

Blends of Plasticized Poly(vinyl chloride) and Waste Flexible Poly(vinyl chloride) with Waste Nitrile Rubber Powder

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ABSTRACT: Blends of poly(vinyl chloride) (PVC) with varying contents of plasticizer and finely ground powder of waste nitrile rubber rollers were prepared over a wide range of rubber contents through high-temperature blending. The effects of rubber and plasticizer (dioctyl phthalate) content on the tensile strength, percentage elongation, impact properties, hardness, abrasion resistance, flexural crack resistance, limiting oxygen index (LOI), electrical properties, and breakdown voltage were studied. The percentage elonga-

tion, flexural crack resistance, and impact strength of blends increased considerably over those of PVC. The waste rubber had a plasticizing effect. Blends of waste plasticized PVC and waste nitrile rubber showed promising properties. The electrical properties and LOI decreased with increasing rubber and plasticizer content. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1552–1558, 2004

Key words: poly(vinyl chloride) (PVC); rubber; blends

INTRODUCTION

The disposal of waste rubber is a serious environmental problem. Vulcanized rubber is not biodegradable. Although thermoplastic materials can be reprocessed or recycled, vulcanized rubber cannot be reprocessed by melting because it is crosslinked. The use of such rubber as filler is commercially and academically very attractive. Blends of finely ground rubber tire with thermoplastics have been studied.^{1–7} Most of the rubbers, however, are not compatible with a majority of commodity plastics. Also, grinding the rubber into fine powder is energy-consuming, and the compositions of different tires are different.

Nitrile rubber and poly(vinyl chloride) (PVC) are compatible, and they may form a self-crosslinkable system.^{8–13} A significant quantity of nitrile rubber waste is generated from used rubber rollers from the printing industry. Tipanna and Kale¹⁴ reported a considerable increase in the impact properties and flexural crack resistance of rigid PVC when it was blended with waste nitrile rubber. The processing of PVC is much easier when a plasticizer is compounded with it. Also, waste flexible PVC generated in large quantities contains significant quantities of plasticizer. The utilization of such waste should be of interest to many.

Although PVC and nitrile rubber are compatible, there are no data on the effects of plasticizer content on the properties of such blends. Similarly, the properties of blends made from plasticized waste PVC and waste rubber have not been studied. In this study, we investigated these aspects.

EXPERIMENTAL

Materials

PVC resin (K57-01), with a *K* value of 57 and used for general-purpose extrusion, was supplied by Reliance Industries, Ltd. (Mumbai, India). The *K* value is related to molecular weight,¹⁵ and the higher the *K* value is, the higher the molecular weight is. Tribasic lead sulfate and dibasic lead stearate, used as heat stabilizers, were supplied by Indofil Chemicals, Ltd. (Mumbai, India). Calcium stearate as a processing aid and other proprietary additives such as lubricants were supplied by Fine Organics, Ltd. (Mumbai, India). The plasticizer, dioctyl phthalate (DOP), was procured from a local supplier. The ground nitrile rubber powder was procured from a local manufacturer of rubber rollers (SPASA Industries, Ltd., Mumbai, India). These rollers were made from nitrile rubber, KSR-35-1, with an acrylonitrile (AN) content of 33% (Kumbho Synthetic Rubber, South Korea). The used rubber rollers were machined to fine powder to remove all of the rubber up to a metal mandrel. The new rollers were then recast on these mandrels. The rubber rollers used for the offset printing (lithographic) process normally

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contain 100 parts nitrile rubber; 50 parts phthalate type plasticizer; 60–65 parts fillers; 7–8 parts different additives, including sulfur as a vulcanizing agent; and 5 parts carbon black. The particle size of the waste rubber powder was around 100–300 μm.

The grade of nitrile rubber used in these rubber rollers was KSR 35-1, which contained AN up to 33%. This was as per the specifications of Kumbho Synthetic Rubber. The used rubber rollers may have contained very small amounts of dried offset ink. The amounts, however, should have been very negligible, as a very thin layer of dried ink may have remained on the used rollers. Therefore, the composition of rubber rollers presented earlier should be the same as given previously.

Waste flexible PVC used in making tourist bags was procured from Srijji Plastics (Mumbai, India). The waste PVC was dissolved in the solvent cyclohexanone. The undissolved fillers and some stabilizers were filtered out, dried, and weighed. The filtrate contained PVC and plasticizer. PVC was reprecipitated from this by the addition of methanol. The PVC was filtered, dried, and weighed. Thus, the approximate composition of waste PVC was 33–35 phr plasticizer, whereas the filler content was about 15 phr. The plasticizer used in India is generally DOP or its mixture with dibutyl phthalate. Virgin nitrile rubber used was supplied by APAR Industries, Ltd. (Mumbai, India), with an AN content of 33%.

Compounding

PVC resin, heat stabilizers, processing aids, lubricants, and plasticizer were dry-blended in a high-speed blender (M/s Neoplast, Ahmedabad, India) at 60°C. The speed of blending was 80 rpm. The blending was carried out for 2 min. The waste nitrile rubber powder, predried at 120°C for 10 min to remove any surface moisture, was added to the blender, and mixing was carried out for an additional 8 min. The mixture was then immediately fed to a corotatory twin-screw extruder (MP19TC, APV Baker, United Kingdom), with an length to diameter (L/D) ratio of 25:1. The screw speed was 100 rpm, and the temperature profile for compounding was 130, 140, 150, and 160°C for four zones and 170°C for the die zone. For comparison, the effect of virgin nitrile rubber was also studied. The extrudate from the screw compounder was air cooled and pelletized. Similarly, the properties of blends prepared with waste PVC and waste nitrile rubber were studied. The main aim of this work was to study the blends of waste nitrile rubber. Therefore, a blend of virgin nitrile rubber with waste PVC was not studied. Table I shows the various compositions studied. The additives and plasticizer are expressed as the amount by weight per 100 parts of PVC resin (phr, or per hundred parts of resin). Thus, when the PVC content

TABLE I
Various Compositions Studied

Sample	Composition		
	PVC (%)	Waste rubber (%)	DOP (phr)
1	100	0	10
2	80	20	10
3	65	35	10
4	50	50	10
5	35	65	10
6	20	80	10
7	65	35	40
8	65	35	60
	PVC (%)	Virgin rubber (%)	
9	65	35	10
10	65	35	40
11	65	35	60
	Waste PVC (%)	Waste rubber (%)	
12	65	35	—
13	50	50	—
14	35	65	—

decreased, the amount of additives and plasticizer also decreased proportionately. Thus, the weight ratio of PVC to DOP was always maintained as 10, 40, or 60 parts of DOP per 100 parts of PVC resin. The rubber content was percentage by weight in comparison to the dry PVC resin only.

Testing

The pellets of the blends were dried and molded into thin sheets 2 mm thick with a compression-molding machine (a Sterling hydraulic compression-molding machine, Mumbai, India) with a pressure of 150 kg/cm² and a platen temperature between 170 and 185°C. The specimens for tensile testing as per ASTM D 638 were punched from the sheet. The tensile strength was measured with a universal tensile testing machine (LR50K, Lloyds, Farcham, United Kingdom) with a crosshead speed of 50 mm/min. Charpy impact strength was measured (with an Avery Denison impact tester, Leeds, UK) with 2.7- and 15-J strikers with a striking velocity of 3.46 m/s. Shore hardness (ASTM D 2240), flexural-crack resistance (ASTM D 430), and abrasion characteristics (ASTM D 1242) were determined with a machine supplied by Zwick and Co. K.G. (Einsingen, Belgium). Volume resistivity and breakdown voltage were measured as per ASTM D 257 and D 149, respectively. Similarly, the limiting

TABLE II
Mechanical Properties of Various Rubber Blend Compositions

Sample	PVC (wt %)	Waste rubber (wt %)	DOP (phr)	Tensile strength (MPa)	Elongation at break (%)	Shore hardness (A)	Impact strength (kgcm/cm)	Flex crack resistance (cycles before breaking)	Weight loss due to abrasion (%)
1	100	0	10	43.5	118	52	10.0	1	0.68
2	80	20	10	22.4	227	50	No break	2,922	0.69
3	65	35	10	13.7	406	52	No break	51,021	0.73
4	50	50	10	9.4	511	42	No break	279,360	1.14
5	35	65	10	7.4	675	40	No break	>300,000	1.21
6	20	80	10	3.6	599	24	No break	>300,000	2.16
7	65	35	40	8.8	390	28	No break	>300,000	1.13
8	65	35	60	5.6	423	18	No break	>300,000	1.21
	PVC	Virgin rubber							
9	65	35	10	14.0	616	35	No break	72,196	0.90
10	65	35	40	6.2	554	15	No break	118,652	0.91
11	65	35	60	3.8	474	10	No break	182,569	1.40
	Waste PVC ^a	Waste rubber							
12	65	35	—	10.7	547	30	No break	>300,000	0.57
13	50	50	—	7.6	549	20	No break	>300,000	0.73
14	35	65	—	4.9	620	15	No break	>300,000	0.84

^a Waste PVC contained a total plasticizer content of about 35 phr.

oxygen index (LOI) was determined as per ASTM D 2863.

RESULTS AND DISCUSSION

Effect of rubber content

Table II shows the mechanical properties of different composites prepared with varying rubber and low plasticizer contents (10 phr). As the amount of rubber content increased, the tensile strength decreased considerably but the percentage elongation at break, impact strength, and flexural crack resistance increased substantially. The shore hardness was not seriously affected until the concentration of waste rubber reached 35%, beyond which it decreased noticeably. The percentage weight loss due to abrasion increased as the percentage nitrile rubber increased. It is known that the addition of plasticizer results in increased percentage elongation and impact strength, whereas flexural crack resistance increases only marginally.¹⁵ The increase in impact properties with increasing rubber content, however, appeared to be an order of magnitude higher when compared with reported values for plasticized PVC.

Pena et al.¹⁶ reported the plasticizing action of rubber. From these results, we concluded that waste rubber also has some plasticizing effect on PVC.

Table III shows the electrical and flame-retardant properties of different compositions prepared with varying rubber contents. As the rubber content in-

creased, the breakdown voltage and volume resistivity decreased steadily. The LOI of the composites did not show significant change until the content reached 35%. At higher concentrations, however, it decreased steadily. Waste PVC contains some fillers and the plasticizer can be different than DOP. Although PVC is flame retardant, the incorporation of plasticizer reduces the flame retardancy of PVC. A reduction in LOI with increasing plasticizer is normally observed. The addition of waste nitrile rubber had some plasticizing effect, and the LOI did not change significantly from that for plasticized PVC.

A comparison of the properties of blends containing virgin and waste rubber (compositions 3, 7, and 8 and 9, 10, and 11, respectively) showed that the tensile strength and impact strength appeared to be similar whether virgin or waste rubber was used. The shore hardness was significantly higher for compounds containing waste rubber. At low plasticizer contents, the percentage weight loss due to abrasion seemed to be lower for the blends containing waste rubber. Similarly, the flexural crack resistance at higher plasticizer contents was higher for the blends containing waste rubber. The percentage elongation at break for the compositions containing waste rubber was lower than that for virgin rubber. The breakdown voltage appeared to be higher for the blends containing waste rubber. The volume resistivity seemed to be comparable for compositions containing waste and virgin rubber. The LOI for the blends containing waste rubber

TABLE III
Electrical and Flame-Retardant Properties of Various PVC–Nitrile Rubber Blend Compositions

Sample	Composition			Break down voltage (KV/mm)	Volume resistivity (Ωcm)	LOI at 27°C
	PVC (%)	Waste rubber (%)	DOP (phr)			
1	100	—	10	24.57	3.2×10^{17}	26.9
2	80	20	10	20.54	1.76×10^{17}	27.7
3	65	35	10	17.96	ND	26.1
4	50	50	10	15.30	3.9×10^{16}	25.4
5	35	65	10	13.02	2.3×10^{16}	23.5
6	20	80	10	10.59	3.5×10^{16}	21.3
7	65	35	40	16.66	4.1×10^{16}	22.3
8	65	35	60	15.52	1.4×10^{16}	21.9
	PVC (%)	Virgin rubber (%)				
9	65	35	10	16.15	7.0×10^{16}	23.5
10	65	35	40	13.33	3.9×10^{16}	21.2
11	65	35	60	11.16	1.4×10^{16}	20.4
	Waste PVC (%)	Waste rubber (%)				
12	65	35	—	11.05	3.9×10^{14}	26.8
13	50	50	—	10.28	ND	24.3
14	35	65	—	8.67	ND	21.8

ND = reproducible results could not be determined.

was marginally higher than that for virgin rubber. Thus, the properties of the blends of PVC and virgin or waste nitrile rubber powder were fairly comparable.

Effect of plasticizer content

At a given concentration of rubber (compositions 3, 7, and 8), the tensile strength, shore hardness, and abrasion resistance decreased as the amount of DOP increased. With increasing plasticizer content, the PVC compound became softer, and hence, the abrasion resistance decreased or the weight loss due to abrasion increased. The percentage elongation at break remained relatively unaffected, and the flexural crack resistance increased. Similar effects were observed when the amount of DOP was increased for the blends containing virgin rubber.

In general, the breakdown voltage, volume resistivity, and LOI decreased as amount of plasticizer increased. Waste rubber also had a plasticizing effect, but the decrease in these properties with increasing amounts of rubber was not as much as that with increasing amounts of plasticizer.

IR spectroscopy

Figures 1–4 show the IR spectra for waste nitrile rubber, virgin nitrile rubber, and blends of PVC with

virgin and waste nitrile rubber. The IR spectra did not show significant change when waste nitrile rubber was added. The main aim was to see if there was any chemical reaction between PVC and waste nitrile rubber. The IR spectra shown here did not show any evidence of chemical interaction between waste nitrile rubber and PVC. The reasons for these are discussed now. Because the vulcanization of rubber takes place at the double bond in the main chain, most characteristics of the virgin and waste rubber were comparable except CH₂ stretching.

Manoj and De³ discussed the crosslinking between PVC and nitrile rubber. During this reaction, a nitrile group is involved. However, for such a reaction, a free radical on PVC is necessary, which is normally formed through the degradation of PVC. Also, the temperature should be high, and long reaction times are necessary. In this study, the reaction times, that is, the processing times, were on the order of 5 min, and PVC was stabilized with thermal stabilizers. Therefore, the extent of such a self-crosslinking reaction between PVC and virgin or waste nitrile rubber may have been very small, and it was not detected by IR studies. Thus, the change in the properties of PVC could be attributed to only physical interactions between PVC and waste nitrile rubber. The virgin or crosslinked nature of rubber did not make any difference for such interactions, as suggested by Zytek and Zelinger.¹¹

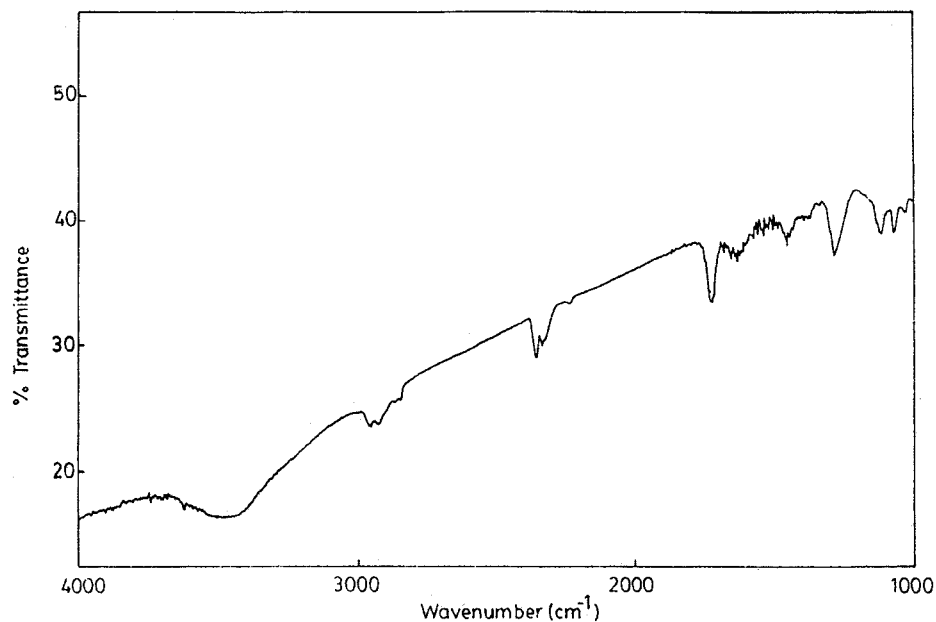


Figure 1 IR spectra of waste nitrile rubber.

Effect of waste rubber content on waste flexible PVC

Tables II and III also show the properties of the blends prepared from waste flexible PVC and waste nitrile rubber. The waste PVC contained about 35 phr plasticizer and 15 phr filler. Therefore, the composition (65/35 waste PVC/waste rubber) was recast in terms of the actual PVC used. Thus, 65 parts

of PVC were made up of about 43 parts PVC, 15 parts of plasticizer, and 5 parts of filler. The tensile strength, percentage elongation, impact strength, flexural crack resistance, LOI, and breakdown voltage of these compounds compared reasonably with those made from virgin PVC. The mechanical properties of these blends also depended on morphology. Meaningful scanning electron microscopy

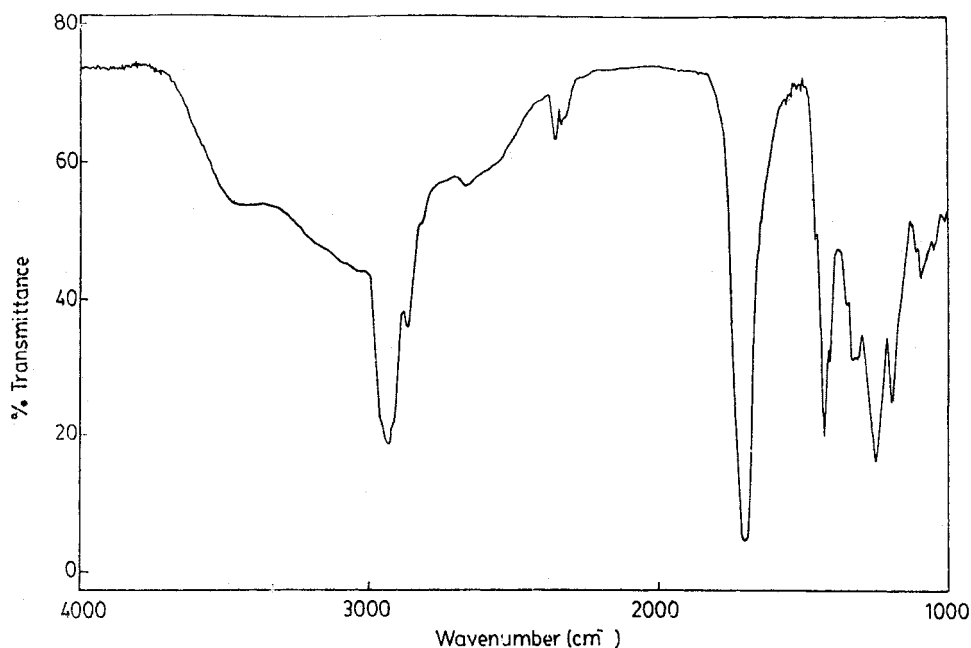


Figure 2 IR spectra of virgin nitrile rubber.

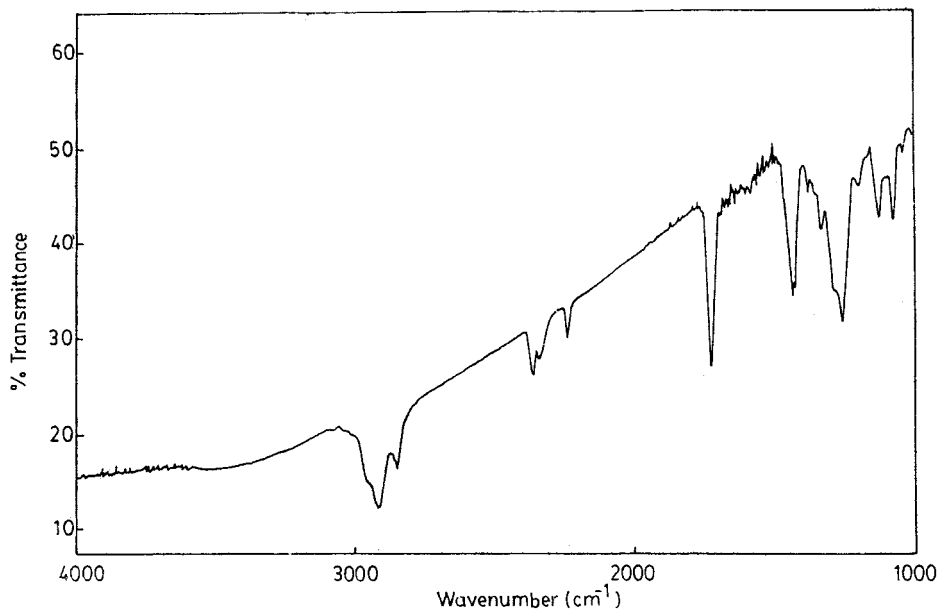


Figure 3 IR spectra of PVC/virgin rubber (65/35/10 phr DOP).

could not be carried out because of the presence of fillers and carbon black.

CONCLUSIONS

We significantly increased the impact strength and percentage elongation of plasticized PVC by blending it with finely ground waste nitrile rubber. The physical interaction or solubility of nitrile rubber in PVC

seemed to be the more likely reason for such changes in the properties of flexible PVC. When the plasticizer content was increased, there was a decrease in tensile strength, shore hardness, abrasion resistance, breakdown voltage, volume resistivity, and LOI. The abrasion resistance and shore hardness decreased. The breakdown voltage, volume resistivity, and LOI decreased when the loading of waste rubber was more than 35%.

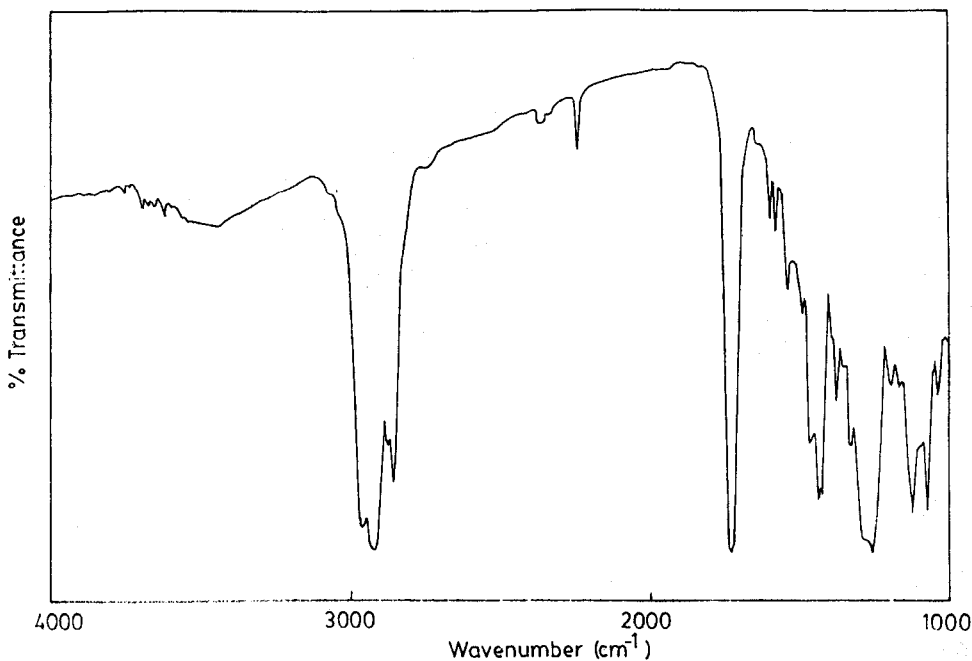


Figure 4 IR spectra of PVC/waste rubber (65/35/10 phr DOP).

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