



Supplementary Information

Strategic optimization of plasticizers, fillers, and blend ratios for enhanced performance of dynamically cured epoxidized natural rubber (ENR)/polypropylene (PP) thermoplastic vulcanizates

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S1. Detailed material descriptions and sources

The materials used in this study, along with their sources, are summarized in Table S1. Additionally, the in-house synthesized epoxidized natural rubber (ENR-20), the compatibilizer (phenolic-modified polypropylene or Ph-PP), and the properties of the thermoplastic component (PP) are described in Sections S1.1–S1.3.

S1.1 Epoxidized Natural Rubber (ENR-20)

ENR containing 20 mol% epoxide (ENR-20) was synthesized in-house via performic acid epoxidation. The process involved diluting high-ammonia concentrated latex from 60% to 20% dry rubber

content (DRC) and then reacted with formic acid (Fisher Scientific, Loughborough, UK) and hydrogen peroxide (Solvay Peroxythai Limited, Rayong, Thailand). The reaction was carried out at 50°C under controlled conditions, as previously reported [21], to achieve uniform epoxidation and a consistent epoxide content of 20 mol%.

S1.2 Compatibilizer (Phenolic-Modified PP or Ph-PP)

Ph-PP was synthesized in-house following previously published protocols [22] and was employed to enhance interfacial adhesion between ENR-20 and PP during dynamic vulcanization and throughout the service life of the TPV materials.

Table S1. Materials used in this study and their corresponding sources.

Chemicals	Sources
Reagents for Synthesis of ENR-20:	
• High-ammonia concentrated latex	Yala Latex Co., Ltd., (Yala, Thailand)
• Formic acid	Fisher Scientific, (Loughborough, UK)
• Hydrogen peroxide	Solvay Peroxythai Limited, (Rayong, Thailand)
Polypropylene (PP)	
	Thai Polypropylene Co., Ltd., (Rayong, Thailand)
Plasticizers and Process Oils:	
• Paraffinic Oil (PO)	Asia Oil Company Limited, (Bangkok, Thailand)
• Epoxidized Soybean Oil (ESO):	Alfa Chemistry, (Holbrook, USA)
• Dioctyl Phthalate (DOP)	DC Chemical Co., Ltd. (Seoul, Korea).
• Di-iso-nonyl Phthalate (DINP):	DC Chemical Co., Ltd. (Seoul, Korea)
Additives and fillers	
• Zinc oxide	Global Chemical Co., Ltd., (Samut Prakarn, Thailand)
• Stearic acid	Imperial Chemical Co., Ltd., (Pathum Thani, Thailand)
• Sulfur	Mahachai Chemicals Co., Ltd., (Samut Sakorn, Thailand)
• Accelerator (TBBS)	Thermo Fisher Scientific Chemicals, (Ward Hill, USA)
• Antioxidant (Wingstay L)	North Wanxing Chemical Co., Ltd., (Beijing, China)
• Silane Coupling Agent (Bis(3-triethoxysilylpropyl)tetrasulfide, Organosilane TF800)	Topflight Co., Ltd., (Bangkok, Thailand)
• Carbon Black (N220)	Thai Carbon Black Public Co., Ltd., (Angthong, Thailand)
• Silica (Ultrasil VN3 GR)	Evonik United Silica (Siam) Co., Ltd., (Rayong, Thailand)

S1.3 Polypropylene (PP)

The thermoplastic phase used to prepare ENR-20/PP TPVs was El-Pro P700J grade polypropylene homopolymer, which has a melt flow rate of 12.0 g/10 min (measured at 230°C under a 2.16 kg load), a density of 0.910 g·cm⁻³, and a melting temperature of 163°C.

S1.4 Chemical structure and properties of process oil and plasticizers

Paraffinic oils are composed primarily of alkanes, consisting of long straight-chain or branched hydrocarbons (Figure S1(a)). Most paraffinic oils contain carbon chains ranging from C14 to C40. This molecular structure imparts high thermal stability and low volatility, making them particularly suitable for high-temperature processing and applications. In contrast, epoxidized soybean oil (ESO) is a bio-based plasticizer derived from soybean oil through the epoxidation of

unsaturated fatty acid chains, introducing multiple epoxide (oxirane) groups, as illustrated in Figure S1(b). These polar epoxy groups enhance compatibility with polar rubbers like ENR and can participate in secondary interactions or even covalent crosslinking. Similarly, dioctyl phthalate (DOP) is a widely used phthalate-based plasticizer composed of a phthalic acid core esterified with two branched 2-ethylhexyl groups (Figure S1(c)). Its molecular structure features both aromatic and ester functional groups, resulting in moderate polarity and excellent compatibility with polar polymers such as ENR.

Likewise, di-iso-nonyl phthalate (DINP) is another phthalate-based plasticizer, in which the phthalic acid core is esterified with two branched iso-nonyl alcohol chains, each containing nine carbon atoms with varying branching patterns (Figure S1(d)). Its bulky branched side chains reduce crystallinity, enhance flexibility, and improve migration and volatility resistance, while its ester and aromatic components maintain moderate polarity and good compatibility with polar elastomers.

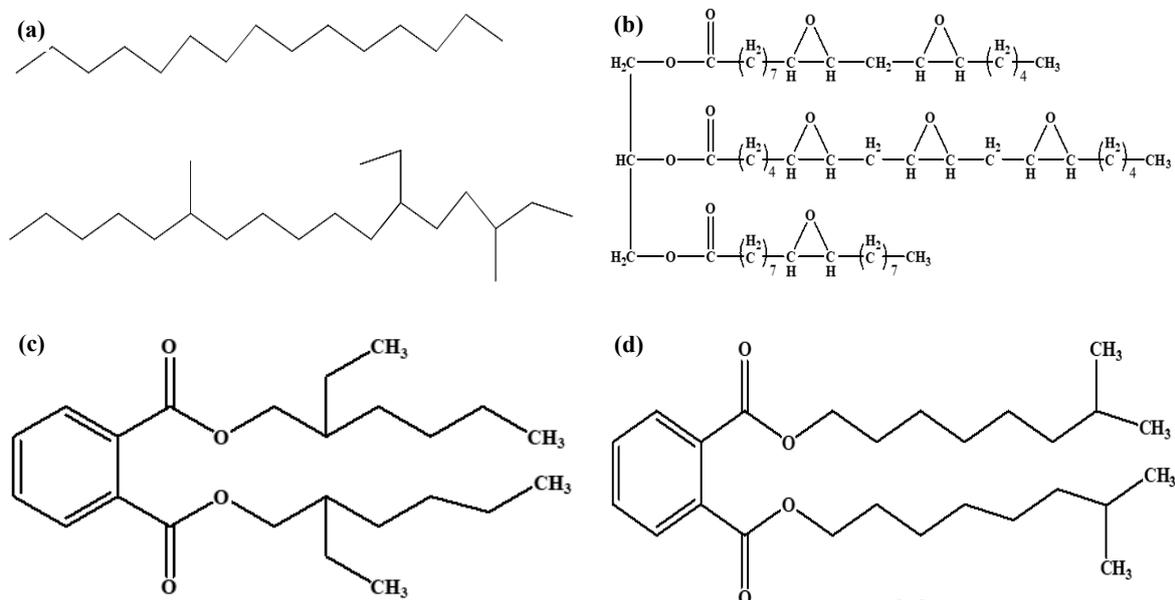


Figure S1. Chemical structures of the process oil and plasticizers: (a) paraffinic oil, (b) epoxidized soybean oil (ESO), (c) dioctyl phthalate (DOP), and (d) di-iso-nonyl phthalate (DINP).



Figure S2. Dumbbell-shaped specimen used for tensile testing, prepared in accordance with ASTM D412 specifications.

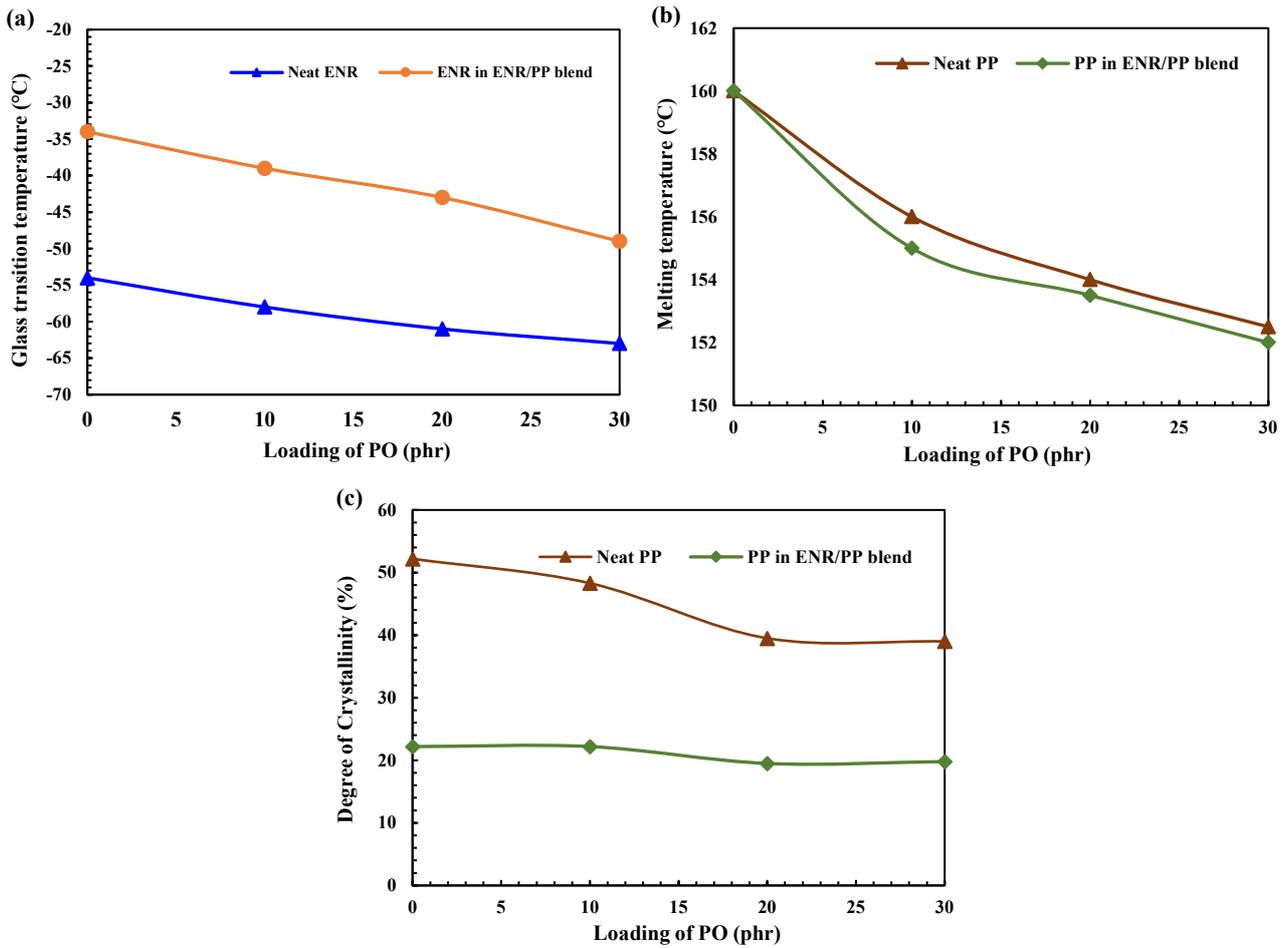


Figure S3. (a) Glass transition temperature (T_g) of ENR and ENR in ENR/PP blends, (b) crystalline melting temperature (T_m) of PP and PP in ENR/PP blends, and (c) degree of crystallinity of PP and PP in ENR/PP blends, each containing PO at 0, 10, 20, and 30 phr.

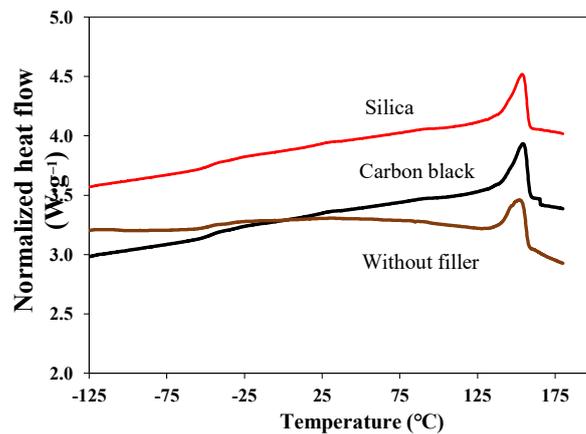


Figure S4. DSC thermograms of 60/40 ENR-20/PP blends with 30 phr of PO and 30 phr of carbon black and silica loadings.

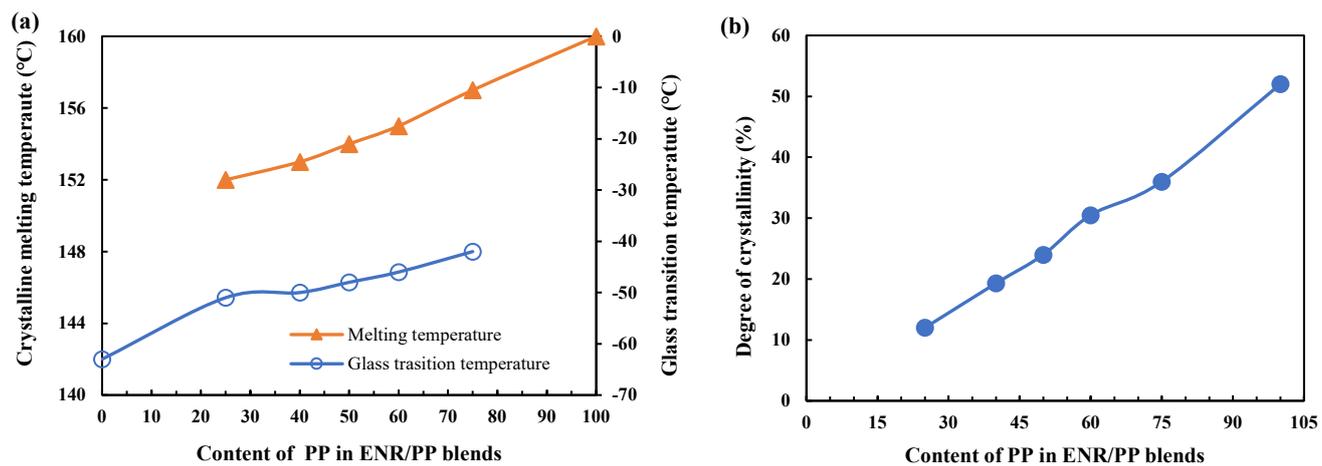


Figure S5. (a) Glass transition temperature (T_g) of the rubber phase and crystalline melting temperature (T_m) of the PP phase, and (b) degree of crystallinity of the PP phase in dynamically cured ENR-20/PP blends containing 30 phr of PO and 30 phr of silica (Ultrasil VN3) at varying blend proportions.