

Chemical treatment for rubber waste to recycle by degradation and obtain sustainable products

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INTRODUCTION

In response to the high demand and wastes of industrial rubbers, a global effort has been made to reduce elastomeric, plastic, and microplastic pollution by studying various mechanisms of polymer degradation, including thermal degradation, mechanical treatment, UV exposure, and chemical processes. Recently, innovative techniques have emerged, such as degradation via metathesis, in which they seek to break the polymeric chains of synthetic rubbers and obtain molecules of lower molecular weight [1-3].

This work aims to synthesize polyesters and polyols by metathesis degradation of rubber waste using mild reaction conditions. This process can contribute to reuse and recycling through rubber degradation to obtain sustainable products that can be used for the synthesis of engineering design polymers, intermediates, fine chemicals, and the polyurethane industry.



MATERIALS AND METHOD

Butadiene rubber (BR) was obtained from Goodyear (TX, USA), $M_n = 111259$ g/mol, $M_w = 686799$ g/mol by GPC. Rubber waste from rubber gloves and latex. The fatty alcohol 10-undecen-1-ol and the fatty acid methyl 10-undecenoate as chain transfer agents (CTA); dichloroethane anhydrous (99.8%) as solvent; methanol (ACS reagent) to wash and isolate products; and the HG2 catalyst (Ru) second-generation Hoveyda-Grubbs, were purchased from Sigma-Aldrich, Inc. (St. Louis, MO, USA), and used as received.

01

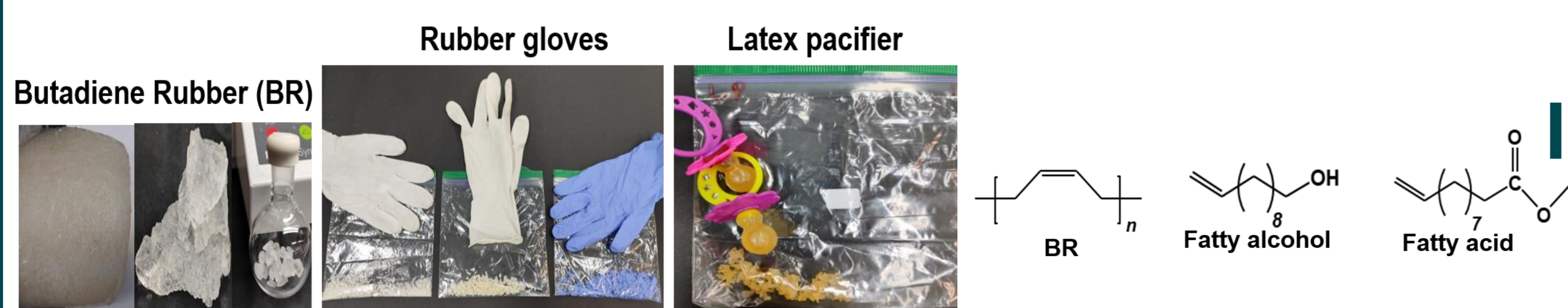
The synthesis of polyesters and polyols was carried out via metathesis degradation reaction from BR or rubber waste using the fatty alcohol 10-undecen-1-ol for polyols and the fatty acid methyl 10-undecenoate for polyesters, as shown in Fig. 1 and 2.

02

The molar ratios of double bonds of rubber waste (2g) to CTA used were [Rubber]/[CTA] = 1:1, 1:4, 1:13, and 1:32 to control the molecular weights.

03

All reactions were carried out in a flask under a dry nitrogen atmosphere at 45 °C for 12 h. Finally, the polyols and polyesters were washed three times with methanol, isolated, and dried under a vacuum oven.



ACKNOWLEDGEMENTS

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RESULTS AND DISCUSSION

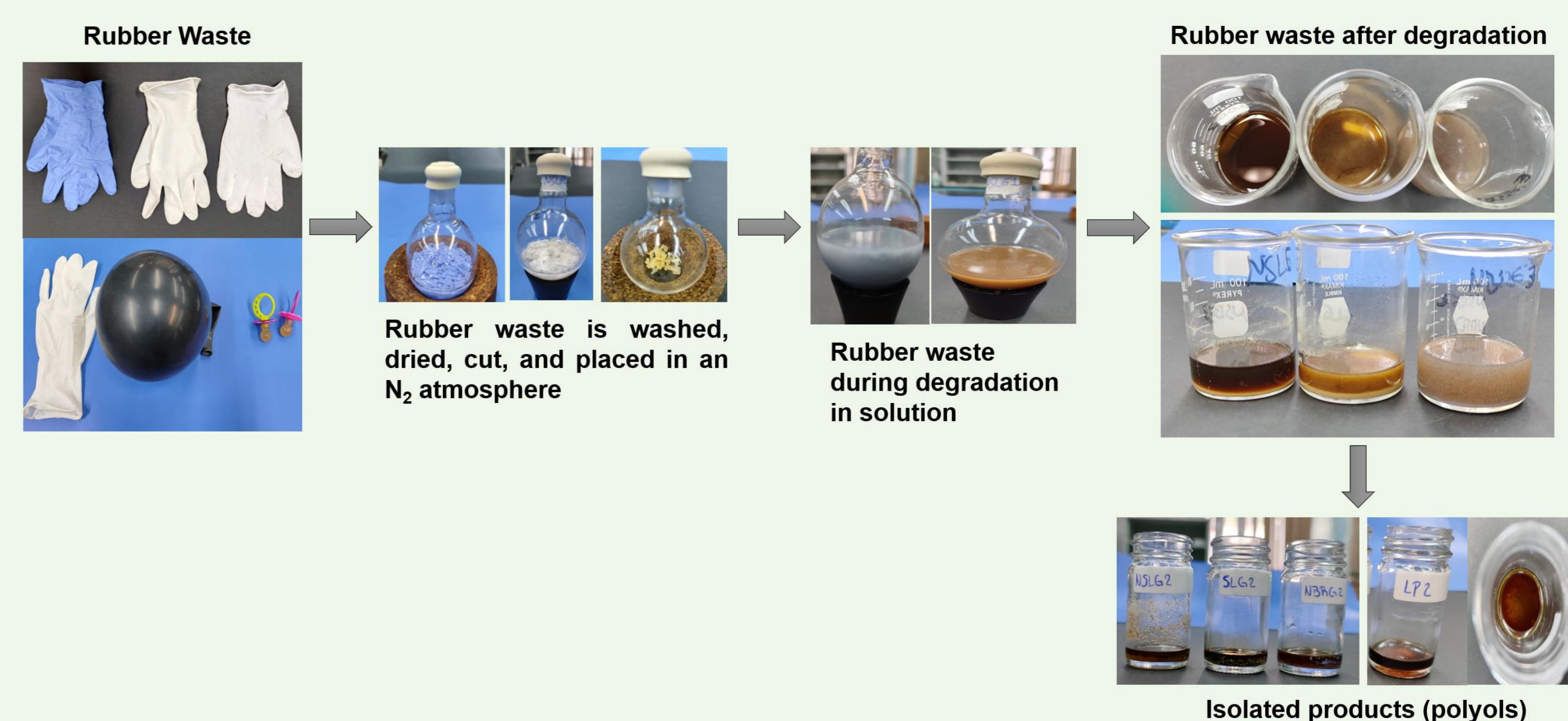


Fig. 1. Chemical treatment for rubber waste to recycle by degradation and obtain sustainable products.

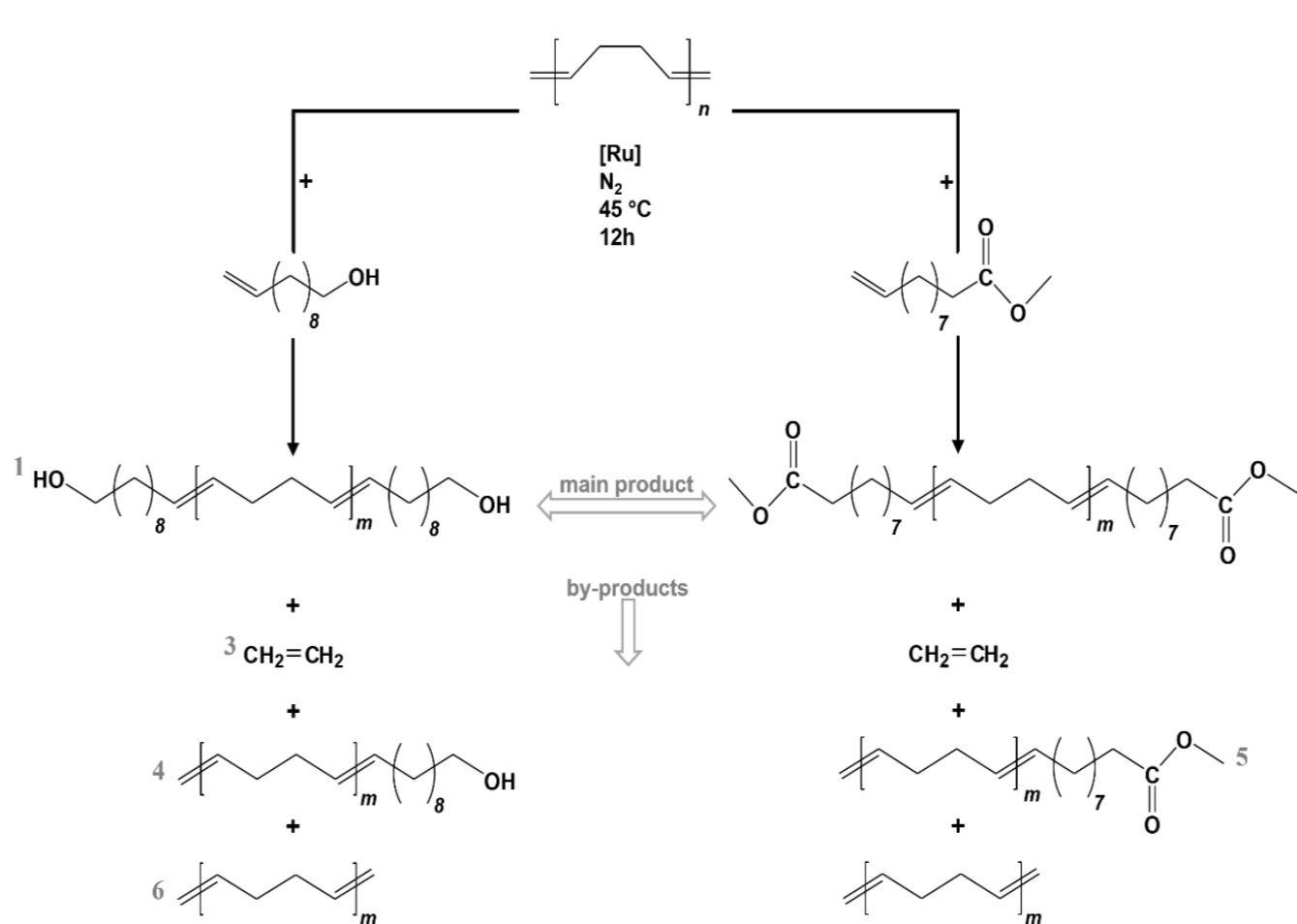


Fig. 2. Synthesis of polyols (1) polyester (2) by degradation via metathesis of rubber waste.

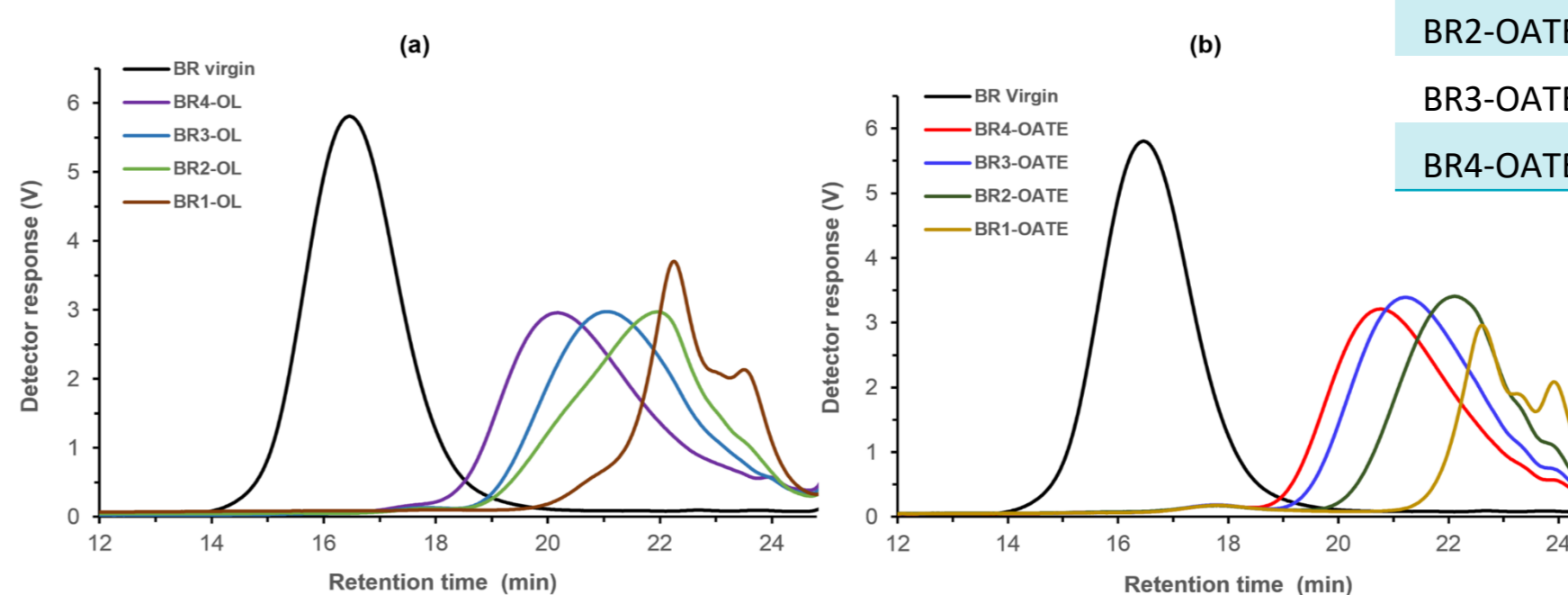


Fig. 3. Retention time comparison of rubber before degradation (black line), polyols (a), and polyesters (b) synthesized.

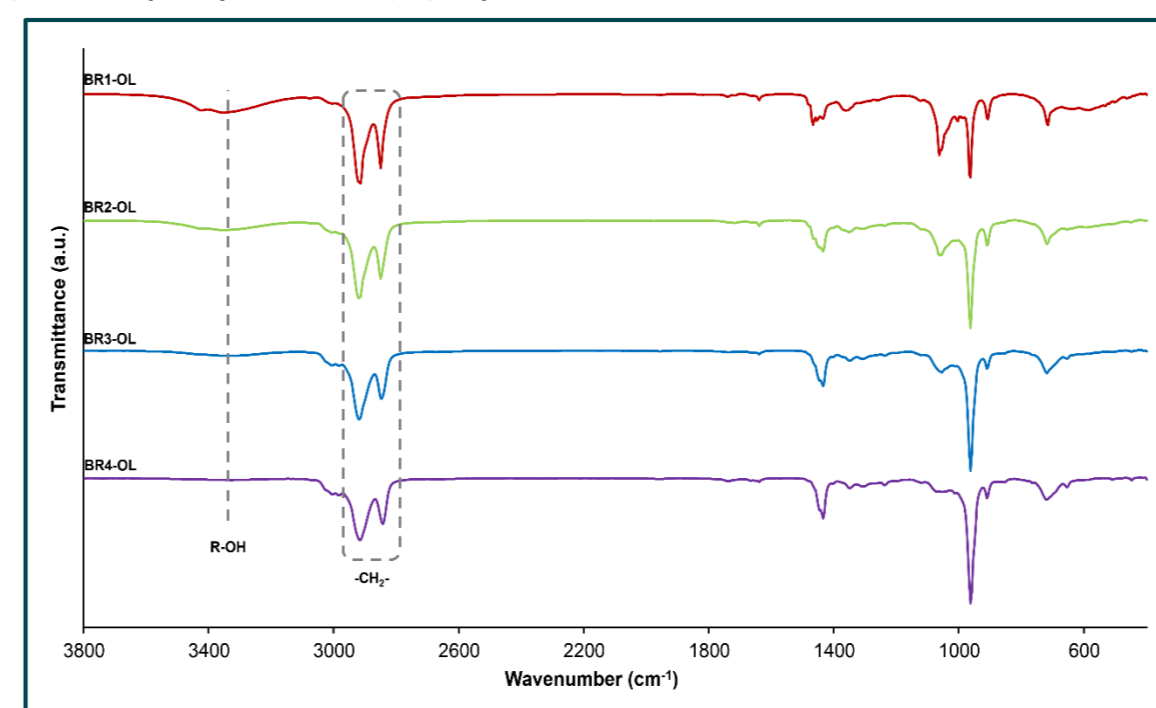


Fig. 4. FT-IR spectra corresponding to polyols obtained (samples BR1-OL to BR4-OL).

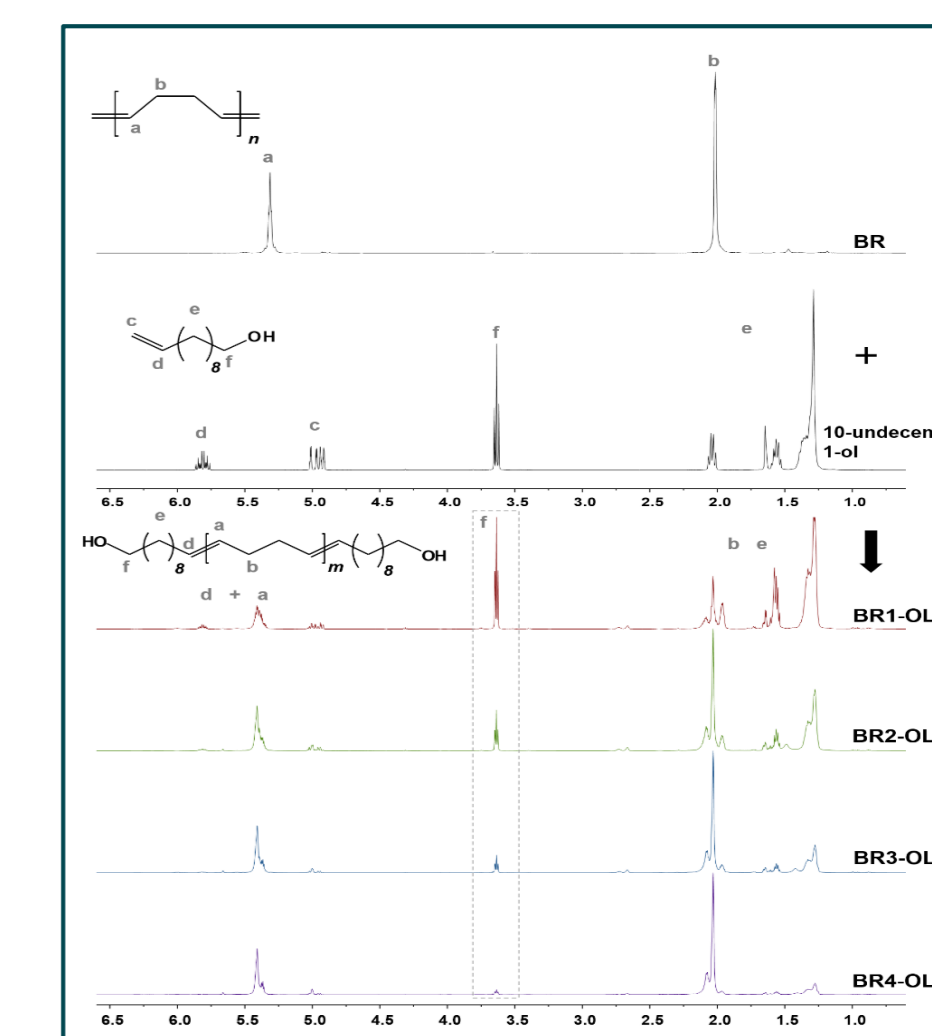


Fig. 5. ¹H-NMR spectra of rubber (BR), 10-undecen-1-ol as CTA, and the polyols obtained from the reactions (samples BR1-OL to BR4-OL).

Table 1. Results of the synthesis of elastomeric polyesters and polyols by GPC.

Sample	[BR]/[CTA] (mol/mol)	Theoretical molecular weight Mw	Molecular Weight by GPC			
			Retention time (min)	M_n (g/mol)	M_w (g/mol)	PDI
BR Virgin			16.5	111259	686799	6.2
Polyols (CTA: 10-undecen-1-ol)						
BR1-OL	1:1	366	22.2	687	797	1.2
BR2-OL	1:4	528	21.9	871	1460	1.7
BR3-OL	1:13	1014	21.0	1083	1852	1.7
BR4-OL	1:32	2040	20.2	1629	3963	2.4
Polyesters (CTA: Methyl 10-undecenoate)						
BR1-OATE	1:1	422	22.6	585	605	1.0
BR2-OATE	1:4	584	22.1	696	872	1.3
BR3-OATE	1:13	1070	21.2	965	1452	1.5
BR4-OATE	1:32	2096	20.8	1201	2000	1.7

CONCLUSIONS

- Polyesters and polyols were successfully synthesized with 94-97% yields. The formation of polyol and polyester was confirmed using FT-IR and NMR, and the main products' different functional groups and structures were assessed.
- The results indicate that the molecular weight of polyols and polyesters could be controlled using different molar ratios of 1, 4, 13, and 32. Polyols with Mw ranging from 797 to 3963 g/mol and polyesters from 605 to 2000 g/mol were obtained, with polydispersity index from 1.0 to 2.4 calculated by GPC.
- This process can contribute to reuse and recycling through the degradation of rubber waste to obtain sustainable products that can be used for the synthesis of engineering polymers, intermediates, fine chemicals, elastomers, and the polyurethane industry.



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