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Grupo Sado

**STUDY OF THE MECHANISMS OF THERMAL DESPOLIMERIZAÇÃO OF THE
POLI(METHYL METHACRYLATE)**

Selection of solvent compatible with PMMA

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Abstract

The mechanism of depolymerisation of the PMMA was studied in this work as well as the incidence of formation of by-product with negative effect in the yield of MMA. A bibliographical study of patents and processes for depolymerisation of the PMMA was described. A theoretical and experimental study of dissolution of the PMMA in different organic solvent was developed, for selection of solvent that can serve of base for acrylic adhesive preparation. The depolymerisation mechanism of PMMA has been studied for more than 6 decades. It consists of three distinct stages: the initiation, depropagation and termination. The initiation can occur by chain end scission, random chain scission, or by elimination of metoxicarbonil side-chains, originating macro-radicals that during the depropagation promote the formation of the MMA. The PMMA degrades thermally almost exclusively in MMA with yields up to 97%. The main by-products are CO₂, CO, CH₄, CH₃OH, light Hydro-carbons and char. The amount of by-products depends on the temperature of depolymerisation. The processes of depolymerization of the PMMA are based on the pyrolysis, differentiating for the way as the necessary heat to the reaction is transmitted. Two groups are distinguished: processes of direct heating and processes of indirect heating. The forecast of dissolution PMMA made from the three-dimensional method of Hansen and of the energy of Gibbs of mixture, agrees to the experimental results, except in the cases of the Nitrometane and Acetonitrile. As potential solvents for the acrylic adhesive preparation we can use: CH₂Cl₂/CH₃NO₂; CHOOC₃/CH₃NO₂; CHOOC₂CH₃/CH₃NO₂; CH₃COOCH₃/CH₃NO₂; CH₃COOCH₂CH₃/CH₃NO₂; CH₃COOCH₃/C₃H₇NO; CH₃COOCH₂CH₃/C₃H₇NO and CH₃COO(CH₂)₃CH₃ /C₃H₇NO.

Keywords: Depolymerization, Pyrolysis, PMMA, Thermal Degradation, dissolution

1. Introduction

In recent years, the global search and consumption of the plastic have grown exponentially. The management and elimination of the wastes resultants in the use of these materials are a challenge each time bigger, especially in the great urban centres. Until now the residues were deposited in landfill areas or incinerated. However, due to the increase of the costs of these operations, and of the ambient legislation each time more rigorous because of the ambient problems related with these activities, are required alternative and more efficient methods for the recovery and recycling of plastic materials. The controlled thermal degradation of the polymer or pyrolysis is a viable alternative to the traditional methods of treatment. Into this process the residues can be converted into valuable products as fuels, or into monomers through the depolymerization.

The adhesives for acrylic materials are presented on the most varied forms, such as adhesive in volatile solvent, adhesive based on esters and polyesters acrylic or methacrylic in organic solutions, water based emulsions, suspensions etc. The Poly(methyl methacrylate) is widely used as adhesive when dissolved in an appropriate solvent , or its monomer. The use of monomer prevents the

necessity to remove solvent as well as the fast drying of junctions. Usually small amounts of catalysts and plasticizers are added. This composition is appealed when are intended adhesives of high resistance for adverse ambient conditions.

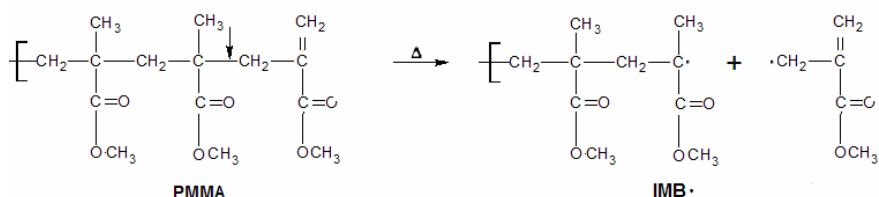
This work is divided in two independent parts. In the first one, it was studied the mechanisms and the main processes of depolymerization of the PMMA. And the second part, it was presents a theoretical and experimental study of dissolution of the PMMA in different organic solvents, for the selection of a set of organic solvents that can serve of base for the acrylic adhesives preparation.

2. Mechanisms of depolymerization of the Poly(methyl methacrylate)

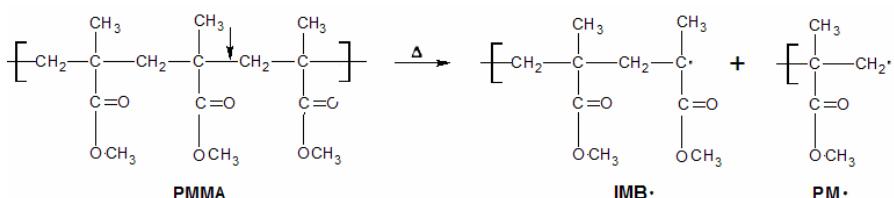
Definition: "Despolimerização is a process by means of which a polymer is decomposes in monomer pure from which was gotten originally" [13].

The mechanism of despolimerização of the PMMA consists of three distinct stages, nominated, the initiation, depropagation and termination. The initiation can occur by chain end scission, or random chain scission, or by elimination of metoxicarbonil side-chains. In equations 1 to 3 and *scheme I* present the 3 types of initiation.

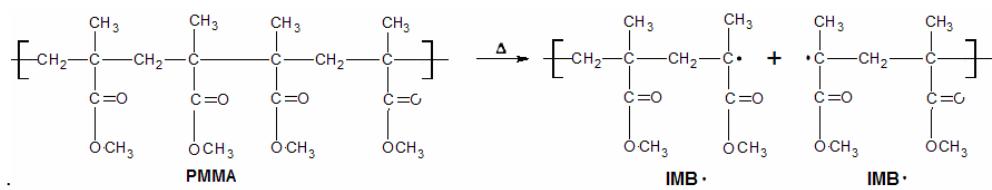
Equation 1: chain end scission



Equation 2: Random chain scission

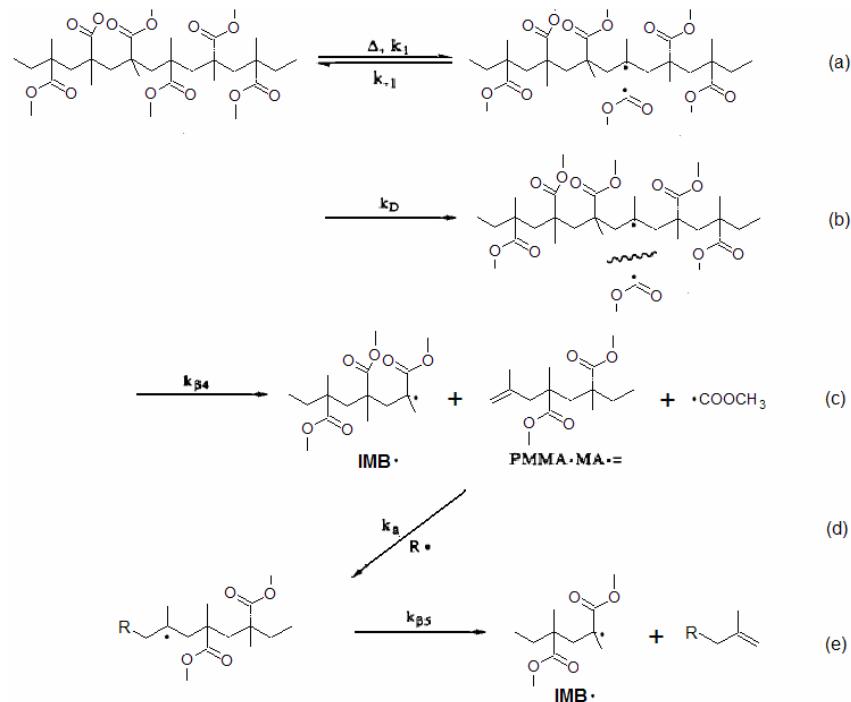


Equation 3: Initiation in chains with head-head linking's



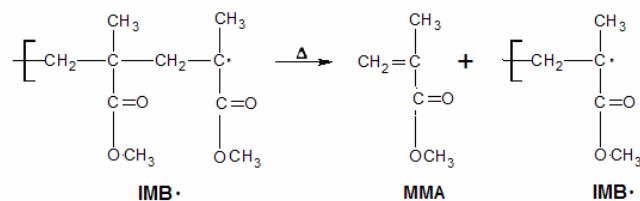
According Manring [5], the PMMA degrades by elimination of metoxicarbonil side-chains such as presented in scheme I [5].

Schema I



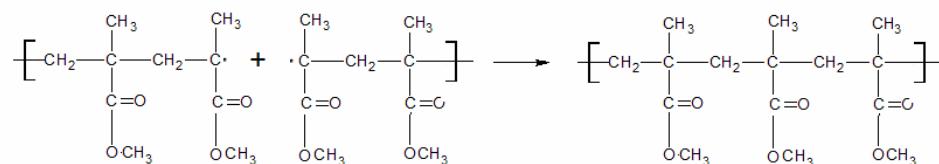
The originated macroradicals in the previous stage, nominated, the tertiary macroradical isobutyryl ($IMB\bullet$) and primary macroradical ($PM\bullet$), are degraded during the stage of depropagation producing the MMA.

Equation 4: Depropagation stage



The depropagation process can be interrupted if two radicals recombine inhibiting its continuation.

Equation 5: termination stage



2.1. Inhibiting action of the oxygen and catalytic effect of the sulphates on the depolymerization of the PMMA

The thermal decomposition of the PMMA depends on the structure of polymer, such as the type groups esters, way of termination, formation or not of copolymers with other monomers, degree of polymerization, presence of oxygen etc. In atmospheres with oxygen, the macroradical isobutryl (*IMB* •) can eventually react with Oxygen, forming the radical peroxide that is thermally more steady and inhibits the depolymerization. The presence of metallic sulphates speeds the thermal degradation of the PMMA. The catalytic action must the interaction between metallic ion of the sulphates and the oxygen of the carbonyl group of polymer that weakens the conjugated effect of the group ester and inhibits the transference of electron inside of the radicals. The order of catalytic activity determined experimentally for the 5 sulphates used as catalysts is: $\text{Fe}_2(\text{SO}_4)_3 > \text{Al}_2(\text{SO}_4)_3 > \text{MgSO}_4 > \text{CuSO}_4 > \text{BaSO}_4$ ^[7].

2.2. Occurrence of bys-product with negative effect in the yield in methyl methacrylate

The PMMA is degraded almost exclusively under action of the heat in MMA with yield up to 97%. The main by-products formed are CO_2 , CO, CH₄, CH₃OH, light Hydro-carbons and char. The ratio of these products depends on the temperature of depolymerization. In Table 1 are presented the percentages of the main products of the pyrolysis of the PMMA gotten in the different temperatures of depolymerisation.

Table1. Main products of the pyrolysis of PMMA^[9]

Produto % (p)	450 °C	490 °C	590 °C
Gás	1.37	2.63	42.46
Metano	11.8	10.3	9.2
Eteno	4.7	4.4	5.87
Etano	3.4	2.6	1.6
Propano	1.3	6.8	16.3
Iso-butano	0.21	1.85	4.9
CO_2	75.8	55	20.4
CO	0.78	14.3	31.9
Líquido	98.48	97.08	57.27
Metanol	0.03	0.07	0.06
Metilisobutanol	0.11	0.13	0.54
MA	0.28	0.34	2.18
MMA	98.66	98.34	95.8
MMA-dimero	0.14	0.26	0.51
Char	0.15	0.29	0.27

3. Processes of Depolymerization of the Poly(methyl methacrylate)

The thermal degradation of the PMMA is controlled at low temperature (below of 230°C) by kinetic of the reaction and at high temperatures by the flow of transferred heat^[9]. In the industry the majority of the processes operate with temperatures more than 230°C. Thus, the guarantee of an adequate flow of heat is one of the factors most important. The necessary heat to the reaction can be

directly transferred to the polymer through hot walls of a metallic reactor, or indirectly through an organic liquid, melted metal, a fluidized bed or metallic spheres.

Two groups are distinguished: processes of direct heating ("Dry" distillation and Extrusion process) and processes of indirect heating (Processes of indirect heating with organic liquids; Processes of indirect heating with melted metal; Processes of indirect heating with fluidized beds; and Processes of indirect heating with metallic spheres).

4. Selection of solvent compatible with the PMMA

Based on the theoretician methods described in literature for forecast of the dissolution of polymers in solvent organics (nominated, energy of Gibbs of mixture and method of Hansen) and in experimental assays, were selected the following solvents for acrylic adhesive preparation:

- Dichloromethane and 1,1-Dichloroethane (the addition of 10 to 65% of Nitromethane/Nitroethane improves the quality of these solvents).
- Methyl acetate, ethyl acetate and butyl acetate (the addition of 10 to 50% of Nitromethane/Nitroethane improves the quality of these solvents).
- Methyl acetate, ethyl acetate and butyl acetate (the addition of 50 to 90% of N,N-Dimethylformamide improves the quality of these solvents).
- Methyl formate and Ethyl formate (the addition of 10 to 75% of Nitromethane/Nitroethane improves the quality of these solvents).

5. Conclusions

The PMMA depolymerization mechanism consists of three distinct stages, nominated, the initiation, depropagation and termination. The initiation can occur by chain end scission, or random chain scission, or according Manring by elimination of metoxycarbonyl side-chains, originating macro-radicals that during the depropagation promote the formation of the MMA

The thermal decomposition of the PMMA depends on the structure of polymer, such as the type groups esters, way of termination, formation or not of copolymers with other monomers, degree of polymerization, presence of oxygen etc. In atmosphere with oxygen the despolimerização is more difficult, on the other hand the presence of metallic sulphates speeds the thermal degradation, ex $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$, MgSO_4 , CuSO_4 , e BaSO_4 ,

In the PMMA depolymerization to the industrial level the guarantee of adequate flows of heat is the factor most important. The necessary heat to the reaction can directly be transferred to the polymer through hot walls of a metallic reactor, or indirectly through an organic liquid, melted metal, a

fluidized bed or metallic spheres. The processes of indirect heating are most common; among these the process of Clementi and the processes of fluidized bed are distinguished. However, due to problems associates to the lead presence the first process is falling in disuse.

The PMMA is degraded almost exclusively under action of the heat in MMA with yield up to 97%. The main by-products formed are CO₂, CO, CH₄, CH₃OH, light Hydro-carbons and char. The ratio of these products depends on the temperature of depolymerization.

The forecast of dissolution PMMA made from the three-dimensional method of Hansen and of the energy of Gibbs of mixture, agrees with the experimental results, except in the cases of the Nitromethane and Acetonitrile. As potential solvents for the acrylic adhesive preparation are the following mixtures: CH₂Cl₂/CH₃NO₂; CHOOCH₃/CH₃NO₂; CHOOCH₂CH₃/CH₃NO₂; CH₃COOCH₃/CH₃NO₂; CH₃COOCH₂CH₃/CH₃NO₂; CH₃COOCH₃/C₃H₇NO; CH₃COOCH₂CH₃/C₃H₇NO and CH₃COO(CH₂)₃CH₃/C₃H₇NO.

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