Rheology, Morphology, and Mechanical and Thermal Properties of Recycled PVC Pipes

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ABSTRACT: This article demonstrated the possibility of recycling PVC pipes by investigating the effect of adding PVC pipes (varying from 0 to 80 % wt) into two commercial PVC virgin grades on the rheological, morphological, mechanical, and thermal properties of the PVC blends. The results obtained showed an increase in the melt viscosity and no change in the die swell ratio as the concentration of the recycled PVC was increased. The die swell ratio was observed to increase with temperature, this being associated with the presence of gelation that occurred at high temperature. The optimum tensile and impact strengths were detected, the impact strength being explained by use of SEM micrographs of the fracture surface. The hardness result corresponded well to the density of the compounds. The glass transition, degradation, and heat-deflection temperatures were also found to shift with the recycled PVC loading. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2478–2486, 2001

Key words: polyvinyl chloride (PVC); recycling; gelation; rheology; mechanical properties

INTRODUCTION

A considerable body of literature has been published concerning the recycling of plastic waste due to the pressure of resource conservation, reduced landfill availability, and increasing stringent legislation. PVC is regarded second behind polyethylene in respect to worldwide polymer consumption, but recycling of postconsumer PVC is not as widespread as for polyethylene due to its long-term applications. Recently, recycling PVC products has become demanding, and attempts have been made to recycle PVC materials. Summers et al.[1] discussed a number of examples to assess the feasibility of recycling PVC products. The article suggested that vinyl products can be recycled into a variety of applications including bottles, drainage pipes, and drainage pipe fittings with good appearance and properties. Thomas and Quirk[2] showed that recycled PVC bottles can be used successfully in stabilized PVC foam formulations to produce profiles. It was also found that the profile properties were unaffected when virgin PVC was replaced by PVC bottle recyclates.

The recycling of PVC material encounters difficulties because the material itself is very sensitive to temperature and the environment, involving continuous changes in its morphological structures and properties.[3] Generally, it has been known that PVC structural changes take place during processing. While sheared, the degree of fusion of PVC particles affected the mechanical properties such as tensile and impact strengths and hardness.[4] The original PVC particle structure progressively changed into a network of entanglement and primary and secondary crystal-

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linity during processing, both significantly affecting optimum physical and mechanical properties. Recent evidence[4] found that increasing the degree of PVC gelation seems to improve the properties to either a plateau being reached or a maximum value being passed, this involving interparticle interaction and the destruction of the primary crystallinity of the PVC compound. Wenguang and Mantia[5] studied the mechanical and processing properties of recycled PVC (collected from bottles and pipes) blended with pipe-grade virgin PVC. They found that the particle size and restabilization of the recycled PVC during processing were the two important factors controlling the properties of the PVC blends. The impact strength and processing behavior of the virgin PVC were improved with the addition of the recycled PVC due to the presence of modifier agents in the recycled pipes, whereas the thermal resistance was slightly lowered. Ulutan[6] conducted spectroscopic studies such as infrared and ultraviolet and differential scanning calorimetry curves of recycled PVC bottles under heat impact at 160–180°C temperature. It was found that the recycled PVC was considerably affected at 180°C heat treatment, this being indicated by color changes, loss of volatile components, and decomposition products formed. The study suggested that reclaimed PVC bottles were recyclable for real process time.

So far, the demand of using PVC is still increasing, around 40% of PVC being used for making pipes.[5] It is then interesting to assess the possibility of recycling processed PVC products. The idea of incorporating PVC scrap in a virgin PVC compound is not new but it still needs more study for seeking a wider range of applications. The objective of this article was to seek and assess the optimum properties of recycled PVC pipes blended with two different commercial grades of virgin PVC compounds, one being the pipe grade (the same as used to produce the recycled PVC pipes) and the other being a bottle grade. The results were explained in terms of the effect of the recycled PVC content on a variety of properties including thermal, physical, mechanical, rheological, and morphological properties.

EXPERIMENTAL

Raw Materials

Three different materials were studied in this present work, these being

Table I Blending Composition (Percent by Weight)

| No. | Composition (% wt) | | |
	V-P	V-B	R-BP
1	100	—	—
2	—	100	—
3	—	—	100
4	80	—	20
5	60	—	40
6	40	—	60
7	20	—	80
8	—	80	20
9	—	60	40
10	—	40	60
11	—	20	80

- Virgin PVC pipe compound (Grade Y5902BLA), supplied in granule form by Thai Plastics and Chemicals, Co. Ltd., Bangkok, Thailand, *sample code V-P*. The compound comprised 1.2 pph calcium stearate, 1.2 pph tetrabasic lead sulfate, 0.1 pph polyethylene wax, and 4 pph $CaCO_3$.
- Virgin PVC bottle compound (grade B0303CLA), supplied in granule form by Thai Plastics and Chemicals Co. Ltd, *sample code V-B*. The compound comprised 1.6 pph liquid thiotin (stabilizer), 12 pph MBS impact modifier, 2 pph processing aid (acrylic type), and 1.5 pph fatty acid.
- Recycled PVC flake, material reclaimed from PVC cold-water blue pipes that had been collected after being used for 5 years from building sites, the original compound used to produce pipes being the same as the V-P compound. The collected PVC pipes were washed to remove any contaminants and then crushed in a granulator, supplied by Thai Union Co., Ltd. (Bangkok, Thailand) to give recycled PVC flake prior to further use, *sample code R-BP*.

PVC Compounding

In this work, recycled PVC flake was added to each virgin PVC compound at concentrations ranging from 0 to 80 % wt as shown in Table I. The recycled PVC pipes were granulated in a granulator (2835 Bosgo Engineering Co. Ltd.) before blending with virgin PVC in a twin-screw

extruder manufactured by HAKKE Co. Ltd (Germany). The head of the extruder contained a three-strand die (each strand having a diameter of 3 mm), this producing three extrudates at the die exit. The extrudates were then passed through a water bath via the use of a pull-off unit before undergoing a pelletizer to produce compounded granules. The screw rotating speed was 100 rpm, with the barrel temperature setting on zone one (near the hopper) at 140°C, on zone two at 150°C, and on the die at 160°C. The drive torque during mixing in the twin-screw extruder was recorded to follow the mixing performance of the PVC compounds.

Test Piece Fabrication

The resultant blends in the form of pellets were compression-molded at 180°C and 5000 kPa for 5 min into sheets approximately 1 mm thick (for tensile test) and 3 mm thick (for impact test) before being cooled to room temperature. From the sheets, dumbbell specimens, according to the standard tensile test JIS K6732 (1987), the impact test ASTM D256 (1990), and the heat-deflection temperature test ASTM D648 (1990), were die-stamped to produce test pieces for mechanical tests.

Characterization

Rheological Properties

The rheological properties of the PVC compounds were determined using an Instron 4467 extrusion rheometer (barrel diameter of 9.5 mm) fitted with a die 1.25 mm in diameter and 44 mm in length. Flow curves (relationship between shear stress, shear rate, and apparent viscosity) were constructed, whose the calculations can be found elsewhere.[7] In this article, the test temperature used was 190°C and the shear rates ranged from 42 to 280 s^{-1}.

A Kayeness Galaxy Series melt flow indexer (Model D7053) was used to assess the melt flow index of the PVC compounds. The test procedure followed was as specified in ASTM D3364 (1990). The test temperature used was 180°C and the applied load was 20.5 kg with a die of *L/D* 8/2.

Die Swell Determination

The die swell ratio of the compound was determined using an Instron 4467 capillary rheometer for various test temperatures (190, 200, and 210°C). The die swell of the extrudate was directly measured by calculating the ratio of the diameter of the extrudate to that of the die (*L/D* ratio of 44/1.5), the extrudate diameter being based on the size of the extrudate diameter in the fully swollen extrudate.[8]

Thermal Properties

A Perkin–Elmer DSC-7 instrument was used to determine the glass transition temperature (T_g) of the PVC compound. The temperature was scanned from room temperature to 120°C with a heating rate of 5°C/min. The degradation temperature (T_d) of the compound was determined using a Perkin–Elmer TGA-7 using a temperature range of 50–600°C with a heating rate of 20°C/min. The heat-deflection temperature (T_h) of the compound was examined using a Rosand HDT instrument from a starting temperature of 32°C with a heating rate of 2°C/min. The test procedure was carried out according to ASTM D648 (1990).

Density Measurement

The density of the PVC compound (granule) was determined using a Rosand density column according to ASTM D 1505 (1990), the solvents used being toluene and CCl_4.

Tensile Testing

The ultimate tensile stress (UTS) of the PVC blends was of our interest, determined from dumbbell samples after conditioning for 24 h in a controlled environment of 23°C and 50% relative humidity. All tests were performed on an AGS-500D (SHIMADZU) tensile testing machine at a crosshead speed of 20 mm min^{-1}.

Impact Testing

The Izod impact tests were carried out according to ASTM D256 (1990). The samples were tested on a Yasuda impact tester with the notched side facing the pendulum. The results are reported in terms of the impact strength.

Hardness Testing

The hardness of the compound was evaluated using a Durometer Shore D (Model 409) supplied by PTC Instruments Co. Ltd. The test procedure followed was specified as ASTM D2240 (1990).
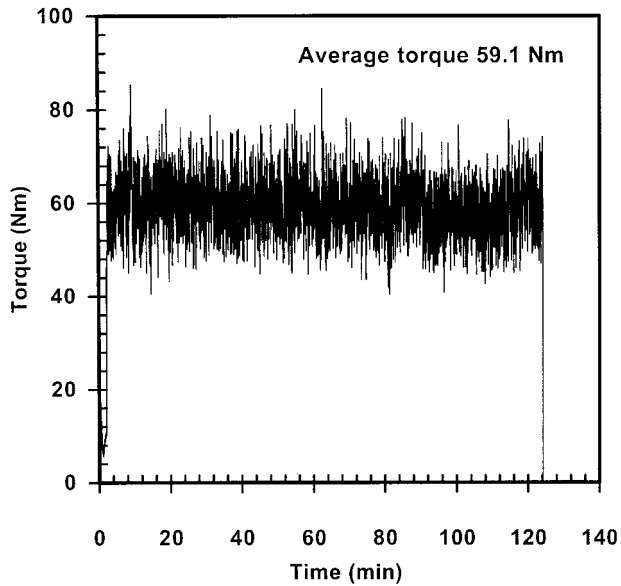
Figure 1 Example of torque curve during compounding in the twin-screw extruder (R/BP:V-P = 40:60 % wt).

SEM Investigations

Failure mechanisms were investigated using a JEOL (JSM-6301F) SEM machine at a 15-kV accelerating voltage, examining fracture surfaces obtained from ultimate tensile testing at 23°C. The samples were mounted onto an aluminum stub and coated with carbon to reduce the charging effect, the carbon coating being performed using a vacuum coating unit (JEOL JEE-400) operated at 15A.

RESULTS AND DISCUSSION

The torque curve measured during blending the PVC compounds in the twin-screw extruder was typically of the form shown in Figure 1. It can be seen that the torque stabilized over the blending period, which indicated the homogeneity, consistency, and quality of the blend. This typical behavior was also seen for all blends (not shown), but the average torque value varied with the compositions of the blends. Figure 2 shows the average torque values encountered during blending for the V-B and V-P systems, respectively, with different R-BP loadings added. In the case of the V-B system, the average torque values of the V-B and R-BP compounds were 93 and 56 Nm, respectively, this reflecting the differences in the rheological properties of the compounds. Varying the

R-BP content resulted in a change in the torque value. The torque level seemed to stabilize at the initial stage and started to reduce sharply as the R-BP content was increased between 40 and 80%. In the case of the V-P system, the initial torque values of the R-BP and V-P were the same, indicating that there was no difference in the rheological nature of the compounds. Therefore, varying the R-BP concentration did not change the torque level of the compounds. This may be expected since the R-BP and V-P were the same grade. This also implied that the processability of the recycled PVC pipes did not change over a period of time during service.

Figures 3 and 4 show the rheological properties of the compounds after blending in the extruder. It can be seen from Figure 3 that as the R-BP content increased the MFI value progressively decreased, the effect being more pronounced in the case of the V-P system. The decrease in the MFI value due to the addition of R-BP indicated an increase in the overall viscosity of the compounds. This was found to be true when considering the flow curves in Figure 4, which shows that, for a given shear rate, the shear stress of R-BP was higher than that of V-P and V-B, indicating a larger compound viscosity. In comparing the viscosities of R-BP and V-P (which were orig-
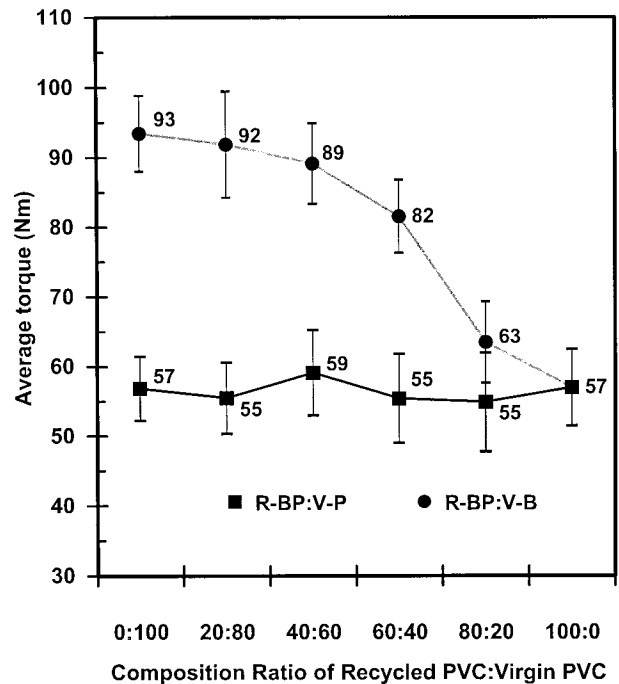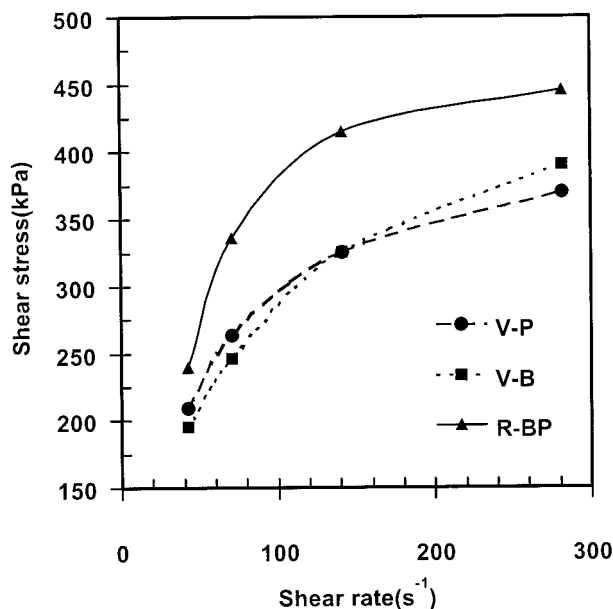

Figure 2 Average torque versus composition ratio of recycled to virgin PVC.
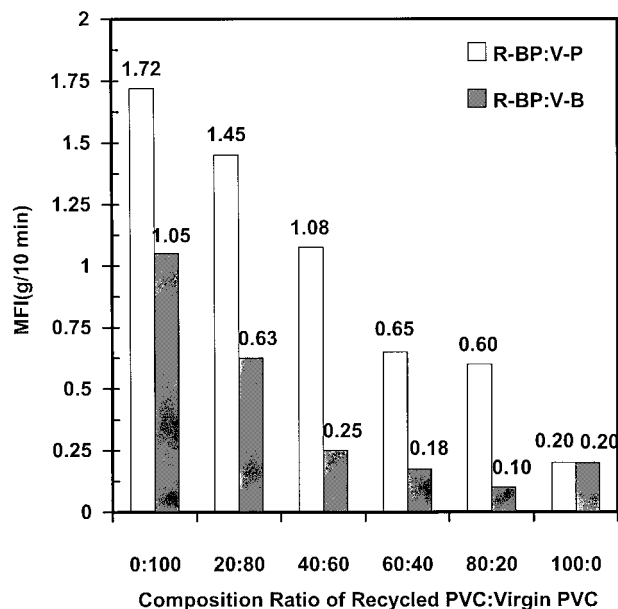
Figure 3 Effect of recycled PVC content on MFI value at 190°C.
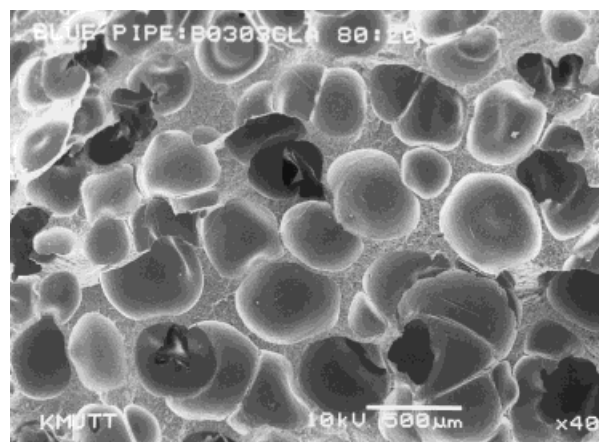
Table II **Effect of Test Temperature on Die Swell Ratio for Different Blending Compositions at Shear Rate 280 s^{-1}**

	Die Swell Ratio		
Composition	190°C	200°C	210°C
100% V-P	1.3	1.2	1.2
100% V-B	1.1	1.1	1.2
100% R-BP	1.2	1.2	1.3
20% R-BP : 80% V-P	1.2	1.2	1.2
40% R-BP : 60% V-P	1.1	1.1	1.2
60% R-BP : 40% V-P	1.2	1.1	1.3
80% R-BP : 20% V-P	1.1	1.2	1.4
20% R-BP : 80% V-B	1.2	1.1	1.2
40% R-BP : 60% V-B	1.1	1.1	1.2
60% R-BP : 40% V-B	1.2	1.2	1.4
80% R-BP : 20% V-B	1.2	1.2	1.6

inally the same grade), the greater viscosity of R-BP may probably be because R-BP had experienced more processing times (thermal history), making its molecular structure (particles) more compacted and densified.[4,9] This statement can also be used to explain the differences in the change of the MFI values in the V-P and V-B systems.

Table II shows the effects of the composition and blending temperature on the die swell ratio. It can be seen that adding R-BP did not change the die swell ratio within the experimental error ($\pm 2.5\%$) except for the R-BP/V-B system between 60 and 80% R-BP loading at 210°C, the swelling ratio being about 1.4–1.6. The very high swelling ratio resulted from two sources: First, it was due to a decomposition of the PVC that produced HCl gas and thus porosity (due to expansion of the HCl gas) in the compound during high-temperature processing as shown by an SEM micrograph of the extrudate at 210°C (Fig. 5). This led to an increased die swell ratio. Second, the increase in the die swell was caused by PVC gelation. The

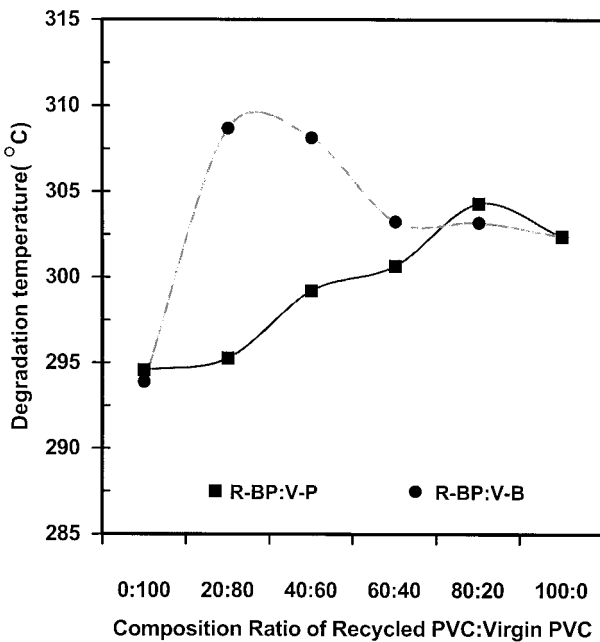**Figure 4** Flow curves for PVC compounds at 190°C.

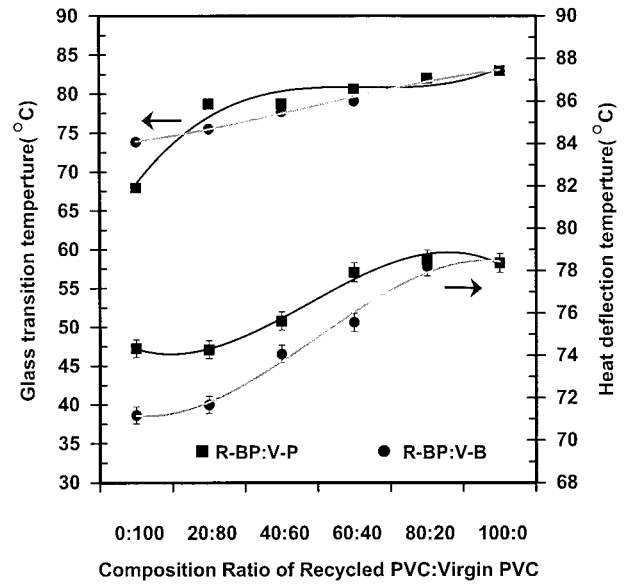

Figure 5 SEM micrograph of the extrudate at 210°C test temperature.

Table III   Effect of Shear Rate on Die Swell Ratio for Different Blending Compositions at 210°C

| | Die Swell Ratio | | | |
Composition	42 s^{-1}	70 s^{-1}	140 s^{-1}	280 s^{-1}
100% V-P	1.2	1.2	1.2	1.2
100% V-B	1.1	1.2	1.2	1.2
100% R-BP	1.1	1.2	1.2	1.3
20% R-BP : 80% V-P	1.2	1.2	1.1	1.2
40% R-BP : 60% V-P	1.2	1.2	1.1	1.2
60% R-BP : 40% V-P	1.2	1.2	1.2	1.3
80% R-BP : 20% V-P	1.2	1.3	1.3	1.4
20% R-BP : 80% V-B	1.1	1.2	1.2	1.2
40% R-BP : 60% V-B	1.1	1.1	1.2	1.2
60% R-BP : 40% V-B	1.1	1.1	1.2	1.4
80% R-BP : 20% V-B	1.3	1.3	1.4	1.6

Figure 7   Effect of recycled PVC content on glass transition and heat-deflection temperatures.

latter could be substantiated by considering the effect of the test temperature; the die swell ratio seemed to slightly increase with temperature. Generally, the die swell ratio decreases with the temperature due to a reduction of the elastic characteristic.[3] However, this was not the case for this work. Huneault et al.[10] suggested that the die swell characteristic of PVC material behaved dif-

ferently from that of other polymers. In their work, the die swell increased as the temperature was increased in association with an increase in the level of PVC gelation due to temperature and shear and, thus, increased swelling. In relation to this work, it was possible that at 210°C the PVC experienced gelation. Table III shows the effect of the shear rate on the die swell of recycled PVC at 210°C. It was found that the die swell increased

Figure 6   Effect of recycled PVC content on degradation temperature.
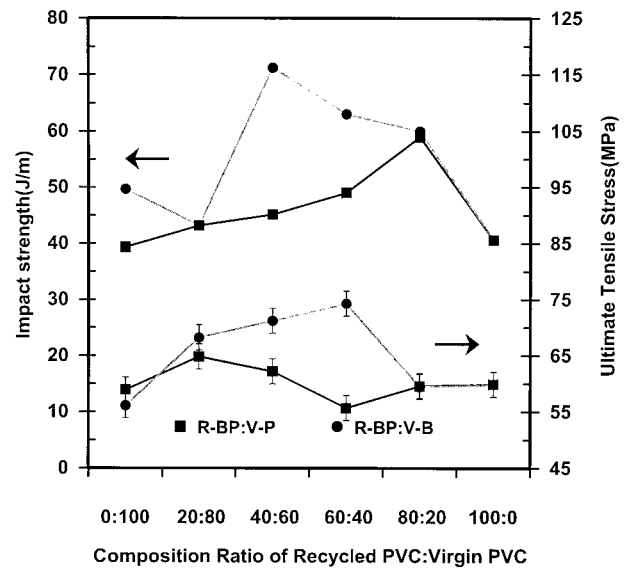
**Figure 8**   Effect of recycled PVC content on impact strength and UTS.
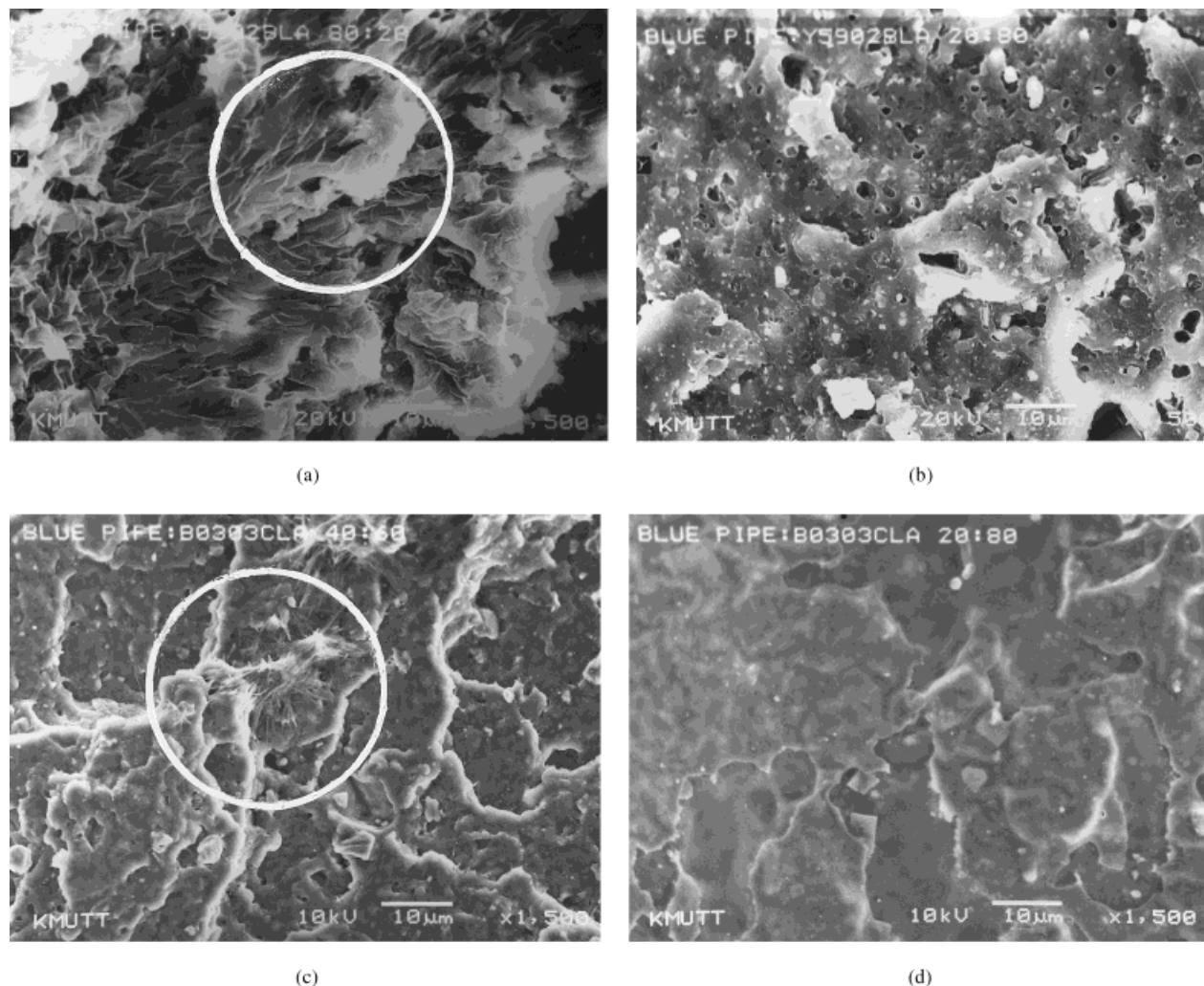
Figure 9 SEM micrographs of fracture surface of PVC blends (a) 80% wt R-BP : 20% wt V-P. (b) 20% wt R-BP : 80% wt V-P (c) 60% wt R-BP : 40% wt V-B (d) 20% wt R-BP : 80% wt V-B.

with the shear rate due to the increased elastic characteristic and gelation.[8–10]

Figure 6 shows the changes in degradation temperature (T_d) as a function of the R-BP content in V-P and V-B systems. In the case of the V-B system, the T_d gradually increased with increasing PVC recyclate (R-BP), while the T_d in the V-P system sharply increased at the initial stage (between R-BP loading of 20–40%) and decreased for further loadings of R-BP. For a given R-BP loading, the T_d of the V-P system was much higher than that of the V-B system, except for the 80% R-BP loading. The change in the T_d value was thought to be caused by the particle compaction and densification as stated earlier. The changes in the glass transition temperature (T_g)

and the heat-deflection temperature (T_h) are shown in Figure 7. It can be seen that the T_g and T_h increased with the R-BP loading. Work by Ulutan[6] suggested a shift of the T_g from 62 to 80°C as the PVC was reprocessed under a temperature range of 160–180°C, accompanied by a slow cooling, this T_g shift being due to the depletion of some ingredients, to a certain extent, acting as a plasticizer.[6] In relation to this work, the R-BP had a thermal and shear history while it was first processed, as compared to the two virgin grades. It was possible that the amount of the depletion of its ingredients in R-BP was relatively large. Therefore, increasing the content of the R-BP may result in the shift (increase) in the T_g and T_h values in the blends.
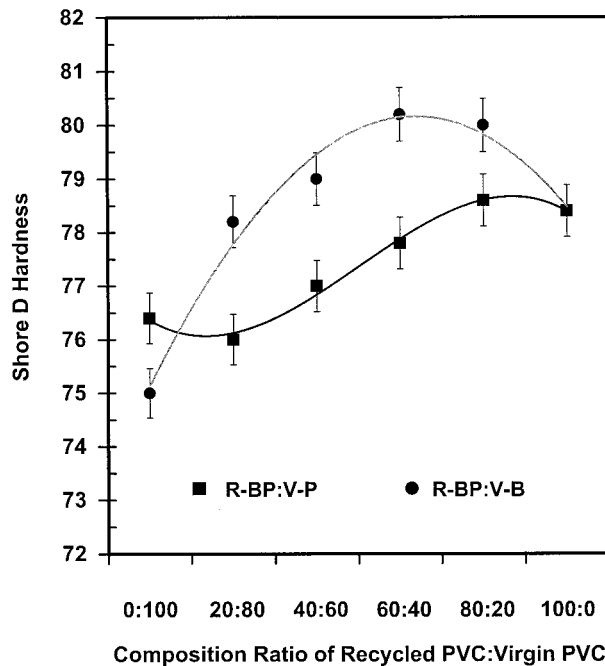
Figure 10 Plots of hardness and blending composition.

Figure 8 shows the changes in UTS and impact strength as a function of the composition ratio of R-BP/V-P and R-BP/V-B systems. It can be observed that both properties changed with variations in the composition ratio. For the impact strength, a maximum was reached for R-BP contents of 40 and 80% for the V-B and V-P systems, respectively. In the case of tensile properties, the optimum UTS was 60% R-BP for the V-B system and 20% R-BP for the V-P system. Higher impact strength may also be due to the presence of modifier agents in the recycled pipes (R-BP).[5] Mechanical properties have been, therefore, well defined and this study was further supplemented by scanning electron microscopic studies of the selected fracture surfaces. Figure 9(a,b) shows the selected fracture surfaces of samples with the highest (80% R-BP) and the lowest (20% R-BP) impact strengths, respectively, in the V-P system. It can be seen that the surface of the sample with 80% R-BP shows ductile fracture, observed from the orientation or elongation of the PVC molecules [represented by a white phase as circled in Fig. 9(a)] in the direction to the impact force applied, whereas that of the sample containing 20% R-BR exhibited brittle fracture shown by the clear-cut fracture of the surface. Figure 9(c,d) shows selected fracture surfaces of samples with the highest (60% R-BP) and the lowest (20%

R-BP) impact strength, respectively, in the V-B system. The sample with the higher impact strength showed some indications of ductile fracture [as circled in the Fig. 9(c)] compared to that with a lower impact strength giving a brittle fracture surface. In addition to the SEM studies, the optimum tensile and impact properties for the particular R-BP loadings found were probably due to the existence of a network morphology, with the presence of primary and secondary crystallinity, this being also supported by many authors.[4,9,11]

Figure 10 illustrates the hardness property of PVC compounds containing different PVC recyclate contents. It can be observed that the hardness progressively increased with increasing R-BP content. For a given R-BP content, the V-B compound had higher hardness than that of the V-P compound. This behavior was mirrored to a certain extent by the density of the compounds as shown in Figure 11. In general, the higher the density, the greater the hardness.[4] The increase in the compound density was possibly associated with the degree of gelation which occurred during compounding. It was thought in this work that the R-BP compound, which had a greater processing time, had a more compacted and densified structure as compared to the two virgin grades tested, and, therefore, adding R-BP into the virgin compounds would lead to the increase in the apparent density and hardness of the compounds.
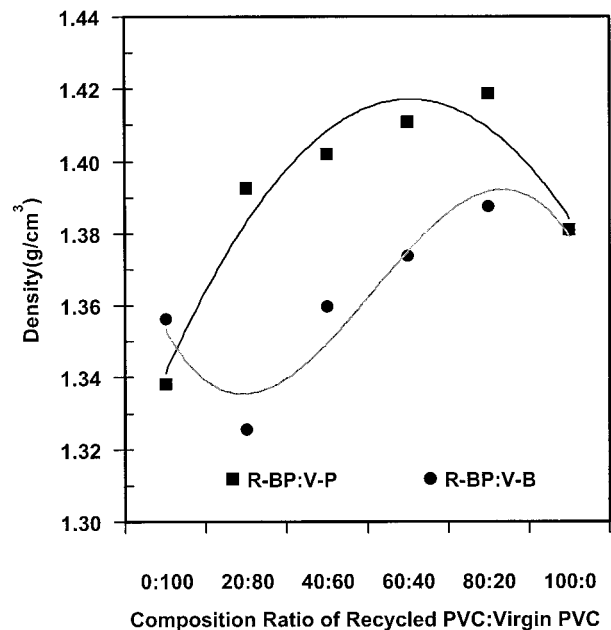
Figure 11 Effect of recycled PVC content on density.

CONCLUSIONS

The recycling of PVC pipes by adding them into two commercial PVC virgin grades for various concentrations was possible according to the following findings:

- Adding the PVC recyclate into the virgin PVC caused an increase in melt shear stress (or viscosity) and a decrease in the melt flow index. The die swell ratio did not change with the recycled PVC loading, but an excess swelling ratio was observed at a very high temperature (210°C) due to due to the PVC gelation characteristic.
- It was recommended that the virgin PVC bottle and PVC pipe grades be added by 40 and 80% wt PVC recyclate, respectively, to give the optimum impact strength and by 60% wt and 20% wt PVC recyclate, respectively, for the optimum UTS. The impact strengths can be explained using the morphological structure of the blends. The hardness corresponded well to the density of the blends: The higher the recycled PVC loading, the greater the hardness and density of the blends.
- The glass transition, degradation, and heat-deflection temperatures were also found to shift with the recycled PVC loadings.

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