Recycling of High Density Polyethylene/Poly(vinyl chloride)/Polystyrene Ternary Mixture with the Aid of High Energy Radiation and Compatibilizers

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ABSTRACT: Ternary mixtures of waste plastics of high density polyethylene (HDPE), poly(vinyl chloride) (PVC), and polystyrene (PS) was recycled using a single-screw extruder. Poly(ethylene-*co*-vinyl acetate) and poly(styrene-*b*-ethylene/butylenes-*b*-styrene) were introduced as compatibilizers for HDPE/PVC and HDPE/PS, respectively. After the polymer blends was prepared via extrusion, they were subjected to high energy irradiation. The morphology and the mechanical properties of the hybrid blends were examined. Scanning electron micrographs and transmission electron micrographs showed that both compatibilizers and irradiation improved the uniformity and dispersion of the system. The heterogeneous crosslinking generated by irradiation resulted in an optimum impact strength. High elongation at break was achieved by using compatibilizers. The improvement of tensile strength was moderate. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2756–2762, 2003

Key words: recycling; blend; irradiation; compatibilizer

INTRODUCTION

Pushed by ecological and environmental requirements, plastics recycling has attracted more and more attention. Approaches to plastic recycling mainly include three options: (1) mechanical or material recycling, (2) chemical recycling, and (3) energy recovery.[1–4] In the modern sense, plastics recycling does not simply mean "to remove the trash" or "to make use of the waste," but "to yield useful materials." The recycling of industrial plastic scraps has been an ongoing practice in many manufacturers. Industrial scrap is relatively easy to deal with for the simple reason that contamination from other plastics is unlikely. This does not hold true for municipal plastic waste because it is often a mixture of several plastics. In the recycling of this plastic waste, people have to deal with two issues: (1) the molecular weight of the plastics was decreased during the service time, and (2) they are usually mixtures of several different immiscble plastics, which result in inferior mechanical properties. A number of approaches are currently being investigated for dealing with plastic waste: to introduce compatibilizers[5–7] and to subject the mixture to high energy irradiation[8–10] constitute two main measures to improve the properties of the mixture.

High density polyethylene (HDPE), poly(vinyl chloride) (PVC), and polystyrene (PS) are three most frequently used plastics, whose scrap and used packages are often mixed together. The recycling of a mixture of the three is difficult, because each one is not compatible with the other two—blending of the three will definitely result in phase separation and hence poor mechanical properties. In order to improve the compatibilization, compatibilizers have been employed in polymer blends. For instance, chlorinated polyethylene (CPE) has been used as a compatibilizer for HDPE and PVC pairs[11–14]; the styrene–ethylene block copolymer (SEP) has been used for HDPE and PS pairs.[15,16] However, compatibilizers for binary systems are not always satisfactory for ternary ones, and few attempts were made to recycle the mixtures of three or more plastics.

In this work, an investigation was conducted to recycle a ternary mixture using compatibilizers combined with high energy irradiation. Poly(ethylene-*co*-vinyl acetate) (EVA) was introduced to compatibilize HDPE and PVC; poly(styrene-*b*-ethylene/butylenes-*b*-styrene) (SEBS) was introduced to compatibilize HDPE and PS. Various doses of ^{60}Co γ-irradiation was carried out after the components were blended using an extruder. High energy irradiation constitutes a powerful method to generate crosslinking and/or grafting, and to produce functional group on the surface of some polymers, though the mechanism of the reaction under irradiation was not clearly known. In many research works the irradiation was carried out before or during the plastics were blended.[8–10] However, in the former procedure, no mutual crosslinking can be generated; in the latter one, the equipment was

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expensive and complicated. In this work, the irradiation was carried out after the blends were prepared. The mechanical properties and the morphology of the blends were examined.

EXPERIMENTAL

Materials

Waste HDPE and PVC [plasticized with 50 parts of dioctyl phthalate (DOP)] were received as films. Waste PS was received as transparent cases. All the waste plastics were carefully washed, dried, and cut into small pieces before use. EVA and SEBS were supplied by Japan Chemical Co. Ltd.

Specimens preparation

Waste plastics were machanically mixed and fed into the barrel of a single-screw extruder. The materials were extruded at a screw speed of 40 rpm. The temperature at 3 zones of the barrel and at the die was 160, 190, 200, and 190°C, respectively . The strands extruded were quenched into water and cut into small granules by a pelletizer. Using these pellets, impact bars and dumbell tensile specimens were injection molded with an injector (Auckland M20-55, Switzerland). The injection pressure was 179MPa.

Irradiation

The γ-irradiation was carried out directly on the specimens using ^{60}Co industrial equipment at room temperature in the air before they were tested. The samples were exposed to 50,100,150, and 200 kGy doses.

Mechanical property measurement

The tensile properties were determined with an Instron Universal Testing Machine (model 1130) according to ASTM D638 at room temperature. The notched Izod impact strength was determined using a Sumitomo impact tester according to ASTM D256. The thickness of the Izod impact specimens was 1/8 in. Five determinations were carried out for each data point.

Electron microscopy observation

Scanning electron microscopy (SEM) was used to examine the fractured surfaces of impact bars. The fractured surfaces were sputter coated with gold before examination with an electron microscope instrument (Cambridge S250, UK).

Morphology was determined by transmission electron microscopy (TEM). Samples were cryogenically microtomed using a diamond knife and stained with ruthenium tetroxide (RuO_4). A Hitachi H-800 (Japan) transmission electron microscope was used to view and photograph these samples.

RESULTS AND DISCUSSION

The effects of the compatibilizers and irradiation are discussed below. Since an effective ternary compatibilizer for the HDPE/PVC/PS system was not available, two binary compatibilizers, SEBS and EVA, were used instead. It was well known that SEBS is a good compatibilizer between HDPE and PS, and EVA is a good one between HDPE and PVC; their combination was considered as a substitutive of a ternary compatibilizer. For this reason, the two compatibilizers are considered as one component in this paper and are not be treated separately.

The waste PVC used in this paper is plasticized with 50 parts of DOP. During the recycling, DOP may migrate into other components, and thus affect the properties and morphology. However, since neither HDPE nor PS is polar, the migration was rather limited. For this reason, PVC resin and DOP are considered as a single component, which covered the effect of DOP.

Morphology

The morphologies of the fractured surface of the samples based on various compositions and different doses of irradiation are presented in Figure 1. We may find that both the compatibilizers and the irradiation improved the compatibility of the components. Comparing the pictures horizontally (different compatibilizer content, constant irradiate dose), we may find the effects of the compatibilizers were the improvement of the dispersion of the components and the flexibility of the system. The improvement in dispersion is best demonstrated by Figures 1-2a, 1-2b, and 1-2c in the second row. When the amounts of EVA and SEBS were increased to 7.5 parts, foam-like structures were observed, which were formed by pulling off the dispersed phase from the continuous one. When the amount of the compatibilizers was 15 parts each, the foam became even finer, which means the size of the dispersed domain was greatly decreased. The increase in flexibility was indicated by the deformation of the fractured surface. It can be seen in each row that the deformation during the fracture became larger as an increasing amount of the compatibilizers was introduced. Comparing the pictures vertically (different irradiation dose, constant composition), we may conclude that the irradiation possessed more powerful effects on the compatibilization than the compatibilizer. Figures 1-1a to 1-1c showed that when the samples were subjected to no irradiation, large particles of dispersed phase could be identified at the fractured

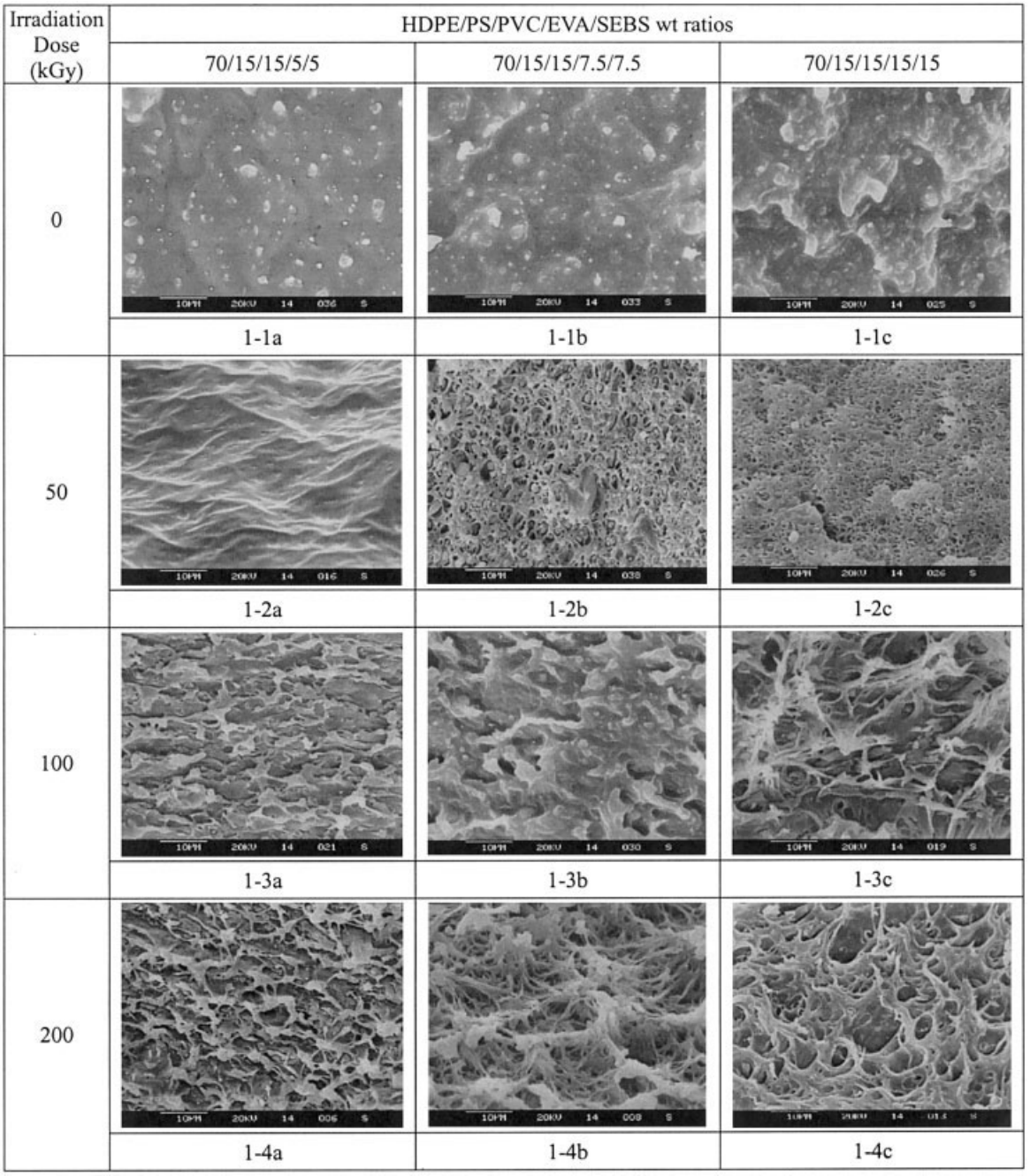

Figure 1 SEM microphotographs of the fractured surfaces of the blends.

surface, even when large amounts of compatibilizers were used. As the dose of the irradiation increased, the systems became more uniform, and at the same time deformation on the fractured surface became larger. When the amount of the compatibilizers were 7.5 parts or more, the increase in deformation became more remarkable. The increase of deformation for the systems without irradiation was the contribution of the compatibilizers alone, because they are rubbery materials. However, when the irradiation was performed, heterogeneous combination of rigid chains and flexible ones may contribute more deformation. This is probably the reason for the simultaneous improvement of the uniformity and the flexibility.

The compatibilizing effect is better shown by TEM micrographs in Figure 2. Because the staining rates of PS and PVC are much faster than that of HDPE, the staining time was controlled such that the domains PS and PVC looked black and those of HDPE white or gray. When no compatibilizers introduced, the size of the black domains is large and the edge of them is sharp. As the amount of compatibilizers increased, the edge of the domains became smeared, and the domains became smaller and more uniformly dispersed.

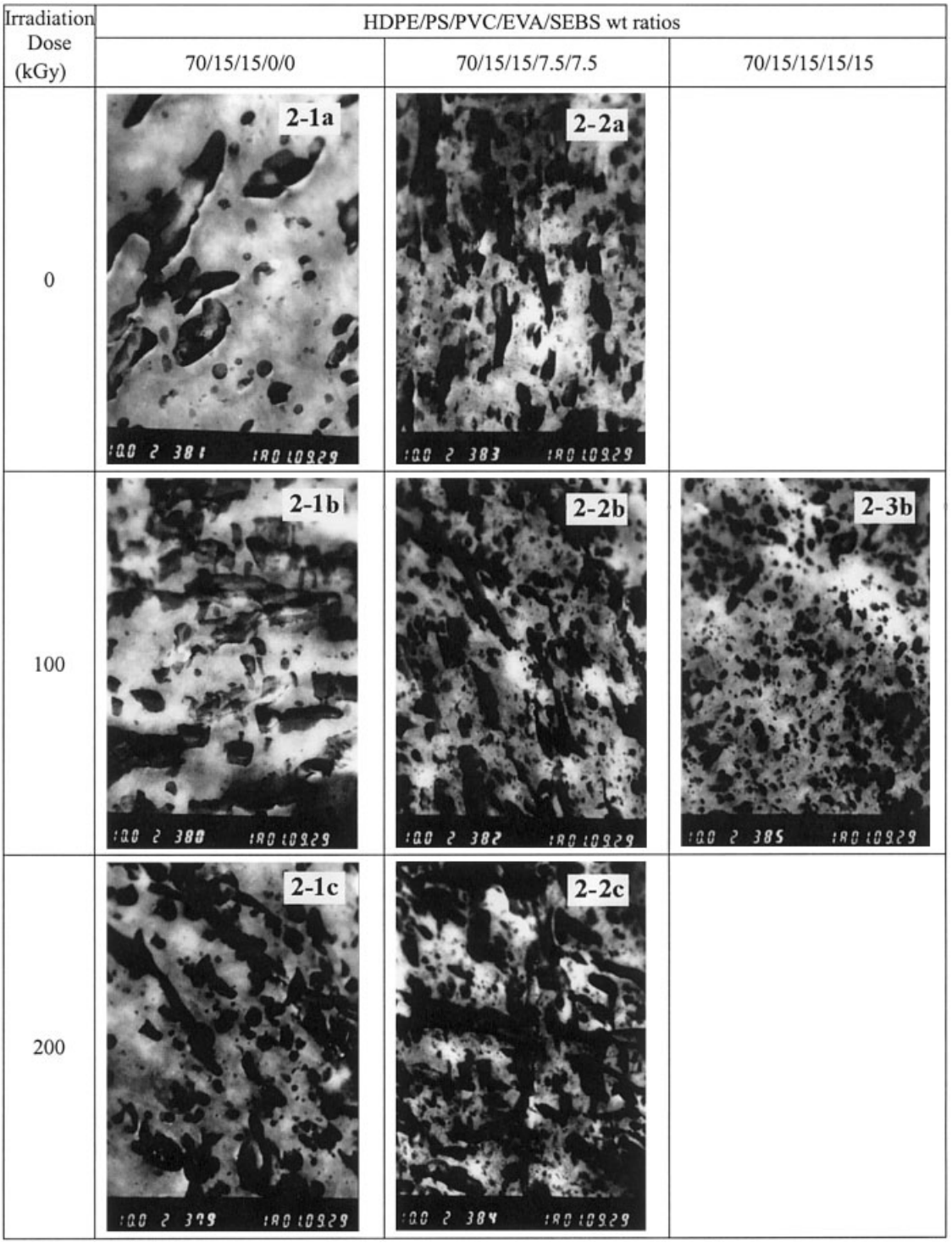

Figure 2 TEM microphotographs of the ternary blends.

The effect of irradiation is similar, which is indicated by the increase of the area of the black region. As shown in columns 1 and 2, Figure 2, for the same composition, the area of the black region became larger as increasing dose of irradiation. As mentioned above, this can also be attributed to the combination of different chains, which improved the dispersion.

Impact strength

Table I shows that the impact strength depends on the composition, the amount of compatibilizers, and the irradiation. Among the three waste plastics, HDPE constitutes the tough component, which provides the flexibility of the mixed system; PS and PVC constitute

the brittle components, and they are not compatible with HDPE. As seen in column 2 of Table I, the impact strength of waste HDPE alone was 14 J m^{-1}, that of the blends of 90 parts of HDPE and 10 parts of PS or PVC decreased to 7.11 or 6.30 J m, respectively. PS and PVC are not compatible with each other. When the three components were mixed together, the toughness became even lower. A ternary blend of HDPE/PS/PVC (wt ratios 75/15/15) possessed impact strength of only 2.39 J m^{-1}. As can be noticed, the effect of the compatibilizers on the impact strength is moderate. When the amounts of the compatibilizers were 15 parts each, the impact strength had been increased by a factor of only 1.85. This increase in toughness can be attibuted to the increase in the flexibility. Both compatibilizers EVA and SEBS are rubbery materials, and they may cause large deformation when the material was fractured, as shown in Figures 1-4b and 1-4c. Such deformations increased the consumption of external energy during the fracture. However, as mentioned above, they are binary compatibilizers only, not ternary ones. EVA was employed for HDPE/PVC and SEBS for HDPE/PS, respectively. The segment repulsion between HDPE and PVC or PS can be reduced; however, that between PVC and PS remained, and EVA and SEBS themselves are not compatible, too. The incorporation of compatibilizers eliminated some segment repulsion, but at the same time produced some new repulsion. The phase separation caused by the segment repulsion constituted the potential cracks, and a material is sensitive to cracks when subjecting to an impact load. As a result of the potential cracks, the improvement in toughness was moderate.

TABLE I
Impact Strength (J m^{-1}) of Various Systems

Ingredients wt ratios	Irradiation dose (kGy)				
	0	50	100	150	200
HDPE100%	14.00	17.21	23.44	NB[a]	23.62
PS/SEBS 90/10	1.92	2.24	3.065	1.33	1.26
PS100%	0.66	0.66	0.66	0.66	0.66
HDPE/PVC 90/10	6.30	6.45	6.25	5.93	3.44
HDPE/PS 90/10	7.11	7.62	9.03	10.32	8.03
HDPE/PS/PVC/EVA/SEBS wt ratios					
70/15/15/0/0	2.39	2.43	3.34	2.29	2.15
70/15/15/2.5/2.5	3.09	3.33	3.65	2.36	2.22
70/15/15/5/5	3.27	3.57	4.38	2.47	2.54
70/15/15/7.5/7.5	3.38	3.87	4.63	3.69	2.77
70/15/15/10/10	3.96	5.00	5.38	7.22	4.86
70/15/15/15/15	4.44	5.82	8.18	NB	7.54
90/5/5/7.5/7.5	21.27	23.74	NB	NB	NB
80/10/10/7.5/7.5	6.75	7.94	10.95	8.61	6.62
70/15/15/7.5/7.5	3.38	3.87	4.63	3.69	2.77
60/20/20/7.5/7.5	2.06	2.15	2.82	2.20	1.94
50/25/25/7.5/7.5	1.88	1.97	2.35	2.08	1.70

[a] NB: no break.

TABLE II
Gel Content (wt %) of HDPE/PVC Systems (HDPE/PVC = 70/30 w/w)

Content of EVA (wt %)	Irradiation dose (kGy)			
	50	100	150	200
0	20.2	52.1	50.0	46.3
5	23.0	62.6	58.9	43.5
10	38.5	65.2	61.2	46.3
15	50.5	66.5	63.3	47.9
20	41.4	69.2	60.3	49.0
Neat PVC	13.8	39.7	39.2	25.6
Neat HDPE	45.5	70.7	58.5	41.4

For these reasons, irradiation constituted a major approach to the toughening of the system in addition to the compatibilizers. Under γ-radiation, the polymer chains scission may take place and free radicals may be generated. The recombination of the chain radicals produced some crosslinked structures. The crosslinking can be homogeneous (among the same polymer chains) or heterogeneous (among different polymer chains). The former may be harmful to the compatibility; however, the latter may improve the compatibility. The chain scission and recombination were competitive. When the irradiation dose was moderate, sufficient amounts of heterogeneous crosslinking were generated, which bridged the gaps due to phase separation and thus toughened the blend. When the irradiation dose was too high, chain scission may prevail, the strength of the material decreased. Indeed, for each composition, the impact strength exhibited a maximum with increasing irradiation dose, which occurred between 100 and 150 kGy.

The degree of the crosslinking was measured with gel content. Since PS was not affected by the irradiation (shown in Table I), the gel content of HDPE/PVC binary system was determined, which is listed in Table II. It shows that the gel content also exhibited a maximum with increasing irradiation dose, which is coincident with that for impact strength in Table I. We may conclude that it was the heterogeneous crosslinking that bridged the gap between the phases of HDPE and PVC resulting in toughening. Comparing the gel content of neat HDPE and neat PVC, we may conclude that under γ-radiation, HDPE preferred crosslinking to chain scission, and the opposite for PVC. We notice that at high irradiation doses, the gel contents of some blends were higher than that of neat HDPE. This is probably attributed to the heterogeneous recombination between radials of HDPE and PVC, which constituted the main factor of compatibilization.

Tensile properties

From the data in Table III, some general tendencies can be concluded (though there are a few exceptions)

TABLE III
Elongation (%) at Break of Various Systems

Ingredients wt ratios	Irradiation dose (kGy)				
	0	50	100	150	200
HDPE100%	297.46	214.52	180.28	159.23	144
PS100%	15.48	11.33	8.85	8.92	17.53
HDPE/PVC 90/10	219.77	153.4	151.29	148.62	108.33
HDPE/PS 90/10	219.59	164.7	151.25	147.24	109.63
HDPE/PS/PVC/EVA/SEBS wt ratios					
70/15/15/0/0	32.50	30.07	26.15	25.65	18.79
70/15/15/2.5/2.5	31.22	29.54	28.89	27.97	16.38
70/15/15/5/5	57.46	47.46	40.63	87.50	26.13
70/15/15/7.5/7.5	235.93	202.56	189.5	178.68	126.4
70/15/15/10/10	395.94	250.87	248.42	240.46	142.92
70/15/15/15/15	332.15	306.76	262.5	241.99	183.62
90/5/5/7.5/7.5	282.58	254.26	226.68	192.86	161.67
80/10/10/7.5/7.5	366.72	352.62	233.96	215.83	172.50
70/15/15/7.5/7.5	235.93	202.56	189.5	178.68	126.40
60/20/20/7.5/7.5	139.22	133.37	127.09	106.11	103.90
50/25/25/7.5/7.5	103.35	88.33	88.33	78.91	68.98

for the elongation at break: (1) At constant HDPE/PVC/PS wt ratio, the higher the compatibilizer fraction, the higher the elongation at break. (b) At constant compatibilizer amount, the higher the HDPE fraction, the higher the elongation at break. (3) At constant plastics composition, the larger the irradiation dose, the lower the elongation at break. Among the three waste plastics, HDPE is the most flexible one and it constitutes the main part of the mixture. Virgin HDPE possesses an elongation at break of higher than 400%, though the value for used ones is much lower. When HDPE was mixed with PVC and PS without or with a low amount of compatibilizers, the flexibility decreased sharply because of the rigidity of PS and the immiscibility. However, when the amount of compatibilizer was sufficient, the elongation at break increased rapidly, even surpassed that of used HDPE. Although the binary compatibilizers were not completely suitable for the ternary system, as discussed in the preceding section, under slow tensile loading, the effect of compatibilization was satisfactory. In addition, the increase in elongation at break could also be attributed to the rubbery nature of the compatibilizers, whose flexibility is much higher than that of HDPE.

TABLE IV
Tensile Strength (MPa) of Various Systems

Ingredients wt ratios	Irradiation dose (kGy)				
	0	50	100	150	200
HDPE100%	33.37	30.11	29.59	29.02	29.98
PS100%	58.68	56.15	59.76	57.25	61.58
HDPE/PVC 90/10	28.15	27.52	27.70	27.03	28.02
HDPE/PS 90/10	30.35	30.49	20.40	29.52	29.66
HDPE/PS/PVC/EVA/SEBS wt ratios					
70/15/15/0/0	28.68	28.54	28.53	29.52	29.79
70/15/15/2.5/2.5	29.31	29.20	29.50	30.29	30.16
70/15/15/5/5	29.87	28.74	29.31	28.80	27.44
70/15/15/7.5/7.5	28.11	26.96	26.98	26.96	27.63
70/15/15/10/10	27.53	26.65	26.49	26.27	25.73
70/15/15/15/15	27.44	24.95	25.44	24.93	24.59
90/5/5/7.5/7.5	26.46	25.11	24.42	23.95	23.94
80/10/10/7.5/7.5	26.62	25.18	25.15	25.07	25.31
70/15/15/7.5/7.5	28.11	26.96	26.98	26.96	27.68
60/20/20/7.5/7.5	27.56	27.27	26.89	27.43	27.91
50/25/25/7.5/7.5	28.61	28.25	28.26	28.58	29.19

Once the system was reasonably compatibilized, its elongation at break was greatly increased. The effect of irradiation is twofold. The crosslinking caused by the irradiation may improve the compatibilization, which may increase the elongation at break. However, the crosslinking itself would greatly impede the motion of the segments, and the sample would break at a lower elongation. As a result, the net effect of the irradiation is a decrease of the elongation at break.

Unlike impact strength and elongation at break, Table IV shows that the tensile strength of the blends remained almost unchanged as the composition or irradiation dose changed. Of all the components, PS is the only one possessing a tensile strength higher than 50 MPa; its incorporation, especially after compatibilizing by irradiation, should increase the tensile strength. From Table IV one can find that PS improved the tensile strength only moderately. This is because (1) PS exists in the system as a dispersed phase, and its contribution to the tensile strength is much less than that of the continuous phase; (ii) although the compatibility was improved by the compatibilizer and irradiation, the more PS introduced, the more immiscibility was also introduced, which is also harmful to the tensile strength. The other components, including the two compatibilizers, are all weak ones. No matter how they are compatibilized, the tensile strength would not be increased to a high level.

CONCLUSION

A mixture of waste HDPE, PVC, and PS can be recovered as useful materials via a method using both compatibilizers and high energy irradiation. The two means made the morphology of the material more uniform and finer. The elongation at break may be higher than 300% when a sufficient amount of compatibilizers was used. The high energy irradiation constituted a powerful means to toughen the ternary system. Impact strength of the system exhibited a maximum with increasing irradiation dose, which was attributed to the heterogeneous crosslinking generated. However, the tensile strength was only improved moderately.

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