ENHANCING ECO-EFFICIENCY OF THE IMPACT MODIFIED ACRYLIC CAST SHEET PRODUCT BY DEPROTEINIZED NATURAL RUBBER

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Abstract

Acrylic, trade name of poly(methyl methacrylate): PMMA, is a transparent thermoplastic, which widely used in many fields such as automobile parts and transparent roofs. The increase of product performance is an important strategy for companies to enhance market share. The impact modification of acrylic cast sheet presents a significant increase of material performance and economic value of product. The incorporation of elastomeric particles such as rubbers into the bulk of thermoplastic brittle polymers is a well-know technique used to improve toughness. This paper presents the enhancing eco-efficiency, which performs in both of economic and environmental aspects, of the impact modified acrylic cast sheet product by using deproteinized natural rubber (DPNR) as an impact modifier. The influence factors, such as monomer ratio and concentration of DPNR, on the preparation of impact modified acrylic sheet were studied. The physical and mechanical properties of the impact modified acrylic cast sheet by using DPNR were compared with that of using natural rubber (NR) as an impact modifier. It was found that the highest impact strength of impact modified acrylic cast sheet was shown at the 2.0% by weight of DPNR. The physical and mechanical properties of the impact modified acrylic cast sheet by using DPNR were better than that of using natural rubber. Finally, the eco-efficiency of the impact modified acrylic cast sheet by using DPNR was evaluated by using the life cycle inventory (LCI) data for material grouping according to environmental and material properties. The using of DPNR as an impact modifier compared to the using of NR and synthetic rubber shows the decrease of natural consumption, pollutions, and investment cost, which demonstrates the enhancing eco-efficiency of the acrylic cast sheet production.

Keywords: Eco-efficiency; Acrylic cast sheet; Deproteinized natural rubber; Natural rubber waste; Life cycle inventory

1. Introduction

Rapid economic progress has brought a positive change in the social conditions but at the same time has resulted in changing and unsustainable patterns of consumption of consumer goods and raw materials. Resource management and eco-efficiency are the key issues and challenges for making the patterns of consumption and production more sustainable [1]. Eco-Efficiency is a new environmental management tool, which can be implemented both as concept and measurable indicator. It is expressed as the ratio of the product value of a system to its environmental influence [2].

NR obtained from *Hevea brasiliensis* is an elastomer, which has very high green strength in comparison with synthetic rubbers. This difference in the green strength has been attributed to the crystallizability derived from the isoprene unit and non-rubber constituents present in NR. Non-rubber in NR could be removed by the enzymatic and transesterification deproteini--zations [3].

Methyl methacrylate (MMA) is a monomer, which is commonly used for free radical chain polymerization. After polymerization, MMA monomer is converted to acrylic plastic, trade name of poly (methyl methacrylate) (PMMA), which has a highly amorphous structure and relatively high glass transition temperature making the resultant polymer rigid, brittle and transparent. PMMA is a thermoplastic, which is widely used in many fields such as automobile parts and transparent roofs. With the excellent properties of PMMA, such as transparency, lightness, and safety, the consumption volume of PMMA are relatively high compared to those of other monomers and plastic. Polystyrene (PS), which is prepared from styrene monomer (S), is a thermoplastic, which has similar properties to PMMA. In order to decrease the cost of PMMA sheet production, the use of S-MMA copolymerization method has been considered [4]. The impact strength of thermoplastics can be improved by the addition of elastomeric materials. The impact modification of S-MMA copolymer cast sheets by using NR [5], synthesis rubber [6], and polyurethane [7] were reported.

Chemical reactions directly of NR also can be influenced by presence of the proteins. These proteins could act as free radical scavengers and terminate the free radicals species during the polymerization reaction [8] and protein allergy [9] therefore, DPNR is an obvious choice in copolymerization.

In this research, the non-rubber components in natural rubber were eliminated by saponification. The prepared DPNR was used as an impact modifier for the acrylic cast sheet. The S monomer was copolymerized in order to dissolve the DPNR and decrease the cost of acrylic cast sheet. The impact modified acrylic cast sheet was prepared by bulk copolymerization of MMA and styrene monomer with a small amount of deprotienized natural rubber (DPNR). The mechanical and physical properties and environment impact of the impact modified acrylic cast sheet by using DPNR as the impact modifier were investigated. Finally, the economic and environmental impacts from the preparation of impact modified acrylic cast sheet were evaluated following to the eco-efficiency indicator assessment method.

2. Experimental

2.1 Materials

MMA monomer was purchased from the Thai MMA Co.,Ltd. S monomer was supplied by the Shell Co.,Ltd. (Thailand). Solid NR (STR 5L) was purchased from the Chana Latex Co., Ltd. The free radical initiators, benzoyl peroxide and azo-bis-2,4-dimethylvaleronitrile were purchased from Merck. Sodium hydroxide (NaOH), acetone, 1,2-dichlorobenzene and chloroform were purchased from Aldrich. All chemicals were used as received.

2.2 Preparation of DPNR

The DPNR was prepared by using saponification technique NR was dissolved in toluene under reaction glass vessel. The addition of NaOH solution with 5% w/v was performed, while slowly stirring at the temperature of 70°C for 3 hr. After that the solution was washed by distilled water and coagulated by ethanol. The DPNR was dried in the oven at 60°C. The basic copolymer composition of the DPNR was characterized by using the Fourier Transform Infrared (FT-IR) Spectrophotometer.

2.3 Characterization of DPNR

2 g of DPNR sample was dissolved in 10 ml of chloroform. The DPNR solution was dropped on NaCl cell. The FT-IR spectra of DPNR were recorded using a Nicolet PRO-TEGE 460 FT-IR spectrophotometer.

2.4 Preparation of the impact modified acrylic cast sheet by DPNR

The DPNR was first dissolved in a mixture of S and small amount of MMA monomers under viscous agitation. Once the DPNR was dissolved, the solution was then mixed with the MMA monomer until the homogeneous solution was performed. The pre-polymerization of solution was carried out by using BPO as initiator (0.1% by weight) at 115°C with continuous stirring. The viscous solution was then cooled down until room temperature and after that 0.03% of ABVN was added in the viscous solution and agitated for 15 min. The viscous solution was poured into the polymerization casting calls and left in a water bath at 60°C until approximately 90% monomers conversion had taken place (viscous solution in casting cells turned to solid). Finally, the polymerization casting cells were placed in an oven at 100°C for 2 h. in order to complete polymerization.

2.5 Mechanical tests

The Notched Izod impact strength was measured according to ASTM D256. The specimens were cut from the mid section of the acrylic cast sheet. The Izod samples were notched by using V-Notch sampling machine (GOTECH: GT-7045-I). The impact speed was 3.46 m/s, and the energy of the hammer was 150 kg cm. The Izod impact tests were carried out in an air-conditioned room at 25°C. The Shore D hardness was determined according to ASTM D2240 and was tested by using Shore D durometer (TECLOCK GS-7206). Tensile strength sample was prepared equaling to ASTM D638 type I. The test was performed at room temperature and at a cross-head speed of 1.28 mm min^{-1} by using universal testing machine (CHUN YEN).

2.5 Physical properties

The opacity and hest resistances of the acrylic cast sheets were investigated according to the Pan Asia Industrial Co.,Ltd, standard. Copolymer cast sheet specimens (6 cm x 6 cm) determined the opacity by using color matching machine (GretagMacbeth: COLOR iMATCH) before placed in an oven for 25 min at 165°C. The change in yellowness of the specimens was examined by using color matching machine. UV resistance of the copolymer cast sheet specimens (5 cm x 20 cm x 3 mm) were recorded color change by using color matching machine. After that the specimens were placed in QUV cabinet using ultraviolet at wavelength 280 nm to 320 nm for one day. The color changing of the specimens were examined by using color matching machine (GretagMacbeth: COLOR iMATCH) again.

2.6 Eco-efficiency evaluation of the impact modified acrylic cast sheet

The economical cost of the impact modified acrylic cast sheet production was assessed. The environmental impact of the impact modified acrylic cast sheet was also calculated based on the material balance of the acrylic cast sheet production process [10]. The economical and environmental impact data were obtained from the Pan Asia Industrial Co., Ltd. and the Life Cycle Inventory (LCI) data from previous literatures [4, 10, 11]. Finally, the eco-efficiency was evaluated according to the BASF's method [12].

3. Results and discussions

3.1 Characterization of the deprotienized natural rubber

Infrared spectroscopy has been used as a method of studying intermolecular interactions caused by hydrogen bonding, because the vibrational modes of the donor and acceptor groups are sensitive of this interaction leading to a change in a vibrational characteristic [13].

The IR spectrum of NR in Figure 1a. indicates appearance characteristic of the amide group at 3282 cm^{-1} (N-H stretching), 1629 cm^{-1} (amide I vibration), and 1544 cm^{-1}, which can be attributed to the signals of proteins [14]. These signals are not found in the spectrum of DPNR in Fig.1b.This evidence can be qualitatively used to confirm that the proteins in the NR were eliminated.

3.2 Mechanical properties of the impact modified acrylic cast sheet

Mechanical properties of the acrylic cast sheet containing DPNR were examined. The effects of DPNR and S copolymer on the mechanical properties, such as impact strength, hardness and tensile properties, of the acrylic cast sheet are shown in Figure 2 a-d.

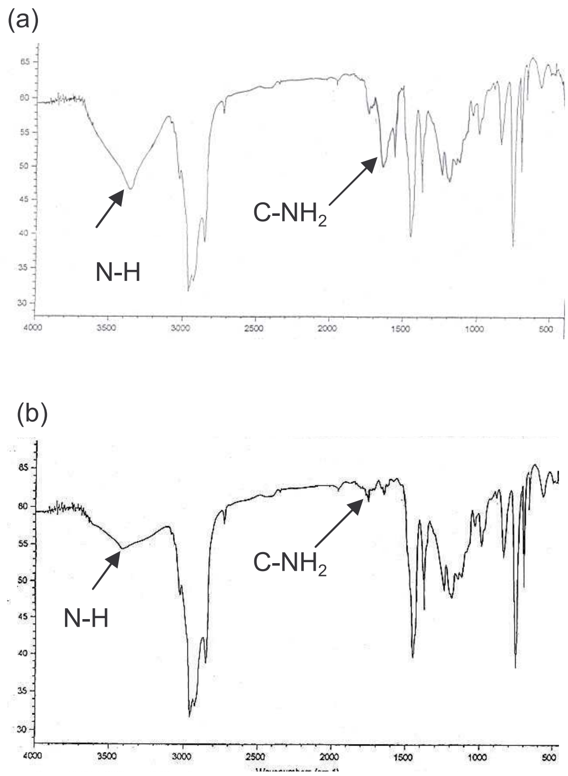


Figure 1. The FT-IR spectrum of rubber (a) NR (b) DPNR

From Figure 2a. it can be seen the Izod impact strength of the modified acrylic cast sheet containing DPNR increased with the increasing of the S and DPNR contents. In addition, the impact modified acrylic cast sheet with DPNR illustrated the higher Izod impact strength compared with the specimens containing NR (Figure 3a)

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation or scratching. Most hardness tests for plastics are based on resistance to penetration by an indenter pressed into the plastic under a constant load [15]. The shore D hardness is a standard hardness test for the brittle thermoplastic [16]. Figure 2b showed that the shore D hardness values of the modified acrylic cast sheet containing DPNR remain relatively constant in the range of 80-86, the trend of shore D hardness decreased when the amount of S monomer and DPNR increased.

Figure 2c presents effects of S monomer and DPNR on the tensile strength of the modified acrylic cast sheets. It can be seen that the increasing of rubber has affected the trend of tensile strength decreased. However, it was found that the tensile strength at yield of the modified acrylic cast sheet containing NR (Figure 3c) was higher than that of the modified acrylic cast sheet containing DPNR. It was due to the removal of mixed fatty acids and linked fatty acids in addition to the decomposition of chemical branch points formed by phospholipids [17].

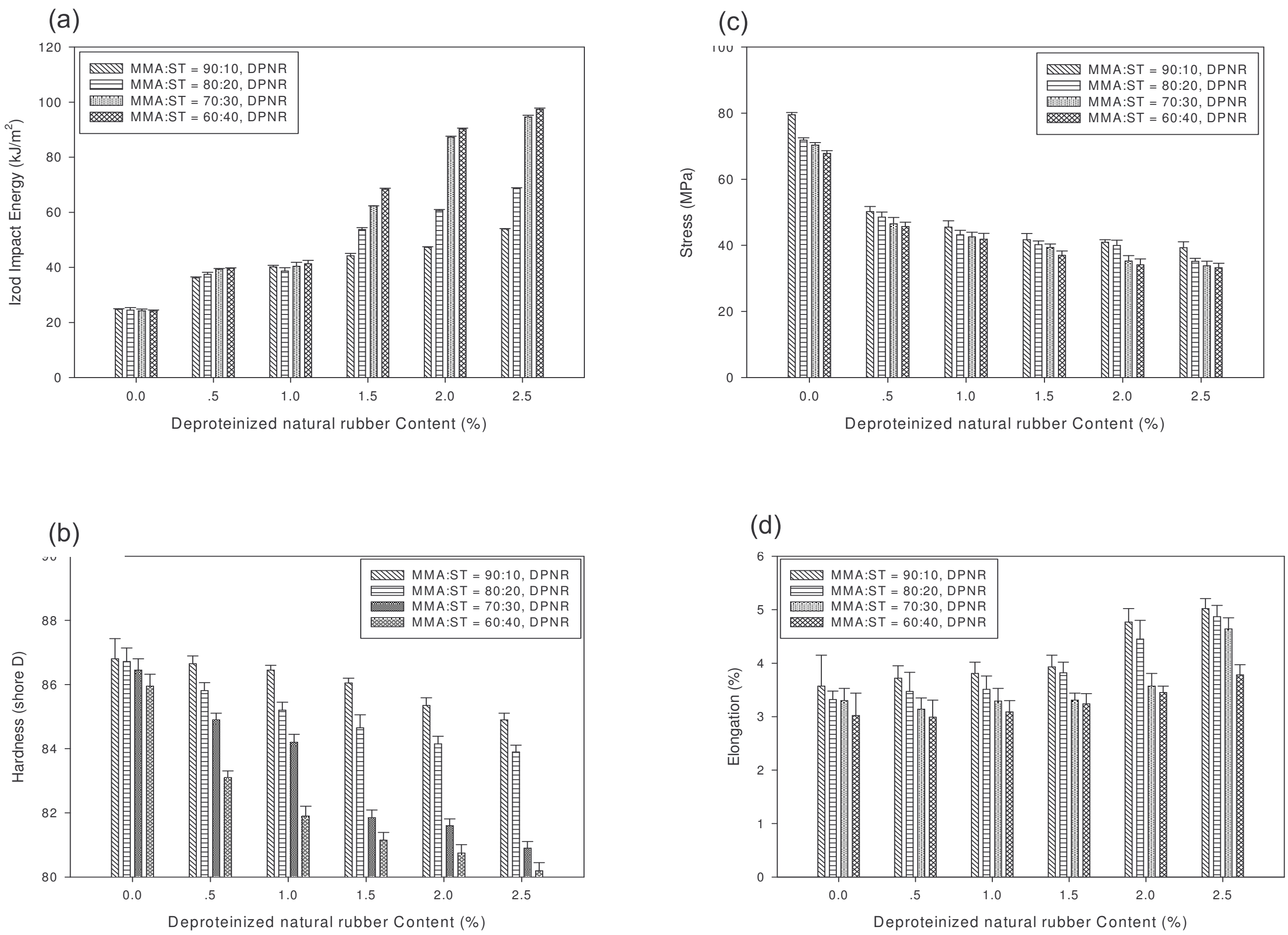


Figure 2 Mechanical properties of the impact modified acrylic cast sheet containing various DPNR and S monomer contents (a) Izod impact strength (b) Shore D hardness (c) tensile strength (d) elongation at break

This suggests that the chlorine group in the phospholipid had no predominant role in the formation of branch point at the α-terminal of the rubber chain [13].

The effects of S monomer and DPNR on the elongation at break of the modified acrylic cast sheet are illustrated in Figure 2d. It can be seen that the elongation of the modified acrylic cast sheet samples increased with increasing the amounts of DPNR and S monomer. It was found that the elongation at break of the modified acrylic cast sheet containing NR (Figure 3d) was higher than that of the modified acrylic cast sheet containing the DPNR.

3.3 Physical properties of the impact modified acrylic cast sheet

Transparency is an important property for acrylic cast sheet product. Average 15% of the opacity value is expected for the acrylic cast sheet of the Pan Asia Industrial Co., Ltd [4]. The influences of the S and DPNR concentrations on the opacity value of S-MMA copolymer cast sheet are shown in table 1. In the range of 0.5 - 2.5% of the DPNR and 10% and 40% of the S monomer concentration, the opacity values were observed in the range 12.73 - 13.83. In summary, the DPNR and S monomer did not affect the transparency of the modified acrylic cast sheet.

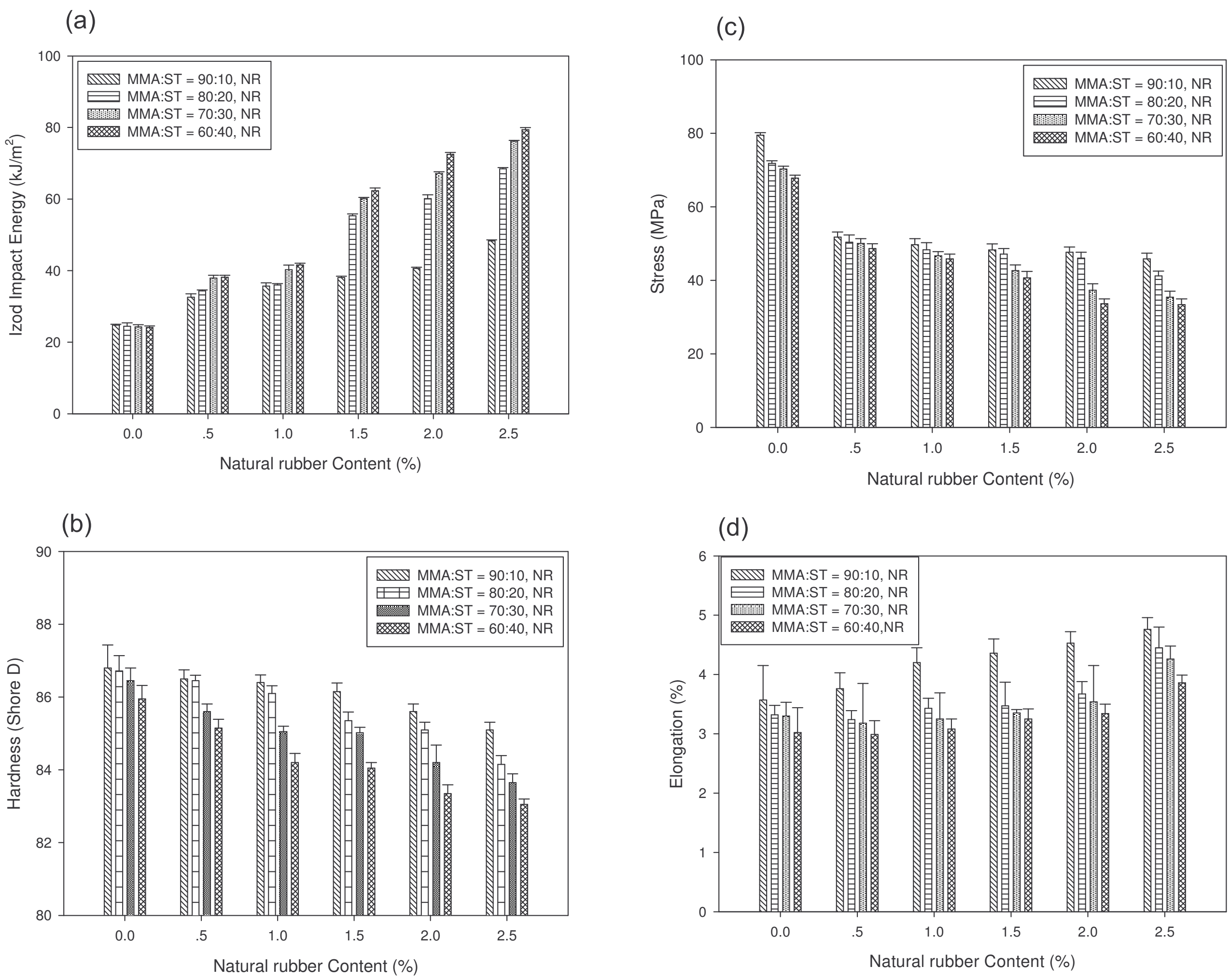


Figure 3 Mechanical properties of the impact modified acrylic cast sheet containing various NR and S monomer contents (a) Izod impact strength (b) Shore D hardness (c) tensile strength (d) elongation at break

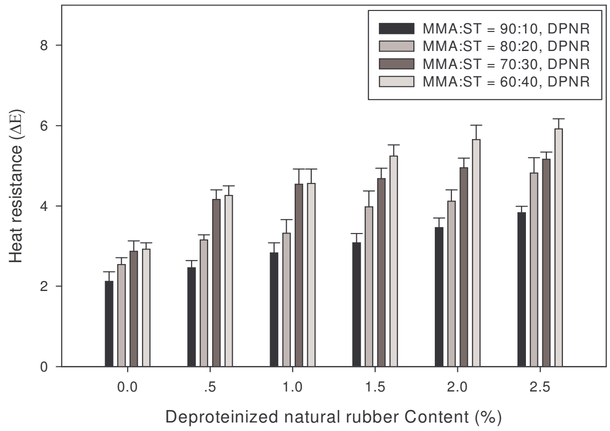
Table 1. The effects of S monomer and DPNR concentrations on the opacity property of the impact modified acrylic cast sheet.

Exp.	S (%)	DPNR (%)	Opacity (%)
1	0	0	12.16 ± 0.04
2	10	0.5	12.73 ± 0.12
3	10	1.0	12.83 ± 0.11
4	10	1.5	12.94 ± 0.19
5	10	2.0	13.17 ± 0.12
6	10	2.5	13.28 ± 0.18
7	40	0.5	13.43 ± 0.09
8	40	1.0	13.46 ± 0.10
10	40	1.5	13.56 ± 0.13
11	40	2.0	13.66 ± 0.13
12	40	2.5	13.83 ± 0.09

Heat resistance was applied to investigate the weathering property of the acrylic cast sheet. The heat resistance was examined by monitoring the yellowness shifts of the test specimens, which are reported in the terms of color difference (ΔE). The effects of S monomer and DPNR concentrations on the heat resistance of the modified acrylic cast sheet are shown in Figure 4a. It can be seen that the ΔE of the modified acrylic cast sheets increased as the S concentration increased. This agreed very well the previous observation [4]. The ΔE values of the modified acrylic cast sheets were also slightly increased with the increasing of the DPNR concentration.

The effects of S monomer and DPNR concentrations on the ultraviolet resistance of the modified acrylic cast sheet are shown in Figure 4b. It can be seen that the ΔE of modified acrylic cast sheets increased as the DPNR and the S monomer increased. This can be explained by the structures of DPNR and S, which contain a double bond left in the rubber and the polymer structures.

(a)



(b)

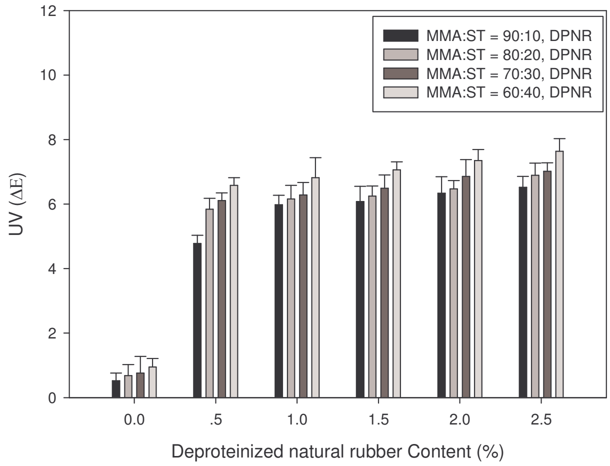


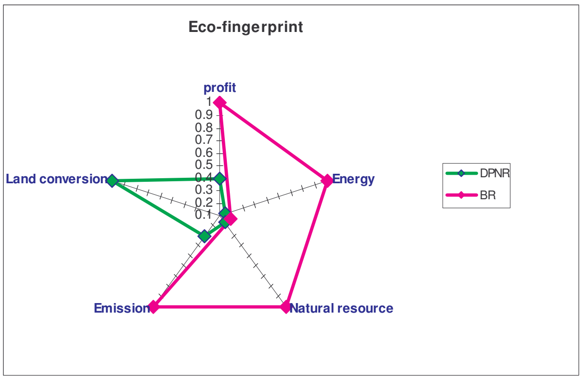
Figure 4. The effect of styrene monomer and DPNR concentration on the physical property (a) heat resistance property and (b) UV resistance property

4. Eco-Efficiency evaluation of the impact modified acrylic cast sheet

It can be said that the specific environmental data for acrylic cast sheet and NR in Thailand are not available yet. In this research, we can estimate the environmental impact of the impact modified acrylic cast sheet by using the material grouping for a simplified product life cycle assessment [18]. The material grouping for simplified life cycle assessment provides the average data for mechanical properties and environmental impact of 17 material group, which can be used as estimates when LCI data for specific materials are missing [4]. The economical cost of the impact modified acrylic cast sheet production was evaluated from the database of the Pan Asia Industrial Co., Ltd and the previous literatures [4,10]. The economical and environmental assessment results from this step were used as a data for evaluation of eco-efficiency following to the BASF's method [12].

The eco-efficiency is the relation between environment and economic. The eco-efficiency evaluation of the impact modified acrylic cast sheet by using DPNR compared with by using synthetic butadiene rubber (BR) is shown in Figure 4a and b. Figure 4a demonstrates the profit and environmental factors consisted of energy, emissions, natural resource and land conversion of the impact modified acrylic cast sheet by using DPNR compared with by using BR. It was observed that the impact modified acrylic cast sheet by using DPNR can reduced the consumption of energy, emissions, natural resource and increase the land conversion with compared to the impact modified acrylic cast sheet by using BR. Figure 4b shows the eco-efficiency portfolio of the impact modified acrylic cast sheet by using DPNR compared to the using of BR. It can be seen that the eco-efficiency of the impact modified acrylic cast sheet containing DPNR process had better than that of containing BR.

(a)



(b)

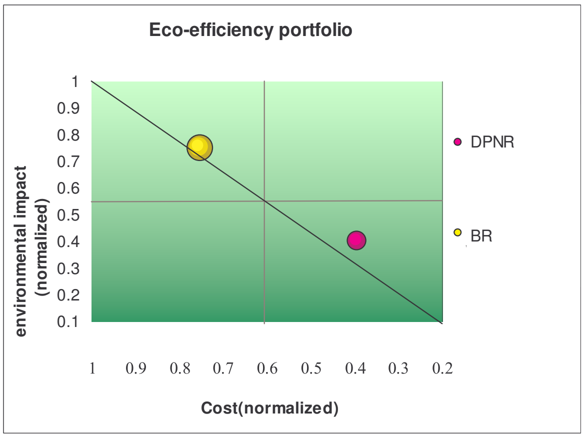


Figure 5. Eco-efficiency of the modified S-MMA copolymer cast sheet containing NR comparing with synthesis rubber. (a) Eco-fingerprint (b) eco-efficiency portfolio.

5. Conclusions

DPNR can be used as an impact modifier for the acrylic cast sheet. The effect of S monomer and DPNR concentrations on the mechanical properties of the acrylic cast sheet indicate that the shore D hardness and tensile strength of the acrylic cast sheets were decreased when the concentrations of S monomer and DPNR increased. The impact strength and elongation at break increased with increasing the S monomer and DPNR contents. DPNR and S monomer concentrations did not affect the transparency of the acrylic cast sheet. The physical properties, such as heat and ultraviolet resistance properties, of the modified acrylic cast sheets were increased with the increasing of S monomer and DPNR concentrations. The eco-efficiency evaluation of the modified acrylic cast sheet by using DPNR as an impact modifier compared to the using of BR illustrates the decrease of natural consumption, pollutions, and investment cost.

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7. References

[1] Chiu, A. S. F., Ward, V. J., and Massard, G. (2009). Introduction to the special issue on Advance in Life-Cyhcle Approaches to Business and Resource Management in the Asia-Pacific Region, *Journal of Cleaner Production*, Vol. 17, pp. 1237-1240.

[2] Pil-Ju Park, Tahara, K. and Inaba, A. (2007). Product quality-based eco-efficiency applied to digital cameras, *Journal of Environmental Managemen*t, vol. 83, pp. 158-170.

[3] Amnuaypornsri, S., Sakdapipanich, J. and Tanaka, Y. (2009). Green strength of natural rubber: The origin of the stress-strain behavior of natural rubber, *Journal of applied polymer science,* vol. 111, pp. 2127-2133.

[4] Charmondusit, K. and Seeluangsawat, L. (2009). Recycling of poly(methyl methacrylate) scrap in the styrene-methyl methacrylate copolymer cast sheet process, *Recources, Conservation and recycling*, doi 10/1016/j. resconrec. 2009.07.005 (in press).

[5] Prasertpong, P. and Charmondusit, K. (2008). Impact modification of styrene methylmethacrylate copolymer sheet by using natural rubber via casting process, Proceedings of the 2nd Technology and Innovation for Sustainable Development Conference 2008, Khon Kean, Thailand.

[6] Charmondusit, K. and et., al. Preparation of transparent styrene-methyl methacrylate copolymer by casting process, Thai Patent 0601002635. June 8, 2006.

[7] Heim, PH., Wrotecki, C. and Avenel, M. (1993). High impact cast sheets of poly(methyl methacrylate) with low of polyurethane, *Polymer,* vol. 34, pp. 1653-1660.

[8] Siti Hajjar Che Man, Azanam, S. and Hazizan Md. Akil. (2008). Properties of styrene-methyl methacrylate grafted DPNR latex at different monomer concentrations, *Journal of Applied Polymer Science,* vol. 109, pp.9-15.

[9] Yeang, H-Y., et. al. (2006). Allergen concentration in natural latex, *Clinical and Experimental Allergy,* vol. 36, pp. 1078-1086.

[10] Chaikaew, P. and Charmondusit, K. (2007). Life cycle inventory of poly (methyl methacrylate) cast sheet production process, Paper presented in the 2nd Thai LCA workshop and seminar, March 15-16, 2007, Chiang Mai, Thailand.

[11] Rydh, C. J. and Sun, M. (2005). Life cycle inventory data for materials group according to environmental and material properties, *Journal of Cleaner Production*, vol. 13, pp. 1258-1268.

[12] Saling, P. and et. al. (2002). Eco-efficiency analysis by BASF: The method, International

Journal Life Cycle Assessment, vol. 7, pp. 203-218.

[13] Tarachiwin, L., Sakdapipanich, J. and Tanaka, Y. (2005). Structure characterization of α-Terminal group of natural rubber Decomposition of branch-points by phospholipase and chemical treatments, *Biomacromolecules,* vol. 6, pp. 1858-1863.

[14] Phetphaisit, W. and Phinyocheep, P. (2003). Kinetice and parameters affecting degradation of purified natural rubber, *Journal of Applied Polymer Science,* vol. 90, pp. 3546-3555.

[15] Vishu, S. (1998). Handbook of plastics testing and failure analysis, 3rd ed. ISBN 978-0-471-67189-3, John Wiley and Sons, Inc.New Jersey.

[16] Hinchiranan, N. and et. al. (2007). Improving properties of modified acrylic sheet via addition of graft natural rubber, *Materials Letters,* vol. 61, pp. 3951-3955.

[17] Kawahara, S., Kakubo, T. and et. al.(2000). Crystallization behavior and strength of natural rubber : skim rubber, deprotienized natural rubber, and pale crepe, *Journal of Applied Polymer Science,* vol. 78, pp. 1510-1516.

[18] Sun, M., Rydh, C.J. and Kaebernick, H. (2003). Material grouping for simplified product life cycle assessment, *Journal of Sustainable Product Design,* vol. 3, pp. 45-58.