Processing and Mechanical Properties of Recycled PVC and of Homopolymer Blends with Virgin PVC

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SYNOPSIS

Mechanical and processing properties of recycled polyvinylchloride (PVC, from bottles and pipes) were compared with those of virgin pipe grade PVC. Blends of recycled and pipe grade PVC were also prepared and characterized. It was found that the particle size and the restabilization of the recycled PVC are the two main points to be considered for obtaining virgin/recycled PVC blends with uniform and good mechanical properties. In general, recycled PVC not only does not significantly reduce the modulus and tensile strength, but also improves the impact strength and processing behavior of pipe grade virgin PVC. Only the thermomechanical resistance is slightly lowered. The latter points hold, of course, only when the recycled PVC contains both reinforcing and modifier agents. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyvinylchloride (PVC), as the second largest volume plastic used worldwide, plays an important role in the plastic industry and is an integral part of plastic recycling opportunities. Because of its compounding versatility, PVC can be processed into many short-life products, such as beverage packaging bottles, and long-life products such as appliances and pipes. Much research and industrial effort has been made for recycling PVC beverage bottles and other disposable goods like pipes, windows, and other semidurable and durable items.[1-5]

About 40% of PVC is used for making pipes. It should be appealing to blend the recycled PVC materials with virgin pipe grade PVC powder to make new pipe products. This study evaluates thermal stability and mechanical properties of the recycled PVC from postconsumer beverage bottles and pipes, and then reports the effects of recycled PVC on the processing and mechanical properties of recycled/virgin PVC blends in view of its use as pipe grade PVC.

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EXPERIMENTAL

Materials

Virgin pipe grade PVC powder (VPPVC), K value about 75, contains 2.4% $CaCO_3$ powder and 2% stabilizer and lubricant, and represents the typical formulation for pipes. Postconsumer PVC beverage bottles (RBPVC) were granulated into pieces through 9, 5, and 3 mm screens. The typical formulation of PVC for beverage bottles is reported in Table I. Recycled rigid PVC pipes (RPPVC), used about 5 years, were granulated into pellets through a 3-mm screen. The composition of the resin used for these products is unknown and different from that previously reported as VPPVC. Some qualitative tests suggest the presence of small amounts of rubber and larger contents of $CaCO_3$ (about 5%).

Processing

Before processing pure virgin and recycled PVC samples, 2–3 parts of stabilizer (dibasic lead hydrophosphite hemihydrate) were added to 100 parts of VPPVC, RBPVC, and RPPVC by using a Brabender laboratory twin screw Brabender Compounder model 42/7 attached to a Plasti-CORDER PLE651. This

Table I Typical Composition of Beverage Bottle PVC

	phr
PVC (K = 55–57)	100
MBS	6–10
Epoxidized soya oil	3–6
Stabilizers (Ca, Zn salts)	<1.5
Lubricants	<2

lead stabilizer is commonly used in Europe, mostly in pipe compounds and in general in nonfood PVC items. Virgin/recycled PVC blends were also prepared using this twin screw extruder. The composition of these blends is reported in Table II. The thermal profile was 140–155–165°C for RBPVC because of its low K value, 150–165–180°C for VPPVC, RPPVC, and for all blends. The screw speed was 60 rpm.

The samples for mechanical tests were obtained by compression molding in a laboratory press at 190°C for RBPVC, 195–200°C for VPPVC/RBPVC blends, and 200–205°C for VPPVC, RPPVC, and their blends.

Characterization

The dynamic thermal stability time (DTST) and the melt torque at equilibrium were measured using a Brabender mixer, 65-g sample, running at 190°C and 60 rpm. DTST is the time at which the torque in a mixing test starts to rise. The increase of the torque is a sign of the change of the structure. The material then can be processed for times lower than DTST.

Tensile measurements were carried out by means of an Instron machine (model 1122) at room temperature. A crosshead speed of 10 mm/min and a gauge length of 3 cm were used in all the measurements. Impact strength was determined using a Fractoscope (CEAST) in Izod mode with a notch of 2.54 mm. All the reported results are an average of at least seven measurements.

Dynamic mechanical properties were obtained by using a direct reading dynamic viscoelastometer, RHEOVIBRON Model DDV-II. The test frequency was 100 Hz and the heating rate about 2°C/min.

RESULTS AND DISCUSSION

Thermal Stability of Recycled PVC

The main disadvantage of PVC is the rather limited thermal stability that requires the addition of heat stabilizers to prevent extensive degradation. The stabilizer in PVC will be consumed both during processing and sometimes during the lifetime. Therefore the thermal stability is remarkably reduced in recycled PVC that undergoes more processing steps. It is then interesting and necessary to get information about the remaining stability of RBPVC and RPPVC before recycling.

The DTST is a good index for evaluating the thermal stability. The curves of torque vs. time of RBPVC, RPPVC, and those of the recycled PVC samples with 1–3 phr of stabilizer were determined and reported in Figures 1 and 2. DTST of RBPVC is less than 4 min and DTST of RPPVC is about 6 min. Some authors[4] consider that if DTST of rigid recycled PVC is less than 12–15 min, some stabilizer should be added to the material.

Figures 1 and 2 show that DTST of RBPVC in-

Table II Composition and Sample Code of Investigated Blends

Sample Code	Composition (phr)	Composition (%)
VRB20	VPPVC 100, RBPVC 20	VPPVC 83, RBPVC 17
VRB40	VPPVC 100, RBPVC 40	VPPVC 71, RBPVC 29
VRB60	VPPVC 100, RBPVC 60	VPPVC 62, RBPVC 38
VRB80	VPPVC 100, RBPVC 80	VPPVC 56, RBPVC 44
VRB100	VPPVC 100, RBPVC 100	VPPVC 50, RBPVC 50
VRP20	VPPVC 100, RPPVC 20	VPPVC 83, RPPVC 17
VRP40	VPPVC 100, RPPVC 40	VPPVC 71, RPPVC 29
VRP60	VPPVC 100, RPPVC 60	VPPVC 62, RPPVC 38
VRP80	VPPVC 100, RPPVC 80	VPPVC 56, RPPVC 44
VRP100	VPPVC 100, RPPVC 100	VPPVC 50, RPPVC 50

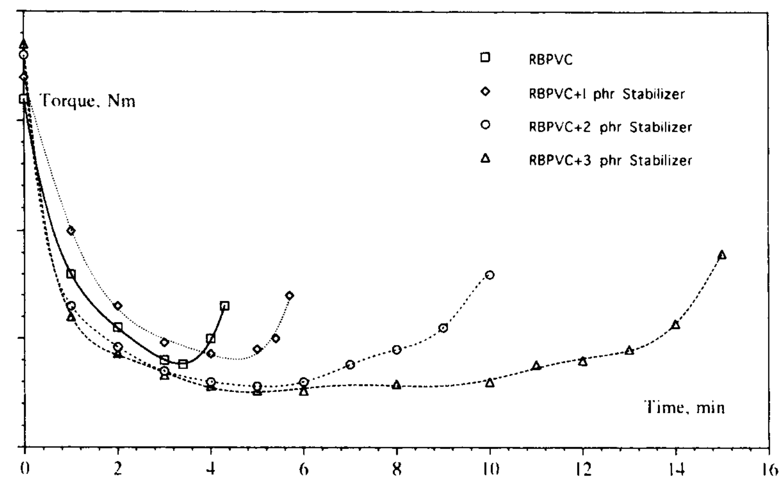

Figure 1 Torque values versus time for RBPVC at 190°C and 60 rpm.

creases to about 14 min by adding 3 phr of stabilizer; DTS of RPPVC increases to about 20 min by using 2 phr stabilizer. In the following, 3 phr of stabilizer were used for RBPVC and its blends, and 2 phr of stabilizer were used for RPPVC and its blends. It is worth noting that for processing times less than DTST, the material does not show any discoloration; significant discoloration is observed for larger processing times.

Processing and Properties of Virgin and Recycled PVC

The extrudability of the virgin and recycled PVC is an important point in view of possible applications of blends of these materials as pipe grade polymer. The torque can be considered a good parameter for evaluating the processability in this operation. The torques of these materials are reported in Table III. VPPVC shows the higher value of torque while RBPVC has the lower one. This result was expected on the basis of the lower molecular weight of the bottle grade PVC (K about 55 vs. about 75 for pipe grade) and of the presence of some modifiers. Much more surprising is the considerable difference between the torque values of VPPVC and RPPVC that can be attributed both to some difference in the K value and to the presence of modifier agents in this type of pipes.

The stress–strain curves of virgin and recycled

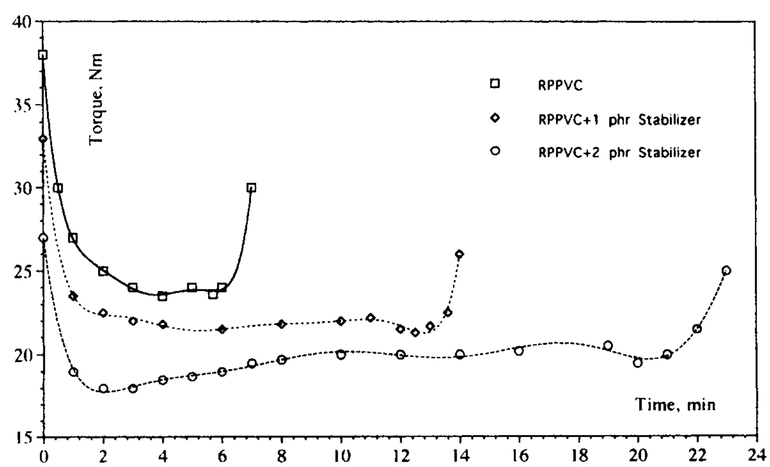

Figure 2 Torque values versus time for RPPVC at 190°C and 60 rpm.

Table III Torque at Equilibrium of Virgin and ecycled PVC

Sample	Torque (Nm)
VPPVC	25.5
RPPVC	20.0
RBPVC	18.0

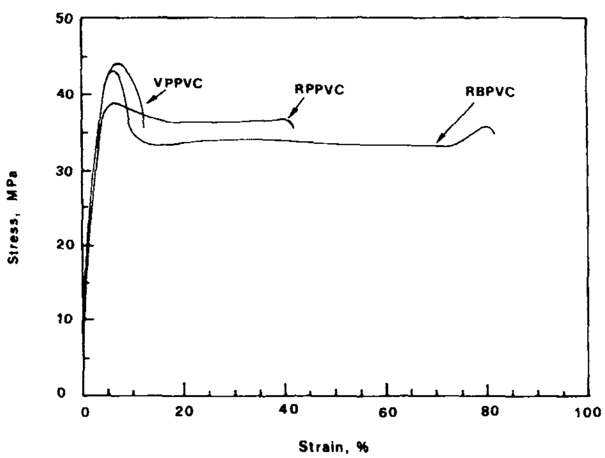

Figure 3 Stress–strain curves of virgin and recycled PVC samples.

PVC are shown in Figure 3. The stress–strain curve of VPPVC is typical for rigid PVC and shows low values of elongation at break. The curve of RBPVC shows that a recycled PVC bottle is a ductile material due to the presence of a high quality polymer modifier in the RBPVC. The curves of VPPVC and RPPVC are different. In particular the recycled material shows a ductile behavior with high values of elongation at break. This behavior confirms the presence of modifier agents in the recycled pipes.

Both tensile at yield and at break (Fig. 4) show similar values for all materials. This holds also for the strain at yield (Fig. 5); as already discussed, the elongation at break increases from VPPVC to RPPVC to RBPVC because of the increasing amount of impact modifier in the materials. Of course, for the same reason, the impact strength (Fig. 6) increases and the modulus decreases in the same way.

The thermomechanical properties were tested by measuring the storage and loss modulus as a function of the temperature (Figures 7, 8). The rigid VPPVC shows the better thermal resistance and its modulus does not change significantly below 85°C, about 15°C higher than that of RBPVC (Fig. 7). An intermediate behavior is shown again by RPPVC (Fig. 8) because of the presence of the elastomeric impact modifier in the recycled PVC pipe. The same conclusions can be drawn by considering the loss modulus curves reported in the same figures. The decrease of the glass transition temperature, as seen by the maximum in the E''-T curve, of the pure PVC suggests that the modifiers are compatible with the PVC.

Blends of Recycled and Virgin PVC

The blending of virgin and recycled PVC is remarkably influenced by the different size and shape of

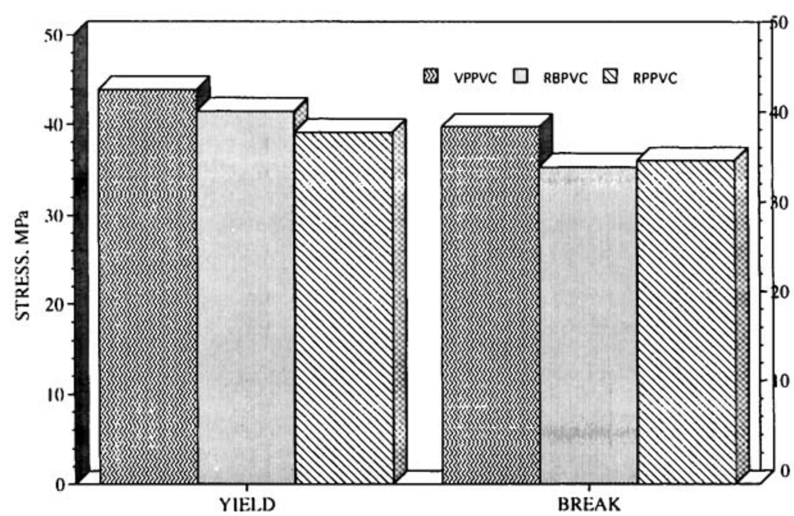

Figure 4 Stress at yield and at break for virgin and recycled PVC samples.

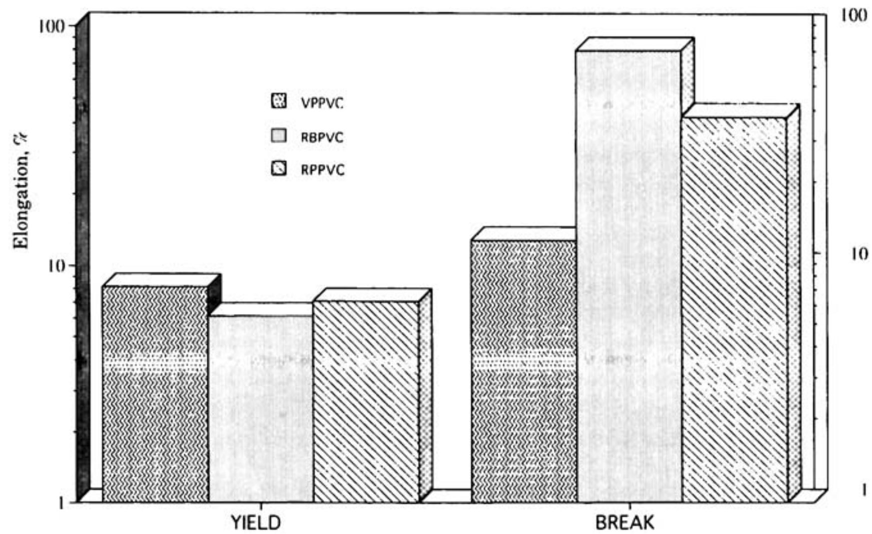

Figure 5 Elongation at yield and at break for virgin and recycled PVC samples.

the two materials. Virgin material is in the form of micronized powders; whereas the particles of the recycled polymer depends on the postconsumer products to be recycled, in this case, thin flakes for bottles and thick particles for pipes. Moreover the dimension depends on the granulation undergone before processing. Powder and particles having different shape, size, and apparent density fall down from the hopper in the extruder without keeping the composition ratio constant, such as the composition of the resulting material changes with time.

Before preparing the blends, the influence of the dimension of the PVC recycled particles and of the blending apparatus was investigated. In particular, flakes obtained from the granulation of the bottles through 3, 5, and 9 mm screens were blended with VPPVC powder in the ratio 80/100 and processed in the twin extruder. For comparison the same blend made with flakes of 9-mm maximum dimension were prepared in a mixer. Because the elongation at break is strongly affected by the inhomogeneity and heterogeneity of the materials, this characteristic was considered a good indication of the best blending conditions.

In Table IV the elongation at break data relative to VPPVC/RBPVC (100/80) blends are reported.

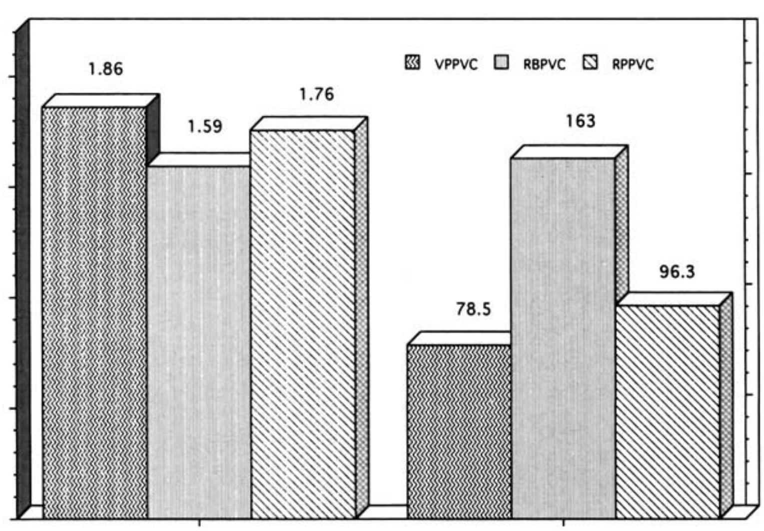

Figure 6 Modulus and impact strength for virgin and recycled PVC samples.

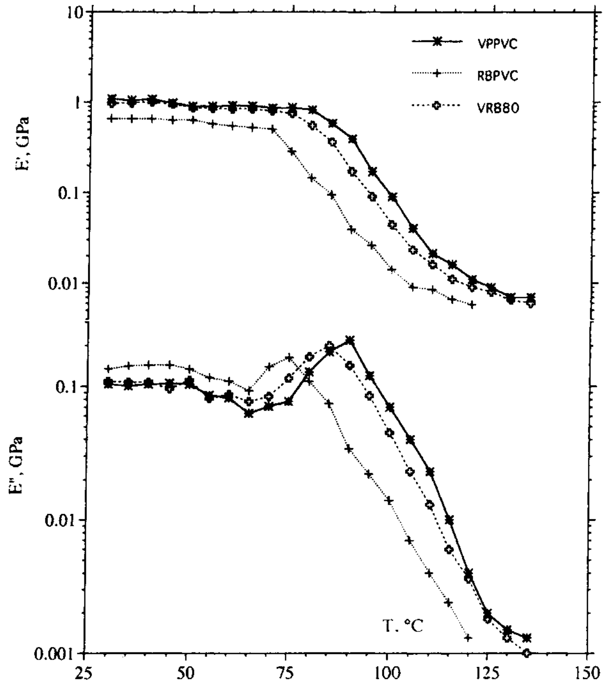

Figure 7 Dynamic modulus versus temperature for VPPVC, RBPVC, and their blends.

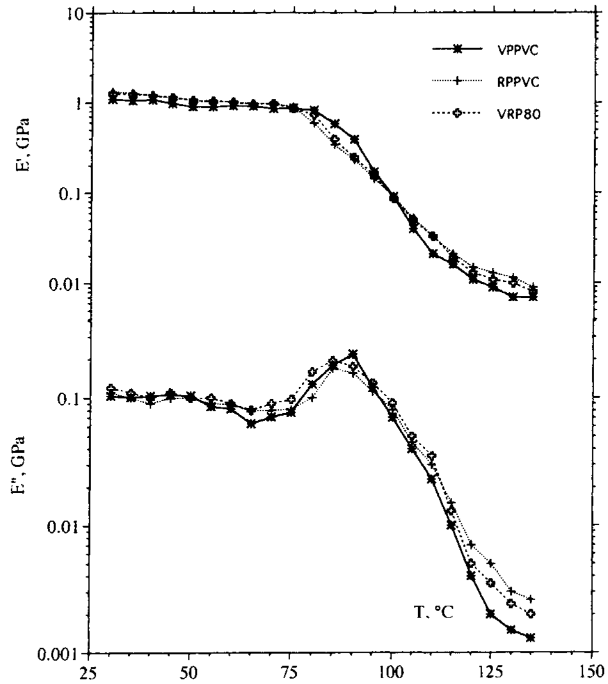

Figure 8 Dynamic modulus versus temperature for VPPVC, RPPVC, and their blends.

For all the blends the range of elongation at break values is quite large, but undoubtedly decreases with decreasing the size of the recycled particles. The scattering of the EB data can be attributed, besides the incompatibility arising from the different molecular weight of the two compounds, to the different composition of the sample caused by the insufficient dry blending and inconstant feeding of the extruder. This suggests that the preparation of the blend in an internal mixer should overcome this shortcoming. The data reported in Table III, which refers to the previous maximum size particle of RBPVC (9 mm), confirms that the elongation at break of samples prepared in the internal mixer are much more reproducible and the average value is higher than that obtained in the extruder, although a quite large scattering of data is still present. These VPVC/RPVC blends have, then, to be considered as biphasic materials with inhomogeneities which give rise to some scattering in the values of the mechanical properties. In the following the mechanical characterization of all the blends will refer to materials prepared in the compounder with RPVC particles granulated through a 3 mm screen.

The mechanical properties of VPPVC/RBPVC and VPPVC/RPPVC blends are shown in Figures 9–14 as a function of the content of recycled PVC. For both systems all the properties of the blends are between those of the two compounds and show an almost additive behavior. Only elongation at break and impact strength are significantly lower than those expected on the basis of an additive rule. However, the impact strength of the blends with high contents of RBPVC again shows an additive behavior.

It is interesting to note that impact strength and EB of these blends are remarkably better than those of the virgin materials for pipe, while the other properties are not significantly modified. This is due, of course, to the modifier agents present in the

Table IV Influence of Maximum Size of RBPVC and of Mixing Apparatus on Elongation at Break (EB) of VPPVC/RBPVC (100/80) Blend

Maximum Size and Mixing Apparatus	EB (%)	Average EB (%)
9 mm, extruder	20–120	60
5 mm, extruder	40–110	70
3 mm, extruder	70–115	80
9 mm, mixer	75–115	85

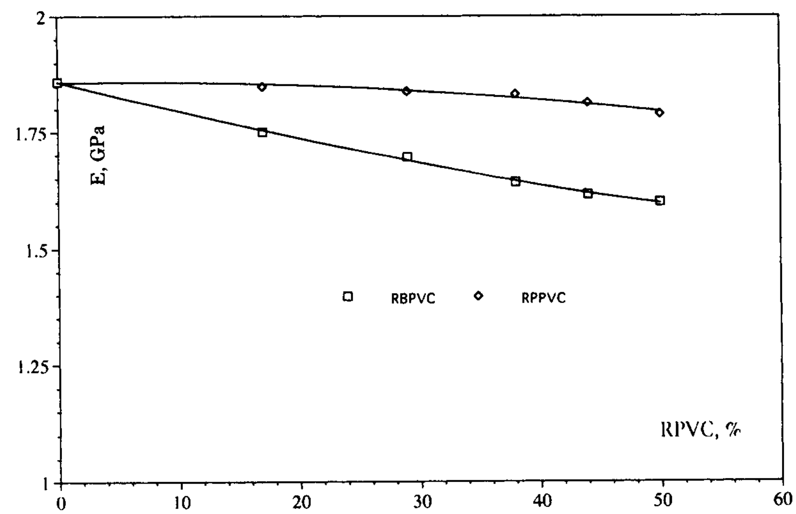

Figure 9 Modulus versus RPVC content in VPVC/RPVC blends.

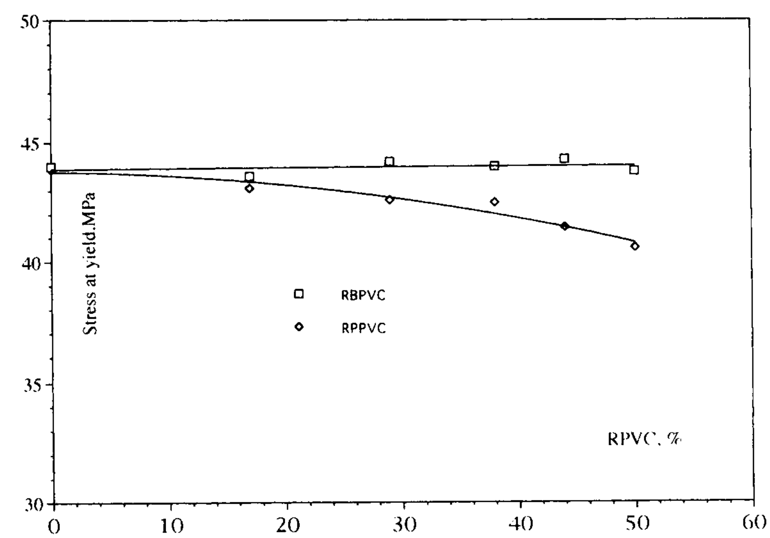

Figure 10 Stress at yield versus RPVC content in VPVC/RPVC blends.

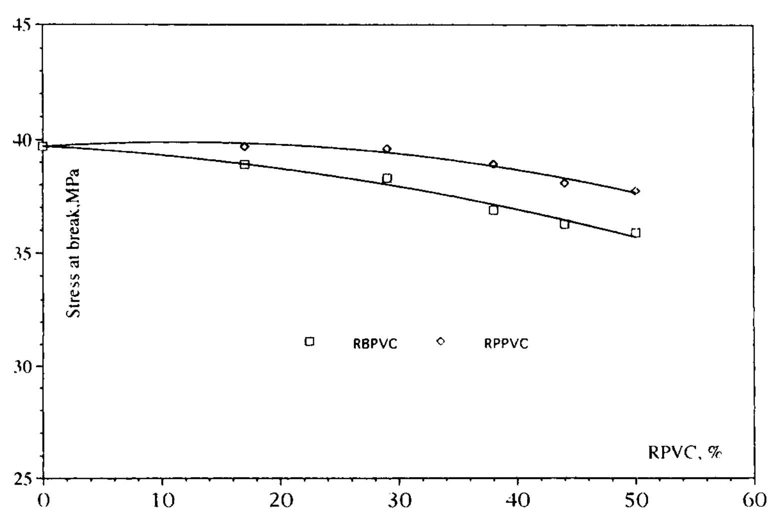

Figure 11 Stress at break versus RPVC content in VPVC/RPVC blends.

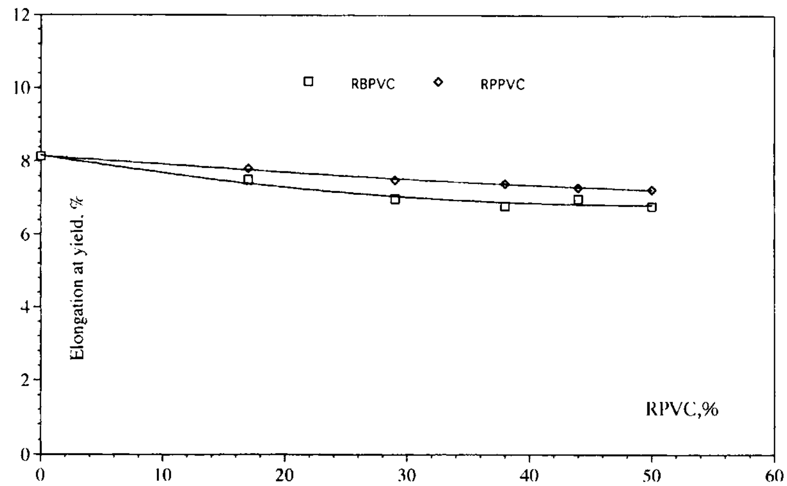

Figure 12 Elongation at yield versus RPVC content in VPVC/RPVC blends.

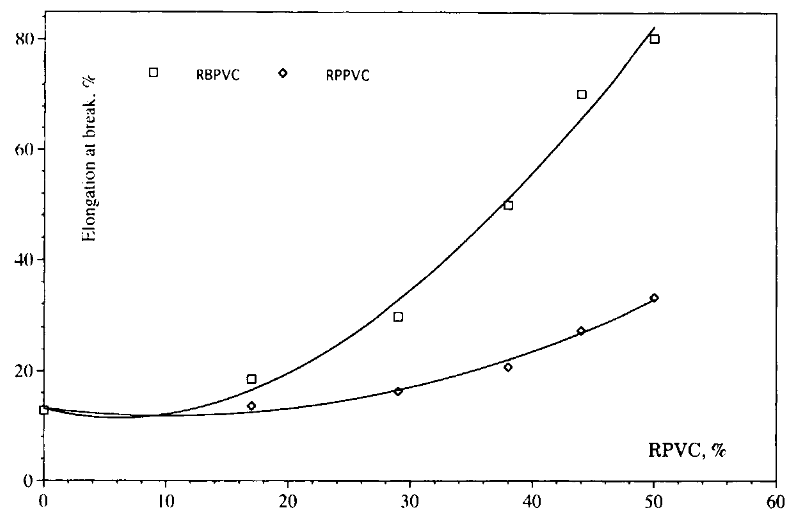

Figure 13 Elongation at break versus RPVC content in VPVC/RPVC blends.

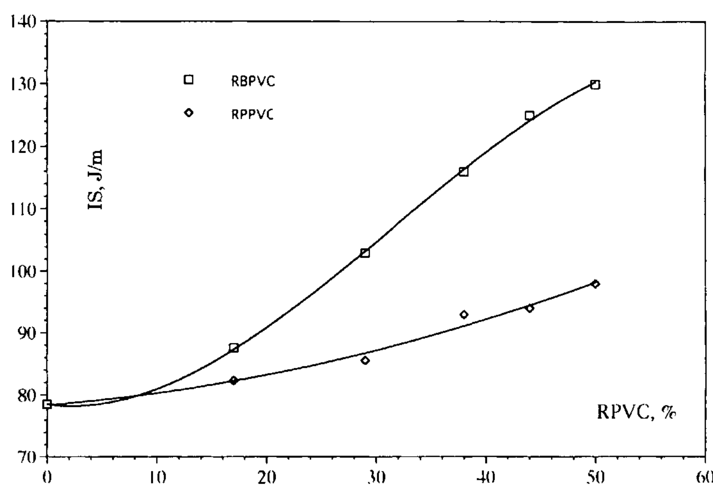

Figure 14 Impact strength versus RPVC content in VPVC/RPVC blends.

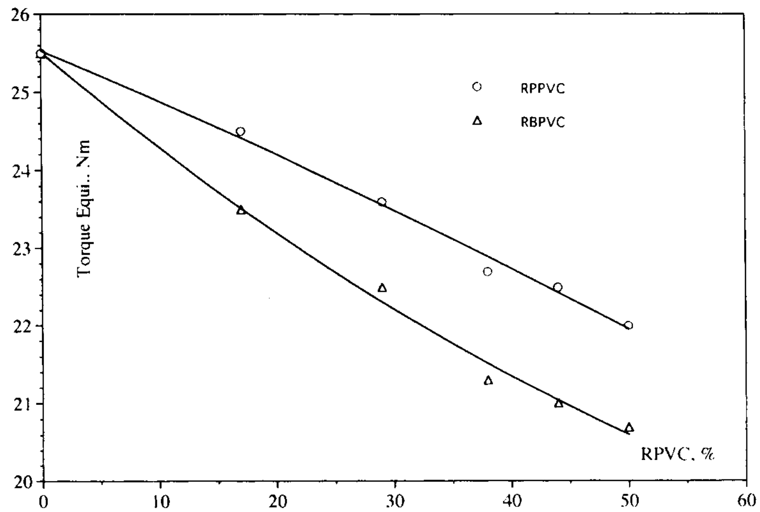

Figure 15 Torque at equilibrium versus RPVC content in VPVC/RPVC blends.

RBPVC. Then, this modifier agent improves some critical properties of the virgin pipe grade PVC, in particular EB and IS, without appreciably worsening other characteristics like the thermomechanical resistance. The curves of dynamic modulus versus temperature for VPVC/RPVC (100/80) blends are shown in Figures 7 and 8. RBPVC reduces the softening temperature of the blend by about 5°C, while the softening temperature of the blend with RPPVC is almost uninfluenced.

The processability of pipe grade PVC can also be improved by adding recycled PVC. Torque at equilibrium during mixing at 190°C and 60 rpm was recorded and reported in Figure 15 or all the virgin/recycled PVC blends. Both recycled PVC samples significantly reduce the values of the torque of VPPVC, and RBPVC is particularly effective. It is also worthwhile to mention that the processing temperature of blends with recycled PVC bottles is lower than that of virgin pipe PVC, allowing a significant energy saving.

CONCLUSIONS

PVC recycled from beverage bottles and from pipes must be stabilized before further processing due to their low thermal resistance caused by the loss of the stabilizer during processing and lifetime. Recycled PVC from bottles possesses lower tensile strength and modulus, and higher elongation at break and impact strength than those of virgin pipe grade PVC because of the presence of impact modifier in the RBPVC. PVC recycled from pipes used for 4–5 years again shows better elongation at break and impact strength values, perhaps for the same reason. These bottles and pipes granulated to small size particles were blended with virgin PVC powder. The properties of the blends with recycled PVC are between those of the compounds, and the IS and EB of the blends with high RBPVC content are very large. Only the thermomechanical resistance is slightly lower. The presence of reinforcing and impact modifier agents in the recycled PVC blends can improve some mechanical properties of pipe grade PVC and also the processability of this material.

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