Compatibilitation of cyclic natural rubber (resiprene-35) with polypropylene in the presence of oleic acid and benzoyl peroxide

B Wirjosentono¹*, Tamrin¹, A H Siregar¹, T I Nasution², K Z Dalimunthe¹, D A Nasution¹

¹Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia
²Department of Physics, Universitas Sumatera Utara, Medan 20155, Indonesia

*E-mail: basuki@usu.ac.id, wirjoseb@yahoo.com

Abstract. Cyclic natural rubber (CNR: Resiprene-35) has been compatibilised with polypropylene in the presence of various contents of oleic acid and benzoyl peroxide in xylene reflux to improve its adhesion as printing binder on the thermoplastic substrate. The dried blends were then compression molded at 175°C for 25 minutes to form specimens according to ASTM D 412. Mechanical testing of the specimens showed optimum tensile strength: 18.13 MPa, elongation: 7.36%, and modulus of elasticity: 246.33 MPa when composition of the blend: polypropylene : CNR : oleic acid : benzoyl peroxide: 80 php : 20 php : 0.05 php : 0.025 php. Analysis of functional group using FTIR spectroscopy of the optimum specimen after exhaustive Sokhlet extraction in n-hexane showed small amount of carbonyl absorption at 1712 cm⁻¹, indicating possible chemical interaction of bound oleic acid with CNR and polypropylene matrices. SEM micrographs of the optimum blend’s specimen surface showed better compatibility when compared to that of blend compatibilised without oleic acid and benzoyl peroxide.

1. Introduction
Natural rubber abundant and low price have paid attention from researchers to produce various byproducts of processing materials for industry. Mirzataheri [1] has reported cyclization process of natural rubber to produce a resinous material. Cyclic natural rubber (CNR) resin produced in North Sumatra, Indonesia, using natural rubber as raw material and under commercial name: Resiprene-35, has been used widely as paint and coating binders. In the market, paint and coating binders for paper, wood, and metal substrates are not hard to find, not like that of for polyolefins materials, since the polyolefins consist of C and H atoms in their backbone and therefore are non-polar polymer, hydrophobic and has low energy surface. To improve water absorption of polyolefins substrates, Cao, et.al., [2], studied mechanical properties and water absorption of kenaf powder filled recycled high density polyethylene/natural rubber biocomposites using mape as a compatibilizer. Schellekens, et.al., [3] prepared block copolymers for waterborne coatings as novel eco-friendly approach for improving coating adhesion to untreated polypropylene based plastics. Zitzenbacher, et.al., [4], reported wetting behavior of polymer melts on coated and uncoated tool steel surfaces.

In this work, The CNR is compatibilised with polypropylene in xylene reflux using oleic acid as compatibiliser in the presence of small amount of benzoyl peroxide as initiator to improve adhesion of the blend as printing binder onto polyolefins substrates. This work is based on modification reaction
reported by various researchers on preparation of compatible polymer blends and composites. Nakason, et.al., [5], have studied grafting of maleic anhydride onto natural rubber. Improved adhesion of various natural fibres with natural rubber, polyolefins, and poly(ε-caprolactone) matrices have been reported by: Ismail, et.al., [6] Ismail, et.al., [7] and Wirjosentono, et.al., [8], as well as by Gea, et.al., [9]. Furthermore improved wetting ability and also biodegradability of polymer composites have also been reported by Suharty, et.al., [10], Gultom, et.al., [11] and Suryani, et al., [12].

2. Experimental

2.1 Materials

Xylene, benzoylperoxide, and oleic acid are all ex. Aldrich Chemicals and were used without any further purification., CNR: Resiprene-35 was ex. PT. Industri Karet Nusantara, Sei Bamban North Sumatra, Indonesia. Polypropylene (Propathene ICI HF26) was supplied by ICI (Plastic Division) Ltd.

2.2 Preparation of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO)

Cyclic natural rubber (CNR) and polypropylene (PP) were dissolved in xylene in a flask connected to condenser and stirrer and added with oleic acid (OA) and benzoylperoxide (BPO). Composition of the solutions were varied as in Table 1:

| Number | Composition of component (per hundred polymer: php) |
|--------|-------------------------------------------------|
|        | CNR | PP | AO | BPO |
| 1      | 80  | 20 | 0  | 0   |
| 2      | 80  | 20 | 0.5| 0.025|
| 3      | 80  | 20 | 1.0| 0.05 |
| 4      | 80  | 20 | 2.0| 0.1  |
| 5      | 80  | 20 | 3.0| 0.15 |

The solution mixtures in the flask were then refluxed with constant stirring for 15 minutes, evaporated, cooled and dried in fume cupboard under nitrogen gas flowing, then grinded. The powdered blends were then hot-pressed to form films at 180°C for 10 minutes, and then cut to form mechanical test specimens according to ASTM D 412.

2.3 Analysis and testing of blend’s specimens

Mechanical tests of the specimens were based on ASTM D 412 using Torsee Electronic System with pulling speed 5 cm/minute and cell capacity 100 kgf. Sample films were morphologically measured using Scanning Electron Microscopy: SEM (JSM-35 C) equipped with Ion Sputter JFC-1100, with magnification 100 and 500 times. Functional group analysis of the sample films were carried out using FTIR (Bruker Alpha-ATR) Spectroscopy before and after exhaustive Sokhlet extraction of the films in n-hexane for 6 hours.

3. Results And Discussions

3.1 Mechanical properties of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO)

Table 2 shows mechanical properties of the CNR/PP blends at various compositions, which include: tensile strength (MPa), elongation at break (%), and modulus of elasticity (MoE: MPa). Figure 1 and Figure 2 are results of tensile strength (MPa) and MoE (MPa) of the blends.
Table 2. Mechanical properties of cyclic natural rubber (CNR) and polypropylene (PP) containing oleic acid (OA) and benzoylperoxide (BPO).

| Number | Composition (php) CNR:PP:OA:BPO | Tensile strength (MPa) | Elongation (%) | Modulus of Elasticity (MPa) |
|--------|---------------------------------|-----------------------|----------------|---------------------------|
| 1      | 80:20:0:0                       | 12.54                 | 5.82           | 215.46                    |
| 2      | 80:20:0.5:0.025                 | 18.13                 | 7.36           | 246.33                    |
| 3      | 80:20:1.0:0.05                  | 11.27                 | 6.48           | 173.92                    |
| 4      | 80:20:2.0:0.10                  | 9.7                   | 6.44           | 72.17                     |
| 5      | 80:20:3.0:0.15                  | 5.4                   | 6.49           | 83.2                      |

Figure 1. Tensile strength (MPa) of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO) with composition variation (per hundred polymer: php)

Figure 2. Modulus of elasticity (MoE: MPa) of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO) with composition variation (per hundred polymer: php)

It was showed that both tensile strength and modulus of elasticity of the blends increased when compatibilised with addition of oleic acid and benzoylperoxide. The oleic acid has functioned as compatibiliser, in which the non-polar and unsaturated alkyl group may bound physico-chemically with PP matrix, whereas the polar carboxylic group bound with the CNR. However at higher peroxide loading the mechanical properties decreased steadily due to degradation and chain scission of the polymer matrices at higher temperature by the presence of benzoylperoxide. Excess of oleic acid also
functions as lubricant for the PP/CNR blends and therefore lowers the mechanical properties. Therefore optimum composition of the CNR/PP blend is that of containing CNR:PP:OA:BPO weight ratio: 80:20:0.5:0.025, in which the tensile strength is 18.13 MPa, elongation at break 7.36 %, and modulus of elasticity 246.33 MPa.

3.2 Functional group analysis using FTIR spectroscopy

![FTIR spectra of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO) at various composition (per hundred polymer: php): (a) PP; (b) CNR:PP:OA:BPO: 80:20:0:0; (c) CNR:PP:OA:BPO: 80:20:0.5:0.025; (d) that of (c) CNR:PP:OA:BPO: 80:20:0.5:0.025 after exhaustive Sokhlet extraction in n-hexane.](image)

When compared to that of PP (a), Figure 3, the FTIR spectrum (b) of PP/CNR (80:20) blend showed increase of peak intensity due to CNR at 1458 cm\(^{-1}\). Whereas that of optimum blend (c) PP/CNR blend compatibilised in the presence of oleic acid (OA) and benzoylperoxide (BPO) showed additional peak due to carboxylic group of the OA at 1712 cm\(^{-1}\). Interestingly FTIR spectrum (d) that of (c) after exhaustive washing in n-hexane also showed small amount of carbonyl peak of the bound OA, which functions as compatibiliser between CNR and PP matrices.
3.3 Morphological measurement using Scanning Electron Microscopy

Figure 4. SEM micrographs of cyclic natural rubber (CNR) and polypropylene (PP) blends containing oleic acid (OA) and benzoylperoxide (BPO): (a) CNR:PP:OA:BPO: 80:20:0:0, magnification 100 times; (b) that of (a), magnification 500 times; (c) CNR:PP:OA:BPO: 80:20:0.5:0.025, after exhaustive extraction in n-hexane, magnification 100 times; (d) that of (c), magnification 500 times

Compatibility of the optimum PP/CNR/OA/BPO (80:20:0.5:0.025) blend was also supported by smoother SEM micrograph of the blend’s surface, Figure 4 (c) and (d), magnification 100 times and 500 times respectively, when compare to that of rougher surface blend without OA and BPO, Figure 4 (a) and (b), PP/CRR (80:20), SEM micrograph magnification 100 times and 500 times respectively.

4. Conclusions
Based on mechanical properties data it is shown that optimum composition of the CNR/PP blend is that of containing CNR:PP:OA:BPO weight php ratio: 80:20:0.5:0.025. In which the tensile strength is 18.13 MPa, elongation at break 7.36 %, and modulus of elasticity 246.33 MPa. The FTIR spectrum of the optimum blend also showed small amount of carbonyl peak of the bound OA even after exhaustive washing in n-hexane, which function as compatibiliser between CNR and PP matrices. This is also supported by smoother SEM micrograph of the blend’s surface when compare to that of rougher surface blend without OA and BPO.
Acknowledgements
The authors would like to thank to University of Sumatera Utara for funding this work through research program of “Penelitian Unggulan Universitas: PUU TALENTA 2017”, also to Physical Chemistry Laboratory and Polymer Chemistry Laboratory of The Department of Chemistry for providing facilities of the work.

References
[1] Mirzataheri M 2000 Iranian Journal of Chemistry and Chemical Engineering, 19 91
[2] Cao X V et al 2011 BioResources, 6 3260
[3] Schellekens M et al 2011 Progress in Organic Coatings, 72 138
[4] Zitzenbacher G et al 2016 J. Appl. Polym. Sci., DOI: 10.1002/APP.43469.
[5] Nakason C et al 2004, Polymer Testing 23 35
[6] Ismail H et al 2001 Iranian Polymer Journal (English Edition) 10(6) p 377-383+415
[7] Ismail H et al 2002 Polymer Testing 21(2) p 139-144.
[8] Wirjosentono B et al 2004 International Journal of Polymeric Materials and Polymeric Biomaterials 53 295
[9] Gea S et al 2010 Journal of Biobased Materials and Bioenergy 4 384
[10] Suharty N S et al 2014 Journal of Physical Science 25 55
[11] Gultom G et al 2017 IOP Conference Series: Materials Science and Engineering 223 012031.
[12] Suryani et al 2017 IOP Conference Series: Materials Science and Engineering, 222 012008.