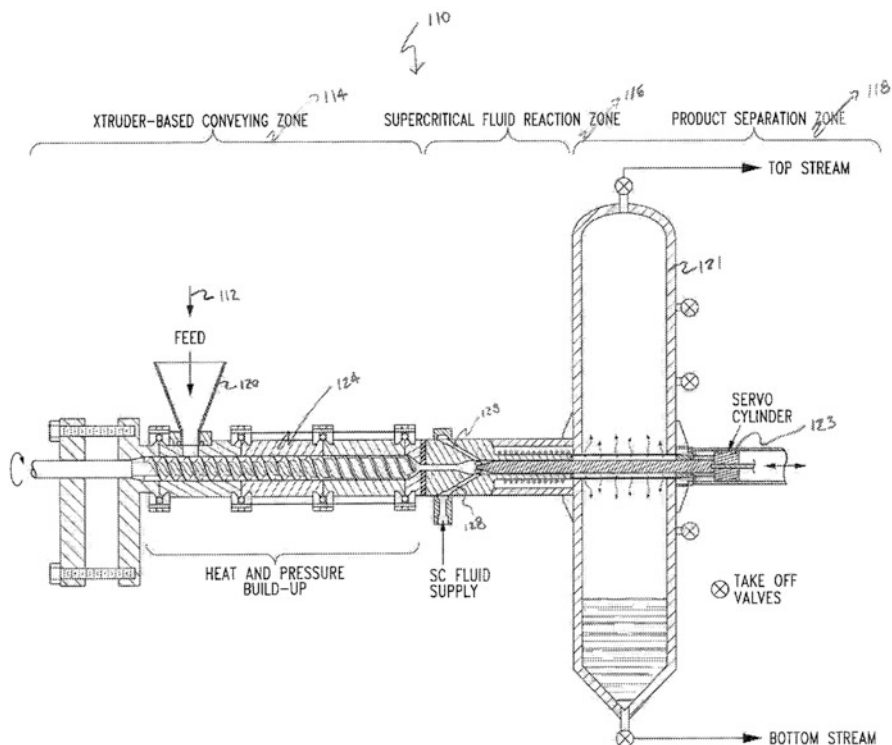
Extruder

In 2015, the extruder-based approach was proposed by Loop et al. for depolymerization of biomass and plastic waste via supercritical water [33]. As shown in Scheme 6, the method comprises several steps as follows:

– Conveying the selected polymeric material through an extruder continuously to a supercritical fluid reaction zone
– Injecting hot compressed water into the supercritical fluid reaction zone
– Retaining the mixture within the reaction zone for a period of time sufficient to yield the plurality of reaction products [33].

Table 7 Yields of the main products obtained in the pyrolysis of PMMA in CSBR at the different temperatures studied [30]

Materials		Yield (wt%)			
		673 K	673 K	673 K	673 K
Gases		0.86	1.95	3.66	9.19
	CO	0.09	0.37	0.72	2.03
	CO_2	0.35	0.99	1.23	2.54
	Methane	0.03	0.04	0.06	0.09
	Ethylene	0.30	0.39	1.07	2.74
	Propylene	0.05	0.13	0.54	1.72
	1,3-Butadiene	0.04	0.03	0.04	0.07
Liquids		99.14	98.06	96.34	90.81
	Acetaldehyde	0.70	0.68	0.52	0.54
	Acrolein (2-propenal)	0.35	0.42	0.57	0.15
	1,3-Cyclopentadiene	0.06	0.06	0.07	0.11
	1,3-Pentadiene	0.09	0.08	0.06	0.07
	Methacrolein	0.02	0.07	0.29	0.04
	2-Pentene	–	0.02	0.11	0.01
	1-Pentene, 2-methyl	0.01	0.02	0.11	0.03
	MA	0.03	0.05	0.41	0.41
	Methyl propionate	–	0.06	0.76	0.52
	1-Pentene, 2,4-dimethyl	–	–	0.10	0.01
	1,4-Cyclohexadiene	0.10	0.09	0.13	0.32
	2,4-Hexadiene	0.05	0.06	0.07	0.10
	Propanoic acid, 2-methyl, methyl ester	0.27	0.40	0.29	0.27
EA		6.19	6.13	4.86	1.52
MMA		86.50	85.26	82.58	77.86
	Propanoic acid, 2,2-dimethyl, methyl ester	–	0.01	0.01	0.02
	1,5-Hexadiene, 2,5-dimethyl	–	0.01	0.02	0.07
	2-Propenoic acid (acrylic acid)	0.08	0.10	0.22	0.34
	2-Butenoic acid methyl ester	0.07	0.07	0.18	0.07
	3-Butenoic acid, 2-Methyl, methyl ester	0.11	0.12	0.03	0.09
	Butanoic acid, 3-methyl methyl ester	0.26	0.24	0.20	0.44
	2-Propenoic acid, 2-methyl, ethyl ester	–	–	0.07	–
	3-Butanoic acid, 3-methyl, methyl ester	0.11	0.15	0.20	0.28
	Methyl tiglate	0.06	0.05	0.15	0.27
Unidentified		4.06	3.91	4.32	6.27

Although the overall scheme of the procedure is somehow defined, but up to our knowledge, there is no data or research available specifically on PMMA. Molecular weight reduction was evidenced when PMMA was fed into extruder. These results can be attributed to the residence time and the actual mechanical stress in the extruder [34].

Scheme 6 Schematic of the extruder-based machinery for PMMA depolymerization [33]

Characterization and Properties of Recycled PMMA

What it is important to notice in recycling process of PMMA is to optimize the recycle approach of waste polymers to minimize the deterioration of product properties in every cycle. Thus characterization of the properties of the product from re-polymerization of recycled PMMA should be paid attention after recycling. As discussed before, analysis of gaseous and liquid products obtained from polymer degradation showed that the oil fraction constituted mainly of the MMA monomer. Thus, the possibility of directly using the liquid product for the reproduction of the polymer was further investigated in the literature [26]. Achilias et al. re-polymerized the pyrolysis oil obtained from fluidized bed reactor and neat virgin MMA monomer with addition of azobisisobutyronitrile as a free radical initiator by raising the temperature in a differential scanning calorimeter. Experimental data of reaction rate versus time at 80 °C (Fig. 7) indicated that the overall profile trend of recycled MMA monomer resembles that of the neat MMA [10]. The reaction rate peak of the recycled MMA monomer occurred at the same conversion amount of recycled one while with a far much larger value.

Fig. 7 Reaction rate versus time at polymerization temperature of 80 °C for neat MMA monomer and recycled one [10]
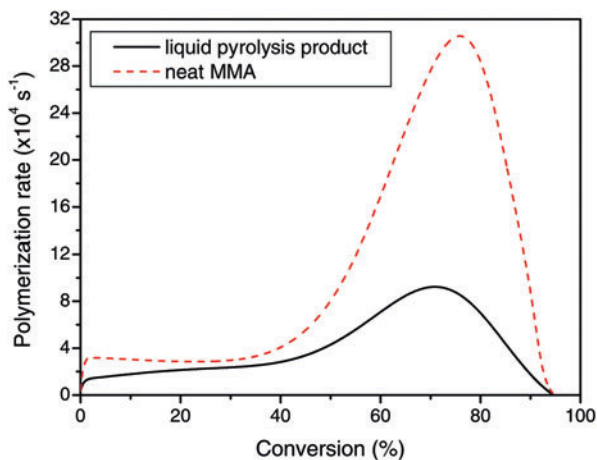
Fig. 8 Molecular weight distribution of the polymer obtained either from pure MMA monomer or from the recycled MMA monomer: number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) [10]
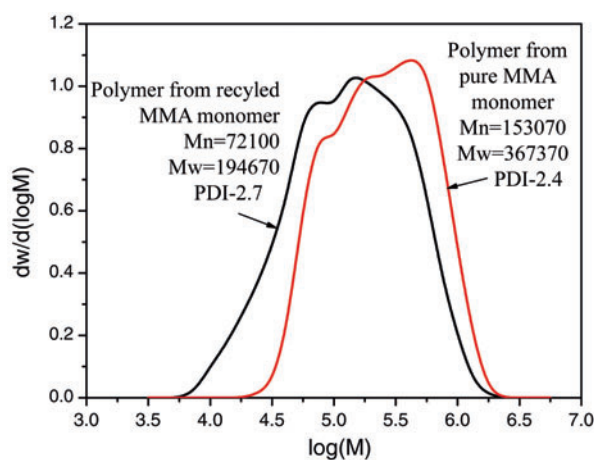
Full molecular weight distribution (MWD) of the polymer obtained either from pure MMA monomer or from the recycled MMA monomer including some statistical data including number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) is presented in Fig. 8. It is revealed from the figure that the MWD of the both types of polymers has almost the same shape, but it is shifted to lower values in the case of recycled monomers. It can be related to lower molecular weight of that polymer due to probable defects form during recycling process. The glass transition temperature (T_g) of the polymer fabricated from neat virgin MMA monomer was measured to be between 103 °C and 106 °C (depending on the polymerization temperature), while that of the polymer produced from recycled MMA monomer was found to be 84–88 °C [10].

It could be concluded from the results that the pyrolysis products can be polymerized and produce a polymer similar to the original PMMA. However, even small amounts of other organic compounds (mainly methyl esters) included in pyrolysis

Table 8 Comparative properties of virgin PMMA and recycled one [21]

Properties	PMMA grade		
	Virgin grade	Recycled from virgin grade	Recycled from decorative sheets
Izod impact strength (KJ/m^3)	1.2	1.3	1.3
Tensile modulus (MPa)	1970	1750	1800
Tensile strength (MPa)	59	53	58
Elongation at break (%)	4	4	4
Melt flow rate (kg/10 min) 0.10^{-3}	1.5	1.6	1.7

product retard the polymerization reaction retardant and alter the reaction rate curve leading to the lower glass transition temperature and average molecular weight of the produced polymer [10].

Gouli et al. employed miscible solvent/nonsolvent system of toluene/n-hexane for solvent recycling of PMMA decorative sheets. Melt flow index and typical mechanical properties of virgin and recycled materials presented in Table 8. The observed slight increase in melt flow rate for the recycled grades possibly can be attributed to the degradation occurring during the measurement itself due to the lack of any antioxidant in the recycled polymer product. It is worthwhile to mention that the mechanical properties of the recycled grades resemble closely to the virgin material and the difference is quite negligible [21].

Popescu et al. researched on a question that if MMA obtained by thermal cracking of PMMA waste can be used to produce PMMA, without any purification before polymerization. The depolymerization results showed that MMA was the predominant fraction of liquid depolymerization product with over 90%, while dimer derivatives and MMA esters are by-products of this degradation. These impurities caused retardation in polymerization process of recycled MMA compared with that of pure MMA. Also the impurities in PMMA based on recycled MMA made the repolymerization products opaque, while the products of virgin PMMA and PMMA obtained from commercial MMA were clear and transparent. As the scanning electron microscopy (SEM) micrographs (Fig. 9) reveal, the monomer impurities affect the microstructure of the polymers. Commercial PMMA and PMMA from virgin MMA have a uniform morphology, while PMMA obtained from recycled MMA contain big aggregates than cause light scattering and very fine (0.5 μm) bubbles [25].

On the other hand, these impurities obtained from recovered MMA improve the compression strength of the obtained PMMA (191.35 MPa), comparing to PMMA obtained from virgin MMA (137.46 MPa). It seems that the impurities in recycled MMA play the role of plasticizer in polymerization process of the obtained recycled MMA, leading to higher compression strength [25].
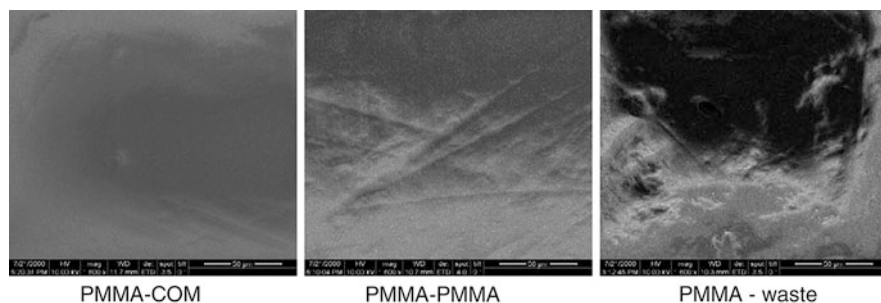
Fig. 9 SEM micrographs of PMMA samples: (left) commercial PMMA, (middle) PMMA from virgin MMA and PMMA from recycled MMA [25]

Recycle of Filled-PMMA

Nowadays most polymers are filled by fillers in order to make them suitable for special applications. This obstructs the reprocessing of high molecular weight polymer material. Therefore, researchers are looking to evaluate the recycling methodologies or modify them especially for highly filled PMMA. The effect of some filler such as quartz (SiO_2) and alumina trihydrate (ATH) on the pyrolysis of PMMA in fluidized bed reactor was reported in the literature [13, 35]. The pyrolysis of filled PMMA and for the sake of comparison pure PMMA pellets were carried out in two plants, a laboratory plant (with feeding rate of 300 g h^{-1}–3 kg h^{-1}) and a mini pilot plant (with feeding rate of 30 kg h^{-1}). At a temperature of 450 °C, pure PMMA yielded 98 wt.% of MMA, while PMMA containing over 60% of SiO_2 filler was pyrolyzed to 91% MMA. Other compounds are given in Table 9. The results showed that great potential of fluidized bed reactor to recover the monomer MMA and the fillers in an acceptable quality. Besides, in comparison to pure PMMA as feed, the amount of side products are two to three times higher in SiO_2-filled PMMA [13].

PMMA is commonly filler by over that 66% of ATH for bathroom and kitchen applications. A higher content of saponification products is expected from pyrolysis of ATH-filled PMMA due to the chemical structure of ATH as a Lewis acid, the separation of water during reaction and the chemical adsorption of methacrylic groups at the ATH surface. The pyrolysis of ATH-filled PMMA at typical condition (450 °C at a laboratory plant) led to a yield of just 53% of MMA instead of more than 90% in case of pure PMMA. Thus the way to prevent saponification was investigated by Grause group [35]. They proposed optimized conditions where MMA yield of 80% was obtained including reduction of partial pressure of the reactants MMA and water, reduction of the feed rate of PMMA, reduction of temperature to 400 °C, and also reduction of the residence time of the products in the reactor.

Table 9 Process conditions and product of pyrolysis in pure and filled PMMA in both laboratory and mini pilot plants of fluidized bed reactor at 450 °C [13]

Plant	Lab	Lab	Lab	Pilot	Pilot
Filler (SiO_2) (wt.%)	71	62	–	71	–
Feeding rate (kg/h)	2.0	1.9	0.9	34	16
Feed (kg)	5.8	2.8	4.2	389	575
Reaction time (h)	2.9	1	1.5	11.5	37
Sand in reactor (kg)	8	8	8	200	160
Gas flow (m^3/h)	3.9	5.2	3.4	50	65
Residence time in fluidized bed (s)	1.2	1.0	1.3	2.9	1.6
Products (wt.%)					
Gas	2.6	2.0	0.4	1.6	0.5
MMA	86.6	90.5	98.4	83.5	96.7
Other liquids	8.1	5.7	0.8	9.4	1.6
Water	1.4	0.6	0.4	4.3	0.8
Carbon black	1.3	1.2	0.01	1.2	0.1

Application of Recycled PMMAs

PMMA/Montmorillonite (MMT) Nanocomposites

Martin et al. employed recycled PMMA to fabricate PMMA/montmorillonite (MMT) nanocomposites containing several types of nanoclay. Clays were dispersed by sonication in ethanol and added into recycled PMMA/dichloromethane solution. After solvent evaporation, PMMA nanocomposite different clay contents were precipitated and then extruded and molded into sheets. A comparative study of the optical transparency for all analyzed PMMA nanocomposites in Fig. 10 shows that an increment of the content of clay in the nanocomposite leads to a decrease in the opacity [36].

The morphology and composition of the nanocomposites have an important influence on light transmittance of nanocomposites. With a higher dispersion degree, nanocomposites appear to show higher transparency extent. The dispersion state of nanoclay in PMMA matrix observed by atomic force microscopy (AFM) in Fig. 11 revealed that the most homogeneous and exfoliated distribution of the clays took place for the sample with organo-modified clay (cloisite 30B). The results are in complete agreement with the evolution of transparency degree shown above [36].

Mechanical behavior of PMMA nanocomposites (Fig. 12) showed that tensile modulus is increased in the case of all the clays in comparison to pristine PMMA. It occurred without sacrificing transparency and thermal properties of the pristine matrix which suggests that recycled PMMA as a suitable low-price matrix for preparing nanocomposites with interesting properties [36].

**Fig. 10** Effect of nanoclay content on relative variation of opacity of PMMA/nanoclay nano-composites [36]

Recycled PVC/PMMA Blends

Recently, biologically derived materials draw a great deal of attention in the polymer research and development area owing to their renewability and environmental concern. In 2017, Suresh et al. considered the effect of bio-based epoxidized soybean oil (ESO) in compatibilization and value addition of recycled PVC/ PMMA blend for the first time. The blends of mechanically recycled PVC and PMMA were prepared through melt blending technique where each component was recovered from the data cables and the computer LCD display, respectively [37]. The results revealed that ESO could act as a promising material for compatibility improvement of the recycled PVC/PMMA blend by interacting with polar functionalities present in the blend. The effect of such compatibilization can be detected in fractured surface morphology of the samples with SEM (Fig. 13). Upon the addition of ESO, surface roughness showed progressive increase which was an indication of good interfacial adhesion between the different polymeric materials [37].
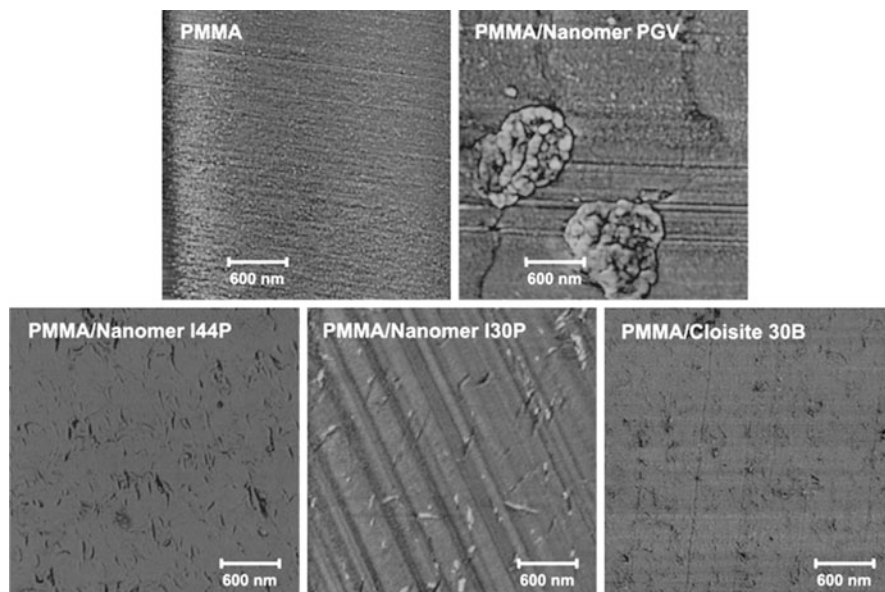
Fig. 11 Phase images of PMMA nanocomposites containing 5 wt% of different types of nanoclays [36]

Fig. 12 Tensile properties of PMMA nanocomposites with different types of nanoclay [36]
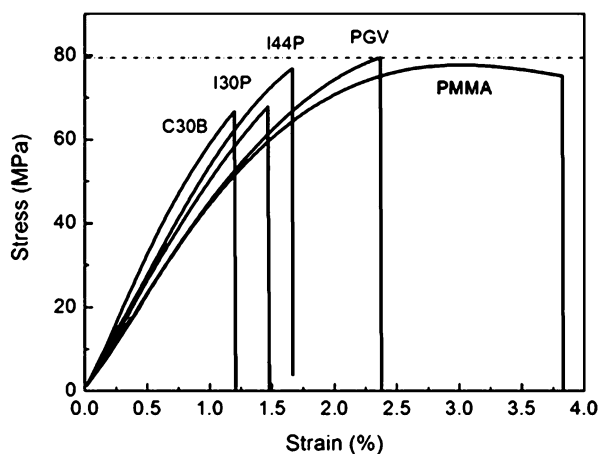
Interaction between α-hydrogen of recycled PVC with the carbonyl (-C=O) group of the recycled PMMA could be identified using Fourier transform infrared spectroscopy (FTIR) analysis (the band at 1726 cm^{-1}). Figure 14 revealed that after the addition of ESO into the recycled PVC/PMMA blend, the related peak shifts to the higher wave length (1729 cm^{-1}) with enhanced intensity. This proposes the
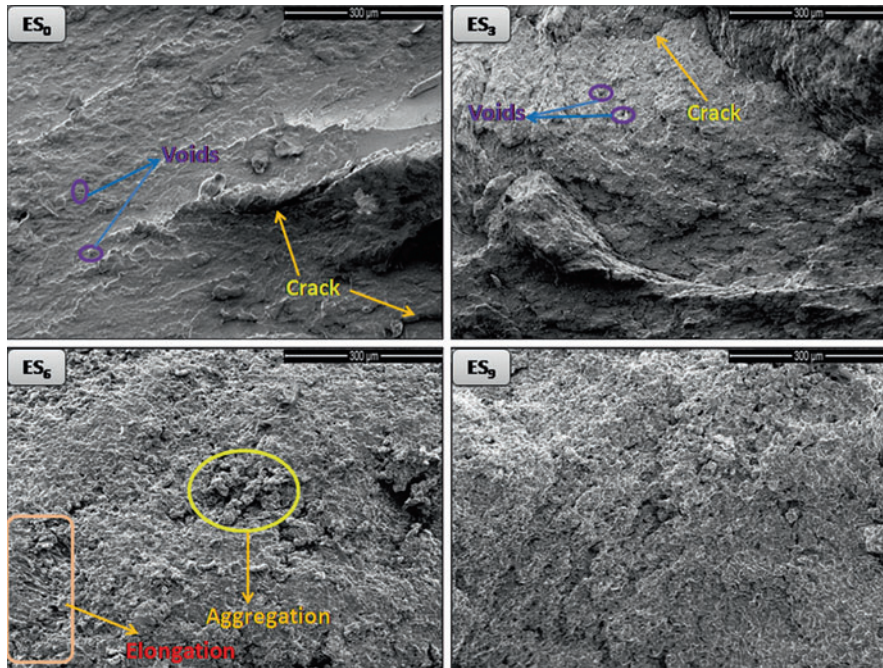
Fig. 13 SEM micrographs of fractured surface of recycled blends with various ESO content [37]

possibility of the dipole interactions increase between the carbonyl group of ESO and recycled PMMA with chlorine atom of recycled PVC existing in the blend [37].

This interaction plays a key role in mechanical properties of recycled materials. It was noted that for the pure recycled blend, notched impact strength showed a lower value (31.06 ± 0.3 J/m) as compared to ESO-modified recycled blend (61.08 ± 1.3 J/m for the sample with 9 wt.% of ESO). Moreover, the improved compatibility between PVC and PMMA was evidenced from the shift in the T_g values of polymeric phases after incorporation with ESO as compared with recycled blend [37].

Conclusion

In this chapter, methods for recycling of PMMA have been studied. The most prevalent process of PMMA depolymerization appears to be degradation of the polymeric wastes using heat in the inert environment in the absence of oxygen (pyrolysis). The products of PMMA depolymerization via pyrolysis range from the monomer preponderantly to other secondary products such as crude oil-like material. Thermal cracking of PMMA follows radical reaction where thermal stability of the reaction can be guaranteed by using mercaptans by saturation of unstable double bonds. Catalytic cracking is introduced as far more advanced approach to enhance
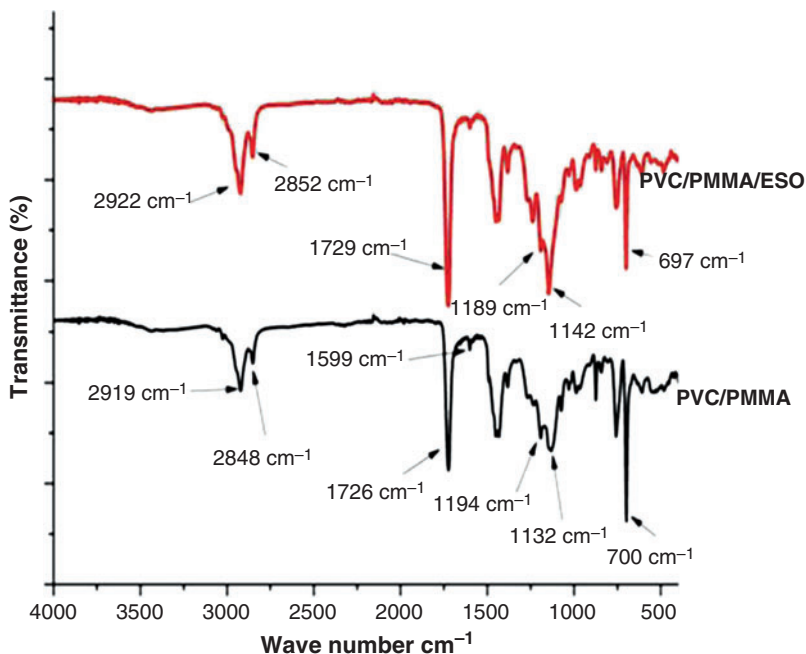
Fig. 14 FTIR spectra of pure recycled PVC/PMMA blend ESO-filled one [37]

the processability and efficiency of thermal cracking. The leading advantage of catalytic cracking is to yield of more useful fractions in comparison with conventional thermal cracking. Zeolite is the most frequently used catalysts for degradation of PMMA. GC-MS data showed that the optimal temperature in catalytic cracking of PMMA is 270 °C, while that of the process is about 450 °C in the absence of catalyst. In regard to recycling apparatuses of waste PPMA, it should be noted that the molten media process is an efficient one to recycle acrylic polymers because of high heat capacity. However, metal contamination of the monomer product and consequently further purification process are the main drawback of molten media process. Another imperative recycling apparatus is fluidized bed reactor which produces uniform products, and its great potential to recover often expensive fillers is the key feature of this method. High energy consumption is the disadvantage faced using fluidized bed reactor. The other apparatus is conical spouted bed reactor that can handle particles with a wide size with excellent hydrodynamic behavior. PMMA pyrolysis in this reactor is carried out at temperature range of 400–550 ° C which is lower than fluidized bed reactor. Characterization of re-polymerization reaction rate of recovered MMA monomer from waste PMMA recycle indicated that its overall reaction rate versus time profile trend resembles that of the neat MMA. The molecular weight distribution of the both types of polymers (recycled and neat) has almost the same shape, but it is shifted to lower values in the case of recycled monomers. It is worth to be mentioned that the mechanical properties of the recycled grades resemble

closely to the virgin material and the difference is negligible in normal applications. SEM micrographs revealed that the monomers impurities affect the microstructure of the polymers. Uniform even morphology is obtained for commercial PMMA, and PMMA produced from virgin MMA and very fine (0.5 μm) bubble formation is confirmed by light scattering in PMMA from recycled MMA. These impurities further found to act as plasticizers in polymerization process leading to higher compression strength. PMMA/montmorillonite (MMT) nanocomposites and PVC/PMMA blends were given as examples for the applications of recycled polymers using the characteristics of above. Nanocomposites appear to show relatively lower transparency and simultaneously higher tensile modulus in the case of all types of the clays in comparison to pristine PMMA.

References

1. Slone RV (2007) Methacrylic polymers. Kirk-Othmer Encyclopedia of Chemical Technology. In: Arza Seidel (ed), Wiley Online Library, New Jersey, USA
2. Research GV (2014) Polymethyl methacrylate (PMMA) market analysis by product (Extruded sheets, pellets, and acrylic beads), by end-use (Automotive, construction, electronics, signs & displays), Competitive landscape, and segment forecasts 2014–2025
3. https://www.basf.com/en.html (2018)
4. Perugini F, Mastellone ML, Arena U (2005) A life cycle assessment of mechanical and feedstock recycling options for management of plastic packaging wastes. Environ Prog Sustain Energy 24(2):137–154
5. Scheirs J (1998) Polymer recycling: science, technology and applications. Wiley, Journals, Baffins Lane, Chichester, Sussex PO 19 1 UD, UK, p 591
6. Kikuchi Y et al (2014) Design of recycling system for poly (methyl methacrylate) (PMMA). Part 1: recycling scenario analysis. Int J Life Cycle Assess 19(1):120–129
7. Kikuchi Y et al (2014) Design of recycling system for poly (methyl methacrylate)(PMMA). Part 2: process hazards and material flow analysis. Int J Life Cycle Assess 19(2):307–319
8. Sasse F, Emig G (1998) Chemical recycling of polymer materials. Chem Eng Technol 21(10): 777–789
9. Alibert D et al (2017) Effect of oxygen concentration on the combustion of horizontally-oriented slabs of PMMA. Fire Saf J 91:182–190
10. Achilias DS (2007) Chemical recycling of poly (methyl methacrylate) by pyrolysis. Potential use of the liquid fraction as a raw material for the reproduction of the polymer. Eur Polym J 43(6):2564–2575
11. http://polymerdatabase.com/ (2015)
12. Ahmad Z, Al-Awadi N, Al-Sagheer F (2008) Thermal degradation studies in poly (vinyl chloride)/poly (methyl methacrylate) blends. Polym Degrad Stab 93(2):456–465
13. Kaminsky W, Eger C (2001) Pyrolysis of filled PMMA for monomer recovery. J Anal Appl Pyrolysis 58:781–787
14. Kang B-S, Kim SG, Kim J-S (2008) Thermal degradation of poly (methyl methacrylate) polymers: kinetics and recovery of monomers using a fluidized bed reactor. J Anal Appl Pyrolysis 81(1):7–13
15. Barlow A et al (1967) Polymethylmethacrylate degradation – kinetics and mechanisms in the temperature range 340° to 460 °C. Polymer 8:537–545
16. Smolders K, Baeyens J (2004) Thermal degradation of PMMA in fluidised beds. Waste Manag 24(8):849–857
17. Arandes JM et al (2007) Catalytic cracking of waxes produced by the fast pyrolysis of polyolefins. Energy Fuel 21(2):561–569

18. Raseev S (2003) Thermal and catalytic processes in petroleum refining. CRC Press, New York, USA
19. Khangkham S (2012) Catalytic degradation of poly (methyl methacrylate) by zeolites and regeneration of used zeolites via ozonation, in Institut National Polytechnique de Toulouse (INP Toulouse). Universite de Toulouse, Toulouse
20. Papaspyrides C, Gouli S, Poulakis J (1994) Recovery of poly (methyl methacrylate) by the dissolution/reprecipitation process: a model study. Adv Polym Technol 13(3):213–218
21. Gouli S, Poulakis JG, Papaspyrides CD (1994) Solvent recycling of poly(methyl methacrylate) decorative sheets. Adv Polym Technol 13(3):207–211
22. Rahimi A, García JM (2017) Chemical recycling of waste plastics for new materials production. Nat Rev Chem 1(6):0046
23. Zhang L, Xu Z (2016) A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J Clean Prod 127:19–36
24. Newborough M, Highgate D, Vaughan P (2002) Thermal depolymerisation of scrap polymers. Appl Therm Eng 22(17):1875–1883
25. Popescu V et al (2009) The characterization of recycled PMMA. J Alloys Compd 483 (1):432–436
26. Kaminsky W, Menzel J, Sinn H (1976) Recycling of plastics. Conserv Recycl 1(1):91–110
27. Weiss H-J et al. (2002) Method for depolymerizing polymethylmethacrylate. Google Patents
28. Kaminsky W, Predel M, Sadiki A (2004) Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polym Degrad Stab 85(3):1045–1050
29. King DM et al (2007) Atomic layer deposition on particles using a fluidized bed reactor with in situ mass spectrometry. Surf Coat Technol 201(22):9163–9171
30. Lopez G et al (2010) Recycling poly-(methyl methacrylate) by pyrolysis in a conical spouted bed reactor. Chem Eng Process Process Intensif 49(10):1089–1094
31. Zhou J (2008) Characterizing and modeling the hydrodynamics of shallow spouted beds. In: Tennessee research and creative exchange. University of Tennessee, Knoxville
32. Moliner C et al (2017) Modelling of spouted and spout-fluid beds: key for their successful scale up. Energies 10(11):1729
33. Loop TE et al. (2015) Biomass and waste plastics depolymerization machine and methods via supercritical water. Google Patents
34. Capone C et al (2007) Thermal and mechanical degradation during polymer extrusion processing. Polym Eng Sci 47(11):1813–1819
35. Grause G, Predel M, Kaminsky W (2006) Monomer recovery from aluminium hydroxide high filled poly (methyl methacrylate) in a fluidized bed reactor. J Anal Appl Pyrolysis 75(2): 236–239
36. Martin L et al (2008) A comparative study of nanocomposites based on a recycled poly (methyl methacrylate) matrix containing several nanoclays. Polym Compos 29(7):782–790
37. Suresh SS, Mohanty S, Nayak SK (2017) Bio-based epoxidised oil for compatibilization and value addition of poly (vinyl chloride)(PVC) and poly (methyl methacrylate)(PMMA) in recycled blend. J Polym Res 24(8):120