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# STRUCTURE AND PROPERTIES OF CELLULAR POLYPROPYLENE/NATURAL RUBBER BLENDS COMPATIBILISED WITH BISMALEIMIDE

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***RINGKASAN:*** *Adunan berbusa polipropilena dengan getah asli (PP/NR) yang telah disebatikan dengan N,N-m-phenylenebismaleimide (HVA-2) telah disediakan melalui adunan leburan menggunakan penyemprit skru berkembar, diikuti oleh pengacuanan mampatan menggunakan Azodicarbonamide yang telah diubahsuai sebagai agen tiupan (CBA). Adunan yang mempunyai struktur sel yang berlainan telah diperolehi dengan mempelbagaikan peratusan HVA-2 dan CBA, dan pengaruh saiz purata sel dan peratus lompang ke atas ketumpatan, tenaga kegagalan hentaman dan faktor redaman adunan telah dikaji. Pemerhatian ke atas mikrograf SEM mendapati bahawa sistem adunan yang menggunakan 0.5% HVA-2 dan 2.5% CBA mempunyai saiz purata sel yang terkecil, iaitu 260 μm dan peratus lompang yang terbesar sebanyak 60%, mengakibatkan pengurangan ketumpatan ketara yang terbesar berbanding adunan PP/NR tanpa busa. Tenaga kegagalan hentaman adunan PP/NR berbusa pula didapati bertambah dengan bertambahnya peratus lompang dan berada pada tahap maksima pada adunan yang mempunyai saiz purata sel optima sebesar 350 μm. Faktor redaman adunan, yang telah dikaji menggunakan penganalisa dinamik mekanik, didapati bertambah dengan bertambahnya peratus lompang dan berkurang dengan bertambahnya saiz purata sel.*

**ABSTRACT:** Cellular polypropylene/natural rubber (PP/NR) blends compatibilised with N, N-m-phenylenebismaleimide (HVA-2) has been prepared by melt blending in a twin screw compounder followed by compression moulding, using modified Azodicarbonamide as the chemical blowing agent (CBA). Blends with different cell structures were obtained by varying the percentage of HVA-2 and CBA used and the influence of cell size and void fraction on the density, failure impact energy and damping factor of the cellular PP/NR blends were investigated. In this study, a blend system with 0.5% HVA-2 and 2.5% CBA was observed from the SEM micrographs to have the smallest average cell size of 260 μm and the highest void fraction of 60% resulting in the greatest reduction in the apparent density as compared to the unfoamed PP/NR blend. The failure energy of the cellular PP/NR blends during impact, investigated using an instrumented falling weight impact tester were found to increase with an increase in the void fractions and was at its maximum value at an optimum cell size of 350 μm. The damping factor (tan δ) of the blends, determined using a Dynamic Mechanical Analyser, was found to increase with increasing void fraction and decreased with increasing cell size.

**KEYWORDS:** PP/NR blends, TPNR, cellular, cell structure, impact energy, damping factor.

## INTRODUCTION

Cellular plastics, commonly referred to in the industry as foamed or expanded plastics, generally consists of a minimum of two phases, a solid polymer matrix and a gaseous phase derived from a blowing agent. Cellular plastics are known to have considerably greater energy-storing or energy-dissipating capacity than the unfoamed material and possess greater load-bearing capacity per unit weight. They are also good heat insulators by virtue of the low conductivity of the gas (usually air) contained in the system and have a higher ratio of flexural modulus to density than when unfoamed. With these unique properties, cellular plastics are commercially used in a wide range of applications, such as thermal insulation, load bearing structures, packaging and transportation.

Practically all plastics can be made into cellular structures, but only a few are principally used and these include polyurethane, polystyrene, polyethylene and polyvinyl chloride. The foaming of another class of material known as the thermoplastics elastomers (TPEs) has also developed in Europe and the USA towards the end of the 1980s. TPEs, which can be obtained by blending a thermoplastic resin with an elastomer, normally of the synthetic type such as ethylene propylene diene terpolymers (EPDM) and ethylene propylene rubber (EPR), exhibit properties typical of rubbery materials but can be processed like thermoplastics. Typically, the thermoplastic component provides strength, stiffness and thermal resistance, while the elastomer provides impact modification. Foamed TPEs have established themselves as the preferred material for a number of modern applications, and in the automotive sector, they are mainly used for exterior fascias, door-trim panels, self-sealing profiles and airbag covers.

Research and development work on utilising natural rubber as the elastomeric component in TPE, producing a class of material known as thermoplastics natural rubber (TPNR) blends, has long been established and reported (Norzalia *et al.,* 1993; Norzalia *et al.,* 1994; Matthew and Tinker, 1986, Gelling and Tinker, 1988). The impact modification of polypropylene through melt blending with natural rubber has resulted in significant increase in the impact strength of the final blend, especially at sub-ambient temperatures. The use of compatibilisers, such as m-phenylbismaleimide (HVA-2) to enhance the impact properties of PP/NR blends have also been studied. It has been reported that the presence of HVA-2 improved the impact properties of the PP/NR blends via two mechanism that is by promoting good interfacial adhesion between the two phases and by crosslinking the NR phase to a low degree (Norzalia *et al.,* 1993; Matthew and Tinker, 1986).

However, no work has been established on the foaming of PP/NR blends to produce a light-weight material with good impact absorption capability, suitable for engineering applications. In this study, cellular PP/NR blends were prepared and the effect of cell structures on the density, impact and damping properties of the cellular blends were investigated. The chemical

blowing agent (CBA) used was a modified Azodicarbonamide compound, a nitrogen releasing blowing agent which decomposes in a temperature range of 175°C to 215°C.

## EXPERIMENTAL

### Materials

The polypropylene used in this study was Pro-Fax SM240, a co-polymer from Titan Himont Polymers (M) Sdn. Bhd. The natural rubber used was SMR-CV obtained from the Rubber Research Institute of Malaysia. Cellcom-ACMP, a modified grade of Azodicarbonamide, supplied by Kum Yang Company Ltd., Korea was used as the CBA. The compatibiliser used for the blend was N,N-m-phenylenebismaleimide (HVA-2) from DuPont Dow Elastomers.

### Blend Preparation and the Foaming Process

Blends of PP/NR at 70/30 weight ratio were prepared in a Brabender twin-screw compounder at a speed of 50 rpm. The temperature setting of the compounder was at 175°C/175°C/165°C, with the lowest temperature being at the region nearest to the hopper. The temperature profile selected was such that the temperatures from the hopper to the nozzle zone were below the decomposition temperature of the blowing agent used to avoid premature release of gas before the actual foaming process was carried out. The percentage of Cellcom-ACMP added to the blend system were 0.5%, 1.5% and 2.5% by weight of total blend, while the percentage of HVA-2 used were 0.2% and 0.5% by weight of total blend. Incorporating higher levels of CBA into the blend system was found to cause the coalescence of cells during foaming, while adding higher amounts of HVA-2 has been found to show little improvement in the impact properties and only serve to increase the cost of the material (Norzalia *et al.,* 1994).

The foaming of the PP/NR blend was carried out by compression moulding in a 20 tonne hydraulic press machine. The pre-foamed PP/NR pellets with different percentages of HVA-2 and Cellcom-ACMP were pressed at 195°C for 15 minutes. The foaming temperature selected was a compromise between the melting temperature of PP/NR blend (170°C), the degradation temperature of NR (above 200°C) and the decomposition temperature of the CBA used (175°-215°C). 10 bar of pressure was applied throughout the foaming process and after the specified period, cooling of the mould was achieved using circulating water.

### Characterisation of Foam Structures

Density test for the unfoamed samples was carried out according to ASTM D792-91, while the apparent density of the foamed samples was obtained in accordance to ASTM D1622-93. Cell structures of the foamed samples were analysed using a Hitachi S-2500 Scanning

Electron Microscope (SEM) with an accelerating voltage of 10kV. The samples were frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact for examination. The fractured surfaces were then coated with platinum to facilitate examination under SEM. The SEM micrographs obtained were used to calculate the void fraction ($V_f$) and the average cell size ($d$) using the following equations (Matuana *et al.,* 1997):

$$V_f = 1 - \frac{\rho_f}{\rho} \tag{1}$$

$$d = \sqrt[3]{\frac{6V_f}{\pi N_0 (1 - V_f)}} \tag{2}$$

where $\rho$ is the density of the unfoamed samples and $\rho f$ is the apparent density of the foamed PP/NR blend. $N_0$, which is the cell population density per unit volume of the original unfoamed blend, is obtained using the following equation (Matuana *et al.,* 1997):

$$N_0 = \left(\frac{nM^2}{A}\right)^{3/2}\left[\frac{1}{1 - V_f}\right] \tag{3}$$

where n is the number of bubbles in the micrograph and, $A$ and $M$ are the area and magnification factor of the micrograph respectively.

**Impact and Damping Properties**

The drop impact test of the foamed PP/NR blends was carried out according to ISO 6603-2-1989 (E) using a Rosand Instrumented Falling Weight Impact (IFWI) tester. Foamed samples with dimension 60 mm x 60 mm square and 5 mm in thickness were used. The impact head was a stainless steel rod with a fixed 10 mm radius hemispherical head, with a weight of about 18 kg. The test was carried out at room temperature (27°C) with an impact velocity of 4.41 $ms^{-1}$.

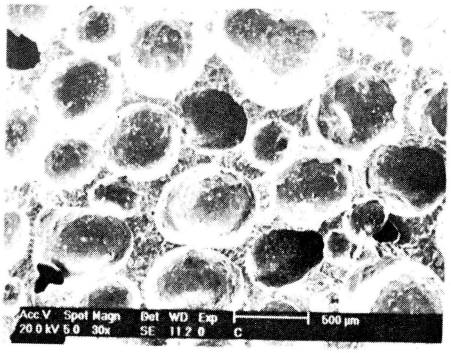
The damping factor of the foamed PP/NR blends was studied using a Perkin Elmer DMA7 dynamic mechanical analyser. The test was carried out in a 3-point bending mode. The dimensions of the specimens were approximately 15 mm x 6 mm x 3 mm. The samples were scanned from -100 to 50°C, at a frequency of 1 Hz and a heating rate of 5°C per minutes with helium as the purge gas. Loss tangent (tan $\delta$) versus temperature curves were plotted and the damping factor, $\Delta Y$, were calculated from:

$$\Delta Y = \tan \delta_{max} - \tan \delta_{min} \tag{4}$$

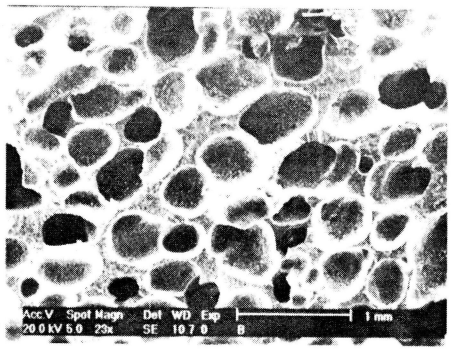
## RESULTS AND DISCUSSIONS

### Cell Structure

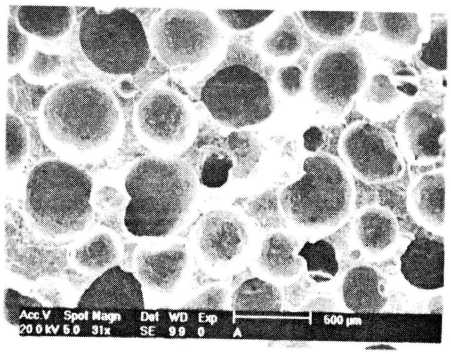
The cell structures of the foamed PP/NR blends with different percentage of CBA are as shown in Figures 1(a) - (c) for samples without HVA-2, Figures 2(a) - (c) for samples with 0.2% HVA-2 and Figures 3(a) - (c) for samples with 0.5% HVA-2. The micrographs obtained show that closed-cell structures were formed in all cases, where the gas phase was dispersed in the form of discrete bubbles in the continuous phase of the blend matrix. All cells were almost spherical in shape and uniformly distributed throughout the solid PP/NR matrix. The calculated apparent density, void fraction and average cell size of the various foamed PP/NR blends produced are given in Table 1.




1 (a)

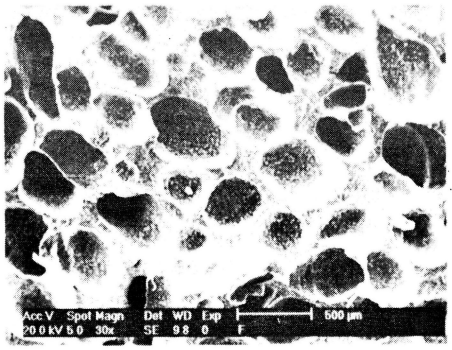



1 (b)

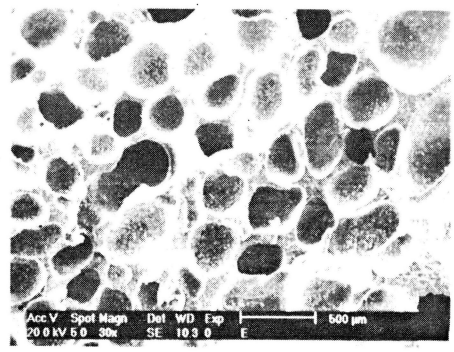



1 (c)

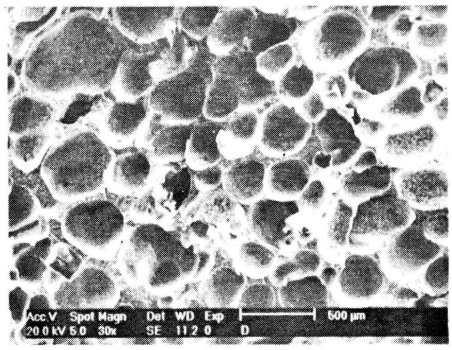
***Figures 1(a) - (c).*** *SEM micrographs of foamed samples without HVA-2 (a) 0.5% CBA, (b) 1.5% CBA, (c) 2.5% CBA*




2 (a)

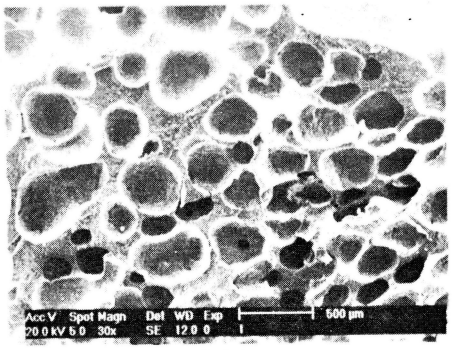



2 (b)

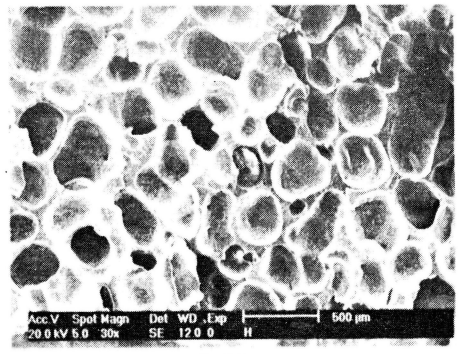



2 (c)

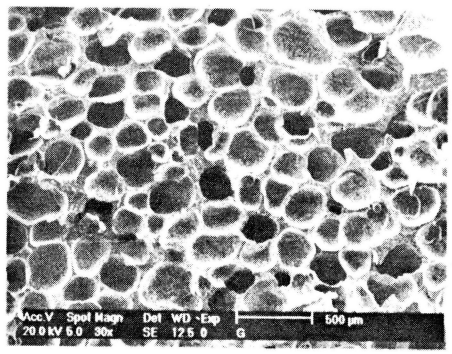
***Figures 2(a) - (c).*** *SEM micrographs of foamed samples with 0.2% HVA-2 (a) 0.5% CBA, (b) 1.5% CBA, (c) 2.5% CBA*




3 (a)




3 (b)




3 (c)

***Figures 3(a) - (c).*** *SEM micrographs of foamed samples with 0.5% HVA-2 (a) 0.5% CBA, (b) 1.5% CBA, (c) 2.5% CBA*

**Table 1.** Apparent density, void fraction and average cell size of the various cellular PP/NR blends

| Blend Formulation | | Apparent Density ($\rho f$), g/cm³ | Void Fraction ($V_f$), % | Average Cell Size (d), µm |
|---|---|---|---|---|
| Percentage HVA-2, wt. % | Percentage CBA, wt. % | | | |
| 0 | 0.5 | 0.408 | 54.5 | 522 |
| | 1.5 | 0.397 | 55.7 | 528 |
| | 2.5 | 0.379 | 57.7 | 466 |
| 0.2 | 0.5 | 0.395 | 56.0 | 442 |
| | 1.5 | 0.381 | 57.5 | 387 |
| | 2.5 | 0.370 | 58.8 | 350 |
| 0.5 | 0.5 | 0.389 | 56.6 | 345 |
| | 1.5 | 0.376 | 58.1 | 348 |
| | 2.5 | 0.368 | 60.0 | 260 |

Note: The density of the unfoamed PP/NR blend used in this study is 0.904 g/cm³

## Effect of Void Fractions and Cell Size on Apparent Density

The apparent density of plastics foam can be defined as the weight per unit volume of the polymer including voids inherent in the material. The range of apparent density obtained for the cellular PP/NR blends were between 0.368 to 0.408 g/cm³. Commercial plastics foam are produced in a great variety of densities ranging from about 0.002 g/cm³ to 0.96 g/cm³. It is known that the mechanical strength of cellular materials are generally proportional to their apparent densities. Lower densities foam are generally suitable to be used as thermal insulators, while higher densities foam are used for more demanding functions, such as energy-absorbing and load-bearing applications.

Void fraction can be defined as the relative amount of air or gas pockets trapped in the dense core of the foamed material. Figure 4 shows the relationship between apparent density and void fractions of the foamed PP/NR blends. As expected the higher the amount of gas trapped in the foam samples, i.e higher percentage of void fraction, the lower is the apparent density of the foam materials produced. For a fixed amount of HVA-2, samples with higher amount of CBA appeared to have higher void fraction, as higher amount of gas has been generated and available for cell growth. Higher void fraction was also produced in the blend with a higher amount of HVA-2. Previous studies has shown that the presence of HVA-2 in the PP/NR blends promotes good interfacial adhesion between the two phases, thus improving the dispersion of the rubber component in the PP matrix (Hanim *et al.,* 1998). This in turn may possibly increase the availability of sites for cell initiation. In this study, the foamed PP/NR blends with 0.5% HVA-2 and 2.5% CBA was found to have the lowest apparent density value of 0.368 $gcm^{-3}$ which corresponds to the highest void fraction of about 60%.

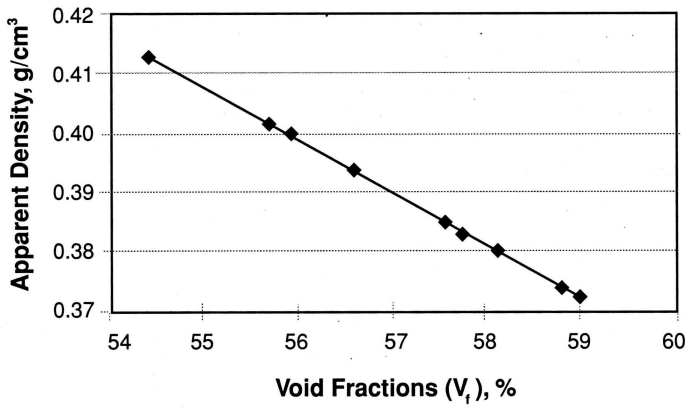



***Figure 4.*** *Relationship between apparent density and void fractions of foamed PP/NR blends*

Figure 5 shows the relationship between the average cell size and the apparent density of the foam PP/NR blends. The higher the average cell size, the greater is the apparent density of the cellular PP/NR blends. From the SEM micrographs, it can be observed that more polymer phase was present in the blends with larger cells per unit area, and this inherently makes the blends more dense. Results also revealed that the size of the cells formed is influenced by the amount of CBA added into the blend. In general, the higher the CBA content, the smaller is the size of cells being formed. This may be due to the higher amount of air bubbles released by the CBA, resulting in smaller cells being formed per unit volume of the blend. It was also observed that the cell size decreases with an increase in the HVA-2 content. Previous studies indicated that increasing the amount of HVA-2 has resulted in a more viscous blend being formed (Hanim *et al.,* 1998). A low viscosity polymer matrix is known to inhibit the rate of cell growth during a foaming process, thus resulting in smaller

cells being formed. It was found that the smallest average cell size formed was 260 μm with 2.5% CBA and 0.5% HVA-2.

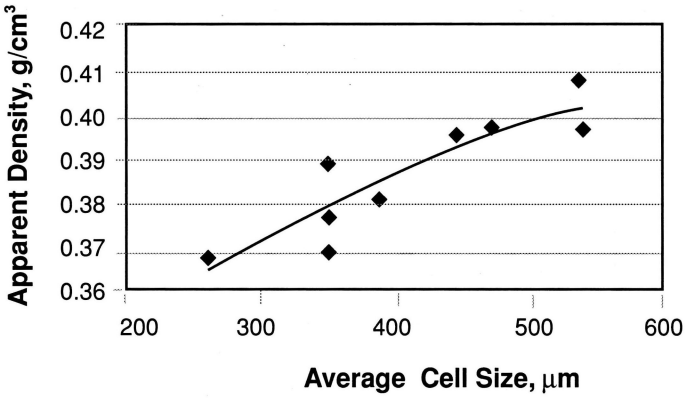



***Figure 5.*** *Relationship between apparent density and average cell size of foamed PP/NR blends*

**Effect of Void Fractions and Cell Size on Total Failure Impact Energy**

Results of total failure energy obtained from an instrumented falling weight impact tests gives indication on the toughness of a material i.e. the tougher the material, the greater is the impact energy needed to initiate and propogate crack which will finally cause failure to the material. This energy absorption capability is essential for materials that are going to be used for applications where they will be subjected to external impact forces.

Figure 6 illustrates the effect of void fraction on the total failure energy of the foamed PP/NR blends. It is observed that the total failure energy of the foamed samples increase with an increase in the void fractions. The blend which exhibits the highest void fractions (60%), i.e. the blend with 2.5% CBA and 0.2% HVA-2, was found to have the highest total failure energy of about 11 J. The increase in the total failure energy may be attributed to the increase in the amount of air voids present in the PP/NR matrix. It is believed that the cellular structure absorbs energy during deformation, therefore as the amount of air present in the matrix increases, the ability of the foam material to absorb energy increases thus increasing the toughness of the foamed PP/NR blends.

Figure 7 shows the effect of cell size on the total failure energy of the foamed PP/NR blend. Results shown in figure 7 indicates that the total failure energy initially increases with the cell size and then decreases after an optimum cell size was obtained. The optimum cell size which give the highest total failure energy (11 J) is found to about 350 μm, which again corresponds to the blend with 2.5% CBA and 0.2% HVA-2. It can be deduced that making

the cell size of the foamed PP/NR blends bigger does not necessarily increase the ability of the samples to absorb impact energy.

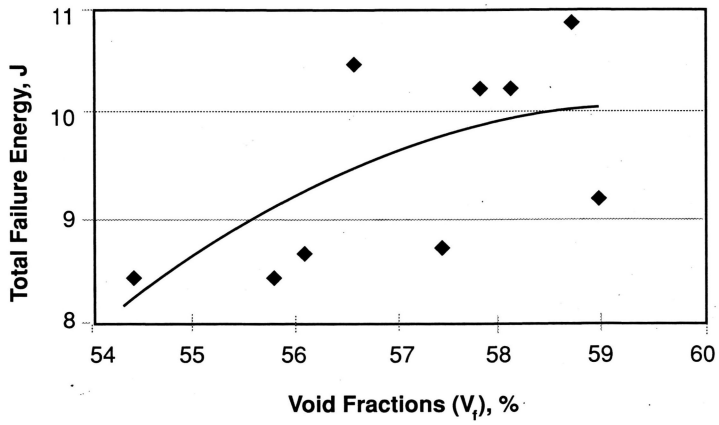



***Figure 6.*** *Relationship between total failure energy and void fractions for foamed PP/NR blends*

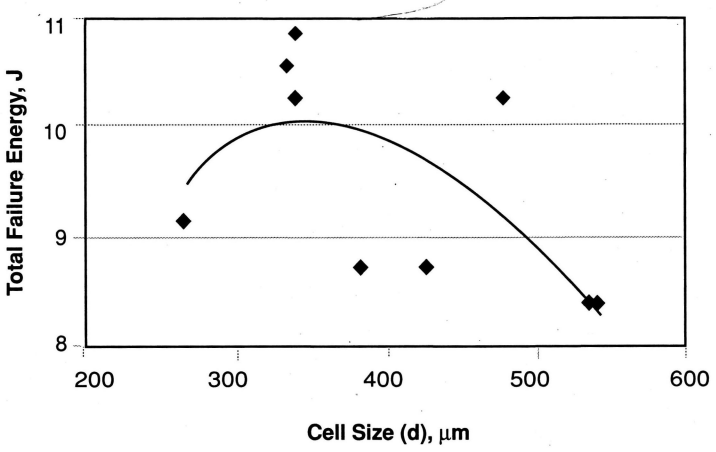



***Figure 7.*** *Relationship between total failure energy and cell size of the foamed PP/NR blends*

**Effect of Void Fractions and Cell Size on Damping Factor**

The damping factor of the foamed PP/NR blends were calculated from the loss tangent (tan δ) curve obtained from the dynamic mechanical analysis (DMA). Tan δ can be defined as the ratio of the energy dissipated to the energy stored when the material is subjected to an oscillatory load. Cellular materials, which are known to possess high damping properties,

has the capability to reduce vibrations and prevents resonance vibrations from building up to dangerous amplitudes.

Figure 8 illustrates the effect of void fraction on the damping factor. The result indicates that the damping factor of the foamed PP/NR blends increases with an increase of the void fractions. This agrees well with the results of the total failure impact energy as the damping characteristic is known to be related to the energy absorption capability of a material.

Figure 9 illustrates the effect of cell size on the damping factor. Results show that the damping factor of the cellular PP/NR blends decrease with increase in the cell size.

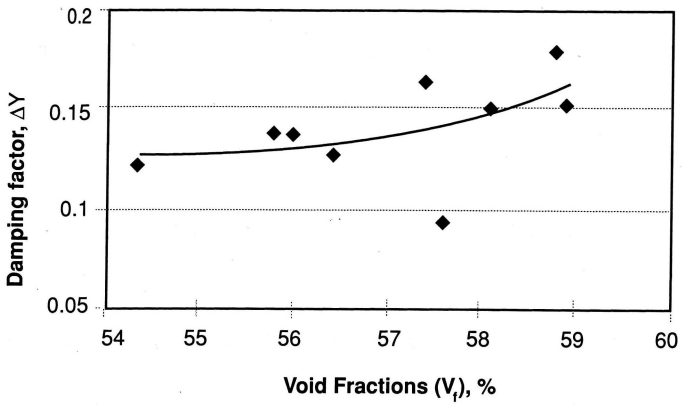



***Figure 8.*** *Relationship between damping factor and void fractions of PP/NR blends*

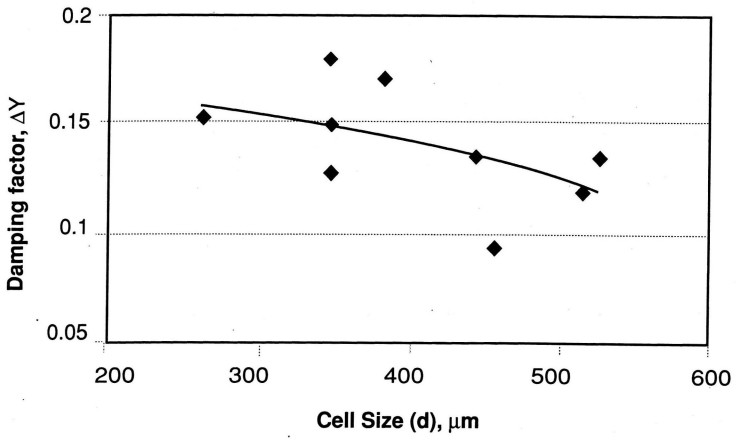



***Figure 9.*** *Relationship between damping factor and cell size of foamed PP/NR blends*

## CONCLUSIONS

This study has shown that properties such as apparent density, failure impact energy and damping factor, of the cellular polypropylene/natural rubber blends compatibilised with HVA-2, are influenced by the percentage of void fraction present in the blend system as well as on the average cell size produced. Blends with high void fractions and small average cell size are found to be more light-weight and exhibit better impact and damping characteristic.

## ACKNOWLEDGEMENT

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