

## Thermoplastic Natural Rubber (TPNR) As a Backbone Polymer for Metal Injection Molding

(Getah Asli Termoplastik (TPNR) Sebagai Polimer Asas  
Untuk Pengacuanan Suntikan Logam)

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### ABSTRACT

*Moldability of metal injection molding (MIM) is dependent on the outward appearance of the resultant feedstock. Properties of the binders used will influence the properties of the feedstock. Stainless steel powder 316L with mean size 22  $\mu\text{m}$  and the binder system consists of three major fractions of paraffin wax, thermoplastic natural rubber and stearic acid with a powder loading of 65 vol. % was investigated. Comparison was also made with existing palm stearin in the binder system replacing the paraffin wax. Kinetic solvent extractions were done to determine the differences between the binder systems. The feedstock was then injected into tensile bar using vertical injection machine. The results showed that there is a slightly time extension during the solvent extraction as a comparison. The feedstock has been successfully injection molded at 190-200°C. Study of thermal analysis such as DSC and TGA has been done as a preparation for the thermal debinding and sintering process. This study demonstrated that a backbone polymer; thermoplastic natural rubber performs best in term of flow stability and compact quality and also saves in processing time.*

*Keywords: Backbone polymer; metal injection molding (MIM); thermal analysis; thermoplastic natural rubber*

### ABSTRAK

*Kebolehan pengacuan suntikan logam (MIM) amat bergantung kepada sifat bahan suapan yang dihasilkan. Sifat bahan pengikat yang digunakan akan mempengaruhi sifat bahan suapan. Serbuk keluli tahan karat 316L dengan purata saiz 22  $\mu\text{m}$  dan sistem bahan pengikat yang terdiri daripada tiga bahagian utama iaitu lilin parafin, getah asli termoplastik dan stearik asid dengan bebanan serbuk logam 65% telah pun dikaji. Perbandingan turut dilakukan dengan kehadiran stearin sawit dalam sistem bahan pengikat menggantikan lilin parafin. Pengekstrakan kinetik larutan dilakukan untuk menentukan perbezaan antara sistem-sistem bahan pengikat tersebut. Bahan suapan kemudian disuntik kepada bentuk bar regangan menggunakan mesin suntikan tegak. Keputusan menunjukkan terdapat perbezaan masa semasa pengekstrakan larutan dilakukan sebagai satu perbandingan. Bahan suapan telah berjaya disuntik pada 190-200°C. Analisis terma iaitu DSC dan TGA telah dilakukan sebagai persediaan untuk penyahikatan terma dan proses pensinteran. Kajian ini telah membuktikan bahawa bahan pengikat iaitu asas (tulang belakang) getah asli termoplastik menunjukkan potensi yang baik daripada segi kestabilan aliran dan kualiti padatan dan menjimatkan masa pemprosesan.*

*Kata kunci: Analisis terma; getah asli termoplastik; pengacuan suntikan logam (MIM); polimer asas*

### INTRODUCTION

Feedstock criterion is a critical factor in metal injection molding (MIM) process; in particular the binders in the feedstock strongly determine MIM quality. The main purpose of binders is to create a thin dense layer on solid particles, which should reduce the attraction force between them without markedly increasing their size and to reduce feedstock viscosity (Kryachek 2004). The homogeneity of the feedstock plays an importance characteristic. Inhomogeneities of feedstock can cause separation phenomenon among binders and powders (Li et al. 2007). In order to prevent this separation the binder should wet the powder surface and have good adhesion with it. German and Bose (1997) noted that the performance of binders depends on the content of the backbone polymer,

which governs the strength of green parts in the injection molding phase, determines the shape of the compact in the debinding phase.

Most works in this field have focused on the percentage of the backbone polymer. LDPE and HDPE are the most favorable polymers for injection molding. Combination of LDPE and HDPE, in the LDPE/HDPE backbone polymer can eliminate the compact defect formed by the evaporation gas and prevent the mass degradation of the backbone polymer in the compacts, which frequently occurs when a single backbone polymer is present (German & Bose 1997). Therefore studies of combination in backbone polymers were carried out with diligence to develop a new binder system which can give good impact by using MIM process in order to produce better performance in green

parts, the brown parts (after thermal debinding process) and also the sinter parts. Scanning electron microscopy (SEM) was applied to monitor the pore structure and binder distribution.

#### EXPERIMENTAL METHOD

The thermoplastic natural rubber (TPNR); Low density polyethylene: Natural rubber (LDPE:NR) with various ratio were compounded out in a laboratory mixer Brabender Plasticoder at 140°C and at speed of 50 rpm for 12 min according to the adequate time for the component to melt and homogenise. Initially the steel powder was mixed with different formulation of binders while the volume fraction of the powder in the mixture kept constant at 65%. The rheological results of the backbone binder; TPNR in term of shear rate, viscosity and pseudoplastic behaviours have been presented using a Capillary Rheometer (CFT-500D, Shimadzu) at 140°C with various shear rates.

Single binders TPNR, PS and PW are compared using differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) in order to study the

decomposition temperature. As an observation of the pore structure scanning electron micrographs were taken and analyzed.

#### RESULTS AND DISCUSSION

##### THERMAL ANALYSIS OF DSC AND TGA

The differential scanning calorimetric is conducted to make an understanding of the viscosity behavior of the binder and to select temperatures for kneading, molding, solvent debinding and melting point (Fan et al. 2009). The DSC curves in Figure 1 shows three different endothermic peaks for each component used in the binder system. The melt temperatures of TPNR, PS, PW and SA are 123.5°C, 68.25°C, 63.95°C and 62.79°C, respectively. Consequently, the injection molding temperature should exceed 123°C and the mold temperature should be lower than 60°C or which is the lowest temperature of the components of the binder. This is also indicating that all three component can be interact together at certain degree whereas TPNR will reacting as backbone binder as it has highest melting temperature compared with other binder.

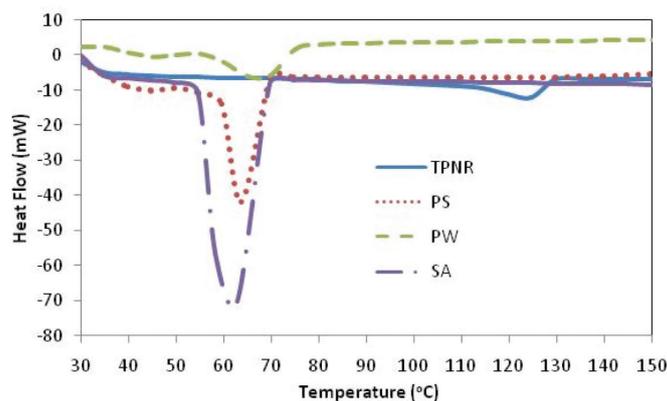


FIGURE 1. The DSC curves of thermoplastic natural rubber (TPNR), palm stearin (PS), paraffin wax (PW) and stearic acid (SA)

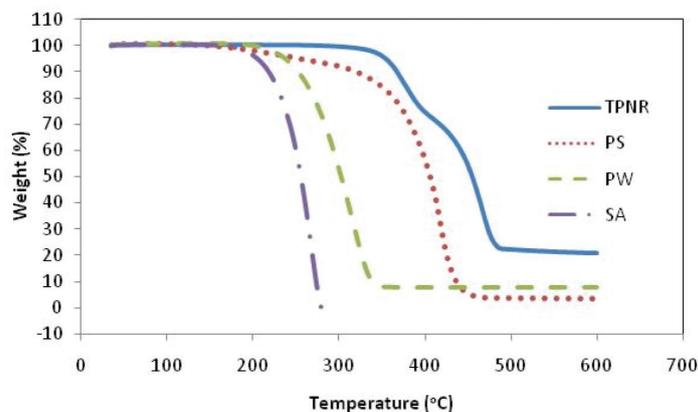


FIGURE 2. The TGA curves of thermoplastic natural rubber (TPNR), palm stearin (PS), paraffin wax (PW) and stearic acid (SA)

The TGA results of the four polymeric additives used in this study are shown in Figure 2. The curves give degradation temperature of each component. SA decompose at 120-280°C, PS decompose at 120-450°C, PW decompose at 170-350°C and TPNR decompose at 260-500°C. The curves separated uniformly in about 50-100°C each. Huang and Hsu (2009) reported that these differences give early information about the binder decomposition analysis while the weight loss data of mixed binder can be traced to a particular binder. This also helps in setting the thermal debinding process parameters.

#### RHEOLOGICAL PROPERTIES

Varying the composition of TPNR showed variation in torque level, indicating differences in viscosity of mixtures. It is clearly illustrated in Figure 3. Among the four types of TPNR, the 40NR/60PE blend system shows the most pronounced because of the significant pseudoplastic behaviour and the blend with 50NR/50PE system the least effect, with 60NR/40PE system being intermediate.

#### KINETIC SOLVENT EXTRACTION

Different in binder composition may effect the debinding rate. Figure 4 shows that as amount of paraffin wax (PW)

decrease, the percentage of the soluble binder that has been extracted increased while the time required would be reduced. Almost complete solvent extraction were done at 60 min leaching time. Even though, there were slightly different at 10 min leaching time, the curve showed that the percentage of binder removed for PS/TPNR/SA is a bit lower than PW/TPNR/SA binder system. However there is a rapid debinding happens at 30 min leaching time for PS/TPNR/SA rather than PW/TPNR/SA system. This was expected, that with less soluble binder, the pore channels become less interconnected. Moreover, a slow debinding rate at the early stage is cause by the swollen backbone binder that might clog the pores.

#### MORPHOLOGY

Observations were made on binder distribution and pore evaluation as shown in Figure 5. The SEM micrograph on the outer surface and fracture surface of the specimen shows equal structure for both PW/TPNR/SA and PS/TPNR/SA binder system. Figure 5(a) and 5(c) demonstrates pores with different size were formed. Pores exits as inter-particle pores and pores within the binder, these indicate that the multicomponent binder system had mixed and interacted to a certain degree while the soluble

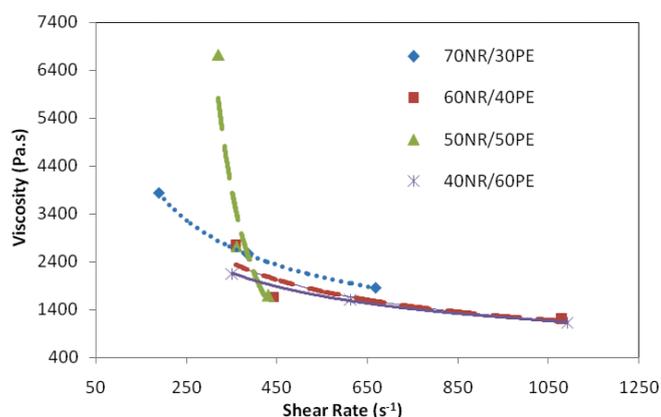


FIGURE 3. Effect of various TPNR binder formulations at 140°C

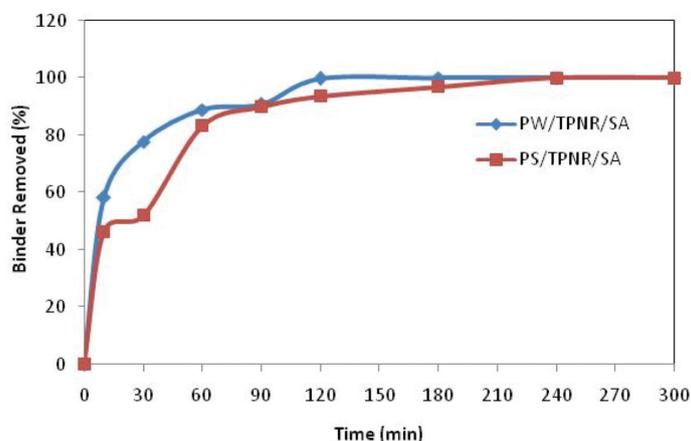


FIGURE 4. Kinetic solvent extraction of different binder formulation

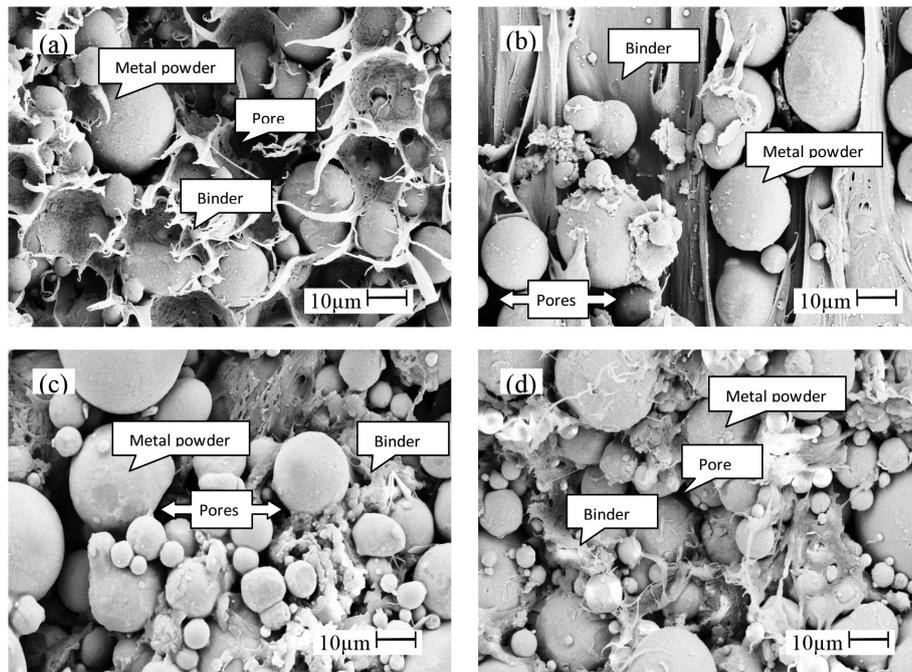


FIGURE 5. SEM micrograph of the specimen that had been solvent extraction for 60 min: PW/TPNR/SA (a) fracture surface (b) outer surface; PS/TPNR/SA (c) fracture surface and (d) outer surface

binder had been removed during solvent extraction. Fine ligament that can be seen in Figure 5(b) and 5(d) shows the remainder insoluble thermoplastic natural rubber holding the powder particle together and maintaining the shape of the specimen.

#### CONCLUSION

Although melt temperature for PW is lower than PS, which is 63.95 and 68.25°C, respectively, but for the debinding process, for PS will need longer time to be debind than PW. This is due to the range of decomposition temperature for PS which is 120-450°C while PW is 170-350°C.

TPNR is considered to be a good polymer backbone as the degradation temperature is higher and might be better than HDPE and LDPE alone. It is also able to sustain till before the thermal debinding process to maintain the shape of the sample.

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