Jurnal Teknologi, 39(A) Keluaran Khas. Dis. 2003: 11–22

RHEOLOGICAL PROPERTIES OF DYNAMICALLY VULCANISED THERMOPLASTIC ELASTOMER COMPOSITES OF POLYPROPYLENE, ETHYLENE PROPYLENE DIENE TERPOLYMER AND WHITE RICE HUSK ASH: TEMPERATURE DEPENDENCE

S. SIRIWARDENA[1], H. ISMAIL[2] & U. S. ISHIAKU[3]

Abstract. The effects of extrusion temperature on rheological properties of dynamically vulcanized and rubber dominant composites of polypropylene (PP), ethylene propylene diene terpolymer (EPDM) and white rice husk ash (WRHA) were investigated. Four different temperatures varying from 170 to 200°C with 10 degree intervals were used. Filler free rubber dominant PP/EPDM blends were also subjected to the same study for the purpose of comparison. The study reveals that the composites could be processed like thermoplastics, if suitable extrusion temperatures and shear rates are used. Study of flow curves and melt fracture of extrudates indicates that increase in extrusion temperature increased the melt viscosity of the composites at low shear rates. At high shear rates, the trend becomes opposite. It was found that PP/EPDM/WRHA composites are pseudoplastic similar to the unfilled PP/EPDM blends. Pseudoplasticity of these vulcanized systems as judged by the power law index (n) increased as the extrusion temperature increases. Furthermore, it was shown that both incorporation of filler and introduction of crosslinked rubber particles induce the pseudoplastic behaviour in the polymer melts. Partial replacement of polymer matrices by WRHA reduces this effect indicating a processing advantage of WRHA filled ternary composites. Overall study suggests that temperature of 180°C is suitable for the extrusion of both these unfilled and filled composites.

Keywords: Rheological properties; dynamically vulcanized; thermoplastic elastomer; polypropylene; ethylene propylene diene terpolymer; white rice husk ash

Abstrak. Kesan suhu pengekstrudan terhadap sifat-sifat reologi pemvulkanan dinamik bagi komposit getah dominan PP/EPDM/WRHA telah dikaji. Empat suhu yang berbeza digunakan bermula daripada 170 sehingga 200°C dengan selang suhu sebanyak 10°C. Adunan getah dominan PP/EPDM tanpa pengisi juga turut dikaji bagi tujuan perbandingan. Kajian menunjukkan bahawa komposit boleh diproses secara termoplastik, jika suhu ekstruder dan kadar ricih yang sesuai digunakan. Kajian terhadap lengkungan aliran dan rekahan leburan ekstrudat menunjukkan peningkatan suhu pengekstrudan telah meningkatkan kelikatan leburan bagi komposit pada kadar ricih yang rendah. Pada kadar ricih yang tinggi, pola yang didapati adalah berlawanan. Didapati komposit PP/EPDM/WRHA adalah pseudoplastik bersamaan dengan adunan PP/EPDM tanpa pengisi. Sifat pseudoplastik bagi system tervulkan ini seperti yang telah ditetapkan oleh indeks hukum kuasa (power law index, n) meningkat dengan peningkatan suhu pengestrudan. Di samping itu telah didapati penambahan bahan pengisi dan partikel-partikel getah tersambung silang mempamerkan kelakuan pseudoplastik di dalam leburan polimer tersebut. Penggantian separa matriks polimer dengan WRHA mengurangkan kesan

[1] Rubber Research Institute of Sri Lanka, Telwala Road, Rathmlana, Sri Lanka; sus_siri@yahoo.com
[2&3] School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia; hanafi@eng.usm.my

ini, menunjukkan kelebihan pemprosesan WRHA terisi komposit. Kajian keseluruhan menunjukkan bahawa suhu 180°C sesuai untuk pengekstrudan kedua-dua komposit tanpa terisi dan terisi.

Kata kunci: Sifat reologi; pemvulkanan dinamik; elastomer termoplastik; poli propilena, etilene poli propilene diena terpolimer; abu sekam padi putih

1.0 INTRODUCTION

Thermoplastic elastomer composites (TPECs) is a blend of rubber, thermoplastic and fillers which could be moulded like thermoplastics at appropriate processing temperatures, but retain some of the characteristics of vulcanized rubbers. Study on TPECs with various types of elastomers and polyolefines have been reported by main researchers [1-3]. However, a significant majority of these studies concentrate on the plastic dominant composites (rubber toughened plastics)[4-5] while less attention has been paid to the rubber dominant composites.

For many end uses, the material should posses good mechanical properties as well as good processability. Dynamic vulcanization is the widely used technology to induce melt blended composites through technological compatibilization [6]. In this process, vulcanized elastomer particles are formed during melt mixing of rubber with molten plastics and any filler incorporated. However, introduction of crosslinked rubber particles and incorporation of filler may affect the processability of the composites.

In general, the viscosities of uncrosslinked polymers and composites decrease with increase in temperature and vice versa [7-8]. However, this does not happen in the case of temperature sensitive crosslinkable polymers and their blends where vulcanized rubber particles are present in the matrix. When these types of materials are extruded at a sufficiently high temperature, crosslinks may formed and subsequently resist the material flow resulting in a high melt viscosity. With respect to the dynamically vulcanized rubber/plastic blends, further crosslinks can be formed, if the extrusion temperature permits. This phenomenon has been observed by Ishiaku *et al.,* [9] who compared the rheological properties of unvulcanised and vulcanized Poly (vinyl chloride) and epoxide natural rubber blends. This effect may lead to a changing of microstructure of the blend affecting mechanical properties as well as the flow properties that produce the unstable polymer melts or thermosets. The effect of post curing is more significant in the elastomer rich composites. Therefore, flow properties of vulcanised elastomer dominant systems may be more sensitive to the extrusion temperature, when they are extruded through a capillary at a high temperature and under shear due to the post curing. Consequently, flow properties characteristics of this class of material may encounter different flow behaviors with respect to the extrusion temperature. Therefore, in this study, the effect of temperature on rheological properties is concentrated on vulcanized elastomer dominant plastic/rubber/filler composites. Both unfilled and filled composites were subjected to this investigation.

2.2 EXPERIMENTAL PROCEDURE AND MATERIALS

2.1 Materials

The polypropylene used was a homopolymer (TITANPRO 6431) with a melt flow index of 7.5 g/10 min at 230°C, and density of 0.9 g/cm^3. The ethylene-propylene-diene terpolymer used was grade "950" with 4.5% of ethylidene-2-norbonene (ENB) as a termonomer and 69% of ethylene content. Mooney viscosity (ML-4 at 100°C) and density of the elastomer were 24 ± 5 and 0.86 g/cm^3 respectively. WRHA with mean particle size 5.4 µm; surface area 1.4 m^2/g and density 2.2 g/cm^3. Details of the WRHA can be found elsewhere [10].

2.2 Preparation of Composites

Unfilled and WRHA filled (30 php (parts per hundred parts by weight)), 30/70:PP/EPDM composites were prepared in a Brabender plasticorder model PLE 331 coupled with a mixer/measuring head (W50H) at a temperature of 180°C and a rotor speed of 50 rpm by melt blending of components for 10 minutes. Details of melt mixing, compression moulding and preparation of test specimens were described in our previous reports [11-12].

2.3 MEASUREMENTS

2.3.1 Determination of Rheological Properties

(a) Flow properties

The flow properties of the blends and composites were determined using the Shimadzu Capillary Rheometer – model CFT-500 as it has an advantage of measuring volumetric flow rate directly over other rheometers, which measure the mass flow rate [7]. The capillary has an l/d ratio of 10 and angle of entry of 90°. The experiment was performed at different temperatures from 170 to 200°C with 10°C intervals employing constant temperature mode. Pre dried samples having dimensions of 2 × 3 × 5 mm (thickness × width × length) were used for the study. They were placed inside the barrel of the extrusion assembly and force down to the capillary with a plunger attached to the moving crosshead. After a warming up period of three minutes at the test temperature the melt was extruded through the capillary. The built-in software calculated and printed the following rheological properties at the end of each run.

At the end of the each run, the extrudate was examined for the presence of any impurities and trapped air bubbles. The exit of the die was inspected for any leakage of the melt. When such problems were observed the run is ignored. The average of three free runs was taken to be the value of therheological property concerned. However, if the shear rate is varied widely, extra two runs were made and an average of five runs was taken.

(b) Extrudate morphology

The extrudate emerging from the capillary was collected, with maximum care taken to avoid any further deformation. Adequate care was taken to avoid effects of the draw down and contraction on cooling. The surface of melt fractures were then examined.

3.0 RESULTS AND DISCUSSION

3.1 Flow Curves

The flow curves of the unfilled and WRHA filled vulcanized EPDM/PP:70/30 systems at 0.4 phr curing agent concentration in log-log scale, over a wide range of shear rate for four different temperatures are presented in Figures 1 and 2 respectively. It is shown that apparent shear stress increases with apparent shear rate for all temperatures for both unfilled and filled systems. The variations were quite linear in general and hence the power–law relationship was observed in the shear rate range studied. Similar observations have been reported for filler free plastic/rubber blends including PP/EPDM blends [13-15]. A ternary composite of carbon black filled PP/EPDM composite has also exhibited the similar behaviors [3].

While all the systems obey the power law, at a constant shear stress, higher shear rate is registered for the blend extruded at 170°C compared with that of other blends (extruded at temperatures above 170°C), until a critical shear rate is generated at which the trend became opposite. A cross over of the flow curve of unfilled blends at

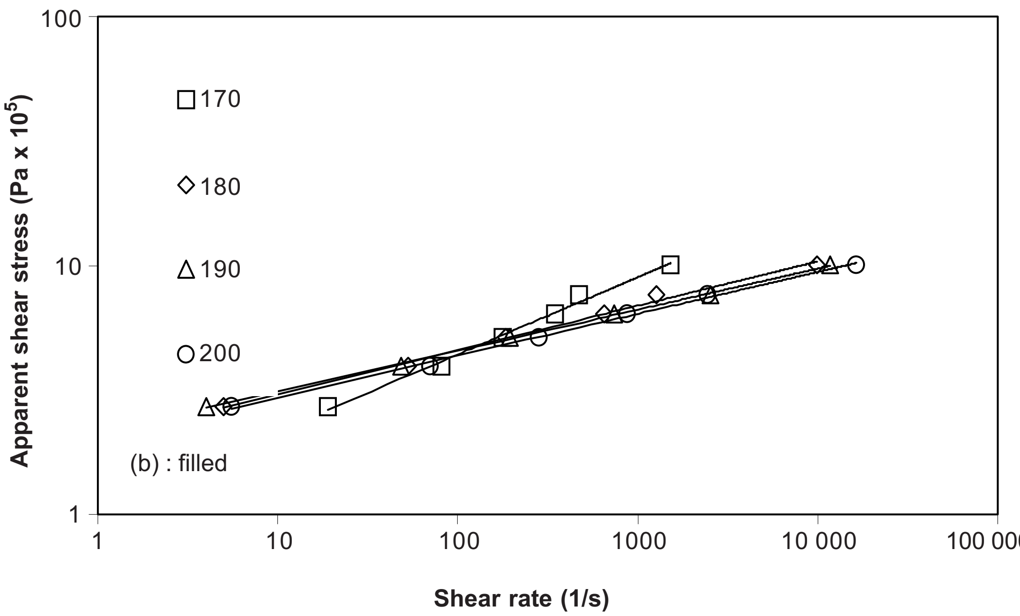

Figure 1 Temperature dependence of apparent shear stress-apparent shear rate plots of dynamically vulcanised EPDM/PP/WRHA (70/30/0) composites at different extrusion temperatures

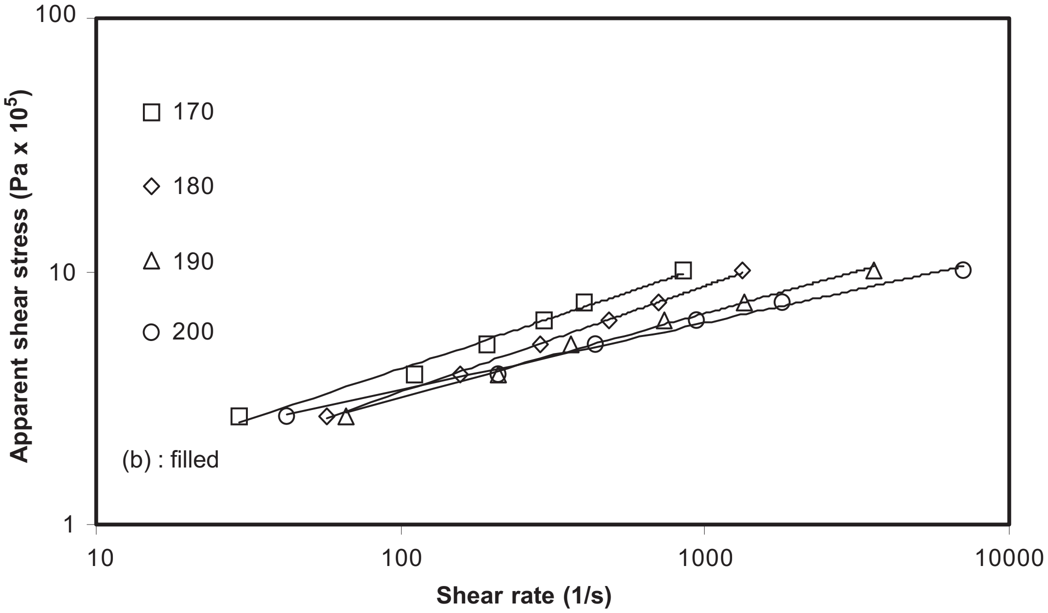

Figure 2 Temperature dependence of apparent shear stress-apparent shear rate plots of dynamically vulcanised EPDM/PP/WRHA (70/30/30) composites at different extrusion temperatures

170°C with the other flow curves shows this effect (Figure 1). When the material was extruded at a higher temperature, but at low shear rate, post curing may have taken place during the prolonged residence time in the reservoir and die under shear. This introduces flow instabilities with increase in temperature and results a poor flow leading to higher viscosity due to increasing crosslinked density. This is proven by the melt fracture of the corresponding extrudate that will be discussed later. In fact, at 200°C, an extrusion was impossible and instead thermoset material was obtained for the vulcanised samples at low shear rate. It is therefore, believed that post curing is significant at temperatures above 170°C at low shear rate. Ishiaku *et al.,* has also reported similar observation on extrusion of dynamically vulcanized PVC/ENR blends at four different temperatures [9]. However, beyond a certain critical shear rate at each temperature, this effect is diminished and composites show increase in shear rate with increase in temperature. This observation suggests that shear rate influences the effect of temperature on the flow properties.

Careful examination of flow curves of WRHA filled systems also show that composites extruded at 180 and 190°C possess slightly better flow properties than at 200°C at very low shear rates. The reduction of the influence of the shear rate on the flow curves of WRHA filled system may be due to the less percentage of crosslinked elastomer particles in the composites compared with the unfilled composites. However, at higher shear rates, again the composites possess the general trend in which better flow is registered with increase in temperature.

The dependence of viscosity of unfilled and filled composites on extrusion temperatures are clearly presented in Figure 3 at two different shear stresses representing low and high shear rates (2.7×10^3 and 1×10^4 Pa). At higher shear stress, filled composites show higher melt viscosities at all temperatures than unfilled composites. On the contrary, at low shear rates, filled composites show a lower viscosity than unfilled ones. The higher shear sensitivity of the viscosity of unfilled composites over the filled ones is indicated by the significant difference between their viscosities at low and high shear rates at all four temperatures. As mentioned before, this is due to the presence of higher amount of elastomer particles in the unfilled composites over the filled composites. Further, it can be seen that the viscosities of both composites follow the general behavior whereby viscosity decreases with increasing shear rate. However, at low shear rate unfilled composites register higher viscosities at temperatures above 170°C and tend to decrease at 200°C possibly due to relatively higher shear rate than at other temperatures.

For the filled composites, viscosity tends to increase at 200°C again possibly due to the post curing phenomenon. Therefore, the temperature dependence of these EPDM/PP blends and composites associated with the post curing phenomenon is obvious. It is also clear that processing of these composites above 180°C does not offer appreciable advantage in term of reduction of viscosity. On the other hand, the temperature below 180°C registers higher viscosity and observes severe melt fracture too.

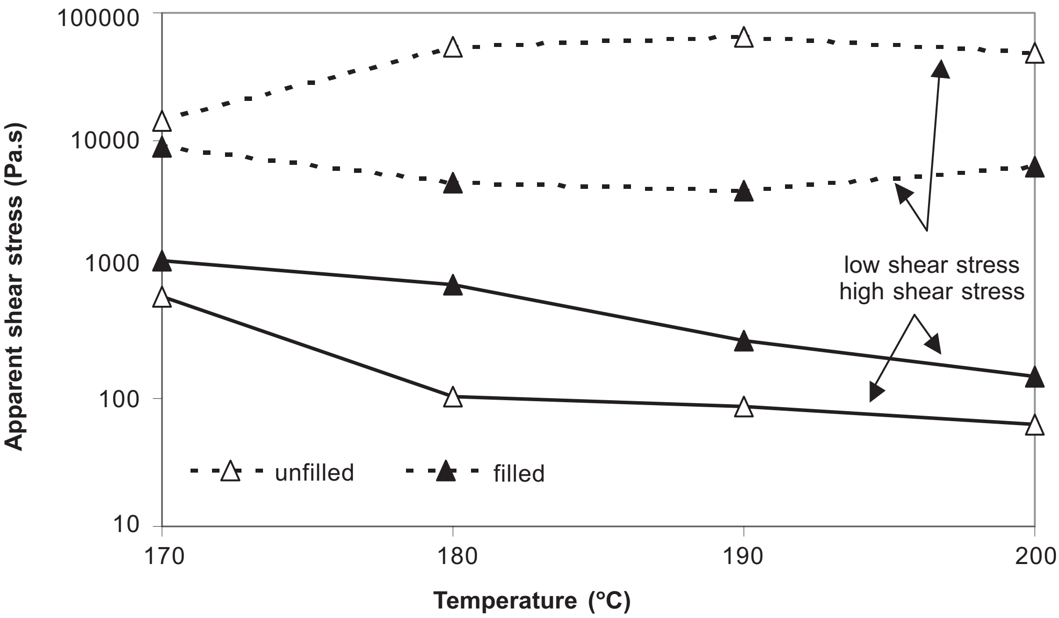

Figure 3 Temperature dependence of apparent shear viscosity of unfilled and WRHA (30 php) filled EPDM/PP (70/30) composites at two different constant shear stresses: - - - - higher shear stress (1 MPa); ——— lower shear stress (0.27 MPa)

3.2 Power-Law Model Parameters

Plots of apparent shear stress versus apparent shear rate discussed earlier was used to derive the power-law index (n) for both composites, which values are reported in Table 1 at different temperatures. These plots indicated regression coefficient more than 0.9. Value of n lower than unity indicates a pseudoplastic behaviour of all the composites studied. These data explain the extent of pseudoplasticity or non-Newtonian behaviour of the composites. For unfilled composites, it can be observed that a sudden decrease of n value as temperature increases from 170 to 180°C and beyond 180°C, n value is almost independent from the temperature. The low values of n suggest that these vulcanized composites show strong pseudoplasticity at higher temperatures. In contrast, filled composites also exhibit a gradual reduction of n value as temperature increases while possess higher n values than unfilled counterparts at each temperature indicating their less pseudoplastic characteristics. A similar trend of decreasing values of n with an increase in temperature has been reported elsewhere for plastic and elastomer composites as well as plastic/rubber blends [16-17]. Therefore, it is clear that ternary composites also show the same trend. This reduction of n values with increasing temperature suggests that increase in temperature confer pseudoplastic characteristics that are opposite to the general trends reported for some uncrosslinked plastic/rubber blends [18]. When the vulcanized composites are subjected to a higher thermal energy (high temperature), post curing occurred resulting the increasing of crosslink density. This may lead to enhance pseudoplastic characteristics and hence reduction of n value. It is reported that increase of crosslink density by increasing the curing agent concentration used for vulcanisation process offers more pseudoplastic characteristics to the blends of elastomer/plastics as characterised by the reduction of n value [19-20]. Although both incorporation of filler and introduction of crosslink particles induce pseudoplastic behavior in the polymer melts, the significant reduction of n value of unfilled composites over filled system as given in Table 1 suggest, that crosslinked rubber particles confer a more prominent effect than WRHA particles on the deviation from Newtonian character.

Table 1 Power – Law model parameters of unfilled and WRHA filled (30 php) EPDM/PP (70/30) composites

Temperature °C	**Unfilled composites *n***	**Filled composites *n***
170	0.31	0.40
180	0.18	0.42
190	0.17	0.36
200	0.17	0.26

3.3 Melt Fracture

The surfaces of the extrudate at two different constant stresses are presented in Figure 4 to show the effect of temperature on the distortion of extrudate surfaces of

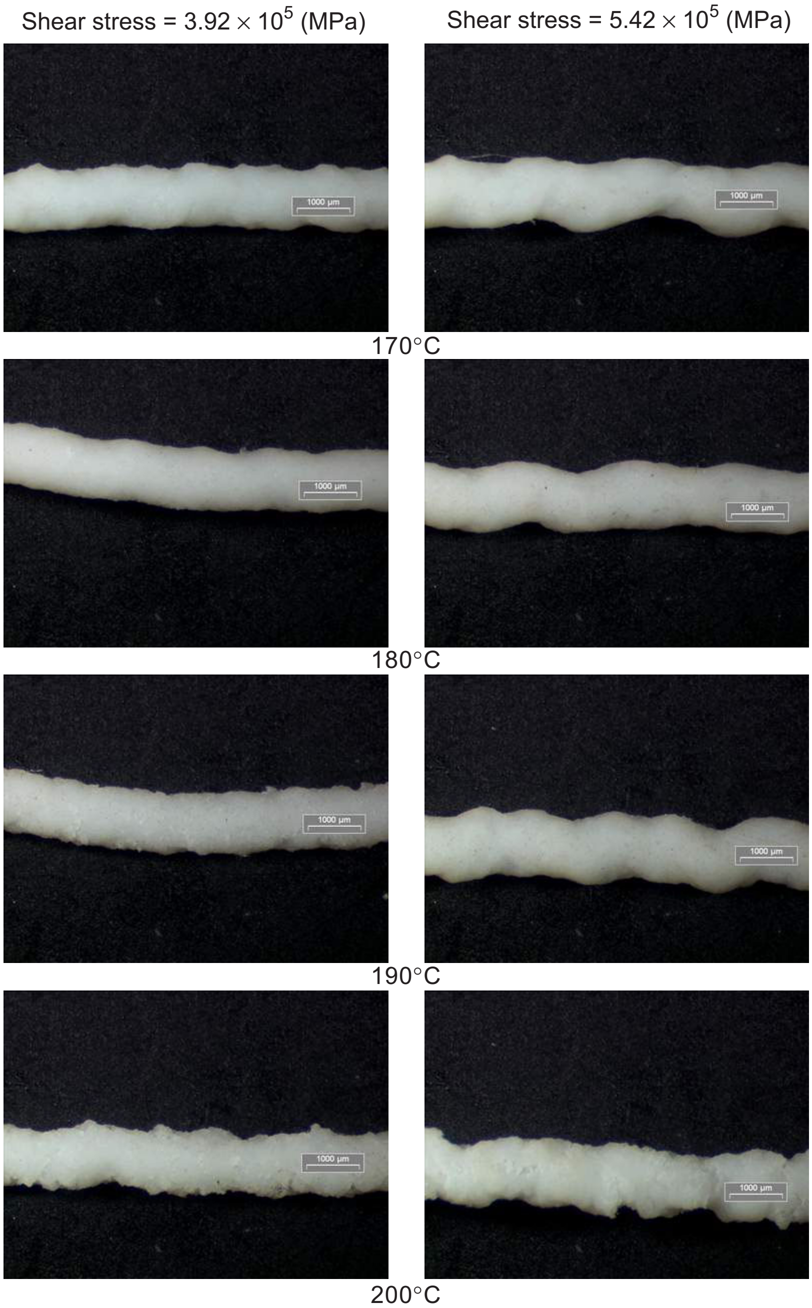

Figure 4 Melt fracture surfaces of unfilled EPDM/PP : 70/30 composites vulcanised at 0.4 phr at four different extrusion temperatures and two different shear stresses

dynamically vulcanized (0.4 phr) filler free EPDM/PP composites. At low shear rate, a smooth extrudate was obtained at 170°C. Extrudate surfaces at all other higher temperatures show a melt fracture phenomenon, which becomes more pronounced

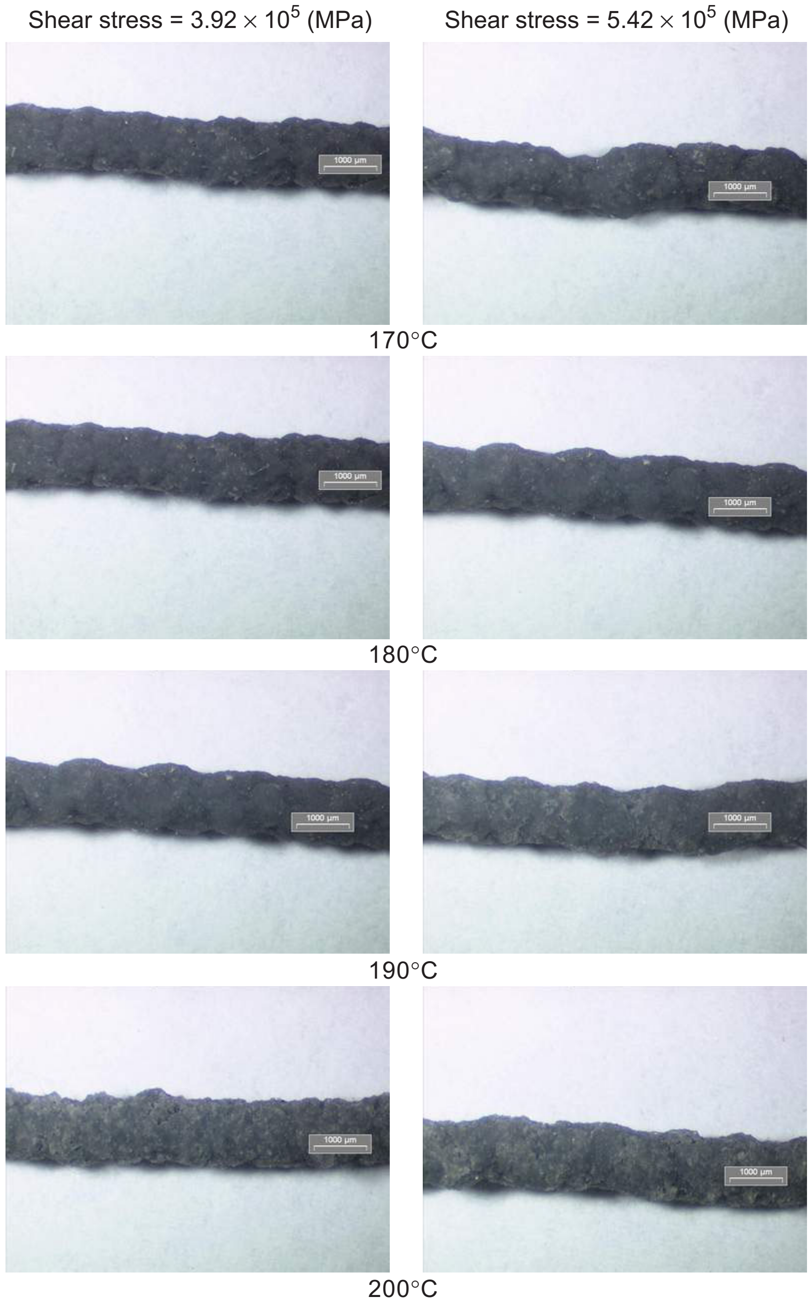

Figure 5 Melt fracture surfaces of EPDM/PP/WRHA : 70/30/30 composites vulcanised at 0.4 phr at four different extrusion temperatures and two different shear rates

with increasing temperature, eventhough there is no significant difference between extrudate surfaces at 17°C and 180°C. The extrudate at 200°C, shows rough surface indicates the deterioration characteristics. This surface therefore confirms the post curing phenomenon discussed earlier.

However, at high shear rate, extrudate surface at 170°C shows rougher surface than that at 180°C. The higher viscosity of the composites at 170°C at high shear rate manifests this difference. As the temperature increased above 180°C, extrudate surfaces again became rougher indicating that shear stress exceeds the strength of the melt [21]. Extrudate surfaces of filled composites extruded at the lower shear rate show no significant difference in surface roughness as the temperature varies [Figure 5]. Filled composites extruded at 170°C exhibits more deformed surface than that of other temperatures for the composites extruded at higher shear rate. This is manifested by the higher viscosity of the composites extruded at 170°C at higher shear rate as indicated in Figure 3. Therefore, depending on the effect of viscosities and melt fracture studies it seems that 180°C temperature is the best among the potential temperatures to study further on the rheological properties of these composites.

4.0 CONCLUSIONS

Rubber dominant dynamically vulcanised EPDM/PP/WRHA composites could be extruded like thermoplastics, if suitable shear rate and temperature are met. It has been shown that post curing play a dominant role at lower shear rate in such a way that its presence causes flow instabilities. However at higher shear rates, rheological properties are controlled by the temperatures i.e. flow improves with increase in temperature. Both unfilled and filled composites obey the power law and exhibits pseudoplastic characteristics. As the shear rate increases, at extrusion temperature of 180^{o}C and above, seems to have little effect on the flow suggesting processing temperature of 180^{o}C is suitable for both these unfilled and filled composites.

REFERENCES

[1] Siriwardena, S., H. Ismail and U. S. Ishiaku. 2002. "Mechanical and Morphological Properties of White Rice Husk and Filled Ethylene – Propylene-diene monomer/polypropylene blends". *J. Appl. Polym. Sci.* 86: 438-453.

[2] Premphet, K. and P. Horanont. 1999. "Influence of Stearic Acid Treatment of Filler Particles on the Structure and Properties of Ternary-Phase Polypropylene Composites". *J. App. Polym. Sci.* 74: 3445-3454.

[3] Ismail, H., L. Mega and H. P. S. Abdul Khalil. 2001. "Effect of a Silane Coupling Agent on the Properties of White Rice Husk Ash-polypropylene/natural Rubber Composites". *Polym. Int*. 50: 606-611.

[4] Ismail, H., Salmah and M. Nasir. 2001. "Dynamic Vulcanization of Rubberwood-Filled Polypropylene/ Natural Rubber Blends". *Polym. Testing.* 20: 819-823.

[5] Hammer, C. O., F. H. J. Maurer, S. Molnar and B. Pukanszky. 1999. "Control of the Structure and Properties of Barium Sulphate–Filled Blends of Polypropylene and Ethylene Propylene Copolymers". *J. Mater. Sci.* 34: 5911-5918.

[6] George, J., K. T. Varughese and S. Thomas. 2000. "Dynamically Vulcanised Thermoplastic Elastomer Blends of Polyethylene and Nitrile Rubber". *Polymer*. 41: 1507-1517.

[7] Nielsen, L. E. 1973. *Polymer Rheology.* New York: Marcel Dekker, Inc.
[8] Utracki, L. A. 1990. *Polymer Alloys and Blends*. New York: Hanser Publishers.
[9] Ishiaku U. S., M. Nasir and Z. A. Mohd Ishak. 1995. "Rhelogical Properties of Poly (vinyl chloride)/ Epoxidised Natural Rubber Blends. Part II: The Effect of Processing Variables". *J. Vinyl Additive Tech.* 1(2): 66-70.
[10] Siriwardena, S., H Ismail and U. S. Ishiaku. 2001. "A Comparison of White Rice Husk Ash and Silica in EPDM Vulcanisates". *Polym. Int.* 50(6): 701-706.
[11] Siriwardena, S., H. Ismail and U. S. Ishiaku. 2001. "White Rice Husk Ash Filled Ethylene–Propylene Diene Terpolymer/Polypropylene Blends: Effect of Dynamic Vulcanization and Filler Loading". *Polym-Plast. Technol. Eng*. 40: 519-538.
[12] Siriwardena S, H. Ismail and U. S. Ishiaku. 2002. "Mechanical Properties and Recyclability of Thermoplastic Elastomers of White Rice Husk Ash/Ethylene–Propylene Diene Terpolymer/Polypropylene". *Plas. rubber & Composite.* 31: 167-176.
[13] Ha, C. S., D. J. Ihm and S. C. Kim. 1986. "Structure and Properties of Dynamically Cured EPDM/PP Blends". *J. Appl. Polym. Sci*. 32: 6281-6297.
[14] Saroop, M. and G. N. Mathur. 1997. "Studies on the Dinamically Vulcanized Polyproplylene (PP)/Butadiene Styrene Block Copolymer (SBS) Blends: Mechanical Properties". *J. Appl. Polym. Sci*. 65: 2691-2701.
[15] Jain, A. K., N. K. Gupta and A. K. Nagpal. 2000. "Effect of Dynamic Crosslinking on Melt Rheological Properties of Polypropylene/Ethylene-Propylene-Dience Rubber Blends". *J. Appl. Polym. Sci.* 77: 1488-1505.
[16] Cheung, M. K., and D. Chan. 1997. "Mechanical and Rheological Properties of Poly (ethylene terephthalate)/ Polypropylene Blends". *Polym. Int.* 43: 281-287.
[17] Asaletha, R., G. Groeninckx., M. G. Kumaran and S. Thomas. 1998. "Melt Rheology and Morphology of Physically Compatibilized Natural Rubber–Polystyrene Blends by the Addition of Natural Rubber – g-Polystyrene". *J. Appl. Polym. Sci.* 69: 2673-2690.
[18] Manchado, M. A. L., J. Biagiotti and J. M. Kenny. 2001. "Rheological Behaviour and Processability of Polypropylene Blends with Ethylene-Propylene–Diene Terpolymer". *J. Appl. Polym. Sci.* 81: 1-10.
[19] Ishiaku U. S., M. Nasir and Z. A. Mohd Ishak. 1994. "Aspects of Miscibility in Poly (vinyl chloride) Epoxidized Natural Rubber Blends. Part II. Dynamic Mechanical Properties". *J. Vinyl Technol*. 16: 226-230.
[20] Mousa, A., U. S. Ishiaku and Z. A. Mohd Ishak. 1999. "Rheological and Viscoelastic Behaviour of Dynamically Vulcanized of Poly (vinyl chloride)–Epoxidized Natural Rubber Thermoplastic Elastomers". *J. Appl. Polym. Sci.* 74: 2886-2893.
[21] Asaletha, R., M. G. Kumaran and S. Thomas. 1999. "Thermoplastic Elastomer from Blends of Polystyrene and Natural Rubber: Morphology and Mechanical Properties". *Eur. Polym. J.* 35: 253-271.