ASEAN J. Sci. Technol. Dev., **32(2)**: 94 – 103

Utilization of Waste from Natural Rubber Glove Manufacturing Line

V. DEVARAJ*, F. I. NUR, A. I. H. DAYANG, H. K. NOR AND M. N. ZAIROSSANI

Malaysia is the largest producer and exporter of examination and surgical gloves in the world and currently faced with mitigating large amounts of waste generated during the glove production process. This waste is mainly generated from glove dipping tanks and is referred as dipping tank coagulum (DTC). It is considered as scheduled waste which requires mandatory disposal by incineration, in compliance to the Scheduled Waste Regulations set by the Department of Environment. Work described in this study showed, DTC samples with a polymer content of >40%, both ash and calcium carbonate content of <10% and curatives <2% (Sulphur, antioxidants, accelerators and ZnO) when blended with virgin rubbers (SMR 10 and SMR 20) were found to be suitable for manufacturing value-added rubber products. DTC samples with polymer contents of <40% and lower in curatives could still be considered for recycling, by adding higher portions of virgin rubber for manufacturing products like shoe soles, carpet underlay and thermoplastic elastomer products. Glove manufactures should ideally set up on-site DTC processing facilities at their factory premises equipped with crepers as well as space to 'air dry' the creped DTC samples. Creped samples could be sent to the Malaysian Rubber Board (MRB) for chemical analyses. Factory owners could also present the analytical results from MRB to the recyclers to obtain a good premium for their processed DTC samples to be used as raw materials.

Malaysia is the largest producer and exporter of examination and surgical gloves in the world and glove industry dominates approximately 70% of all rubber products exports in the country, supplying close to 60% of the world consumptions (MRB 2012). However, with a huge market share of glove export in the world, the latex products manufacturing industry is still faced with mitigating large amount of 'wastes' generated by this industry. These wastes are mainly generated during compounding, dipping and effluent treatment processes (Devaraj & Zairossani 2012). Currently NR glove manufacturers are experiencing serious challenges which include increased raw material and operational costs, coupled with disposal cost incurred when the dipping tank coagulum (DTC) has been classified as Scheduled Waste since 2005. The implementation of Scheduled Waste Regulations (2005) by DOE requires mandatory and costly disposal by incineration (Department of Environment Malaysia 2005).

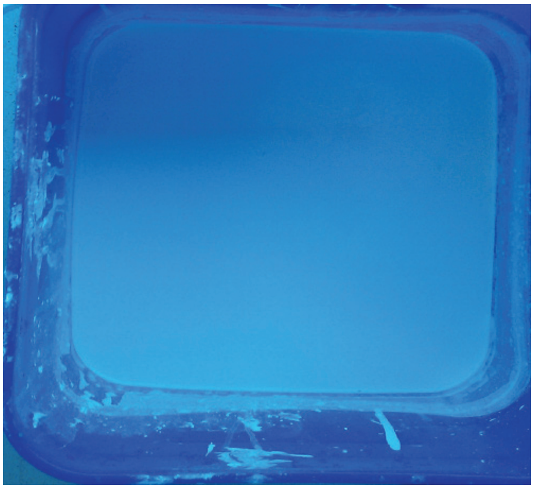
Latex Coagulum and Latex Slurry 'Wastes'

Standard operating procedure of a glove production process requires cleaning (once in every 3–4 weeks) of dipping tank containing formulated pre-vulcanized latex (PVL), into which the ceramic formers dip and subsequently go into the heating chamber to undergo gelling and subsequently curing (*Figure 1a*). The DTC (*Figure 1b*) wastes are separated and stored to be collected by DOE approved recyclers, whereas the latex slurry (*Figure 1c*) is washed

Technology and Engineering Division, RRIM Research Station, Malaysian Rubber Board, 47000 Sungei Buloh, Selangor
* Corresponding author (e-mail: devaraj@lgm.gov.my/veerasamydevaraj199@gmail.com)

(a)

(b)



(c)

Figure 1. (a) Former 'dipping tank'; (b) latex lump and (c) latex slurry in the glove manufacturing line.

into the latex slurry pond to undergo pre-treatment, before the commencement of the effluent treatment cycle. Process flow involved in the dipping tank (DT) cleaning and the 'wastes' generated are as shown in *Figure 2* (Devaraj *et al*. 2014).

Study by the Malaysian Rubber Board

To ease the burden of latex manufacturing industry with regards to waste disposal, MRB recently carried out a study to determine the possibility of turning DTC as a raw material for making other rubber products, with the intention of saving substantial amount of disposal cost if the DTC could be recycled (Devaraj 2011). Therefore the objective of this study is primarily to carry out chemical characterization of DTC and other wastes generated from the dipping process and to identify ideal blending ratios with virgin rubber (SMR 10 or SMR 20) to explore the possibilities of manufacturing value-added rubber products (Kamarulzaman *et al*. 2013.

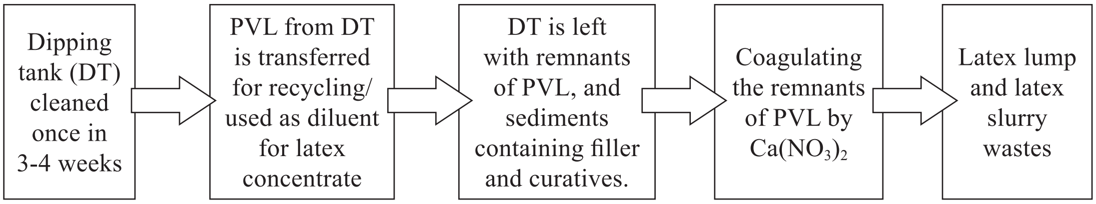


Figure 2. Process flow involved in dipping tank cleaning and 'wastes' generation.

MATERIALS AND METHOD

DTC Sampling and Chemical Characterization

DTC and latex slurry samples were collected from five different gloves manufacturing factories with varying production capacities. For the purpose of carrying out a full chemical characterization on dipping tank wastes, coagulated lump and latex slurry were obtained from participating factories. They were chemically analysed for total solids content (TSC); polymer, calcium carbonate and ash contents by means of thermo gravimetric analysis (TGA) via Mettler Toledo TGA/ SDTA851; sulphur content by Elementar Vario Max CNS instrument; curative agents by thin layer chromatography and the analysis of metals (Ca, Al and Mg) and heavy metal (Zn, Ti, Cd and Pb) by Inductively Coupled Plasma-optical Emission Spectrometry (ICP-OES). The pathway followed for the full chemical characterization of raw dipping tank wastes samples are as shown in *Figure 3*.

Chemical Characterization of Processed DTC

The raw samples (both latex lump and latex slurry) were processed by coagulation (only

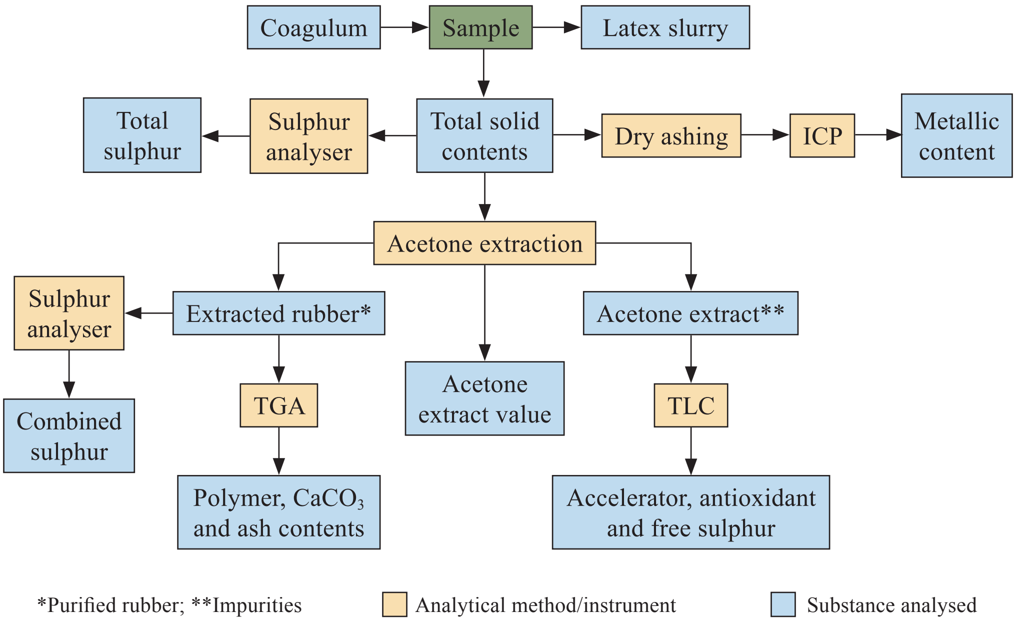
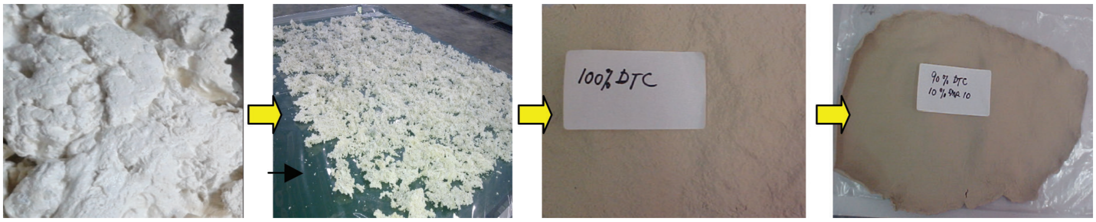


Figure 3. Pathway for full chemical characterization of DTC.



Raw | Creped and washed | Milled | Blended with NR

Figure 4. Various stages of DTC processing and blending with NR.

slurry), creped, washed and subsequently were air-dried at ambient temperature until a constant weight was achieved (*Figure 4*). Air drying at ambient temperature was to prevent the processed samples from undergoing further cross-linking if dried in the heat chamber. Chemical characterizations were also performed on the processed DTC samples using the similar methods as was done on the raw samples, to investigate the variations in their contents.

DTC/NR Blends

The processed DTC samples were milled and observed for its homogeneity visually. Two-roll mill was also used to investigate the blending characteristics of DTC sample from factory A (DTC-A) with NR (SMR 10). Blends of DTC-A/NR (90/10 phr) was compared against DTC-A/NR (100/0 phr), as a non-ideal case scenario. *Figure 4* shows various stages of raw DTC processing and subsequent blending with virgin rubber at 10 phr. Blending was subsequently carried using processed DTC samples from factories A, B and C using three different ratios, which include, DTC/NR (100/0 phr), DTC/NR (70/30 phr) and DTC/NR (50/50 phr).

Study on Cure Characteristics and Physical Properties of DTC/NR Blends

Using the blends of DTC/NR from the three factories at various ratios were compounded and the cure characteristics of the rubber compounds were studied using a Monsanto Moving Die Rheometer (MDR 2000) according to *ISO 6502* at 150°C. The respective cure times were measured by t90, scorch time ts2, maximum torque (MH), minimum torque (ML), etc. were determined from the rheograph. The compounds were then compression-moulded at 150°C using the respective cure times, t90. Dumb-bell samples with the length of 95 mm were cut from a 2 mm-thick moulded sheet. The tensile testing procedure was carried out according to *ISO 37*. An Instron universal testing machine (Model 4206) operating at 500 mm/min was used to determine the tensile properties in terms of ultimate tensile strength and elongation at break. The abrasion resistance (*ISO 4649*) was measured by moving the test piece across the surface of an abrasive sheet mounted to a revolving drum, and the results were normally expressed as abrasion resistance index compared to a reference or standard compound. Three test runs were performed for each compound (Dayang *et al*. 2014).

RESULTS AND DISCUSSION

Chemical Characterization of Raw and Processed DTC Samples

Significant differences in results were obtained from the two types of samples analyzed (latex lump and slurry) for the chemical characterization on raw and processed samples (*Table 1* and *Table 2*) on all parameters tested. From *Table 1*, TSC values for all samples were determined by summing up the

Table 1. Results of chemical characterization of raw DTC.

Factories	A	B	C	D	E
Test parameters	Coagulated lump			Slurry	
Moisture (%)	22.20	32.61	14.67	46.64	55.24
Polymer content (%)	62.50	57.82	61.09	8.69	11.45
Ash (%)	0.30	0.67	8.73	2.15	1.75
Calcium carbonate (%)	12.5	6.60	10.75	36.49	24.62
Zinc oxide (%)	0.16	0.43	1.48	0.82	0.66
Accelerators and antioxidant (%)	0.20	0.61	0.35	2.40	2.82
Total sulphur (%)	1.09	0.81	2.05	2.29	1.75
Others*	1.06	0.45	0.90	0.52	1.71

*Traces of heavy metal (Ti, Cd, Pb), silicates and degraded rubber found in acetone extract which were not analysed.

percentage values for all the parameters as shown, except the moisture content. The dried samples which refers to the TSC, from *Table 1* were subsequently processed and dried to determine values for the parameters as shown in *Table 2*. These values (polymer content and curatives) were used as basis for blending with virgin rubber for making rubber products. For coagulum samples obtained from factories A, B and C, generally had higher polymer content (PC) values; ranging from 57.8% to 62.5%, while the PC values of slurry samples from Factory D and E, where notably much lower, ranging from 8.7% to 11.5%. They had relatively higher filler and curative values, respectively. High in PC values and low in filler and curative values are considered ideal compositions for recycling dipping tank wastes for making value-added rubber products.

From the results of the chemical analyses on the processed DTC-A, DTC-B and DTC-C from the three factories, it was found that the washing and creping of the raw samples managed to release unreacted antioxidant and accelerators, whereas the fillers and others metallic contents which might have been embedded into the rubber matrix during coagulation remained intact. The drying had reduced lots of moisture as compared to the raw samples. This had indirectly increased the polymer content by virtue of more polymers per unit volume compared to the raw DTC. Nevertheless, the processed samples were ideally much cleaner to carry out the virgin NR blending to determine the optimum ratios required for manufacturing other rubber products.

Processability

The chemical analyses of the processed DTC samples (*Table 2*) would have direct effect on the processability and characteristics on any products made from these samples. It was observed that DTC-C with higher percentages of ash, zinc and sulphur and lower polymer content as compared to samples from other two factories, posed difficulties during the processing of this sample, compared to DTC-A and DTC-B. In addition, the sheeted sample after passing through the two-roll mill was found to be quite brittle and powdery.

Cure Characteristics

From the cure characteristics profile of the blending of NR and DTC-A, DTC-B and DTC-C, at various ratios displayed in *Figures 5(a)*, *(b)* and *(c)*, respectively, the minimum and maximum torques increased with increasing level of recycled material (DTC). Theoretically, the increase in the maximum

Table 2. Results of chemical characterization of processed DTC.

Factories	DTC-A	DTC-B	DTC-C
Test parameters		Processed DTC	
Moisture (%)	0.16	0.21	0.20
Polymer content (%)	87.30	88.80	71.60
Ash (%)	2.10	0.70	10.20
Calcium carbonate (%)	4.80	8.00	10.35
Zinc oxide (%)	2.10	0.30	3.40
Accelerators and antioxidant (%)	0.40	–	0.35
Total sulphur (%)	1.70	1.20	2.05
Others*	1.44	0.79	1.85

*Traces elements etc.

torque reflects of an increase in crosslink density and resulting in an additional stiffness of the rubber blend. Similar trend is also observed in NR containing DTC-C whereas, this effect is not very obvious for NR containing DTC-B and DTC-A, respectively. It is also observed that NR containing DTC-C at all ratios tested, showed the highest values for the maximum torque. De *et al*. (2007) highlighted that there is the presence of cross-linked gel in the recycled rubber which remained without dispersing as a continuous matrix with virgin rubber, when these two (virgin rubber and DTC) were blended. As such this phenomenon explains the increase in the stiffness with intermittent presence of cross-linked gel from the recycled rubber, attributing to the maximum torque. Another possible reason could be, with the presence of a high amount of ash in DTC-C sample, which prevented the formation of vulcanized sheet from 100 phr of DTC-C, due to the highly cross-linked rubber becoming stiff and brittle.

A significant decrease in scorch and cure times were also observed with increasing amount of DTC-A, DTC-B and DTC-C loading. A similar trend was also reported by other researchers (George *et al*. 2007; Mathew *et al*. 2001; Edirisinghe *et al*. 2011) with different types of recycled rubbers. This could be due to the unreacted curatives still present in the raw DTC samples. The results were clearly in good agreement with higher amount of sulphur and zinc content in the raw composition analyses of the DTC. This also contributed to the higher crosslinking density in the blends with increased amount of DTC loadings.

Physical Properties

In this study, tensile strength and abrasion resistance were investigated to evaluate the physical properties of the DTC/NR blends. Generally, materials tend to become weak and brittle with increasing concentrations of DTC. *Figure 6* showed that the variations in tensile strength of NR vulcanizates with different blend ratios of DTC from different sources. The inclusion of DTC at 50 phr loading led to a decrease in the tensile strength values and a significant decrease with further increase of DTC loadings. It was found that the maximum values of tensile strength decreased with different samples in the order of DTC-C < DTC-B < DTC-A.

The abrasion resistance of NR containing DTC-A, DTC-B and DTC-C at various ratios are as shown in *Figure 7*. It also could be seen that the abrasion resistance of blended vulcanizates (NR/DTC) gradually decreased as the DTC contents were increased. The declining of abrasion resistance was more pronounced in NR which was blended with DTC-C sample. As mentioned earlier, the high content of zinc

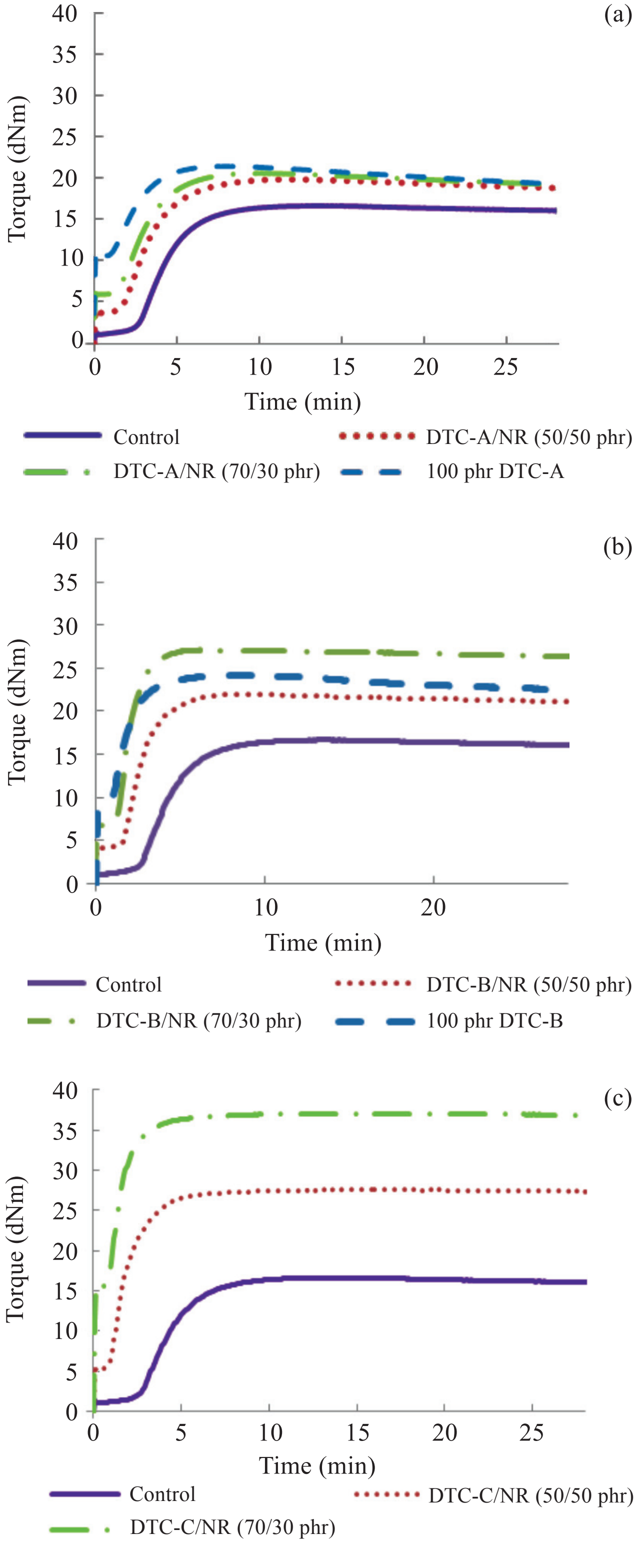


Figure 5. Cure curve of NR and (a) DTC-A; (b) DTC-B and (c) DTC-C at various ratios.

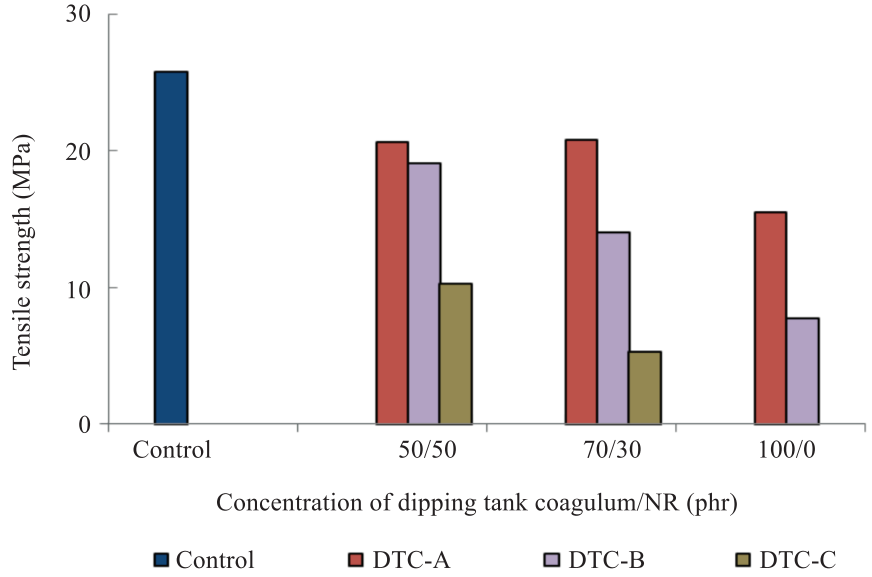


Figure 6. Effect of DTC loading on tensile strength of DTC/NR blends.

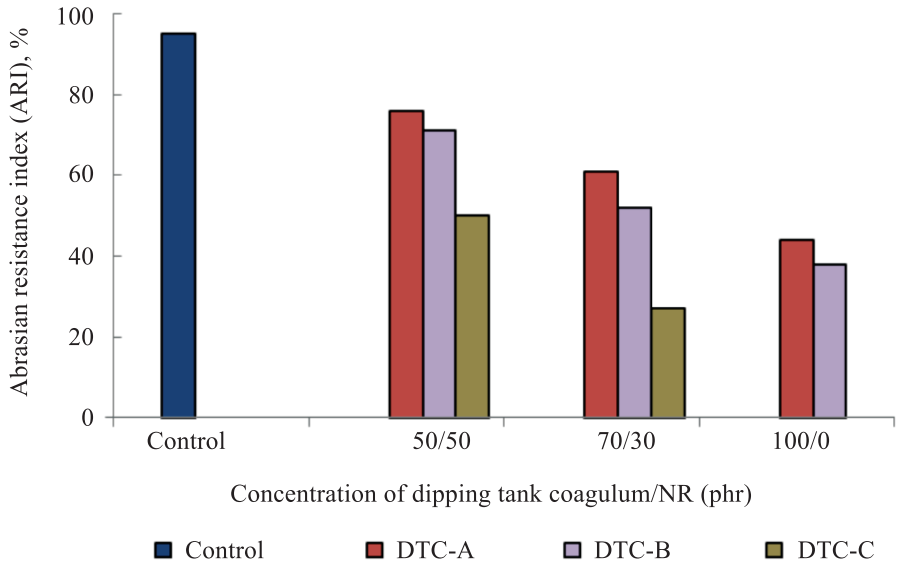


Figure 7. Effect of DTC loading on abrasion resistance of DTC/NR blends.

and sulphur present in DTC-C had caused the increase in crosslink density of the blended vulcanizate which subsequently brought about the deterioration in its physical properties. Therefore, such behaviour confirmed the need to ascertain the ideal blending ratios for inducing optimum degree of crosslinking to incorporate relatively good physical properties.

CONCLUSION AND RECOMMENDATIONS

As a rule of thumb, the highest percentage of recyclable material that could be incorporated for making value added-product is 40%. This was to maintain the quality of the product. Incorporation of 100 parts of recycle material had at least 40 parts of polymer and subsequently 60 parts of virgin rubber that could be added. DTC with lower polymer content needed a higher incorporation of virgin rubber which made it economically non-viable. Results also showed that processed DTC samples with higher polymer content and lower in curatives were ideal for recycling as compared to latex slurry samples with lower polymer and high in filler and curatives. R&D work is currently on-going in MRB to evaluate suitable recycling options for latex slurry samples. Therefore DTC samples with polymer content of >40%; both ash and calcium carbonate contents of <10%; curatives <2 % (Sulphur, antioxidants, accelerators and ZnO) when blended with virgin rubbers (SMR 10 and SMR 20) were found to be suitable for manufacturing rubber products with relatively good physical properties such shoe sole, carpet underlay and solid tyres. *Table 3* summarizes the processed DTC samples' required composition for ideal recycling purposes.

Glove manufactures ideally should set up on-site DTC processing facility at their factory premises equipped with creepers and space to air-dry the creped DTC samples. Creped samples can be sent to MRB (G -TAC_R) for chemical analyses on the six parameters as shown in *Table 3*, periodically. Factory owners can present the analytical results from MRB to the recyclers to obtain a premium price for their processed DTC samples as raw material.

Table 3. Processed DTC sample components requirement for recycling.

No.	Major components	Ideal level (%)
1.	Polymer	> 40
2.	Ash	<10
3.	Zn	<2.0
4.	Sulphur	<2.0
5.	Accelerators and antioxidants	<2.0
6.	Calcium carbonate	<10

DTC samples with polymer contents <40% and lower in curatives could still be considered for recycling by adding higher portions of virgin rubber for manufacturing such as shoe soles, carpet underlay and thermoplastic elastomer products. It is suggested that the inferior properties of recycled rubber from DTC could be compensated by the addition of chemicals (for rapturing the cross-links) with the adjustment of operating conditions, among other remedies. All these add cost to the manufacturing process.

Date of submission: November 2015

Date of acceptance: January 2016

REFERENCES

Abraham, E, Cherian, BM, Elb, PA, Pothen, LA & Thomas, S 2011, 'Recent advances in the recycling of rubber waste', in *Recent developments in polymer recycling*, eds A Fainleib & O Grigoryeva, Transworld Research Network.

Dayang, HAI, Nur, FI, Devaraj, V & Nor, HK 2014, 'Effect of dipping tank coagulum (DTC) on cure characteristics and physical properties of DTC/natural rubber blends', in *International Conference on Plastic, Rubber and Composite (ICPR 2014)*, Langkawi, Malaysia, June 2014, pp. 20–21.

De, D, De, D & Singharoy, GM, 2007, Reclaiming of ground rubber tire by a novel reclaiming agent. I. Virgin natural rubber/reclaimed GRT vulcanizates', *Polymer Engineering & Science*, vol. 47, no. 7, pp. 1091–1100.

Department of Environment Malaysia 2005, *Environmental quality (schedule wastes) regulation 2005*, DOE Malaysia.

Devaraj, V 2011, Report on 'Characterization of dipping tank coagulum (preliminary study)' in *30th JTC Meeting at RRIM Technology Centre*, 21 December.

Devaraj, V & Zairossani MN 2012, 'Sludge-derived fuel from latex products manufacturing industry', *Academy of Sciences Malaysia Science Journal*, vol. 6, no. 1, pp. 15–21.

Devaraj, V, Nur, F, Fadhilah, I, Dayang, HAI & Nor, HK, Hidayaty, K 2014, 'Utilisation of latex coagulum from NR glove manufacturing line', *Malaysian Rubber Technology Developments*, vol. 14, no. 1, pp. 27–33.

Edirisinghe, DG, De Silva, MIA & Premachandra, JK, 2011, 'A novel reclaiming agent for ground rubber tyre (GRT), part II: property evaluation of virgin natural rubber (NR)/novel reclaimed GRT revulcanisates', *Progress in Rubber, Plastics and Recycling Technology*, vol. 27, no. 3, pp. 161–176.

George, RS & Joseph, R 1994, 'The utilisation of latex reclaim rubber in natural rubber', *Die Angewante Makromolekulare Chemie*, vol. 215, no. 3711, pp. 25–33.

Malaysian Rubber Board 1212, 'Malaysia's customs tariff 2012 for rubber and rubber products', Economics and Rubber Market Division, MRB.

Mathew, G, Singh, RP, Nair, NR & Thomas, S, 2001, 'Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber', *Polymer*, vol. 42, pp. 2137–2165.

Kamarulzaman, NH, Idris, NF, Veerasamy, D 2013, 'Characterisation of dipping tank coagulum waste from natural rubber glove factories', in *Proceedings of International Conference on Waste Management and Environment (ICWME)*, August 2013, Kuala Lumpur, pp. 26–27.

Rajan, VV, Dierkes, WK, Joseph, R & Noordermeer, JWM 2006, 'Recycling of NR-based cured latex material reclaimed with 2,20-dibenzamidodiphenyldisulphide in a truck tire tread compound', *J. Appl. Polym. Sci.*, vol. 102, pp. 4194–4206.

Rimez, B, Knappe, S, Pattyn, D & Munck, JD 2008, 'Rubber analysis by advanced thermo-gravimetric', in *Proceeding of British Plastic and Rubber Institute Conference, BPRI*, 22 October.

Saiwari, S 2013, 'Post-consumer tyres back into new tyres: devulcanization and re-utilization of passenger car tyres', PhD thesis, University of Twente, The Netherlands.