



UV-Curable Palm Oil Based-Urethane Acrylate/Clay Nanocomposites

A. M. Salih^{1,2*}, Wan Md. Zin Wan Yunus³, Khairul Zaman Mohd Dahlan⁴,
Mohd Hilmi Mahmood⁴ and Mansor Ahmad¹

¹ Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

² Department of Radiation Processing, Sudan Atomic Energy Commission, Khartoum P.O. Box 3001, Khartoum, Sudan

³ Department of Chemistry, Centre for Defence Foundation Studies, National Defence University of Malaysia, 57000, Sungai Besi Camp, Kuala Lumpur, Malaysia

⁴ Radiation Processing Technology Division, Malaysian Nuclear Malaysia, Bangi, 43000 Kajang, Selangor

ABSTRACT

Synthesis of palm oil based-urethane acrylate (POBUA) resins was carried out by acrylation of epoxidized palm oil (EPOP) using acrylic acid in the presence of a catalyst and followed by isocyanation to obtain the POBUA. Using the monomer as a diluent in the formulation, 4% of photoinitiator and incorporation of organoclay (1-5% wt), nanocomposites were obtained upon UV irradiation. The X-ray Diffractory XRD study revealed that the nanocomposites obtained were of the exfoliation type. The presence of the clay improved the hardness and did not affect the thermal stability. Similarly, it increased the glass transition temperature T_g but reduced the modulus as the clay content was increased. The improvement of the tensile strength was only obtained when the clay concentration was 5 phr.

Keywords: Nanocomposites, Palm oil based-resin, urethane acrylate, UV-curing

Article history:

Received: 27 July 2011

Accepted: 13 January 2012

Email addresses:

ashraf.msalih@gmail.com (A. M. Salih),
wanmdzin@upnm.edu.my (Wan Md. Zin Wan Yunus),
khairul@nuclearmalaysia.gov.my (Khairul Zaman Mohd Dahlan),
hilmi@nuclearmalaysia.gov.my (Mohd Hilmi Mahmood),
mansorahmad@gmail.com (Mansor Ahmad)

*Corresponding author

INTRODUCTION

Vegetable oils are attractive raw materials for many industrial applications as they are renewable resources and can be produced in large quantities at a competitive cost. Moreover they are biodegradable compounds, and can therefore be classified as environmentally friendly products (Perepelkin, 2005; Galià *et al.*, 2009). UV-curable resins are useful for

many applications due to their fast curing and solvent free characteristics, low energy and temperature requirements (Decker, 1996). At present, polymer-clay nanocomposites have attracted a great deal of researchers' attention and many studies have been conducted on this area (Djouani *et al.*, 2010; Jayabalan *et al.*, 2009). Compared to their conventional counterparts, nanocomposites display excellent thermal stability and mechanical properties when a small amount of filler was incorporated into a polymer matrix (Keller *et al.*, 2004).

Preparation of UV cured nanocomposites has been described by Decker *et al.* (2002). The absence of diffraction peak in the XRD patterns of the nanocomposites indicated that they were of exfoliation type (Decker *et al.*, 2002). Intensive investigation on the preparation and characterization of urethane acrylate-clay nanocomposites has been done by Uhl *et al.* (2004). The authors reported that the mechanical properties of the nanocomposites improved, but the thermal stability of these polymer systems was found to be not affected by the addition of the clay (Uhl *et al.*, 2004).

It has been reported that clay-based nanocomposite coatings cured by UV light were obtained by incorporating clay up to 10 wt% and using different dispersion methods. In more specific, both the mechanical and optical properties of the nanocomposite coating were found to be strongly affected by the quality of the clay dispersion (Landry *et al.*, 2009). In addition, the nanocomposite coatings cured by UV were also compared to the electron beam radiation curing. The UV cured coatings were found to have a better abrasion resistance and the hardness increased as the curing dose increased due to the increase of the cross linking density (Nik Salleh *et al.*, 2010). This report describes the preparation and characterization of palm oil based-urethane acrylate-clay nanocomposites.

MATERIALS AND METHODS

Materials

Epoxidized palm oil (EPOP) with oxirane-oxygen value of 3% per gram (Intermed Sdn. Bhd) was used as a raw material to produce palm oil based resin. Meanwhile, acrylic acid (99%, Aldrich) was used in the acrylation reaction of EPOP to synthesize epoxidized palm oil acrylate (EPOLA). Triethylamine (TEA) and 4-methoxyphenol (4-mp) were supplied by Aldrich Chemical Co. Inc, USA. Toluene 2, 4- diisocyanate (TDI) (80% Aldrich) and acrylate monomer (i.e., hydroxyl ethylacrylate or HEA) were used to prepare palm oil based-urethane acrylate prepolymer (POBUA). In the formulation of the UV-curable coating and nanocomposite films, trimethylolpropane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) (Radcure specialties) were used as monomer diluents for POBUA. Darocure ® 1173 (D-1173) was supplied by CIBA Corporation and used as received. Sodium montmorillonite treated with octadecylamine was used as a filler to prepare the nanocomposites.

Synthesis of EPOLA

Epoxidized palm oil (EPOP), triethylamine and 4-mp (0.25% wt) were mixed in a reaction flask that was equipped with a condenser and stirrer for 1 h at 40°C. Acrylic acid was introduced into the mixture (mole ratio 1:1 to EPOP). The mixture was then heated to 110°C. The reaction

was followed by measuring the acid value of the reaction mixture. The reaction was terminated when the acid value was less than 15 mg KOH per gram resin (Hussin & Hilmi, 1990).

Synthesis of POBUA

EPOLA was added to a reaction flask fitted with a condenser and a stirrer, and then mixed with 4-mp (1% wt) for 1 h at 40° C. TDI was introduced to the mixture and heated up to 70°C. Later, HEA was added into the reaction mixture (in mole ratio of 1:1 to EPOLA) and the temperature was kept below 90°C. Synthesis was followed by FTIR spectroscopy to monitor the disappearance of the absorption peak at 2280 cm⁻¹ which indicates the presence of the isocyanate (NCO) group. Fig.1 shows the steps involved in the synthesis.

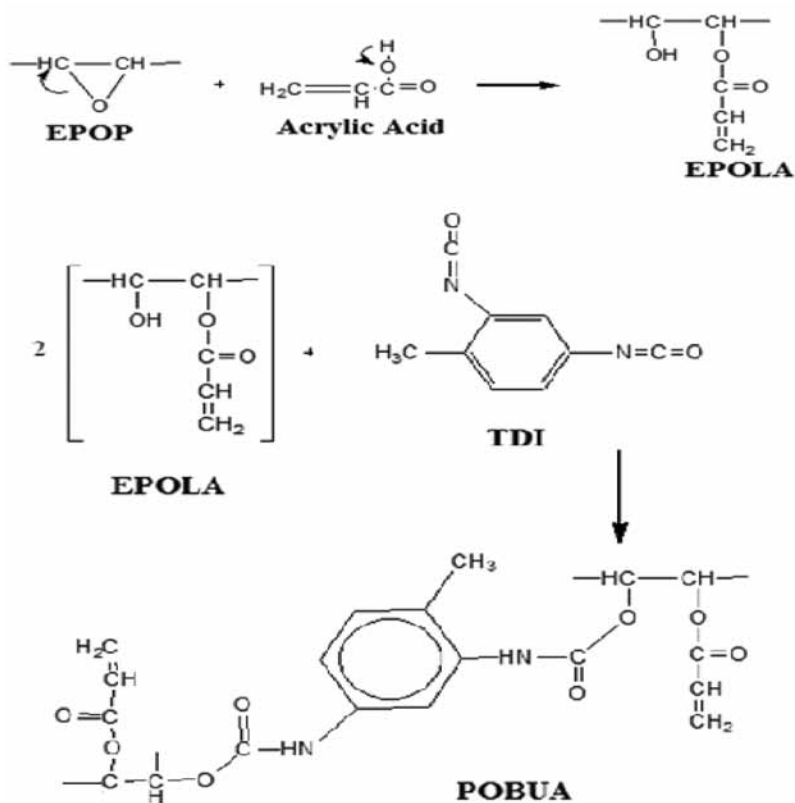


Fig.1: Reaction scheme of palm oil based resin synthesis

Formulation of the UV-nanocomposite Films

Table 1 shows the formulation of the POBUA-organoclay nanocomposites. POBUA was mixed with the monomers (TMPTA and TPGDA) and the organoclay, dispersed by stirring and followed by sonication for 30 min at 25°C. After mixing with the photoinitiator (4% wt.), the mixture was polymerized in an aluminium mould to obtain a polymer film with a thickness of approximately 1 mm or on a glass substrate to produce a film with a thickness of about 80µm.

UV-Curing of the Films

Samples were exposed to UV radiation using an 80 Watt/cm, medium mercury lamp at 5 m/min, with an approximate 1.2 s exposure time.

Table 1: Formulation of the UV-curable nanocomposites films

Sample	POBUA/g	TPGDA/Phr*	TMPTA/ phr	D1173/phr	O-clay/phr
1	15.00	40.00	15.00	4.00	1.00
2	15.00	40.00	15.00	4.00	3.00
3	15.00	40.00	15.00	4.00	5.00
4	15.00	40.00	15.00	4.00	0

*phr – parts per hundred resin

Testing

Measurement of oxirane oxygen content in EPOP and EPOLA samples was done using A.O.C.S Tentative Method Cd 9-57, 1963. Acid value determination (ASTM 974 method) was done by titrating one gram of the resin dissolved in 10 ml acetone. A few drops of phenol red indicator were added and then titrated with 0.1 N KOH and acid values were calculated using the following formula:

$$Av = \text{mg KOH/1g of resin} = 5.61 \times f \times v / w \quad [1]$$

Where f = the factor

v = volume of KOH solution

w = weight of resin sample in grams.

Viscosity of the resins was determined using a Brookfield viscometer model RVTDV-IIICP at 25°C. The molecular weight of resins and POBUA oligomer was determined by GPC (Tosoh made GPC, model HLC-8020). The functional group of the resins and cured films was determined by FTIR spectrophotometer (Perkin Elmer Spectrum 2000).

Meanwhile, the thermal stability of the nanocomposite films was analysed by TGA (Perkin Elmer model TGA 7) and the glass transition temperature of the cured films was determined by DSC (Shimadzu DSC-60). X-ray diffraction test was also carried out using a Shimadzu XRD 6000 diffractometer with Cu-K α radiation ($\lambda=0.15406$ nm). The samples were scanned from 2 to 10° theta at 1°/min.

Universal Tester Machine (Instron) was used to determine the mechanical properties of the cured samples (ASTM 1822 L), while the hardness of the cured films was studied using a pendulum hardness tester (Konig method). The cured films of a known weight (W_1) in SUS 304 stainless steel wire-mesh filter size # 100 was Soxhlet extracted for 16 h using acetone

as a solvent, dried in a vacuum oven and weighed (W_2) until a constant weight was obtained. Gel percentages were calculated as follows:

$$\text{Gel\%} = W_2 \times 100 / W_1 \quad [2]$$

RESULTS AND DISCUSSION

Synthesis of EPOLA

Acrylation reaction was followed by the acid value titration. The acid values before and after 16 hours of the reaction were 51 mg and 10 mg KOH/g, respectively, and this indicated that EPOLA had been successfully obtained. Table 2 shows some properties of EPOP and EPOLA.

Table 2: Properties of EPOP and EPOLA.

Resin	Viscosity/cps at 25°C	Mw g/mole	O _x -O ₂ % per mole
EPOP	240	1664	3.0
EPOLA	1500	2197	0.2

The decrease in oxirane oxygen percentage, i.e. from 3% in EPOP to less than 1% in EPOLA, was due to the degradation of the oxirane rings in the acrylation reaction.

Fig.1 shows the FTIR spectra of EPOP and EPOLA. The absence of the absorption peak at 840 cm⁻¹ in the EPOLA spectrum, which corresponds to the asymmetric bend of oxirane ring and the appearance of peaks at 810 and 1630 cm⁻¹ which indicate the presence of CH out of plane deformation and C=C stretching respectively in the acrylate group of EPOLA, showed that the acrylation of EPOP was successfully carried out. The same observations were also reported by Hussin and Hilmi (1990).

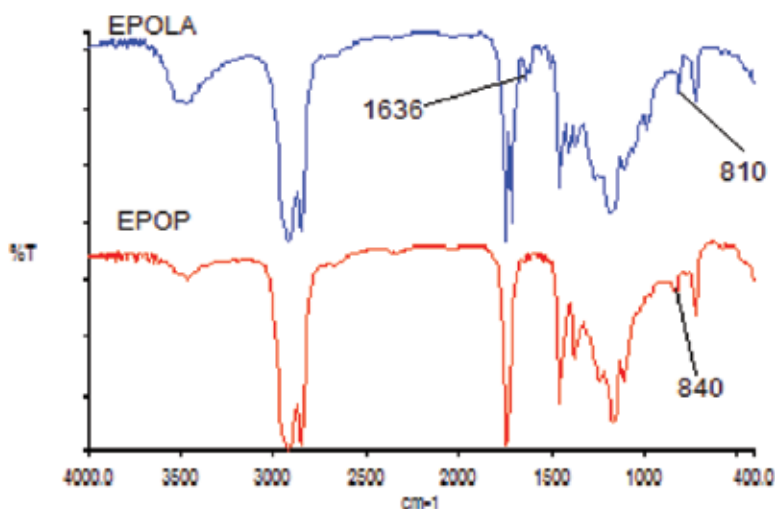


Fig.2: FTIR spectrum of EPOP and EPOLA

Fig.3 displays the FTIR spectra of the reaction mixture from several stages of the synthesis. The disappearance of the absorption peak of the NCO group at 2286 cm^{-1} indicates the isocyanation reaction with OH, which decreases (as shown by 3456 cm^{-1} peak) as the urethane linkage is formed. The molecular weight of POBUA, as characterized by GPC, is around 4500 g/mole with the viscosity of about 700 cps at 25°C .

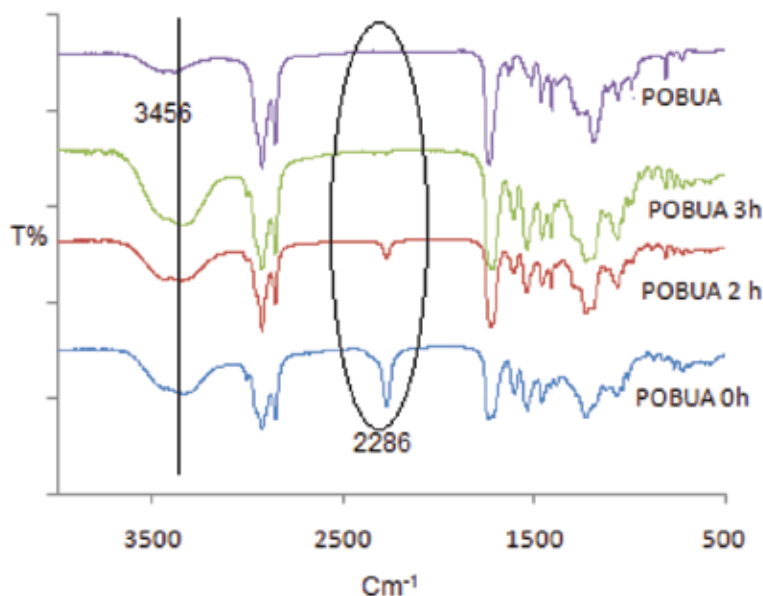


Fig.3: FTIR spectrum of POBUA at different stages during synthesis

Nanocomposite Films

Exfoliated nanocomposites can be obtained if the silicate layers of the clay are completely separated and randomly distributed in a polymer matrix (Keller *et al.*, 2004). The disappearance of the Bragg diffraction peaks in the composite XRD patterns (Fig.4) indicates that the clay layers in the composite have been exfoliated.

The mechanical properties of the nanocomposites were investigated through tensile strength measurements. Fig.5 shows the dependence of the tensile strength and Young's moduli on the clay concentration. The presence of 5 phr of the clay slightly improves the tensile value but reduces the modulus. The DSC results shown in Fig.6 indicate that the glass transition temperature (T_g) has shifted to higher values as the percentage of clay loaded in the nanocomposite films is increased, which is in agreement with the previous reports by Uhl *et al.* (2004) and Uhl *et al.* (2006).

Fig.7 shows the thermograms of the film samples. It was observed that there was no significant effect of clay content on the thermal stability of these polymer composites (Uhl *et al.*, 2004). Meanwhile, the crosslinking density of these composites is more than 80% and increases as the organoclay content is increased, indicating the formation of a strong linkage between the polymer chains and the filler particles. Similarly, the pendulum hardness also increases with the increase in the percentage of the organoclay added (*see* Fig.8).

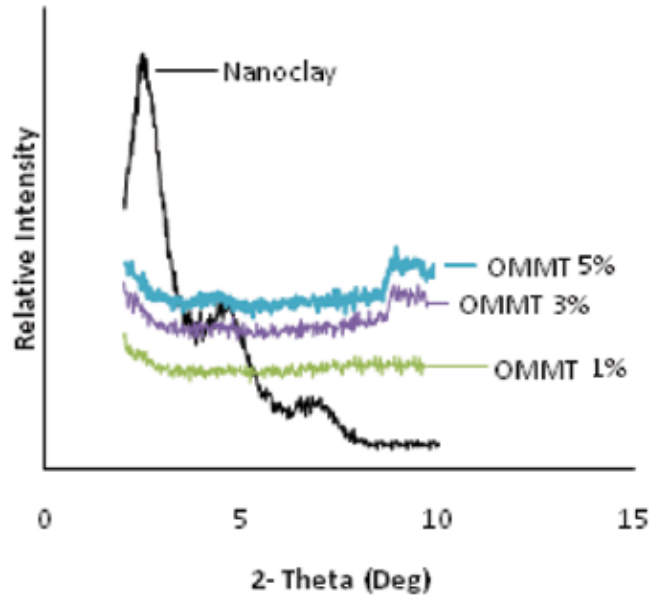


Fig.4: The XRD pattern of POBUA-clay nanocomposites

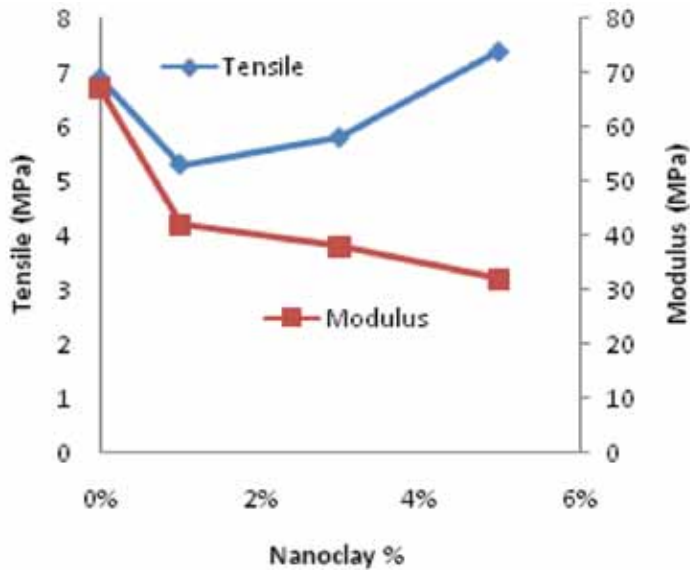


Fig.5: Mechanical properties vs. organoclay (%)

CONCLUSIONS

Palm oil based polyurethane acrylate nanocomposites were successfully prepared. The presence of the clay improves the hardness, T_g , and crosslinking density, but it also reduces the modulus. Higher tensile strength could only be obtained when the clay concentration reached 5wt%.

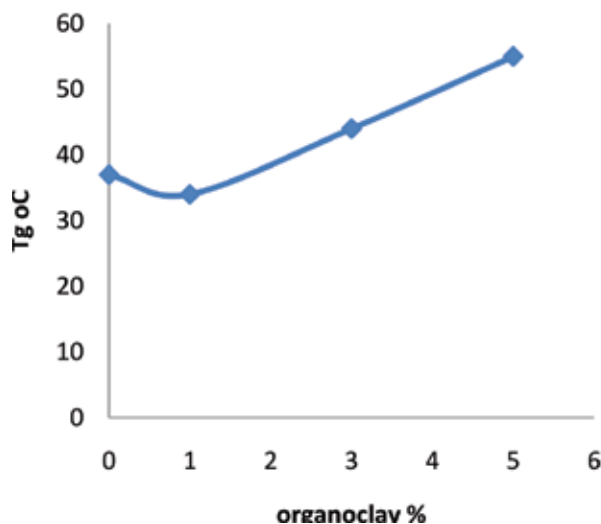


Fig.6: The dependence of the glass transition temperature on the wt% of organoclay

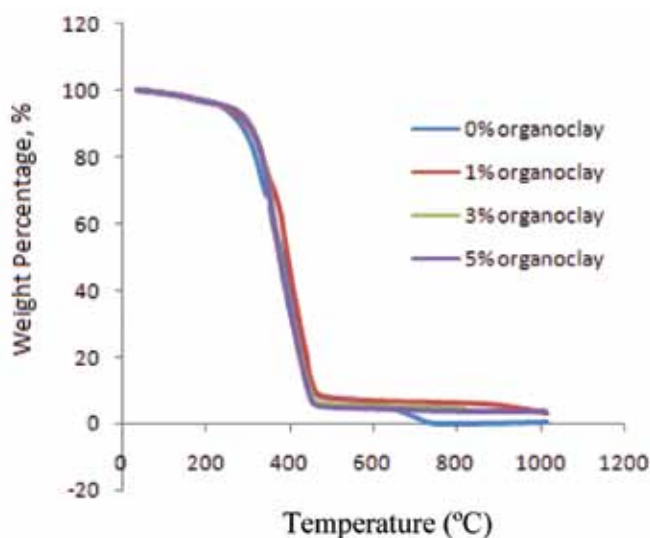


Fig.7: TGA thermograms of the nanocomposites films

ACKNOWLEDGEMENTS

The authors would like to thank Malaysian Nuclear Agency (MNA) for supporting this study and special thanks go to Radiation processing division staff and assistants. Special acknowledgement is also extended Prof. Sabu Thomas from the School of Chemical Sciences, Mahatma Gandhi University, India and Prof. Dean C. Webster from the Department of Coatings and Polymeric Materials, North Dakota State University, USA for their advice and assistance.

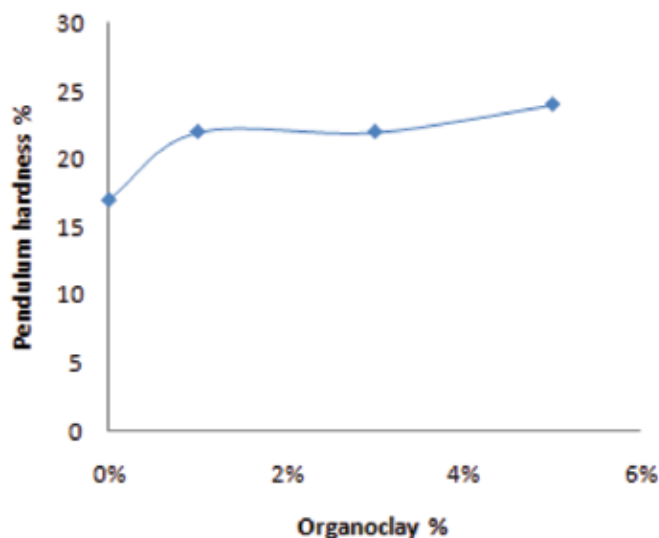


Fig 8: Pendulum hardness percentage Vs. Organoclay (wt.%)

REFERENCES

- Decker, C. (1996). Photoinitiated crosslinking polymerisation. *Progress in Polymer Science*, 21(4), 593-650.
- Decker, C., Zahouily, K., Keller, L., Benfarhi, S., Bendaikha, T., & Baron, J. (2002). Ultrafast synthesis of bentonite-acrylate nanocomposite materials by UV-radiation curing. *Journal of Materials Science*, 37(22), 4831-4838.
- Djouani, F., Herbst, F., Chehimi, M. M., & Benzarti, K. (2010). Synthesis, characterization and reinforcing properties of novel, reactive clay/poly(glycidyl methacrylate) nanocomposites. *Construction and Building Materials*, 25(2), 424-431.
- Galià, M., de Espinosa, L. M., Ronda, J. C., Lligadas, G., & Cádiz, V. (2009). Vegetable oil-based thermosetting polymers. *European Journal of Lipid Science and Technology*, 112(1), 87-96.
- Hussin, M. N., & Hilmi, M. M. (1990). The use of Epoxidised palm oil (EPOP) for the synthesis of Radiation curable resins1. Synthesis of Epoxidised RBD palm olien acrylate. *Japanese Society of Nuclear Medicine*, 8(2), 149-155.
- Jayabalan, M., Shalumon, K. T., Mitha, M. K., Ganesan, K., & Epple, M. (2009). Effect of hydroxyapatite on the biodegradation and biomechanical stability of polyester nanocomposites for orthopaedic applications. *Acta Biomaterialia*, 6(3), 763-775.
- Keller, L., Decker, C., Zahouily, K., Benfarhi, S., Le Meins, J. M., & Miehé-Brendle, J. (2004). Synthesis of polymer nanocomposites by UV-curing of organoclay-acrylic resins. *Polymer*, 45(22), 7437-7447.
- Landry, V., Blanchet, P., and Riedl, B. (2009). Mechanical and optical properties of clay-based nanocomposites coatings for wood flooring. *Progress in Organic Coatings*, 67(4), 381-388.
- Nik Salleh, N.G., Firdaus Yhaya, M., Hassan, A., Abu Bakar, A., and Mokhtar, M. (2010). Effect of UV/EB radiation dosages on the properties of nanocomposite coatings. *Radiation physics and chemistry*, 80(2), 136-141.

- Perepelkin, K. (2005). Polymeric materials of the future based on renewable plant resources and biotechnologies: Fibres, films, plastics. *Fibre Chemistry*, 37(6), 417-430.
- Uhl, F.M., Davuluri, S.P., Wong, S.-C., and Webster, D.C. (2004). Organically modified montmorillonites in UV curable urethane acrylate films. *Polymer*, 45(18), 6175-6187.
- Uhl, F.M., Webster, D.C., Davuluri, S.P. & Wong, S.-C. (2006). UV curable epoxy acrylate-clay nanocomposites. *European Polymer Journal*, 42(10), 2596-2605.