



## Graft Copolymerization of Methylmethacrylate onto *Ximeniaamericana* Seed Oil-Based Polyurethanes using an initiator-accelerator couple system: Effect of initiation time on Mechanical, Swelling and Morphological Properties

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**ABSTRACT:** Graft copolymerization continues to play an important role in the modification of a wide range of polymer materials for industrial application. The objective of this study was to investigate the effect of varied initiation time of benzoyl peroxide-N,N-dimethyl-para-toluidine couple system by free radical solution polymerization on the mechanical, swelling and morphological properties of polyurethane-graft-polymethylmethacrylate copolymer using appropriate standard methods. The tensile and flexural properties for HDPU-1.02-g-PMMA and TDPU-1.02-g-PMMA increased within (20-30 min.) initiation time and decreased thereafter, these parameters for MDPU-1.02-g-PMMA, increased over the whole range of initiation time (20-40 min.). The copolymers showed maximum and minimum swelling in chloroform and propanol respectively, with exception of propanol. MDPU-1.02-g-PMMA copolymer presents the highest swelling in other solvents. HDPU-1.02-g-PMMA and TDPU-1.02-g-PMMA copolymers prepared at 40 min. initiation time showed macrophase separation. In contrast, MDPU-1.02-g-PMMA prepared at identical condition, indicates an encapsulated polymethylmethacrylate chain within the MDPU-polymer matrix. The results showed that *Ximeniaamericana* seed oil was an effective precursor for polyurethane-graft-polymethylmethacrylate copolymers with physico-mechanical properties characterized by structural orientation of the base polyurethane matrix and polymerization initiation time.

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Polymers continue to play important roles in vital sectors of any nation's economy. Grafting has become a veritable chemical tool in the polymer industry to import desired properties into the copolymer to address specific applications. Notwithstanding the remarkable applications of polyurethanes Randall and Lee, (2003), grafting of vinyl monomers onto this polymer backbones is one of the most effective method to improve the performance of its pristine

form relative to resistance towards mechanical stress, chemicals and solvents, with a view to widening and explore broader applications of the copolymer Huang *et al.*, (2006); Pallavi and Nivedita, (2015). Vinyl monomers notably; styrene, vinyl acetate, methylmethacrylate and dialkylfumarates, polymerizes in the vicinity of the polyurethane prepolymer and form grafted chains to the backbone of this step-growth polymer Zoriana *et al.*, (2016).

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Free radical polymerization is usually initiated by dissociation of initiator, which could be of several types including; thermal, photolytic, redox and persulfate initiators Motawie *et al.*, (1995). Among these initiators, thermal initiators, such as organic peroxide and azo compounds are commonly used Hiemenz and Lodge, (2007). When thermal initiator is heated up to a certain temperature, its bond cleaves homolytically into free radicals. Polymerization initiation reaction is limited by speed of initiator decomposition, which gives credence to the use an accelerator in an initiator-accelerator couple system to enhance the speed of initiation reaction Penezek *et al.*, (2005). Although studies have reported the grafting of polystyrene onto the backbone of seed oil derived polyurethanes Naveed *et al.*, (2022); Samuel *et al.*, (2024), to the best of our knowledge, no previous study has been advanced on graft copolymerization of methyl methacrylate onto a seed oil based polyurethane backbone taking cognizance of the effect of varied polymerization initiation time by a initiator-accelerator couple system on the character of the copolymer. Therefore, this research piece was undertaking to investigate the effect of varied initiation time by Benzoyl Peroxide -N, N-Dimethyl-para-toludine initiator-accelerator couple system on the mechanical, swelling and morphological properties of *Ximeniaamericana* seed oil polyurethanes grafted polymethylmethacrylate copolymers.

## MATERIALS AND METHODS

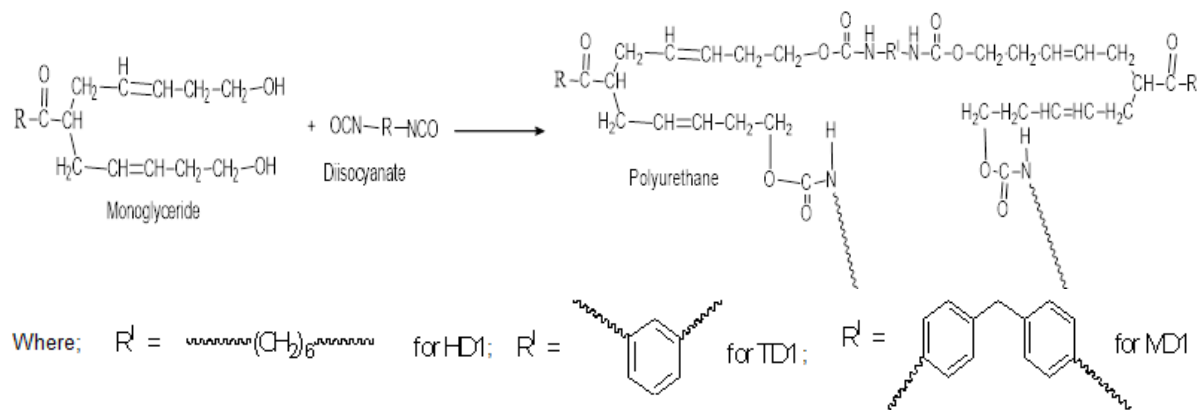
*Extraction of Ximeniaamericana seed oil:* *Ximeniaamericana* seeds sourced from Yola, Adamawa State were cracked, washed with water, sun-dried for 14 days and milled (Binatone, Japan, model BLG-400) into a paste. Oil was extracted from the paste with n-hexane using a soxhlet extractor Samuel *et al.*, (2024). 200 g of paste was packed in a soxhlet thimble and 500 ml n-hexane was poured into the 1000 ml soxhlet round bottom distillation flask. A condenser was connected to the top of the extractor. The heating mantle was switched on (set at 70 °C) and heat was supplied to the distillation flask. Vaporized solvent were generated and condensed as hot liquid solvent in the packed thimble. This process continued for 6 hours and resulted in the extraction of the oil through various siphoning of oil plus solvent into the distillation flask. The mixture of oil and solvent was separated by the use of rotary evaporator.

*Preparation of Ximeniaamericana monoglyceride:* Extracted *Ximeniaamericana* seed oil and glycerol; molar ratio of 1:3 were poured into a 500 ml three-neck reaction round bottom flask equipped with a

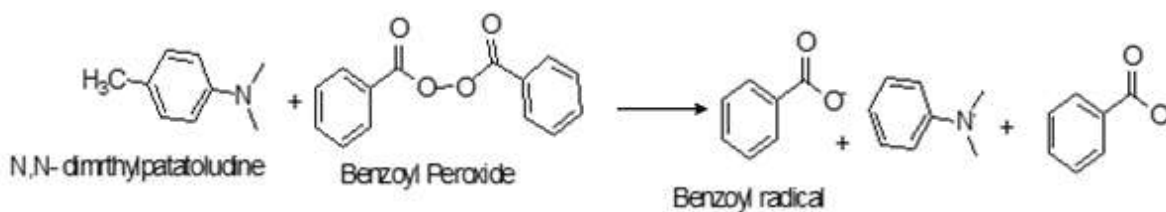
stirrer, a thermometer and nitrogen inlet tube. The mixture was stirred (300 rpm) and heated on a thermostatic heating mantle to a temperature of 200°C for 45 minutes. At this point, calcium hydroxide (0.1 wt % of the oil) was added as catalyst and the temperature raised to 230°C and maintained at this temperature for 3 h, after which an aliquot was withdrawn from the reaction mixture and tested for its solubility in methanol. After, cooling the reaction mixture it was dissolved with diethyl ether and washed first with 0.1 M HCl solution and then with distilled water to remove the catalyst and the residual glycerol. The ethereal layer was then dried over sodium sulphate for 24 h. The residual solvent was removed with the aid of a rotary evaporator.

*Graft copolymerization reaction of methylmethacrylate onto Ximenia polyurethane:* The copolymer was prepared through grafting of methylmethacrylate monomer onto *Ximeniaamericana* seed oil polyurethanes backbone, by free radical solution polymerization initiated by benzoyl peroxide - dimethyl paratoludine couple system. Hexamethylenediisocyanate (HDI) corresponding to 1.02 isocyanate index was fed into a 250 ml three-neck round bottom reaction flask, fitted with a stirrer, thermometer, reflux condenser and a nitrogen inlet tube. *Ximeniaamericanamonoglyceride* dried over silica gel for 24h was added along with 0.002 wt. % of dibutyltindilaurate compared to the weight of monoglyceride. The flask and its accessory were then mounted on a thermostatic heating mantle. The temperature of the mantle was set at 50° C and the polymerization was maintained for 1h with continuous stirring (100 rpm) under nitrogen atmosphere. The initiator (a couple system; 5ml benzoyl peroxide and 2.5ml dimethyl paratoludine) was added slowly, over a period of 2 minutes into the reaction mixture, the temperature of the mantle was adjusted to 120° C and stirred (150 rpm) for 20 minutes initiation time, 5ml of acetone and 20ml of methylmethacrylate was added to the reaction mixture, with the temperature maintained at 105° C for 45 minutes under nitrogen atmosphere. The viscous polymer was then precipitated in acetone to remove free polymethylmethacrylate homopolymer chains. Finally, the precipitated copolymer was poured in to a Teflon mould and covered, to prevent moisture and allowed to cool to ambient temperature. The polymer film was later removed from the mold and conditioned at ambient temperature for fourteen (14) days. This sample was coded HDPU-1.02-g-PMMA. The polymerization was repeated for 30 and 40 minutes initiation time respectively. Other samples coded TDPU-1.02-g-PMMA and MDPU-1.02-g-PMMA was prepared by the same protocol, but with toluene diisocyanate and methylene

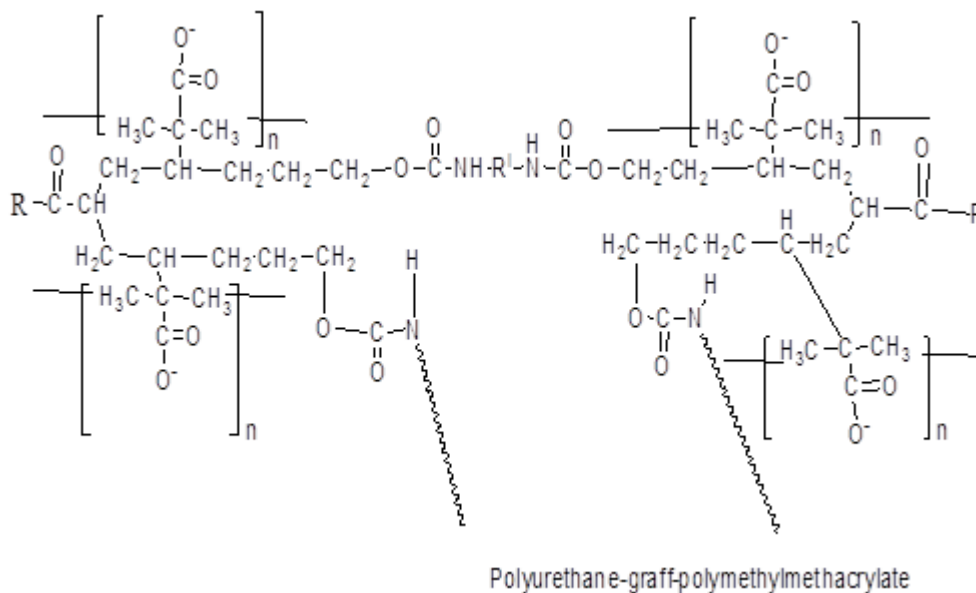
diphenyldiisocyanate respectively, as diisocyanate content for the polyurethane polymer backbone.



Scheme 1: Formation of Ximenia americana Polyurethane



Scheme 2: Redox initiation system



Scheme 3: Methylmethacrylate-Urethane Copolymer

**Characterization of the Methylmethacrylate-Urethane graft Copolymers:** The tensile properties were determined with an electromechanical universal testing machine (INSTRON Model: 5566 USA) at a strain rate of  $10\text{mm min}^{-1}$  using rectangular specimens ( $20\text{mm} \times 10\text{mm} \times 1\text{mm}$ ) at room temperature. Determination of the properties was carried-out in

triplicate and the values reported are the mean and standard deviation respectively. Flexural mechanical properties were determined using Instron Machine model 1190 according to ASTM D-790 and using rectangular specimens  $25\text{mm} \times 15\text{mm} \times 1\text{mm}$  and a cross head speed of  $2\text{mm min}^{-1}$  and a gauge length span of  $40\text{mm}$ . Determination was done in triplicate

and the values reported are the mean and standard deviation respectively. The swelling properties of copolymer samples were determined by gravimetric technique Gopalakrishnan and Fernando, (2011). Copolymer sheets (25mm×10mm×1mm) after taking their dry weight were placed in four different solvents: chloroform, acetone, diethyl ether and Propanol in a standard test-tube stopped with aluminum foil, supported on a rack and maintained at room temperature. The sheets were taken out at 24h interval and weighed immediately and replaced in the solvent. This procedure was repeated on till equilibrium saturation was attained. The swelling mass was evaluated using equation 1;

$$\text{Swellingmassratio}(qm) = \frac{W}{w} (1)$$

Where W is the equilibrium weight of swollen copolymer and w is the weight of dry copolymer. The copolymer micro-graphs were observed with a field emission scanning electron microscopy (FE-SEM Philip XL 30 ESEM-FEG). Sample size of 0.5 mm for each copolymer was immersed in liquid Nitrogen, and coated with Gold before imaging.

## RESULTS AND DISCUSSION

The tensile, flexural and elongation properties of *Ximenia* polyurethanes-graft-polymethylmethacrylate are presented in table 1. The tensile and flexural

properties for HDPU-1.02-g-PMMA and TDPU-1.02-g-PMMA copolymers, increase with initiation time (20-30 min.) and decrease thereafter i.e, at 40 min. the corresponding elongation at break decrease and then increase with initiation time. The tensile and flexural properties for MDPU-102-g-PMMA copolymer increase over the whole range of initiation time, 20-40 min. with a corresponding decrease in elongation at break. The higher tensile and flexural properties of the latter copolymer, may be attributed to the relative reactivities of isocyanate groups in MDI which resulted in the formation of heterocyclic isocyanurate and carbodiimide oligomers Samuel *et al.*, (2023), the unsymmetrical nature of these ring oligomers and their concomitant cyclization occasioned by polycyclotrimerization Samuel (2019), accounts for the amorphous character of MDPU polyurethane backbone, thereby, making the polymer matrix more prone to diffusion of graft initiating phenyl radical moieties and methylmethacrylate monomer into the inner core of MDPU matrix Yong-Chan *et al.*, (2015). Besides, the proximity of grafting sites, occasioned by the presence of vinyl groups in acyl chain of oleic, linolenic and linoleic acids endowed in *Ximenia americana* seed oil Eromosele and Eromosele, (2002), and moisture-toughened heterocyclic isocyanurate and carbodiimide oligomers during the conditioning of the copolymer, suggest, an encapsulated crosslinked polymethylmethacrylate chain with rigid urea and biuret linkages within the copolymer microstructure.

**Table 1:** Mechanical Properties of *Ximenia* Polyurethane-Polymethylmethacrylate Copolymers

Copolymer Sample	Initiation time (Min.)	Tensile strength (MPa)	Tensile modulus (Mpa)	Flexural strength (MPa)	Flexural modulus (GPa)	Elongation @ break (%)
HDPU-1.02-g-PMMA	20	24.87±1.30	0.86±0.01	41.80±8.56	0.84±0.03	11.17±0.05
TDPU-1.02-g-PMMA		23.58±0.13	0.93±0.08	50.76±5.92	1.17±0.08	1.02±0.12
MDPU-1.02-g-PMMA		28.49±1.80	1.24±0.06	59.14±7.25	2.03±0.04	6.56±0.16
HDPU-1.02-g-PMMA		26.75±0.30	0.97±0.01	43.11±3.56	1.03±0.08	9.74±0.51
TDPU-1.02-g-PMMA	30	25.46±0.64	1.11±0.01	52.22±1.19	1.46±0.12	0.99±0.02
MDPU-1.02-g-PMMA		31.61±0.92	1.67±0.14	61.04±2.24	3.91±0.15	5.03±0.96
HDPU-1.02-g-PMMA		25.99±1.30	0.92±0.11	42.41±1.92	0.92±0.04	10.06±2.01
TDPU-1.02-g-PMMA		23.76±0.71	0.96±0.01	49.63±2.22	0.98±0.16	1.04±0.03
MDPU-1.02-g-PMMA	40	35.69±1.36	1.88±0.16	66.22±4.61	5.16±0.82	4.21±0.36

Therefore, on application of mechanical force to this copolymer, these groups in its structural make-up act in concert and hold-on to greater proportion before ruptures Vilela *et al.*, (2010). The increase in tensile and flexural properties for MDPU-1.02-g-PMMA copolymers up to 40 min. initiation time could be attributed to greater stability of its macro-radicals which resulted in more grafted polymethylmethacrylate chain in its microstructure, in contrast, to homopolymer formation, occasioned by Trommsdorf-Norrish effect, and phase separation Odian, (1991); Brian, (2002) for TDPU-1.02-g-PMMA and HDPU-1.02g-PMMA. The foregoing drawback with respect to formation of the

latter copolymers, characterized their macroheterogeneity, which accounts for their low tensile and flexural properties with a corresponding increase in elongation at break, due to reduced mechanical load bearing and force transfer proportions within their structural make-up. The highest elongation for HDPU-1.02-g-PMMA and highest flexural properties for MDPU-1.02-g-PMMA substantiate greater internal plasticization by the whole aliphatic monomers in HDPU and the synergetic effects of the two rigid aromatic rings and aliphatic methylene bridge of MDI in MDPU polymer backbones respectively. The values for MDPU-1.02-g-PMMA copolymer prepared at 20 minutes initiation

time with values for tensile strength and elongation 24.87 MPa and 6.56 % respectively are in close range to 21.87 MPa and 10.2 % for castor oil-based MDI polyurethane graft methylacrylate copolymer from MDI and methylacrylate Zoriana *et al.*, (2016). The

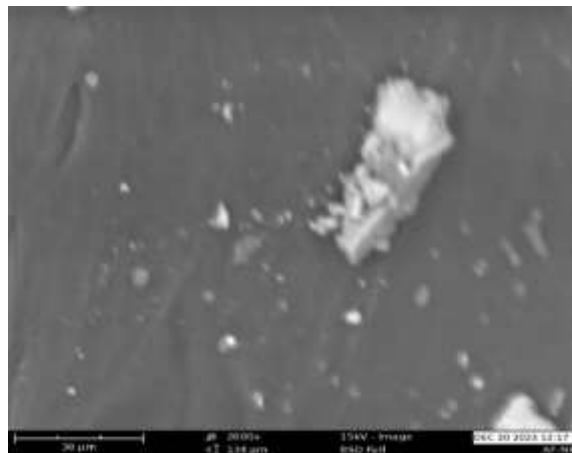
higher elongation for the latter may be attributed to enhanced plasticization by the whole aliphatic chain in castor oil as polyol, compared to a single pendant acyl chain in *Ximenia* monoglyceride monomer in the MDPU polyurethane backbone.

**Table 2:** Swelling Properties of *Ximenia* Polyurethane-Polymethylmethacrylate Copolymers

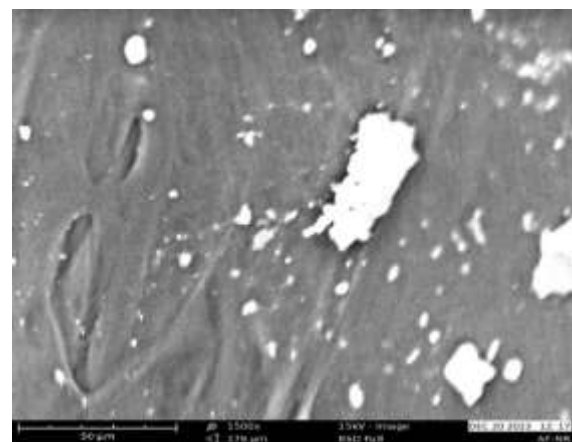
Copolymer	Initiation Time (Min.)	Swelling mass ratio			
		Chloroform	Acetone	Diethyl ether	Propanol
HDPU-1.02-g-PMMA	20	1.82±0.03	1.70±0.01	1.51±0.01	1.94±0.02
TDPU-1.02-g-PMMA		2.34±0.02	2.12±0.01	1.91±0.03	1.75±0.02
MDPU-1.02-g-PMMA		2.64±0.01	2.24±0.03	2.14±0.03	1.41±0.01
HDPU-1.02-g-PMMA	30	1.88±0.02	1.74±0.01	1.55±0.01	1.70±0.02
TDPU-1.02-g-PMMA		2.37±0.01	2.30±0.02	2.11±0.02	1.65±0.01
MDPU-1.02-g-PMMA		2.83±0.02	2.42±0.01	2.39±0.01	1.38±0.02
HDPU-1.02-g-PMMA	40	1.71±0.01	1.66±0.02	1.48±0.02	1.50±0.02
TDPU-1.02-g-PMMA		2.04±0.02	1.98±0.01	1.83±0.03	1.46±0.02
MDPU-1.02-g-PMMA		3.01±0.02	2.59±0.02	2.44±0.02	1.29±0.02

The copolymers were swelled in four solvents namely; chloroform, acetone, diethyl ether and propanol. The swelling mass ratios for the copolymers with exception of propanol increases within 20-30 min. initiation time and decrease thereafter, but all copolymer samples shows a decrease swelling in propanol prepared within 20-40 min. initiation time. However, for HDPU-1.02-g-PMMA and TDPU-1.02-g-PMMA copolymers, in chloroform, acetone and diethyl ether, the decrease is characterized by a minimum for copolymers prepared at 40min. initiation time. In contrast, MDPU-1.02-g-PMMA copolymer shows maximum swelling in these solvent. The decrease in swelling mass ratios of the former copolymers may not be unconnected with increased polymethylmethacrylate homopolymer formations at higher initiation time occasioned by perturbation to graft initiating and chain growth moieties to access reactive sites of their backbone polymers. The maximum and minimum swelling of copolymers in chloroform and propanol respectively as shown in table 2 may be attributed to chloroform being a good solvent having solubility parameter, ( $\delta$ ) 18.7MPa<sup>1/2</sup> which is close to 19.0 MPa<sup>1/2</sup> for polymethylmethacrylate, than 23.8 MPa<sup>1/2</sup> for propanol Carraher, (2010). The closeness of the solubility parameters is expected to increase the osmotic pressure and consequent impregnation of grafted polymethylmethacrylate chains by chloroform owing to the readily convection transport of its molecules. The minimum swelling of the copolymers in propanol relatively to diethyl ether and acetone could be attributed to its higher solubility parameter ( $\delta$ ) of 23.8 MPa<sup>1/2</sup> compared to 15.4 and 19.9 MPa<sup>1/2</sup> for diethyl ether and acetone Carraher, (2010), thereby, impeding sorption of this protic solvent by the hydrophobic polymethylmethacrylate chains. The swelling mass ratios for all copolymers in propanol

decreases with increase initiation time, in the range 20-40 min.



**Plate 1:** SEM Micrograph of HDPU-1.02-g-PMMA at 40 Minutes Initiation Time



**Plate 2:** SEM Micrograph of TDPU-1.02-g-PMMA at 40 Minutes Initiation Time

The decrease which was more pronounced for MDPU-1.02-g-PMMA suggest the overriding influence of the



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