J. Rubb. Res., **16(3)**, 147–161

Preparation and Characterisation of Crosslinked Polycaprolactone and Natural Rubber (SMR CV60) Blends

WAN MD ZIN WAN YUNUS*, LIM CHEE SIONG**#, MANROSHAN, S.***, MOHD ZOBIR HUSSEIN*, MOHAMAD ZAKI AB RAHMAN* AND KHAIRUL ZAMAN MOHD DAHLAN****

Polycaprolactone (PCL) and natural rubber (NR) blends were prepared using a melt blending process, in the absence and presence of an organic peroxide crosslinking agent. The resulting blends were then characterised for their functional groups using Fourier transform infrared analysis (FTIR), surface morphology using scanning electron microscopy (SEM), crosslink degree using gel content measurements, physical properties using tensile measurements and viscoelastic properties using dynamic mechanical analysis (DMA). FTIR analysis revealed the reduction in C=O stretching and C–O bending of PCL due to crosslinking whereas SEM analysis showed rougher and more irregular surfaces with holes and grooves as well as increasing PCL concentration. Similarly, surfaces with holes after extraction with acetone were also observed using SEM. Gel content experiments showed an increase in gel content of the blends with crosslinking, which reduced with increasing PCL concentration. On the other hand, tensile strength and modulus at 300% increased after crosslinking and PCL concentration. However, the elongation at break after crosslinking showed an opposite increasing effect. DMA showed that crosslinking resulted in a more elastic blend behaviour with an increase in the glass transition temperature, T_g for all blend ratios.

Keywords: Polycaprolactone; natural rubber; blends; organic peroxide; tensile properties

Polymer blending is a convenient and attractive route for obtaining new polymeric materials. Compared to the development of novel homopolymers *via* synthesis of new monomers, producing blends of currently available homopolymers offer significant savings in time and cost, while blend properties may be tuned by changing the composition[1,2]. However, this approach is complicated as polymer blends are generally

---

* Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.

** Department of Pharmaceutical Chemistry, International Medical University, No. 126, Jalan Jalil Perkasa 19, Bukit Jalil, 57000 Kuala Lumpur, Malaysia.

*** Rubber Research Institute of Malaysia, P.O.Box 10150, Kuala Lumpur, Malaysia.

**** Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor Darul Ehsan, Malaysia.

Corresponding author (e-mail: cheesiong_lim@imu.edu.my)

thermodynamically immiscible[3]. Thus, achieving compatibilisation of immiscible polymer blends has been a long-standing academic and technological challenge[4].

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point (~ 60ºC) and glass transition temperature of approximately -60ºC[5]. It is therefore compatible with many polymers such as poly(vinyl chloride), chlorinated polyethylene, polycarbonate, poly(amide-6), poly(styrene-*co*-acrylonitrile) and ethylene terephthalate–caprolactone copolyester[6–11]. This is due to carbonyl groups of PCL forming intermolecular hydrogen bonds with hydroxyl groups of the second polymer. However, several researchers have reported incompatibility of PCL with polyester due to weak interactions of polymers at the interfaces, resulting in poorer mechanical and thermal properties[12–15].

So far, there is not much work reported on the blending of PCL with natural rubber (NR). NR contains 93% – 95% *cis*-1,4-polyisoprene and is an elastomer produced from the sap of the rubber tree, *Hevea brasiliensis*. As a renewable natural resource, NR has many excellent properties, such as outstanding resilience, high strength and good processability. It has also been studied and reported extensively in tyre applications because of its superior performance. However, NR has low resistance to heat and ozone but this has been improved significantly by blending NR with a suitable amount of ethylene propylene diene monomer (EPDM)[16–18]. Though so, NR blends generally exhibit poor mechanical properties due to incompatibility and phase separation[19–22].

In order to counter this problem, the use of organic peroxides, such as dicumyl peroxide (DCP) and dibenzoyl peroxide have been recommended as crosslinking agents for some of the polymers (elastomers) in order to improve physical and mechanical properties. In general, the main reaction that takes place is a combination of macroradicals that link macromolecules, therefore generating crosslinks, branching and extension of the chain[23–31]. This reaction is convenient for improving the properties of the polymer. Nevertheless, there are other competitive reactions, such as chain-scission and formation of unsaturations, which affect efficiency of the crosslinking, the molecular structure and final properties of the modified polymer[23–26].

In this study, PCL/NR blends were prepared and crosslinked using an organic peroxide, namely 1,4-di(-2-(tert-butylperoxy)prop-2-yl)benzene. The functional groups resulting from the blending were characterised using Fourier transform infrared (FTIR) analysis. The surface morphology of blends after fracturing and extraction with acetone (Molau test) were obtained through scanning electron microscopy, whereas the crosslink degree was characterised using gel content measurements. Tensile measurement experiments were performed to study the physical properties of the blends, whereas viscoelastic behaviour and glass transition temperatures of the blends were obtained through dynamic mechanical analysis experiments.

EXPERIMENTAL

Materials

Natural rubber (NR) of SMR CV60 grade was supplied by the Rubber Research Institute of Malaysia. Polycaprolactone (CAPA 650) with number-average molecular weight of 80,000 g/mol with a granule size of 5 mm was supplied by Solvay Caprolactone, England. Luperox 40F (1,4-di(-2-(tert-butylperoxy) prop-2-yl)benzene), used as the crosslinking agent was purchased from Sigma-Aldrich Chemicals, England whereas acetone was supplied by BDH, England.

Preparation of Crosslinked Polycaprolactone/Natural Rubber (PCL/NR) Blends

20 g of NR was first melted using Thermo *Haake* Polydrive internal mixer at 60ºC with a rotor speed of 50 r.p.m. for 5 minutes. This was then followed by addition of 20 g of PCL granules. Mixing was continued for another 5 min to form PCL/NR: 50/50 blend. Luperox 40F was added into the PCL/NR blend and mixing was continued for another 5 minutes. Luperox 40F, 5 p.h.r. (parts per hundred resin) and crosslinking temperature of 120ºC were chosen, as preliminary investigation using these conditions gave the required parameters for the PCL/NR blends. The compounded material was then compressed into 1 mm thick films using a hydraulic hotpress with a pressure of 150 kg/cm^2 at 120ºC for 10 minutes. This was then followed by cold pressing at 30ºC for 10 minutes. Similarly, other PCL/NR blends having various ratios (0/100, 10/90, 30/70, 70/30, 90/10 and 100/0) were prepared according to the procedure outlined above.

Fourier Transform Infrared (FTIR) Analysis

The functional groups and types of bonding in the PCL/NR:50/50 blend before and after crosslinking with Luperox 40F, together with pure NR and pure PCL were determined using a Perkin Elmer Spectrum 1000 series Spectrophotometer equipped with attenuated total reflectance (ATR). The infrared spectra of the samples were recorded in the frequency range of 600 to 4000 cm^{-1}.

Determination of Surface Morphology

A Philips XL30 Scanning Electron Microscope operating at 20 kV was used for this study. Micrographs were obtained for 2 sets of samples:

(a) *Tensile fractured samples*: The fractured part of samples after tensile properties measurement was viewed.

(b) *Acetone washed blends*: Sample preparation was according to the Molau test. PCL/NR:50/50 blend was dissolved in acetone for 48 h before it was vacuum dried for 16 h and coated with gold by Bio-rad coating system.

Gel Content Measurement

The crosslinking degree of PCL/NR blends was determined by gel content test. The samples were immersed in xylene and soxhlet extraction was performed for 24 hours. The remaining samples were filtered and vacuum dried to a constant weight for 16 hours. The gel content was calculated using *Equation 1*.

$$\text{Gel content, \%} = \frac{A}{B} \times 100\% \qquad \text{...1}$$

where, A is the weight of sample after extraction and B is the weight of the original sample.

Tensile Properties Measurement

The PCL/NR films were cut into a dumbbell shape and their tensile properties were determined using a universal testing machine, *Instron* 4302 series IX, according to *ASTM D638M-98*. The experiment was performed at room temperature using a crosshead speed of 5 mm/min and a load cell of 1 kN. The average of five best measurements was reported.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis of the PCL/NR blends with dimensions of 40 mm × 10 mm × 1 mm was carried out using a

Perkin Elmer Pyris Diamond DMA Analyzer. The analysis was conducted in a three point bending mode, subjected to an oscillating frequency of 1 Hz at a heating rate of 5ºC/min, from -100ºC to 100ºC.

RESULTS AND DISCUSSION

Determination of Functional Groups

The FTIR spectra of pure NR, pure PCL and PCL/NR:50/50 blends (absence and presence of crosslinking) are shown in *Figure 1*.

Pure PCL spectrum *Figure 1a* showed two peaks at 2940 and 2870 cm^{-1} which indicated the presence of C-H stretching. The peaks at 1718 and 1140 cm^{-1} attributed to C=O stretching and C-O bending. On the other hand, the spectrum of pure NR *Figure 1b* showed strong peaks at 1725 and 863 cm^{-1} which corresponded to the unsaturated C=C stretching and the vinyl out-of-plane bending of C-H. Medium peaks were also observed at 1465 and 1375 cm^{-1} which attributed to $–CH_3$ and $–CH_2$- bending and at peaks of 2930 and 2850 cm^{-1} which corresponded to the C-H stretching of pure NR.

Figure 1c showed peaks at 2930 and 2850 cm^{-1} which corresponded to the C-H stretching of the blend (NR and PCL). It also showed PCL characteristic peaks at 1718 and 1140 cm^{-1} (attributed to C=O stretching and C-O bending) and NR characteristic peaks at 1465 and 1375 cm^{-1} (attributed to $–CH_3$ and $–CH_2$- bending). From *Figure 1c* also, a strong C=C stretching signal at 1725 cm^{-1} and low vinyl out-of-plane bending of C-H signal at 863 cm^{-1} was observed, possibly due to formation of carbon-carbon bonds through radicals of NR chains during melt blending[32–33]. Upon crosslinking (*Figure 1d*), the signal intensity of C=O stretching and C-O bending due to PCL reduced as a result of increase in the crosslinked density of the PCL chains. On the other hand, stronger peaks at 2935,

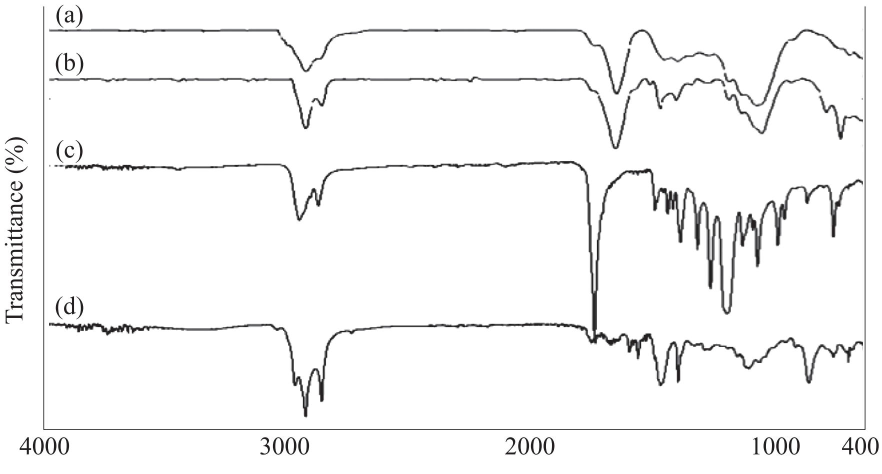


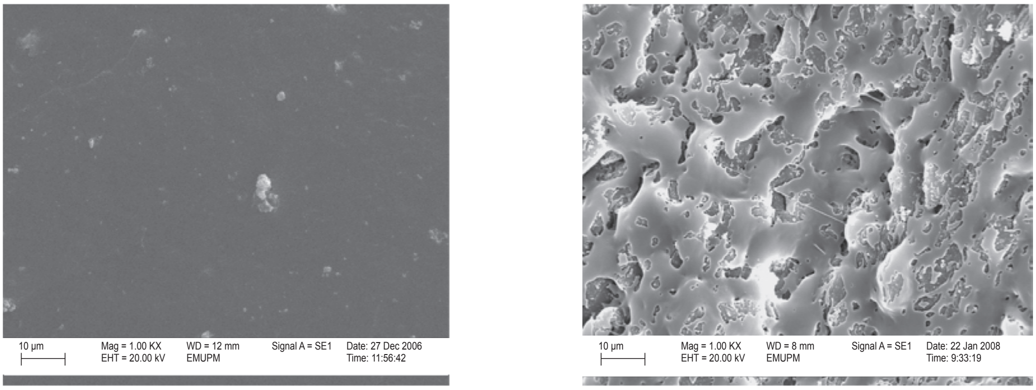
Figure 1. FTIR spectra of (a) pure NR, (b) pure PCL, (c) PCL/NR:50/50 blend in the absence of crosslinking agent and (d) PCL/NR:50/50 blend in the presence of crosslinking agent.

2864 and 2840 cm^{-1} corresponded to the C-H stretching of both NR and PCL.

Determination of Surface Morphology

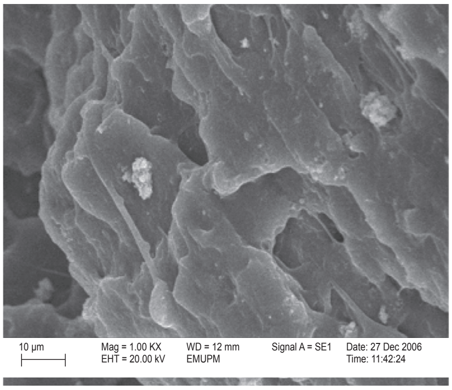
Figure 2 showed the morphology of tensile fractured surfaces of PCL/NR blends at three different ratios, namely 30/70, 50/50 and 70/30. At low PCL concentration (*Figure 2a*), the SEM micrograph showed a smooth fractured surface. However, as the concentration of PCL increased (*Figures 2b* and *c*), the fractured surfaces became rough and irregular with holes and grooves. This was mainly due to the incompatibility of PCL with NR at higher ratios which corresponded to poor adhesion between the two polymers[12–15], unlike at low PCL concentration (*Figure 2a*)[40].

SEM analysis was also performed on the surface of films after extraction with acetone (Molau test) in order to visualise the structure of the crosslinked blends, as acetone dissolves the uncrosslinked PCL. The results for a PCL/NR:50/50 blend before and after the Molau test are shown in *Figure 3*.



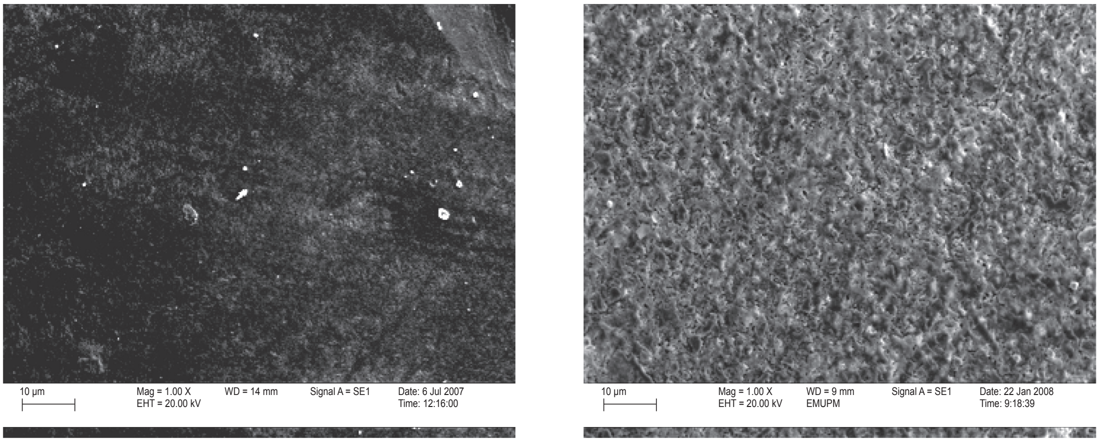
(a) PCL/NR:30/70

(b) PCL/NR:50:50



(c) PCL/NR:70/30

Figure 2. SEM micrographs of tensile fractured surfaces of PCL/NR blends after crosslinking.



(a) (b)

Figure 3. (a) SEM micrographs of PCL/NR:50/50 blend before the Molau test and (b) after the Molau test (Magnification: 100 ×)

As evident from *Figure 3b*, a large number of evenly distributed micro pores were present on the surface of the film after extraction with acetone, indicating the removal of uncrosslinked PCL. This also supports the fact that PCL and NR formed an immiscible blend resulting from a weak interface, as found by other researchers[35–37].

Gel Content Study

Figure 4 shows gel content results of PCL/NR blends in the absence and presence of crosslinking.

In the absence of crosslinking, all PCL/NR blend ratios showed a gel content of 0% as xylene dissolved both polymers. However, upon crosslinking, an increase in the gel content was observed, depending on the ratio of the polymers. In the absence of PCL (PCL/NR:0/100), the crosslinking was highest as network formation occurred between chains in the rubber, restricting its dissolution. Blending with PCL reduced gel content and when only PCL was available, the gel content was 0% as PCL was uncrosslinked. From the results in *Figure 4*, it is evident that PCL hindered the crosslinking of NR.

Mechanical Properties

Figure 5 shows tensile properties of the PCL/NR blends, in the absence and presence of crosslinking. It can be observed that tensile strength (TS) (*Figure 5a*) and the modulus at 300% (M300) (*Figure 5b*) were higher after crosslinking.

In the absence of crosslinking, the tensile strength (*Figure 5a*) and M300 (*Figure 5b*) increased with increasing concentration of PCL, reaching a maximum at PCL/NR:100/0. Upon crosslinking, a similar trend was observed with higher tensile strength and M300. The increase in these properties was

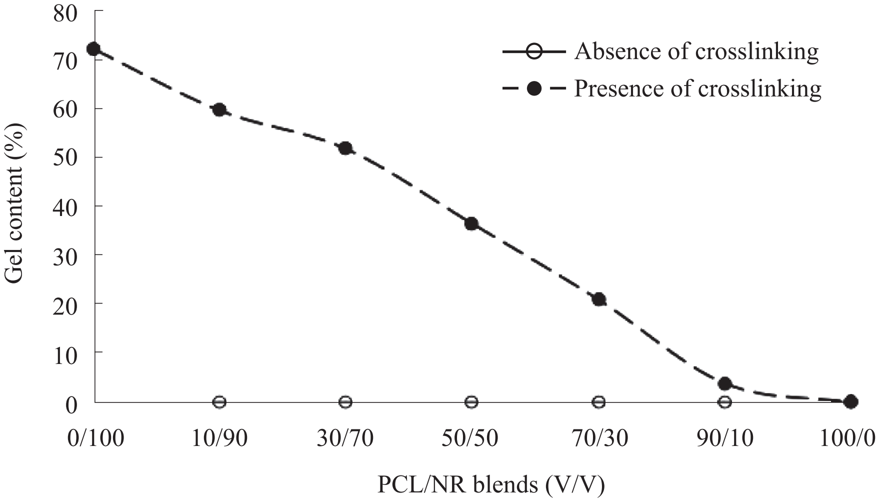


Figure 4. Gel content of PCL/NR blends in the absence and presence of crosslinking.

mainly due to natural stiffness of PCL, which enhanced stress crack resistance and adhesion properties of the blends[39].

Increase in tensile strength upon crosslinking was highest from PCL/NR ratio of 0/100 to PCL/NR ratio 30/70, resulting mainly from the free radical crosslinking of the NR chains. Above this ratio, tensile strength and M300 reduced due to the reduction in the ratio of NR in the blend. Though so, the tensile strength and M300 were still higher after crosslinking, as compared to before crosslinking, probably due to alignment and folding of the crystalline regions of PCL which increased with increasing PCL loadings[38].

A different trend was observed for the elongation at break (EB) as shown in *Figure 5c*. In the absence of crosslinking and PCL, the EB was low mainly as the rubber chains were broken due to the mastication process in the internal mixer. The increase in EB with PCL addition could have been due to contribution of high flexibility of the PCL chains.

The opposite was observed in the presence of crosslinking. From *Figure 5c*, it can be seen that the EB increased in the absence of PCL (PCL/NR:0/100), mainly due to contribution of the crosslinking agent which formed networks of rubber chains through free radical reaction enabling the blend to be stretched further. Addition of PCL however reduced EB of the blend, as PCL caused reduction of crosslinkable material.

Dynamic Mechanical Analysis

Figure 6 shows viscoelastic properties of PCL/NR blends, in the absence and presence of crosslinking. Experiments were performed at 30ºC at an oscillating frequency of 1 Hz. Both results (*Figures 6a* and *b*) showed that storage modulus, G' was higher than the loss

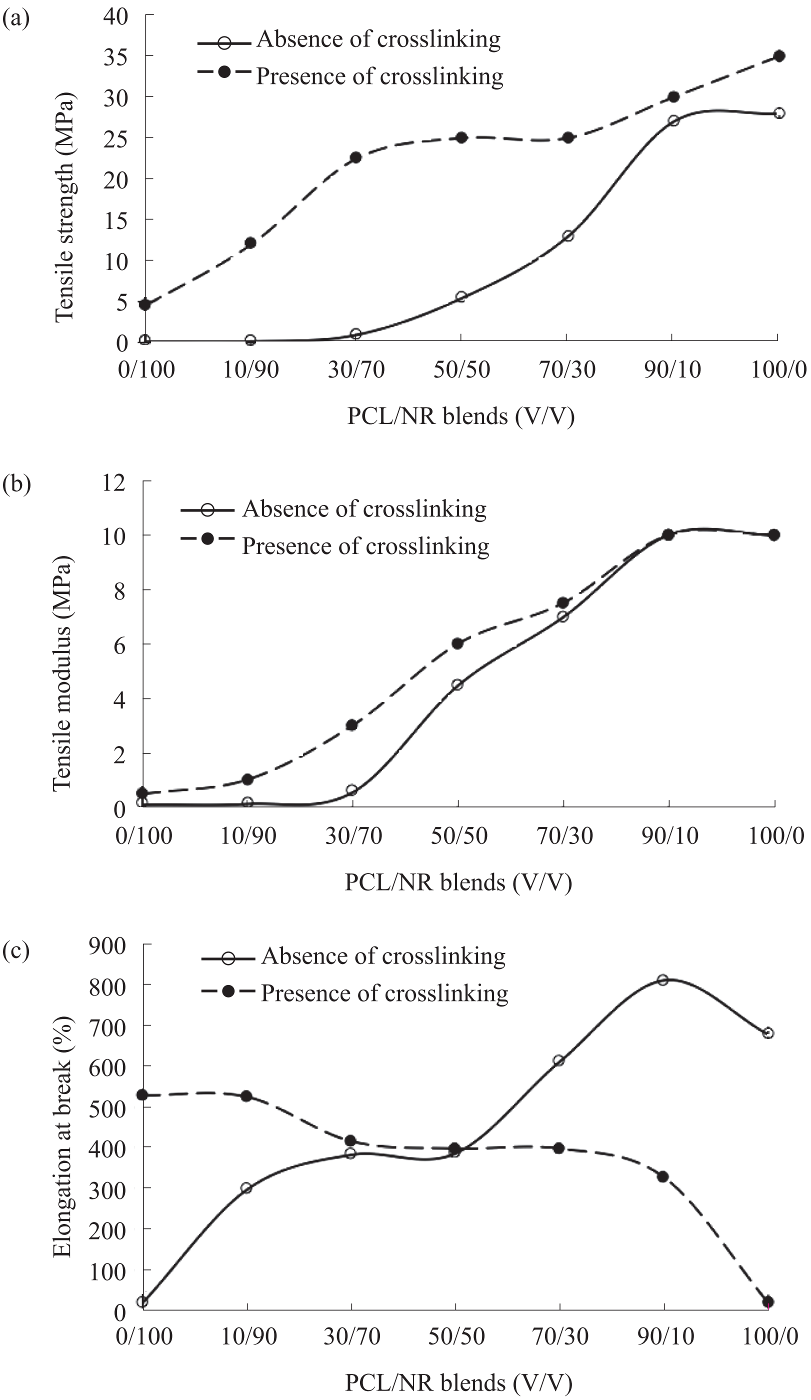


Figure 5. (a) Tensile strength, (b) Modulus at 300% elongation and (c) Elongation at break of various PCL/NR blend ratios in the absence and presence of crosslinking.

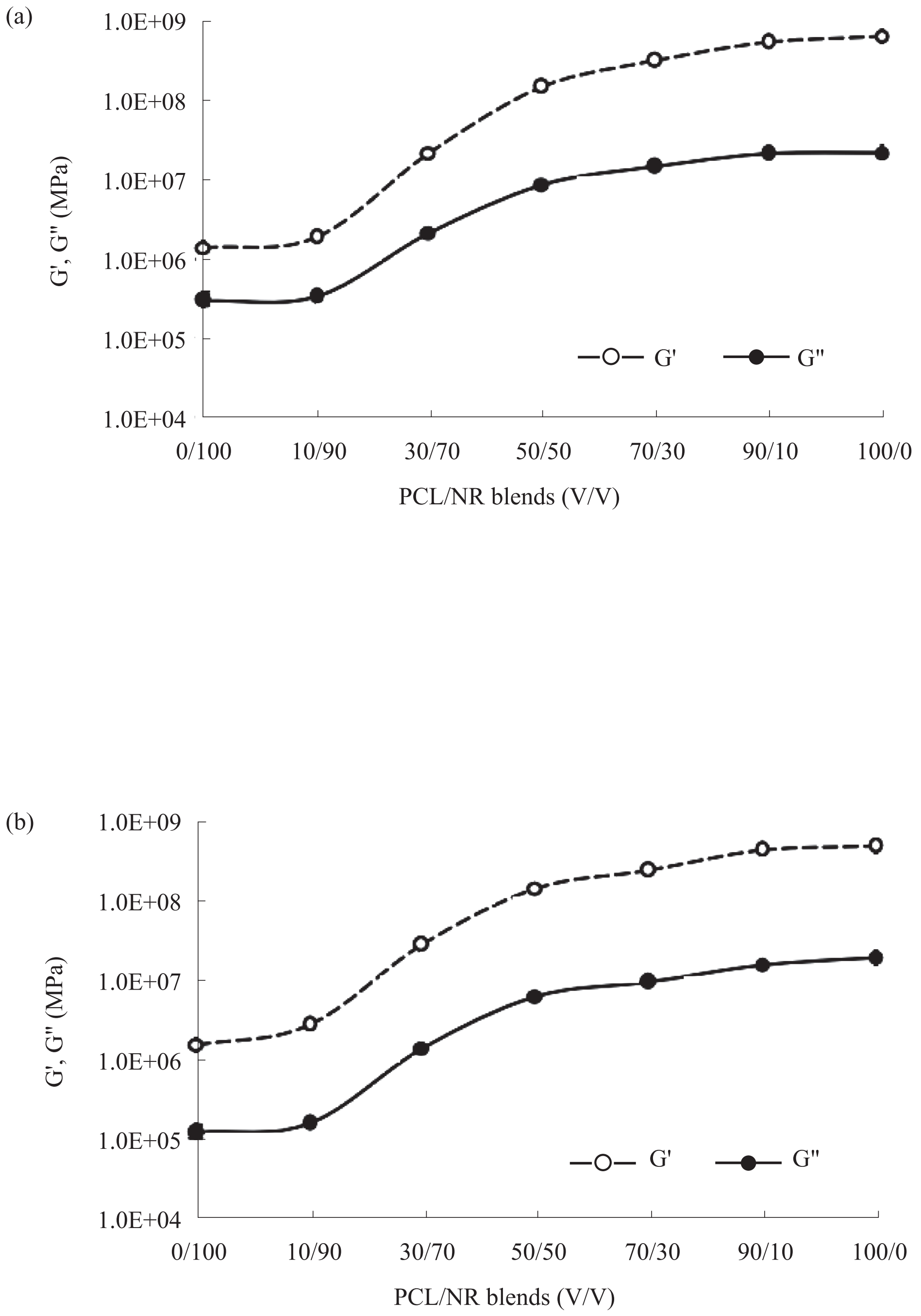


Figure 6. Viscoelastic behaviour of various PCL/NR blends, in the (a) absence of crosslinking and (b) presence of crosslinking.

modulus, G" for all blend ratios indicating a predominantly elastic behaviour. Furthermore, above PCL/NR ratios of 10/90, continuous increase in both G' and G" was also observed with increasing PCL concentration. The increase in modulus values could be attributed to the crystalline structure of PCL.

The above results were further interpreted using tan δ. The tan δ gives an indication of the type of sample behaviour, and the calculation is shown in *Equation 2*.

$$\text{Tan } \delta = \frac{G''}{G'} \quad \text{... 2}$$

where G" is the loss modulus and G' is the storage modulus. Results obtained for the various PCL/NR blends, in the absence and presence of crosslinking are shown in *Figure 7*.

From the results, it can be clearly seen that in the absence of crosslinking and PCL (PCL/NR:0/100), the blends showed a predominantly viscous behaviour. The tan δ however reduced with increasing concentration of PCL indicating a more elastic behaviour of the blend which could probably be contributed by the stiffness of PCL. However, at PCL/NR ratios of 70/30 and above, tan δ was almost independent with further addition of PCL. Similar observations were also obtained upon crosslinking. However, for PCL/NR blend ratios below 70/30 in the presence of crosslinking, a reduction in tan δ was observed, indicating a more elastic sample.

Apart from G' and G", the glass transition temperature (T_g) values can also be obtained from tan δ results. Tan δ results as a function of temperature for PCL/NR blends in the absence and presence of crosslinking agent are shown in *Figure 8*.

From the results, the peak in tan δ represents T_g of the blends. The corresponding T_g for all blends are shown in (*Table 1*).

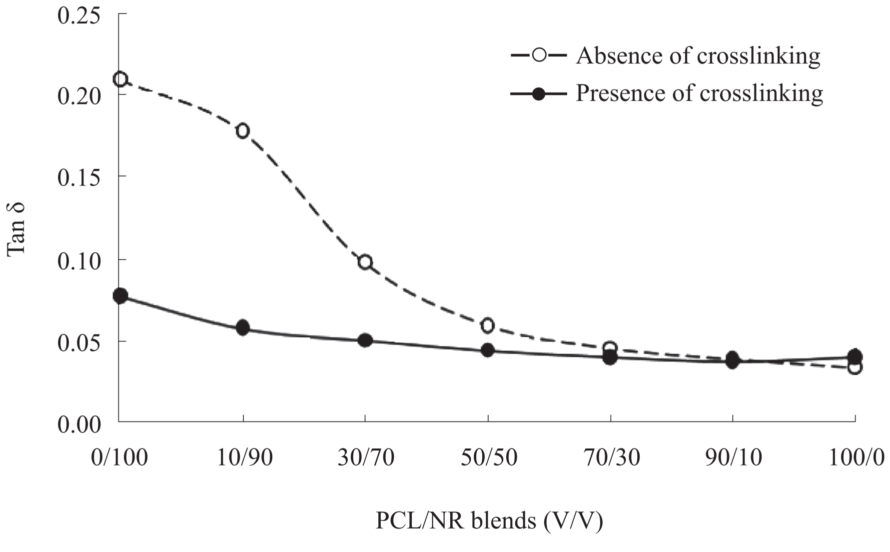


Figure 7. Tan δ *versus PCL/NR blend ratios.*

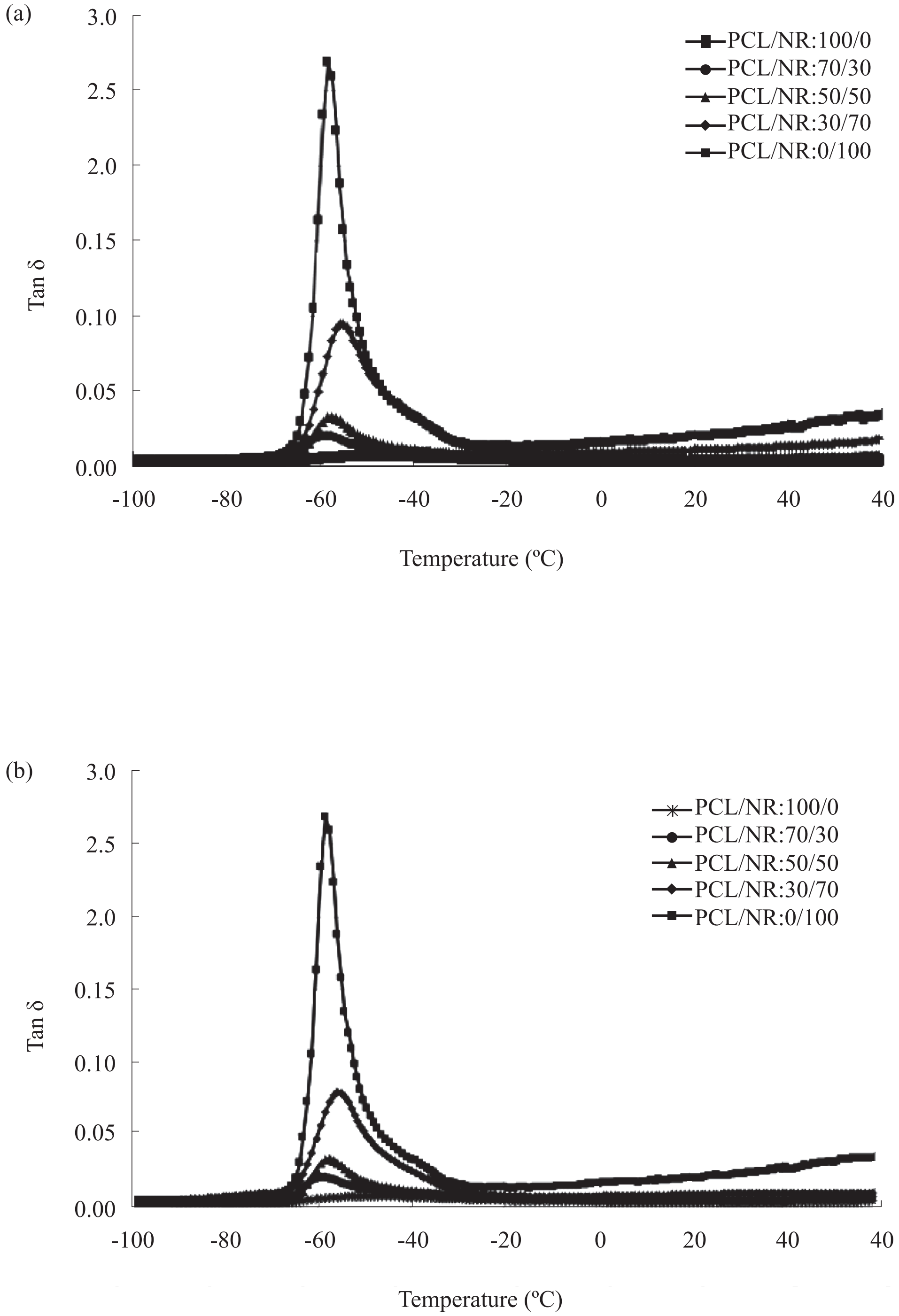


Figure 8. Tan δ *results for the PCL/NR blends in the (a) absence and (b) presence of crosslinking.*

TABLE 1. T_g RESULTS FOR THE PCL/NR BLENDS IN THE ABSENCE AND PRESENCE OF CROSSLINKING AGENT

Blend Ratio (PCL/NR)	Absence of crosslinks	Presence of crosslinks
0/100	-57.5	-55.0
30/70	-58.3	-55.1
50/50	-60.0	-54.0
70/30	-57.8	-53.8
100/0	-53.0	-47.0

Generally, the T_g of a polymer depends on mobility of the macromolecule chain segment. This correlates well with the results in *Table 1* which show that pure PCL (PCL/NR:100/0) has a lower T_g than pure NR (PCL/NR:0/100) because PCL with a longer carbon chain is more flexible than NR, as NR has an unsaturated double bond and a branched $–CH_3$ in its molecule structure causing restriction to its mobility.

As both materials produce immiscible blends when mixed, T_g values should theoretically be evident from DMA results. However, this was not the case with current results, probably because T_g values of both blended materials were very close to each other[47–48]. From *Table 1*, it can be observed that T_g of blends with crosslinks was much higher compared to blends in the absence of crosslinking. This was mainly due to restriction in the polymer chain mobility, resulting from introduction of crosslinks between the chains, unlike in the absence of crosslinking where chains were more flexible[42–46].

CONCLUSIONS

PCL/NR crosslinked blends were successfully prepared through a melt blending method. Fourier transform infrared (FTIR) analysis showed that crosslinking reduced the intensity of C=O stretching and C–O bending due to PCL. Though so, the blends were incompatible with each other, resulting in poor adhesion between the two polymers as observed from the scanning electron microscopy (SEM) analysis. This was also confirmed by the Molau test, where a large number of micropores were evident on the surface of the blend films after extracting with acetone. Gel content experiments revealed that crosslinking increased the gel content. However, this was dependent on the ratio between NR and PCL. NR was crosslinked by organic peroxide whereas blending with PCL hindered the crosslinking of NR. Even so, it was evident from the mechanical properties that tensile strength and modulus at 300% elongation increased with crosslinking and PCL concentration. The elongation at break however reduced after crosslinking. Further evidence of crosslinking was provided by dynamic mechanical analysis, which showed that elastic behaviour of blends increased with crosslinking. As a result, higher glass transition temperature, T_g was observed for the blends.

ACKNOWLEDGEMENTS

We would like to thank Malaysian Rubber Board for supplying natural rubber used in the study and En. Rafiuz Zaman Haroun from the Microscopy Unit, UPM for assisting in the SEM analysis. We would also like to acknowledge the Ministry of Science, Technology and Innovation, Malaysia for financial support through the National Science Fellowship.

Date of receipt: October 2012
Date of acceptance: February 2013

REFERENCES

1. PAUL, D.R. AND BUCKNELL, C.B. (2000) Polymer blends: Formulation & Performance. New York: John Wiley.
2. KONING, C., VAN D.M., PAGNOULLE, C. AND JEROME, R. (1998) Strategies for Compatibilization of Polymer Blends. *Prog. Polym. Sci*., **23**, 707–757.
3. SPERLING, L.H. (2005) Introduction to Physical Polymer Science, *4th Edn*., New York: John Wiley.
4. WANG, D., LI, Y., XIE. X.M. AND GUO B.H. (2001) Compatibilization and Morphology Development of Immiscible Ternary Polymer Blends. *Polym*., **52**, 191.
5. CHANDRA, R. AND RUSTGI, R. (1998) Biodegradable Polymers. *Prog. Polym. Sci*., **23**, 1273–1335.
6. EASTMOND, G.C. (1999) Poly(ε-caprolactone) Blends, *In Adv. Polym. Sci.* **149:** Biomedical Applications Polymer Blends. (*Eds. Eastmond, G.C., Hocker, H. and Klee, D.*) pp 59 – 223. Berlin: Springer-Verlag.
7. KEITH, H.D., PADDEN, F.J. AND RUSSEL, T.P. (1989) Morphological Changes in Polyesters and Polyamides Induced by Blending with Small Concentrations of Polymer Diluents. *Macromol*., **22(2)**, 666–675.
8. KIM, W.N., PARK, C.E. AND BURNS, C.B. (1993) Ternary Blends of Poly (amide-6)/ Polycarbonate /Poly(e-caprolactone), *J. Appl. Polym. Sci*., **49**, 1003.
9. LI, W. AND PRUD' HOMME, R.E. (1994) Orientation and Miscibility of Poly(ε-caprolactone)/poly(styrene-co-acrylonitrile) Mixtures, *Polym*., **35(15)**, 3260–3267.
10. WANG, Z., WANG, X., YU, D. AND JIANG, B. (1997) The Formation of Ring-banded Spherulites of Poly(ε-caprolactone) in its Miscible Mixtures with Poly(styrene-co-acrylonitrile), *Polym*., **38(23)**, 5897–5901.
11. MA, D., LUO, X., ZHANG, R. AND TOSHIO, N. (1996) Miscibility and Spherulites in Blends of Poly(ϵ-caprolactone) with Ethylene Terephthalate-caprolactone Copolyester, *Polym*., **37(9)**,1581.
12. NOTTELET, B., COUDANE, J. AND VERT, M. (2006) Synthesis of an X-ray Opaque Biodegradable Copolyester by Chemical Modification of Poly(ε-caprolactone), *Biomater*., **27(28)**, 4948–4954.
13. NISHIDA, H., KONNO, M., IKEDA, A. AND TOKIWA, Y. (2000) Microbial Degradation of Poly(p-dioxanone) I. Isolation of Degrading Microorganisms and Microbial Decomposition in Pure Culture, *Polym. Degrad. Stabil*., **68(2)**, 205–217.
14. YANG, K.K., WANG, X.L. AND WANG, Y.Z. (2005). Recent Advance in Poly(*p*-dioxanone)-based Biodegradable Polymers. *Proc. 8th Polym. Adv. Technol. Int. Symp*., Budapest.
15. BALSAMO, V., NEWMAN, V., GOUVEIA, L., HERRERA, L., GRIMAU, M. AND LAREDO, E. (2006) Molecular Dynamics and Crystallization Kinetics in PSMA14/PCL Blends, *Polym*., **47(16)**, 5810–5820.
16. MASTROMATTEO, R.P., MIKHELL, J.M. AND BRETT, T.J. (1971) New Accelerators for Blends of EPDM, *Rubb. Chem. Technol*., **44(4)**, 1065–1079.
17. KWEI, T.K., RADIGAN, H.I. AND VOGEL, S. (1977) Ternary Polymer Mixtures, *Macromol*., **10(1)**, 157–160.

18. GOH, S.H. AND SIOW, K.S. (1986) Calorimetric Study of the Miscibility of Poly(styrene-co-acrylonitrile)/poly(methyl methacrylate)/poly(ethyl methacrylate) Ternary Blends, *Thermochimica Acta*, **105(1)**, 191–195.

19. POMPOSA, J.A., CALAHORRA, E., EGUIAZABAL, I. AND CORTAZAR, M. (1993) Miscibility Behavior of Ternary Poly(methyl methacrylate)/poly(ethyl methacrylate)/poly(p-vinylphenol) Blends, *Macromol*., **26(8)**, 2104–2110.

20. SHAH, V.S., KEITZ, J.D., PAUL, D.R. AND BARLOW, J.W. (1986) Miscible Ternary Blends Containing Polycarbonate, SAN, and Aliphatic Polyesters, *J. Appl. Polym. Sci*., **32(3)**, 3863–3879.

21. BARLOW, J.W. AND PAUL, D.R. (1987) The Importance of Enthalpic Interactions in Polymeric Systems, *Polym. Eng. Sci*., **27(20)**, 1482–1494.

22. AMEDURI, B. AND PRUD'HOMME, R.E. (1988) Miscibility Behaviour of Ternary Poly(caprolactone)/poly(vinyl chloride)/chlorinated poly(vinyl chloride) Blends, *Polym*., **29(6)**, 1052–1057.

23. LAZA´R, M., RADO, R. AND RYCHLY´, J. (1990) Crosslinking of Polyolefins, *Adv. Polym. Sci*., **95**, 149–197.

24. ANDREOPOULOS, A.G. AND KAMPOURIS, E.M. (1986) Mechanical Properties of Crosslinked Polyethylene, *J. Appl. Polym. Sci*., **31(4)**, 1061–1068.

25. LAMBLA, M. (1994) Reactive Extrusion: A New Tool for the Diversification of Polymeric Materials, *Macromol. Symp*., **83(1)**, 37–48.

26. KRENTSEL, B.A., KISSIN, Y.V., KLEINER, V.I. AND STOTSKAYA, L.L. (1997) Polymers and Copolymers of Higher A-olefins. Chemistry, Technology, Applications, Munich: Hanser Publishers, 299.

27. LEM, K.W. AND HAN, C.D. (1982) Rheological Properties of Polyethylenes Modified with Dicumyl Peroxide, *J. Appl. Polym. Sci*., **27(4)**, 1367–1383.

28. BREMNER, T., RUDIN, A. AND HARIDOSS, S. (1992) Effects of Polyethylene Molecular Structure on Peroxide Crosslinking of Low Density Polyethylene, *Polym. Eng. Sci*., **32(14)**, 939–943.

29. GLOOR, P.E., TANG, Y., KOSTANSKA, A.E. AND HAMIELEC, A. E. (1994) Chemical Modification of Polyolefins by Free Radical Mechanism: A Modeling and Experimental Study of Simultaneous Random Scission, Branching and Crosslinking. *Polym*., **35**, 1012–1030.

30. SMEDBERG, A., HJERTBERG, T. AND GUSTAFSSON, B. (1997) Crosslinking Reactions in an Unsaturated Low Density Polyethylene. *Polym*., **38**, 4127–4138.

31. PEDERNERA, M., SARMORIA, C., VALLE´S, E.M. AND BRANDOLIN, A. (1999) An Improved Kinetic Model for the Peroxide Initiated Modification of Polyethylene. *Polym. Eng. Sci*., **39(10)**, 2085–2095.

32. WU, Q., LIU, X. AND BERGLUND, L.A. (2002) FT-IR Spectroscopic Study of Hydrogen Bonding in PA6/clay Nanocomposites, *Polym*., **43(8)**, 2445–2449.

33. MOUSA, A. AND KARGER-KOCSIS, J. (2001) Rheological and Thermodynamical Behaviour of Styrene/butadiene Rubber-organoclay Nanocomposites. *Macromol. Mater. Eng*., **286**, 260.

34. COULEMBIER, O., DEGEE, P., HEDRICK, J.L. AND DUBOIS, P. (2006) From Controlled Ring-opening Polymerization to Biodegradable Aliphatic Polyester: Especially poly(ß-malic acid) Derivatives. *Prog. Polym. Sci*., **31**, 723–747.

35. ADRIANA, Y., HARUMI, O., LUÍS, F.C.P., LIMA, B.W.H. ARTEL, D.F., JEFERSON, R.B., RODRIGO, S., MARCELO, F.

AND ADEMAR, B.L. (2007) Study of Polypropylene/polybutene Blends Modified by Gamma Irradiation and High Melt Strength Polypropylene/polybutene Blends. *Mater. Atoms*, **265(1)**, 130–134.

36. JUNGKI, K., HONGYING, Z., NGUYEN, S.T. AND TORKELSON, J.M. (2006) Synthesis and Application of Styrene/4-hydroxystyrene Gradient Copolymers made by Controlled Radical Polymerization: Compatibilization of Immiscible Polymer Blends via Hydrogen-bonding Effects. *Polym*., **47(16)**, 5799–5809.

37. KODAMA, Y., MACHADO, L.D.B., GIOVEDI, C. AND NAKAYAMA, K. (2007) Gamma Radiation Effect on Structural Properties of PLLA PCL Blends. *Nuclear Instruments and Methods in Physics Research, B*, **265(1)**, 294–299.

38. MISHRA, J.K., WOOK C.Y. AND KOOK, K.D. (2007) Green Thermoplastic Elastomer Based on Polycaprolactone/epoxidized Natural Rubber Blend as a Heat Shrinkable Material, *Mater. Lett*., **61(17)**, 3551–3554.

39. CANDRA, R. AND RUSTGI, R. (1998) Biodegradable Polymers. *Prog. Polym. Sci.*, **23**, 1273.

40. VU, Y.T., MARK, J.E., PHAM, L.H. AND ENGELHARDT, M. (2001) Clay Nanolayer Reinforcement of cis-1,4-polyisoprene and Epoxidized Natural Rubber, *J. Appl. Polym. Sci*., **82(6)**, 1391–1403.

41. CHEN, J.S., OBERA, C.K., POLIKS, M.D., ZHANG, Y., WIESNER, U. AND COHEN, C. (2004) Controlled Degradation of Epoxy Networks: Analysis of Crosslink Density and Glass Transition Temperature Changes in Thermally Reworkable Thermosets, *Polym*., **45(6)**, 1939.

42. MISHRA, J.K., CHANGA, Y.W., LEEB, B.C. AND RYUC, S.H. (2008) Mechanical Properties and Heat Shrinkability of Electron Beam Crosslinked Polyethylene Octene Copolymer. *Radiation Physics and Chemistry*, **77(5)**, 675.

43. DAVIES, F.T. (2004) Polymer Chemistry – A practical Approach. London: Oxford University Press.

44. NICHOLSON, J.W. (1997) The Chemistry of Polymer, *2nd Ed*., Cambridge: Royal Society of Chemistry.

45. CARRAHER, C.E. (2003) Polymer Chemistry, *6th Ed*., New York: Marcel Dekker.

46. ALLCOCK, H.A., LAMPE, F.W. AND MARK, J.E. (2003) Contemporary Polymer Chemistry, **3rd Ed.,** Pearson Prentice Hall.

47. MATZINOS, P., TSERKI, T., GIANIKOURIS, C., PAVLIDOU, E. AND PANAYIOTOU, C. (2002) Processing and Characterization of LDPE/Starch/PCL Blends. *Eur. Polym. J*., **38**, 1713–1720.

48. LYON, R.E. AND FARRIS, R.J. (1992) Thermomechanics of Rubber at Small Strains. *Polym*., **28**, 1127–1132.