Compatibility and Wettability of Polypropylene-Cyclic Natural Rubber-NanocrystalCelluloseNanocomposites Containing Methacrylic Acid and Methylacrylateas Coagents

Basuki Wirjosentono1*, Tamrin1, I Putu Mahendra1, Diana Adnanda Nasution1, Hanafi Ismail2, Sukatik3, Jose Alberto Mendez4

1Chemistry Department, University of Sumatera Utara, Medan 20155, Indonesia
2School of Materials and Mineral Resources Engineering, UniversitiSains Malaysia, Engineering Campus, Penang Malaysia
3State Polytechnics of Padang, Padang 25164, Indonesia
4LEPAMAP Research Group, University of Girona, 17003 Girona, Spain

*Corresponding author: basuki@usu.ac.id

Abstract. Cyclic natural rubber (CNR: Resiprene-35) resinhas been used widely as paint and coating binders. However, when used on polyolefin substrates adhesion and mechanical properties of the CNR binders were inferior, and therefore required an adhesion promoter material. In this work, CNR resin was melt blended with polypropylene (PP) using methacrylic acid (MtAc) and methylacrylate (MeAt) as coagents, and filled with nanocrystalcellulose (NCC) to improve compatibility and adhesion on polyolefin surfaces as well as its mechanical strength. Processing conditions of the melt blending were optimized and the resulted (PP/CNR-g-MtAc-MeAt/NCC) nanocomposites were characterized using mechanical testing and Fourier Transform Infrared (FTIR) Spectroscopy. Furthermore, their adhesion characteristics have also been evaluated using Contact Angle Analysis. It was found that the PP/CNR-g-MtAc-MeAt/NCC nanocomposites have increased wettability and adhesion between polyolefin substrates and cyclic natural rubber binder with improved mechanical strength, and may be utilized as adhesion promoter between two substrates.

Keywords: cyclic natural rubber, polypropylene, nanocomposites, modification, paint binders

1. Introduction

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. However, when used as printing on polyolefin substrates adhesion of the CNR binder is inferior due to considerable difference on wettability, and therefore requires an adhesion promoter material. Various polymeric materials have been studied and used commercially as paint binders. Nanocomposite based-on epoxy/polyaniline-camphorsulfonatehas been studied as paint binder to protect corrosion of reinforcing steels in concrete, [1]. On the other hand, nanocrystal cellulose (NCC) prepared from α-cellulose by acid or enzymatic hydrolysis is a nanoscale crystalline material and has been used widely as nanocomposite fillers, [2]. Structure, properties and nanocomposites of cellulose
nanomaterials have also been reviewed, [3]. And a microcrystalline cellulose filled composites has been used as coating for wooden artwork, [4].

In this work, to improve adhesion, wettability and mechanical strength of CNR binder on polyolefin surfaces, polypropylene (PP) was blended with CNR and filled with NCC in the presence of methacrylic acid (MtAc) and methylacrylate (MeAt) as coagents. The reactive blending process was carried out as has been reported by previous researchers. Acrylic acid has been used as compatibiliser in oil palm empty fruit bunch filled polypropylene composites, [5], and trimethylolpropanetriacrylat has been used to enhance tensile properties and biodegradability of rice husk powder-filled recycled polypropylene composite, [6]. Furthermore, grafting of compatibilisers and coagents onto polymer matrices is very important to improve and sustain compatibility in polymer matrices. The effect of bonding agent and filler loading on dynamic properties and swelling behaviour of bamboo filled natural rubber composites has been studied, [7], [8]. When maleic anhydride was grafted onto natural rubber, adhesion of the rubber matrix onto polar filler surface can be improved, [9]. Whereas, preparations using melt blending and characterisations of nanocomposites have also been carried out and studied. Bacterial cellulose can also be used as efficient reinforcing agent on preparation of biodegradable nanocomposites based on poly(ε-caprolactone), [10]. and Mechanical properties of nanocrystal cellulose reinforced polystyrene containing glycerol monostearate as antistatic agent, has also been studied, [11]. Utilisation of inorganic fillers into polymer composites has also been reported in various works. Gultom, et.al., (2017), studied effects of natural zeolite and ferric oxide to electromagnetic and reflection loss properties of polyurethane nanocomposite, [12]. And Suryani, et.al., (2017), improved quality of polylactic acid biopolymer with addition of bentonite as nanofiller, [13].

2. Experimental

2.1 Materials
Cyclic natural rubber was obtained from PT. IndustriKaret Nusantara, in Deli Serdang – North Sumatera, Indonesia. Polypropylene was purchased from SCG Performance Chemicals, Co. Ltd. The compatibilizer, Cyclic natural rubber-grafted-Methacrylic acid-methylacrylate (CNR-g-MtAc-MeAt) masterbatch was prepared using our xylene reflux technique, as reported by Wirjosentono, et.al., (2004), [5], and nanocrystalline cellulose was prepared according to Sumaiyah, et.al., (2014), [14].

2.2 Preparation of Nanocomposites
Polypropylene/cyclic natural rubber-grafted-methacrylic acid-methylacrylate/nanocrystal cellulose (PP/CNR-g-MtAc-MeAt/NCC) nanocomposites were prepared using BrabenderPlastigraph internal mixer, according to procedures reported by previous workers, [7], [8]. Parameters of the processing: rotor speed at 50 rpm/minute, constant heating temperature 170°C, and maximum capacity of loading 35 g. The blending process started with addition of fresh PP for 5 minutes then continued with addition of CNR-g-MtAc-MeAtmasterbatch without and with NCC for another 5 minutes to constant torque, and torque data changes during processing were recorded. The processed nanocomposites were then left at room temperature and conditioned for 24 hours before preparation of test specimens using hot press process.

2.3 Characterisations of Nanocomposites
Characterisations of the nanocomposite samples include: testing for tensile strength, elongation at break, and modulus elasticity. Efficiency of blending process was characterized using Fourier Transform Infrared (FTIR), Bruker Alpha-ATR, spectroscopy and lastly Contact Angle Analysis with water droplet were carried out to measure adhesion and wettability properties of nanocomposite sample films using KRUSS Contact Angle Analyser model DSA25B at 20°C and Kruss Advanced Drop Shape data processing.
3. Results and Discussions

Processing Optimization of Polypropylene/Cyclic Natural Rubber-Methacrylic Acid-Methylacrylate/Nanocrystal Cellulose (PP/CNR-MtAc-MeAt/NCC) Nanocomposites. Processing of Polypropylene/Cyclic Natural Rubber (CNR: Resiprene-35)-grafted-methacrylic acid (MtAc) nanocomposites were carried out using methylacrylate (MeAt) as coagent in the presence of benzoil peroxide as initiator, without and with nanocrystal cellulose (NCC). Based on our previous work experience, variation of loadings of nanocomposite compositions are shown in Table 1, and compared to those of fresh PP and PP/CNR as controls.

Table 1: Variation of modification parameters in processing of Polypropylene/Cyclic Natural Rubber-grafted-Methacrylic Acid-Methyl Acrylate/Nanocrystal Cellulose (PP/CNR-g-MtAc-MeAt/CNN) nanocomposites; (composition unit: php = per hundred total polymer)

| No | Sample Code         | PP (php) | CNR (php) | MtAc (php) | MeAt (php) | NCC (php) |
|----|---------------------|----------|-----------|------------|------------|-----------|
| 1  | PP                  | 100      | -         | -          | -          | -         |
| 2  | PP/CNR              | 80       | 20        | -          | -          | -         |
| 3  | PP/CNR-g-MtAc.MeAt1 | 80       | 20        | 0.01       | 0.02       | -         |
| 4  | PP/CNR-g-MtAc.MeAt2 | 80       | 20        | 0.25       | 0.5        | -         |
| 5  | PP/CNR-g-MtAc.MeAt3 | 80       | 20        | 0.5        | 1          | -         |
| 6  | PP/CNR-g-MtAc.MeAt/NCC1 | 80 | 20 | 0.01 | 0.02 | 1.0 |
| 7  | PP/CNR-g-MtAc.MeAt/NCC2 | 80 | 20 | 0.01 | 0.02 | 2.0 |
| 8  | PP/CNR-g-MtAc.MeAt/NCC3 | 80 | 20 | 0.01 | 0.02 | 3.5 |

When compared to those of fresh PP and PP/CNR specimens, as shown in Table 2, as well as Figures, tensile strength (33.76 down to 18.25 MPa) and Young’s modulus (566.44 down to 410.2 MPa) of blends containing methacrylic acid and methyl acrylate as coagents were lower, which due to addition of the coagents may function as lubricants and formed coagents homopolymers. Therefore, addition of nanocrystal cellulose (NCC) was taken using lowest content of coagents, which showed improved Young’s modulus again (from 566.44 going up to 582.90 MPa).

Table 2. Mechanical properties of Polypropylene/Cyclic Natural Rubber-rafted-Methacrylic Acid-Methyl Acrylate/Nanocrystal Cellulose (PP/CNR-g-MtAc-MeAt/CNN) nanocomposites

| No | Sample Code         | Tensile strength (MPa) | Young’s Modulus (MPa) | Deformation at break (%) |
|----|---------------------|------------------------|-----------------------|--------------------------|
| 1  | PP                  | 33.76                  | 566.44                | 2.98                     |
| 2  | PP/CNR              | 28.78                  | 522.53                | 3.13                     |
| 3  | PP/CNR-g-MtAc.MeAt1 | 26.67                  | 474.1                 | 4.106                    |
| 4  | PP/CNR-g-MtAc.MeAt2 | 20.27                  | 459.2                 | 2.701                    |
| 5  | PP/CNR-g-MtAc.MeAt3 | 18.25                  | 410.2                 | 2.565                    |
| 6  | PP/CNR-g-MtAc.MeAt/NCC1 | 17.89 | 582.90 | 3.03 |
| 7  | PP/CNR-g-MtAc.MeAt/NCC2 | 17.39 | 581.23 | 2.86 |
| 8  | PP/CNR-g-MtAc.MeAt/NCC3 | 15.82 | 499.49 | 2.85 |

Characterizations of PP/CNR-g-MtAc-MeAt/NCC) nanocomposites FTIR Analysis

Then FTIR spectra of the nanocomposite samples were measured (Figure 1). The spectra showed mainly absorption peaks due to polypropylene as the main matrices. Scrutiny of the spectra, however,
they revealed absorption peaks of carbonyl groups in wavenumber of 1600-1700 \text{cm}^{-1}. Especially that of PP/CNR-g-MtAc.MeAt1 (red), i.e.: PP/CNR sample processed with coagents but without NCC showed higher absorption peak at about 1700 \text{cm}^{-1}, which is due to free carbonyl groups (-CO-OH). The absorption peak does not reveal in other spectra of samples containing NCC, since the carbonyl groups have interacted as hydrogen bonding with hydroxyl group of the NCC.

![FTIR spectra of PP/CNR-g-MtAc-MeAt/NCC nanocomposites](image)

**Figure 1.** FTIR spectra of PP/CNR-g-MtAc-MeAt/NCC nanocomposites

**Wettability Assessment**

Data of water droplet contact angle measurement of nanocomposites were shown in Figure 2.

![Contact angle measurements](image)

**Figure 2.** Contact angle measurements of PP/CNR-g-MtAc-MeAt/NCC nanocomposites
Figure 2. Data of water droplet contact angle measurement of nanocomposites; a. PP, b. PP/CNR, c. PP/CNR-g-MtAc.MeAt, d. PP/CNR-g-MtAc.MeAt/NCC1, e. PP/CNR-g-MtAc.MeAt/NCC2, f. PP/CNR-g-MtAc.MeAt/NCC3.

It has been stated that if $\sigma_S$: surface energy of solid, $\sigma_{SL}$: surface energy between solid and liquid, then wettability of a solid surface with the liquid droplet can be defined as $(\sigma_S - \sigma_{SL})$, and can be formulated according to Wenzel equation, [15], as:

\[ r \cdot (\sigma_S - \sigma_{SL}) = \sigma_L \cdot \cos \theta^* \]  

(1)

$r$: surface roughness, \( \sigma_L \): surface tension of liquid, \( \theta^* \): apparent contact angle influenced by surface roughness. Assuming that surface of the sample is relatively smooth, \((r = 1)\), then Wenzel equation can be written as:

\[ (\sigma_S - \sigma_{SL}) = \sigma_L \cdot \cos \theta \]  

(2)

where \( \theta \): measured contact angle of the liquid on the solid surface. Using data of surface tension of water at 20°C, [16], then contact angle and wettability of the samples with water droplet can be assessed as seen in Figure 3.

It is obvious (from Figure 3) that PP surface has lower wettability: $10.90 \times 10^{-3}$ N/m due to its high hydrophobicity, which then slightly goes up to $12.36 \times 10^{-3}$ N/m when blended with CNR without coagent. Interestingly when the PP was blended with CNR in the presence of MtAc and MeAt its wettability increased substantially to $40.00 \times 10^{-3}$ N/m due to the presence of free hydrogen-bonded acrylic acid and ester groups in the blend. Furthermore when NCC filler were added the wettability decreased to $13.82 \times 10^{-3}$ N/m, but then going up again to $(21.82$ and $26.91) \times 10^{-3}$ N/m, respectively, when NCC loading was increased to 2 and 3.5 php, which were because of interaction or hydrogen bonding between acrylic acid and ester groups onto the NCC nanofiller.

Figure 3. Contact angle and wettability of of blend samples
4. Conclusions
Optimum composition of nanocomposite without NCC was found PP/CNR-g-MtAc.MeAt1 (PP: 80 php, CNR: 20 php, MtAc: 0.01 php. and MeAt: 0.02 php). Higher NCC loading improved tensile strength and Modulus of Elasticity but lower elongation of the nanocomposites. When compared to those of PP substrate, PP/CNR-g-MtAc-MeAt/NCC nanocomposites showed lower water contact angle, i.e.: improved wettability, and therefore may be used as adhesion promoter between two substrates.

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