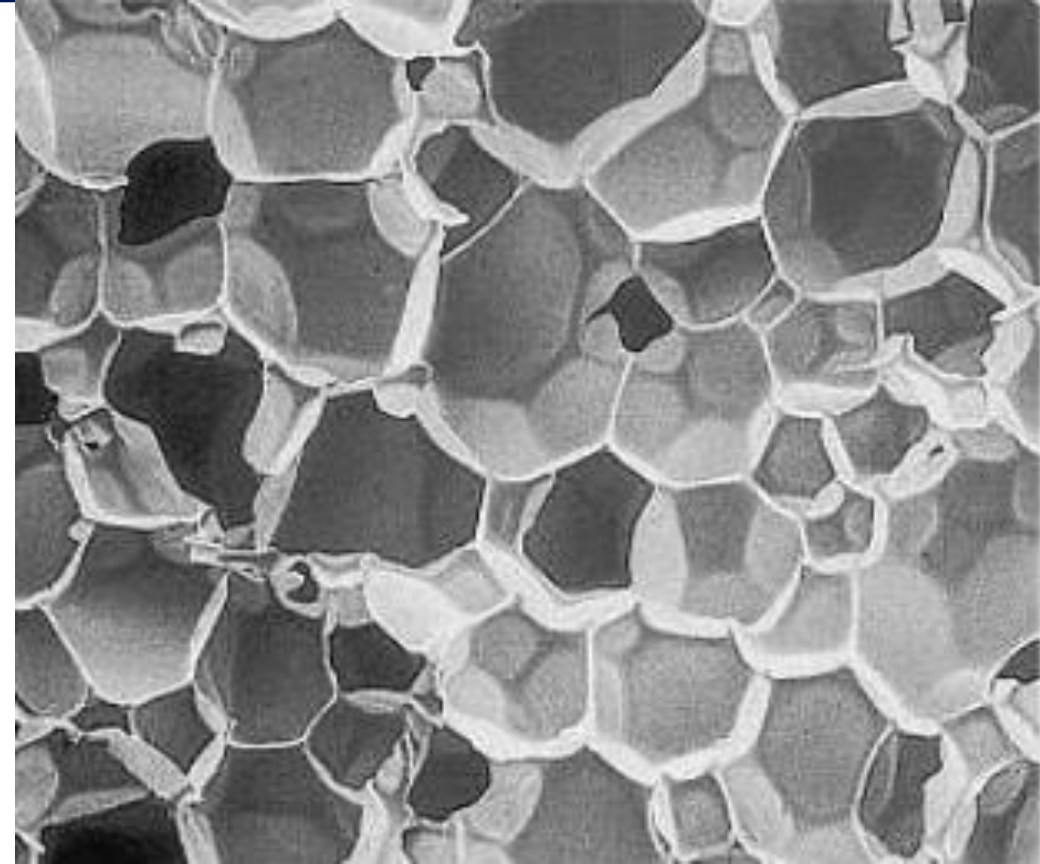


Jornada Reciclatge Químic

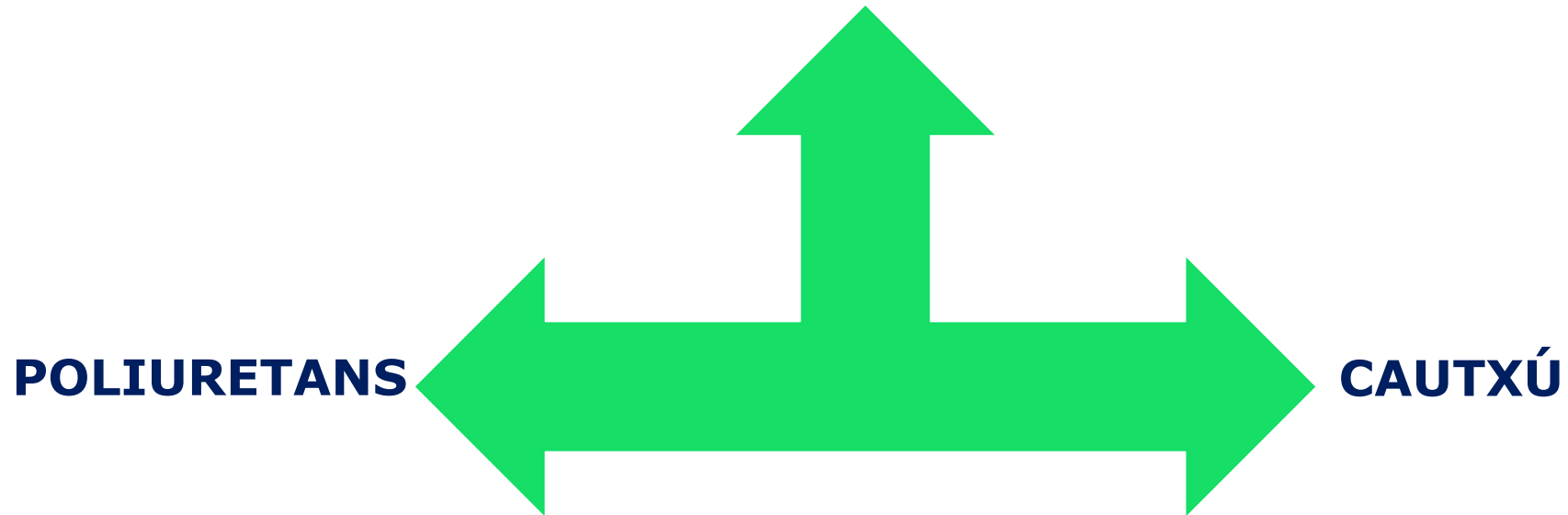
21 d'Octubre 2025

**Reciclatge químic de
termosestables: La
reactivitat no és l'únic
problema**

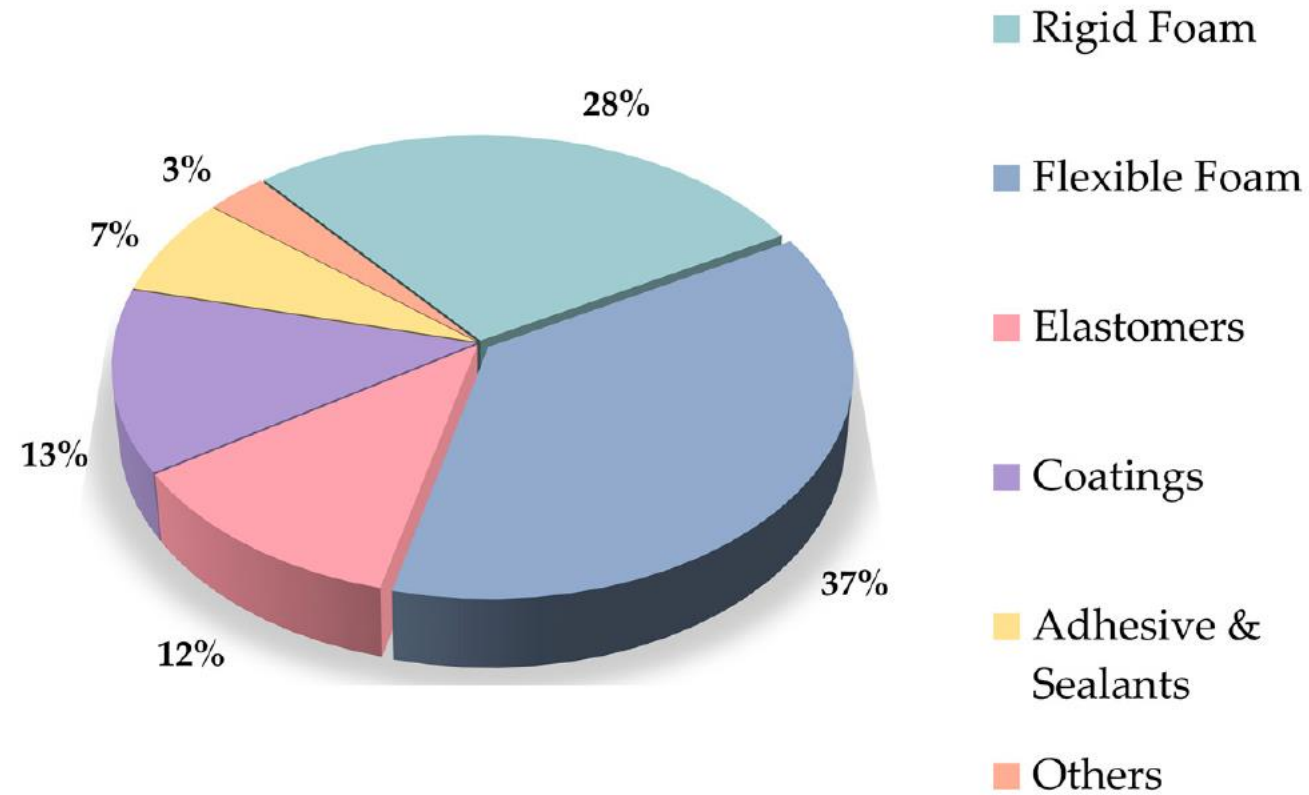


PRIMER DE TOT...

**AVUI PARLAREM DE RECICLATGE QUÍMIC DE
TERMOESTABLES**



Global Polyurethane market



Isocyanate Reactions

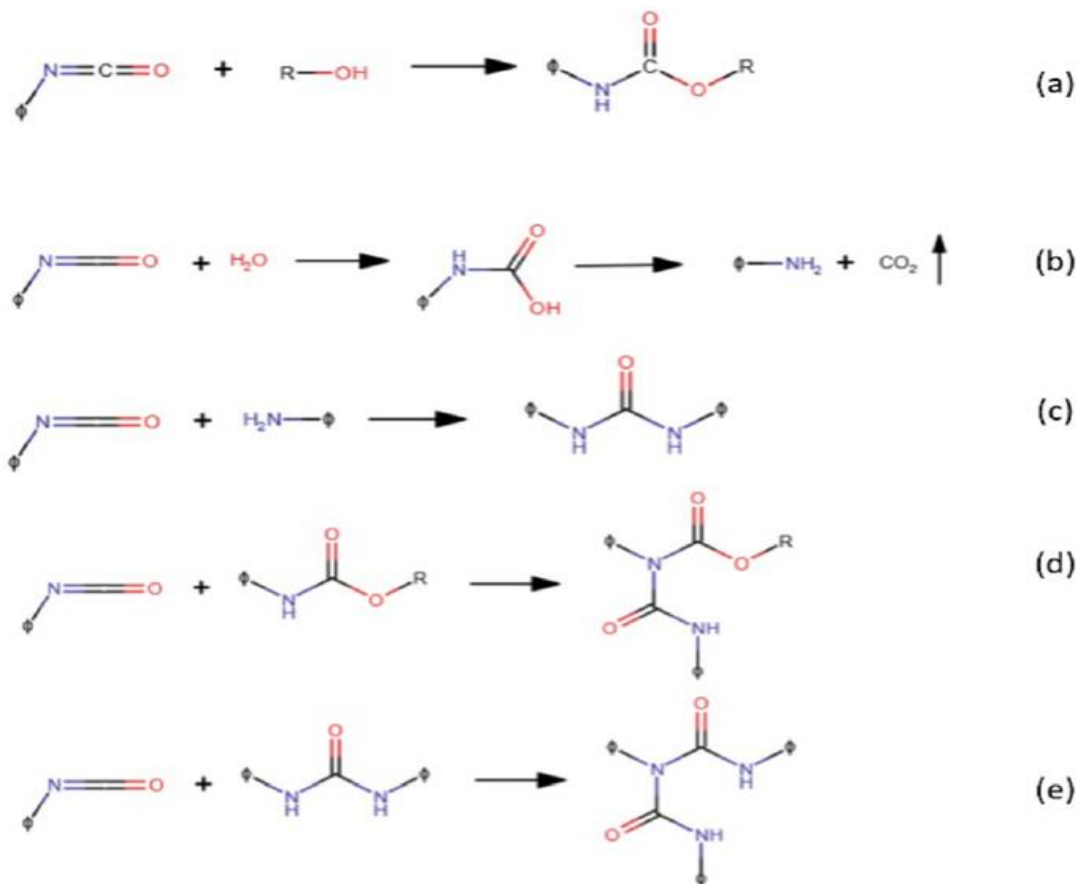


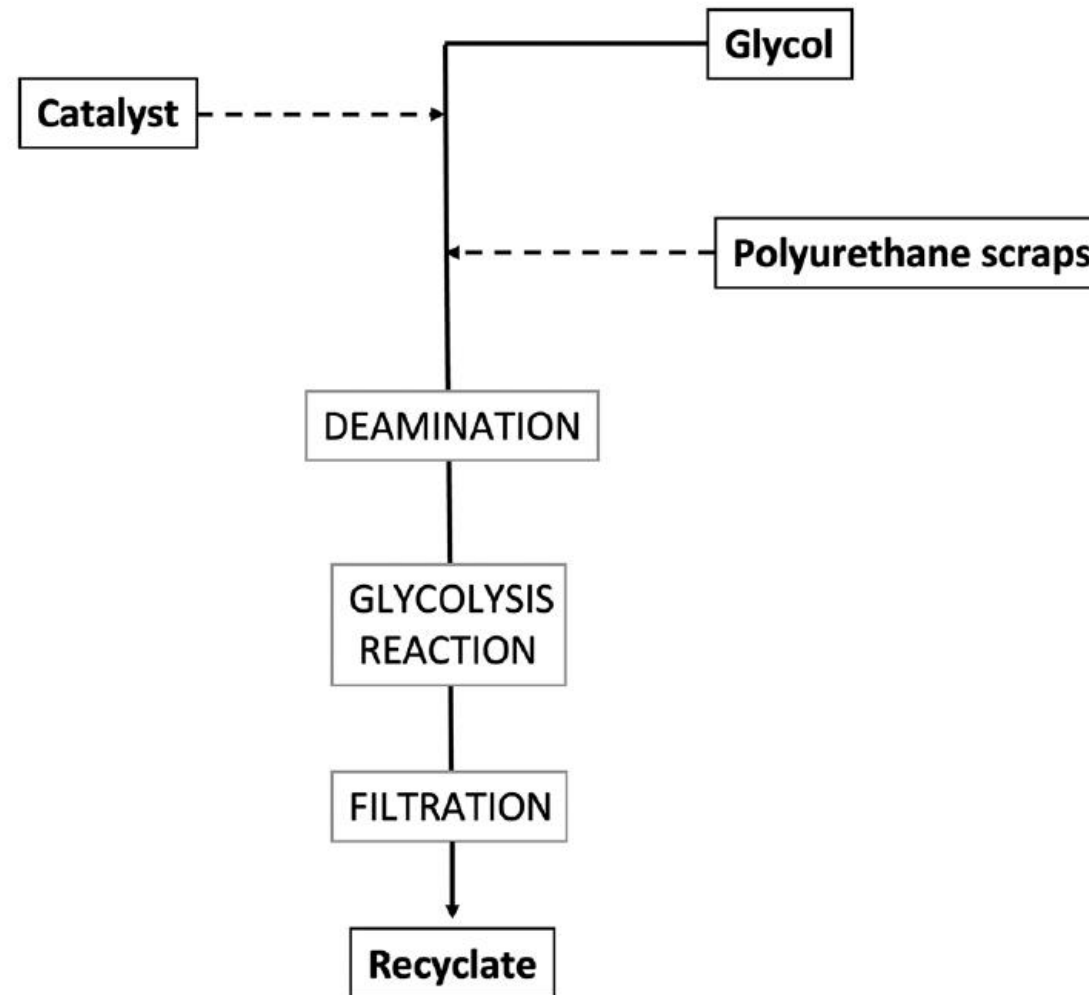
Fig. 1 Reaction between isocyanates and hydroxyl-containing compounds (a), water (b), amine (c), urethane (d), and urea (e).

PU recycling

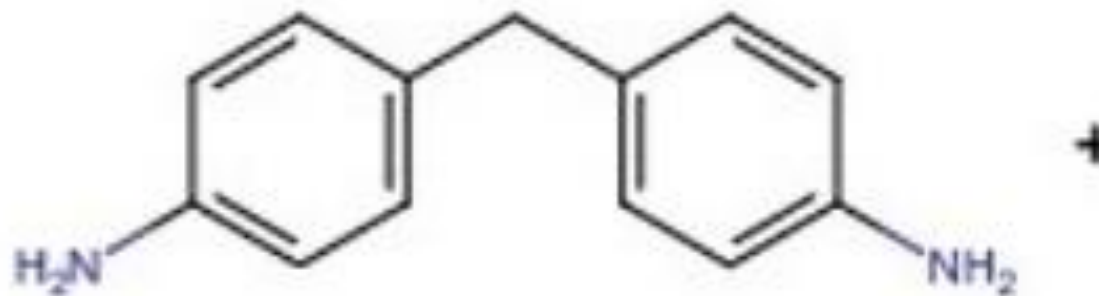
Table 1. Advantages and disadvantages of the possibilities for PU recycling.

Methods of PU Recycling	Advantages	Disadvantages
Physical methods [54]	- Low cost and simplicity of the process - Does not require advanced technological infrastructure - Minimal energy consumption	- Limited processing capabilities—the resulting material can only be used as an additive or filler - Low quality of the recovered material
Thermochemical methods [56]	- Efficient disposal of large quantities of waste - Potential for energy recovery in the form of heat	- Emission of harmful substances (e.g., dioxins, NO_x, CO) - Loss of material—no recovery of original raw materials - High costs associated with flue gas filtration and purification
Hydrolysis [57]	- Ability to obtain basic raw materials that can be reused in production	- Requires high temperatures and pressures, increasing energy costs - The process can be time-consuming. The reaction product is difficult to manage. Low profitability. - Large amounts of carcinogenic amines are formed
Methanolysis [60]	- Ability to obtain basic raw materials that can be reused in production	- The process demands precise control conditions
Aminolysis [61]	- Production of high-quality products such as amines and polyols - Capable of processing different types of PU - Process carried out without an additional catalyst	- Requires the use of toxic amines, posing health and environmental risks - High operational costs
Acidolysis [62]	- Ability to produce products with diverse chemical functionality - The process can be applied to various types of PU	- Involves the use of strong acids, which can be corrosive and difficult to manage
Glycolysis [67]	- High efficiency in recovering high-quality raw materials (polyols) - Applicable to a wide range of substrates and catalysts - Well suited for industrial scale-up - Relatively mild reaction conditions	- Requires the use of catalysts, which can increase process costs - Potential contamination issues with the recovered material

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MDA (the bad guy)



MDA (the bad guy)



4,4'-METHYLENEDIANILINE
CAS # 101-77-9

Agency for Toxic Substances and Disease Registry ToxFAQs

August 1999

This fact sheet answers the most frequently asked health questions (FAQs) about 4,4'-methylenedianiline. For more information, call the ATSDR Information Center at 1-888-422-8737. This fact sheet is one in a series of summaries about hazardous substances and their health effects. It's important you understand this information because this substance may harm you. The effects of exposure to any hazardous substance depend on the dose, the duration, how you are exposed, personal traits and habits, and whether other chemicals are present.

HIGHLIGHTS: Exposure to 4,4'-methylenedianiline occurs mainly in the workplace. Liver damage and skin irritation may occur from exposure to high levels of 4,4'-methylenedianiline. This chemical has been found in none of the 1,445 National Priorities List sites identified by the Environmental Protection Agency (EPA).

What is 4,4'-methylenedianiline?

(Pronounced mĕth'əl-ĕn/ di ān'əlēn)

4,4'-Methylenedianiline is an industrial chemical that is not known to occur naturally. It is also commonly known as diaminodiphenylmethane or MDA. It occurs as a colorless to pale yellow solid and has a faint odor.

4,4'-Methylenedianiline is used mainly for making polyurethane foams, which have a variety of uses, such as insulating materials in mailing containers. It is also used for making coating materials, glues, Spandex® fiber, dyes, and rubber.

What happens to 4,4'-methylenedianiline when it enters the environment?

- ☐ 4,4'-Methylenedianiline is found in tiny particles in air which will settle to land or water in rain or snow.
- ☐ Most of the 4,4'-methylenedianiline in water will attach itself to particles and sink to the bottom sediment.
- ☐ 4,4'-Methylenedianiline in water or sediment will be broken down by bacteria and other microorganisms.
- ☐ It does not build up in the food chain.

- ☐ 4,4'-Methylenedianiline becomes strongly attached to soil and will not easily move into groundwater.
- ☐ It may take as long as 10 days for bacteria and microorganisms in soil to break down 4,4'-methylenedianiline.

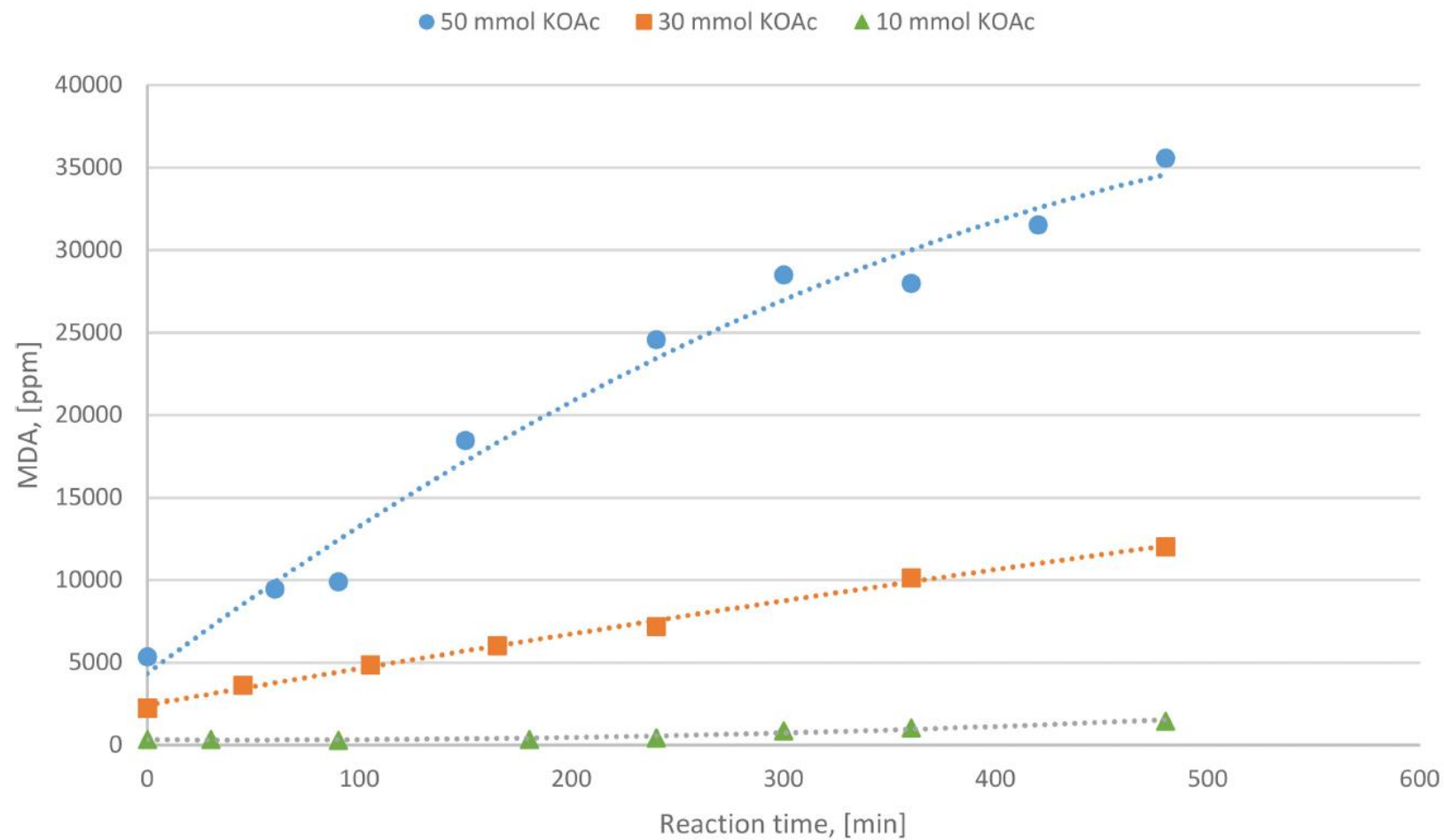
How might I be exposed to 4,4'-methylenedianiline?

- ☐ Working in an industry that makes or uses 4,4'-methylenedianiline.
- ☐ Touching consumer goods such as polyurethane foams that contain it.
- ☐ Living near a hazardous waste site where 4,4'-methylenedianiline is disposed of.
- ☐ Being treated by a kidney dialysis machine. Tiny amounts are released from the polyurethane parts of the machine when it is sterilized by radiation or heat.

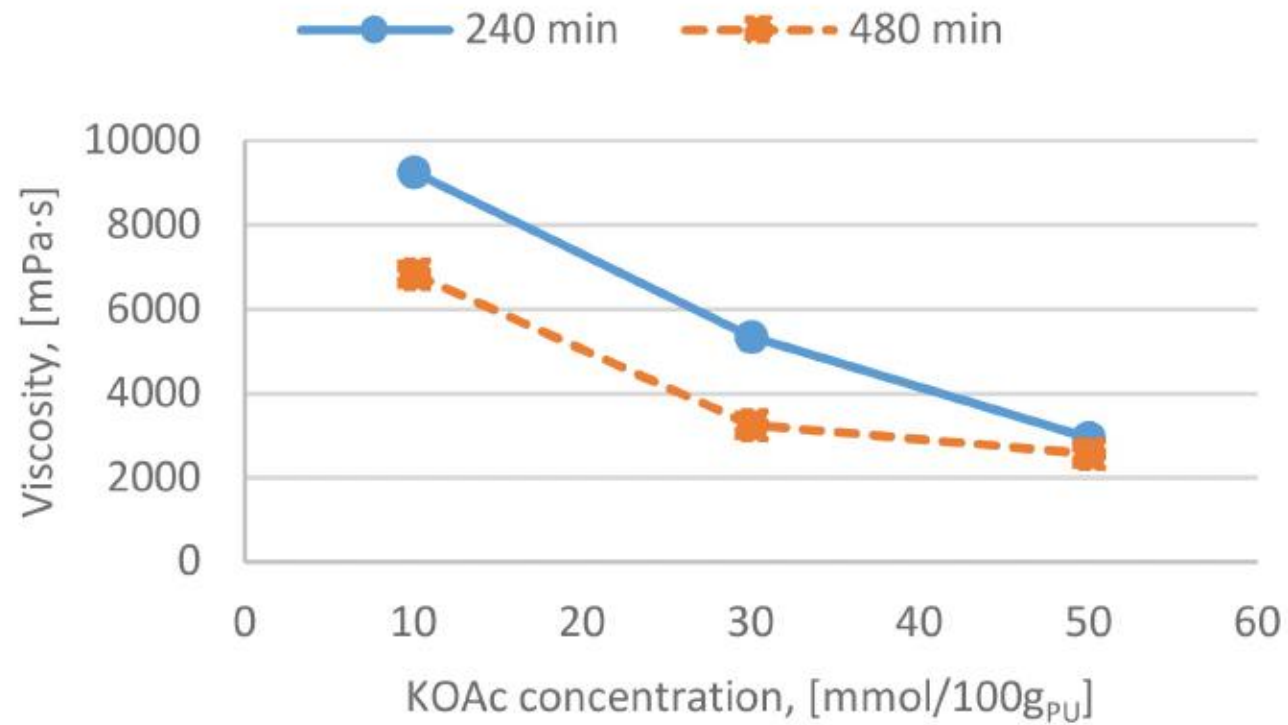
How can 4,4'-methylenedianiline affect my health?

Limited information is available on the effects of 4,4'-methylenedianiline on people's health. The available

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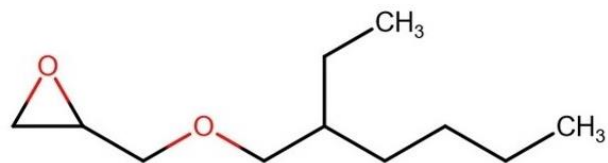
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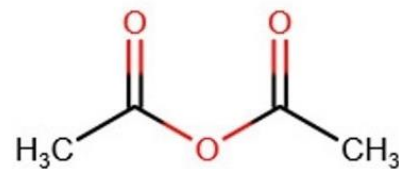
Reducing MDA (the bad guy)

- Air Products, Dow Chemical Company, and McDonnell Douglas diminished MDA content using alkylene oxides such as ethylene oxide (EO) a propylene oxide (PO)[31–34].
- Bayer AG employed low molecular weight urea or carbamic acid esters such as ethyl or methyl carbamate or hydrogen chloride.
- BASF reduced MDA with epoxidized native fatty oils such as soybean oil, linseed oil, rapeseed oil, and nut oils, or adding stepwise small amounts of isocyanate.
- H&S Anlagentechnik GmbH developed an acidolysis process to recycle PU

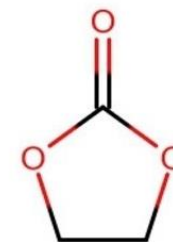
Deamination (the Good Guys)



(A)

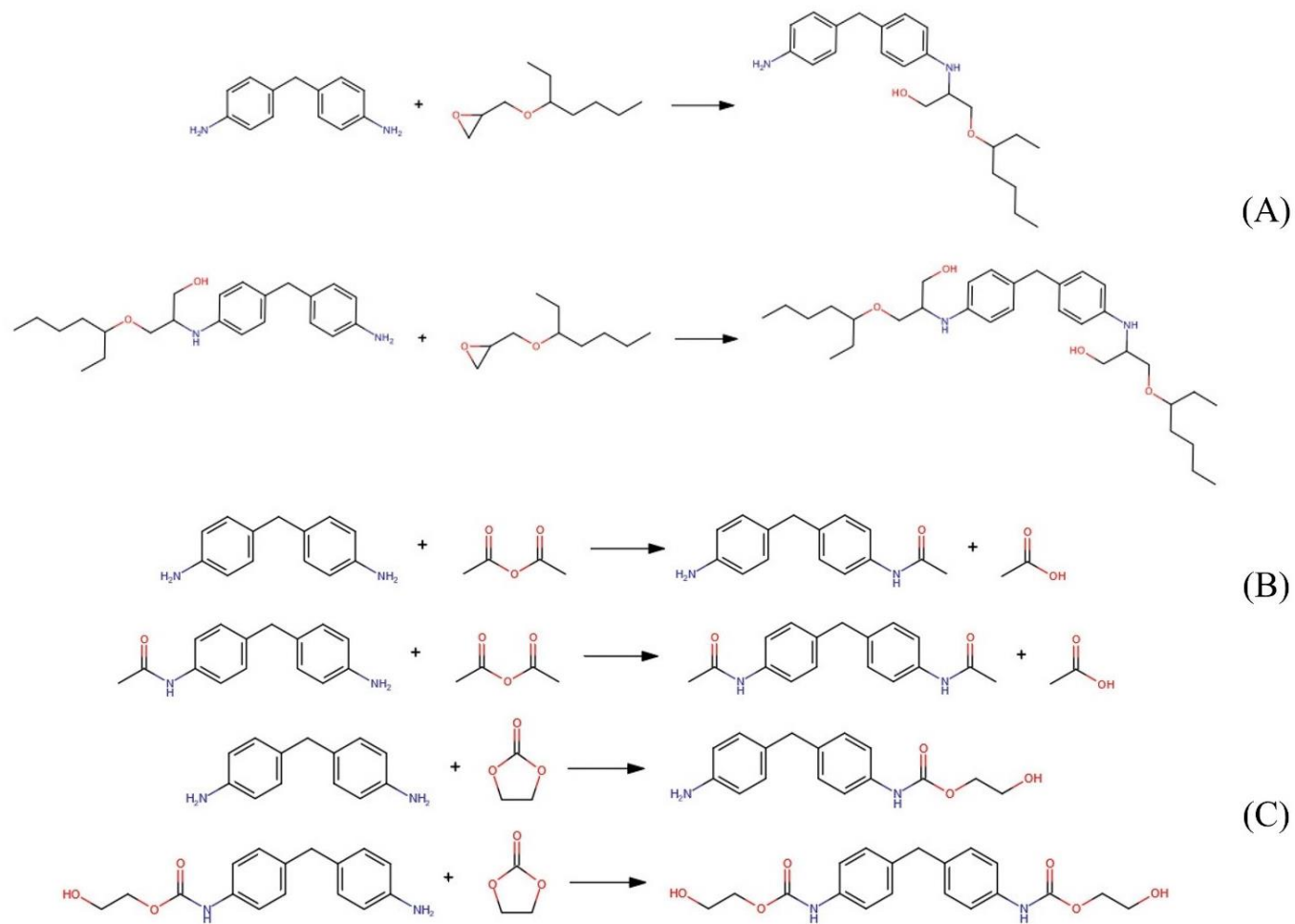


(B)



(C)

Deamination



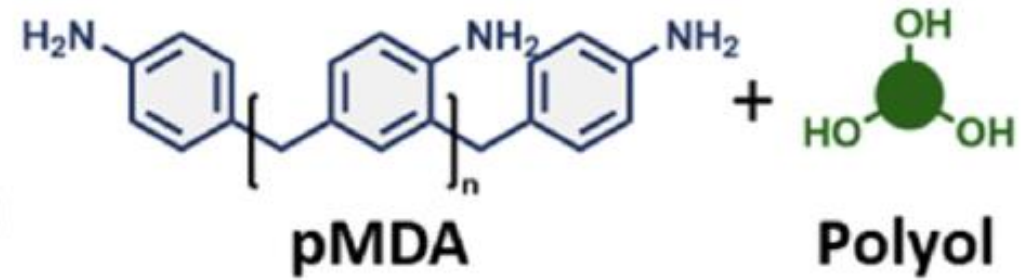
Scheme 1. Reaction schemes of 4,4'-MDA with deaminating agents. (A) 2-EHGE, (B) Ac_2O , and (C) EC.

AMMONOLYSIS



2 g rigid PU

8:1 (NH_3 :IC)
150 °C
→
10 mL THF, 2 h
19 bar



Rubber Recycling



**RECICLAJE Y
REUTILIZACIÓN
DEL CAUCHO**

Rubber Recycling

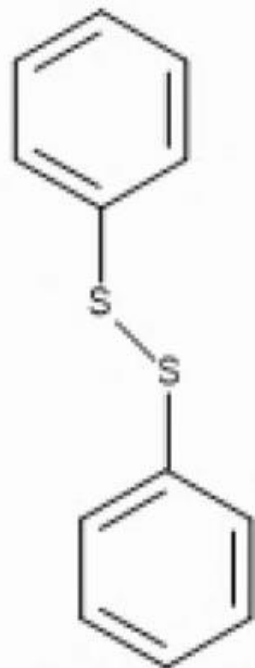


Rubber Recycling

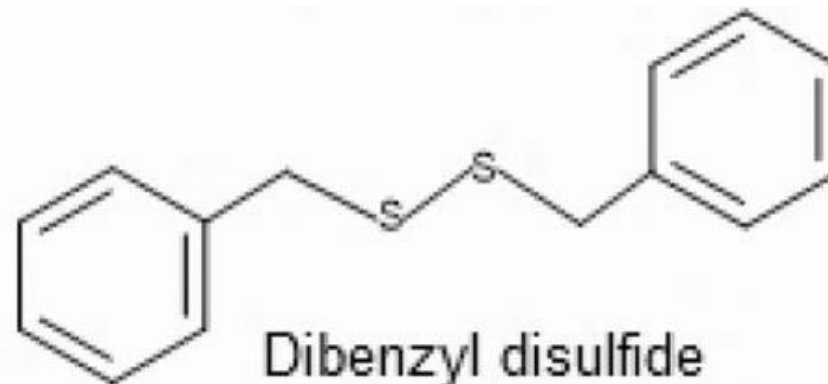
Table 5.1. Dissociation Energy of bonds in rubber crosslinks⁸.

Bond	Dissociation energy, kcal/mol
alkyl- C-C -alkyl	80
alkyl- C-S-C -alkyl	74
alkyl- C-S-S-C -alkyl	54
alkyl- C-S_n-S_m-C -alkyl	34

Rubber Recycling reagents

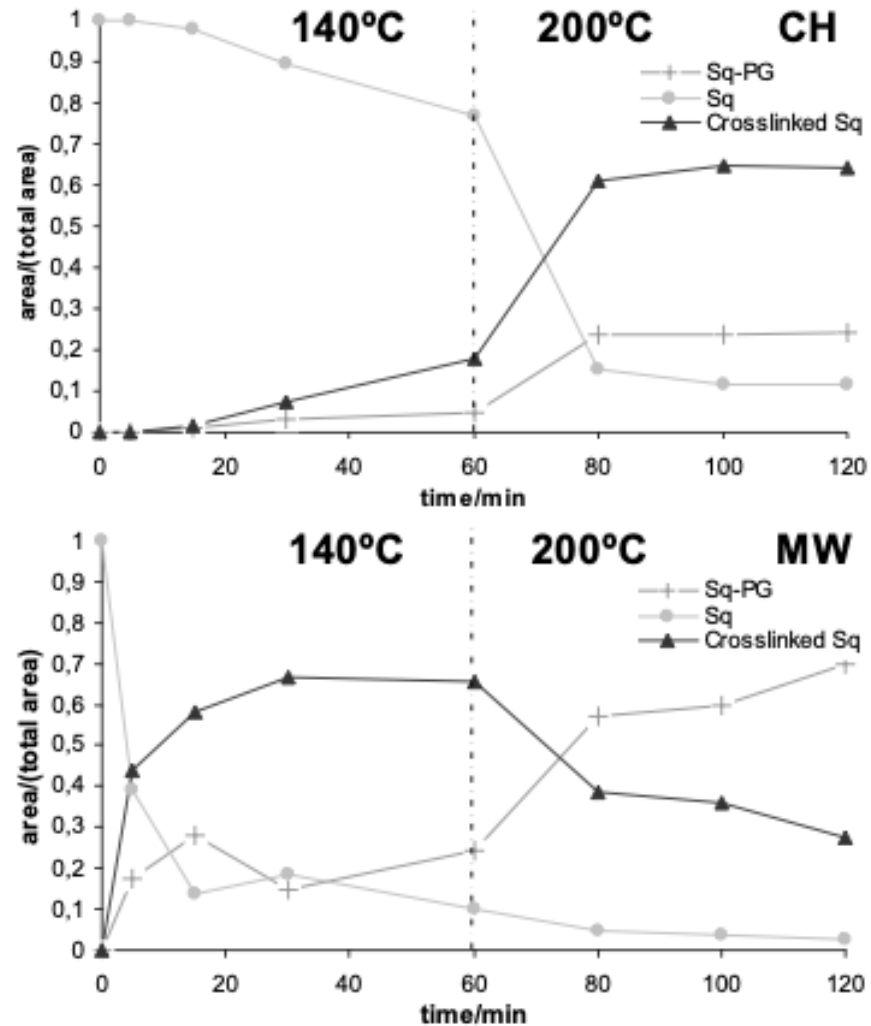


Diphenyl disulfide

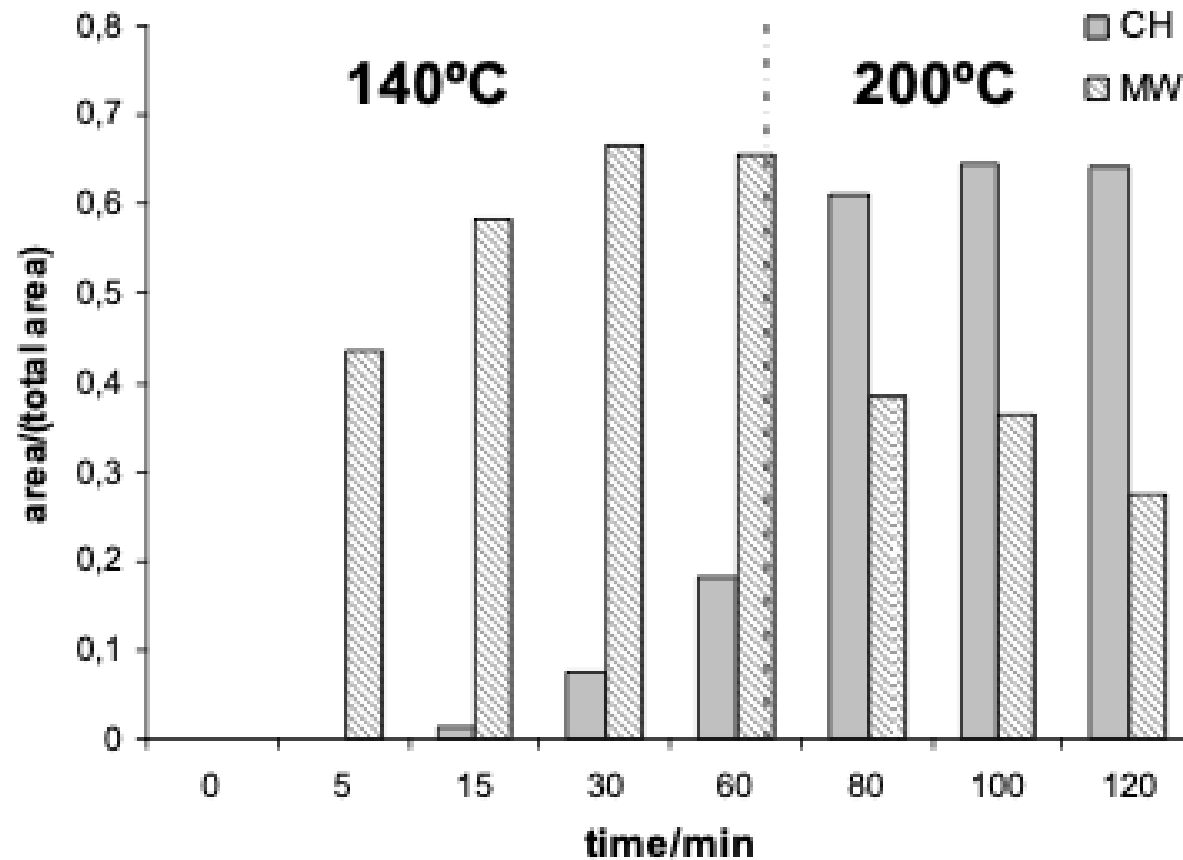


Dibenzyl disulfide

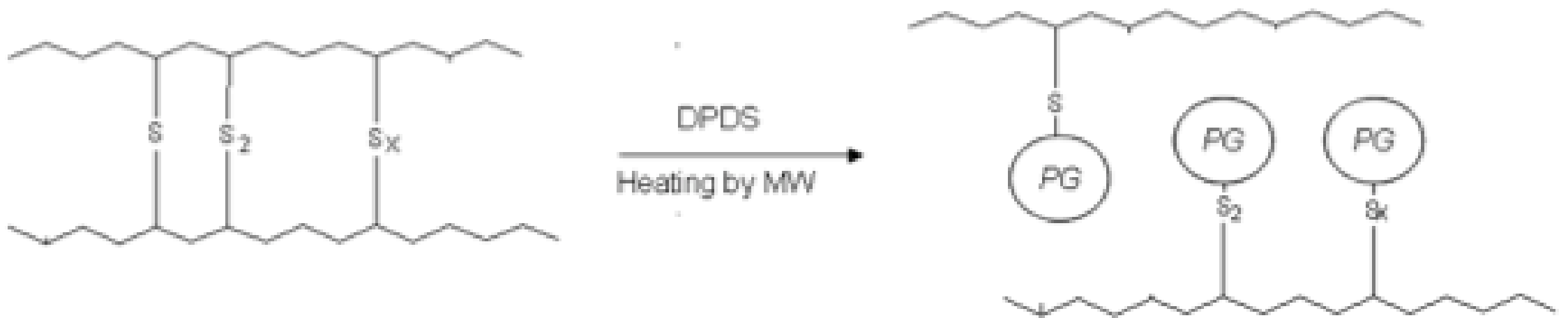
Rubber Recycling Conventional Heating vs Microwaves



Rubber Recycling Conventional Heating vs Microwaves



Rubber Recycling



Take-home Messages

- Reactivity of Thermosets polymers is well known.
- This is not a technology problem.
- Huge problems with by products and post cleaning. Is recycling worse for the environment than the thermoset itself?
- Long way to follow in the design of thermosets for better recycling potential.