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(54) **Thermoplastic resin laminate for vacuum forming**

(57) A structure of a stretched thermoplastic resin film laminated upon an unstretched thermoplastic resin sheet, the structure having a thickness proportion of the film based on the laminated structure of 1.0 to 20%, and being useful in vacuum forming, the sheet being preferably of a polyolefin resin and the film being preferably of a polyolefin resin and prepared by stretching in a draw ratio of 4 times or greater.

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FIG. 1A

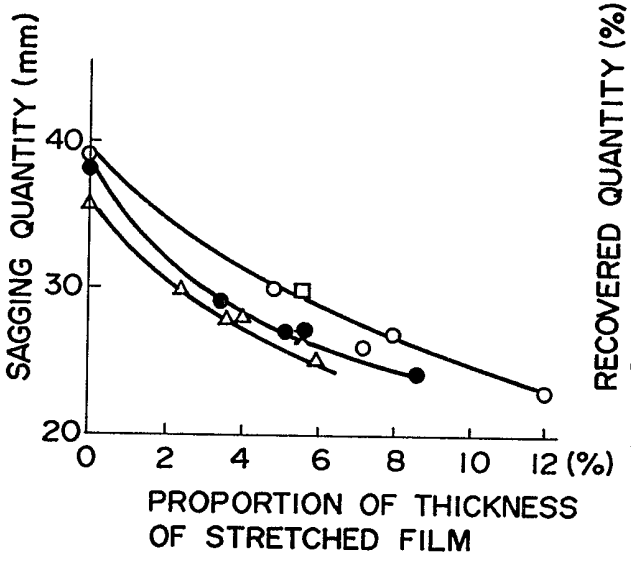


FIG. 1B

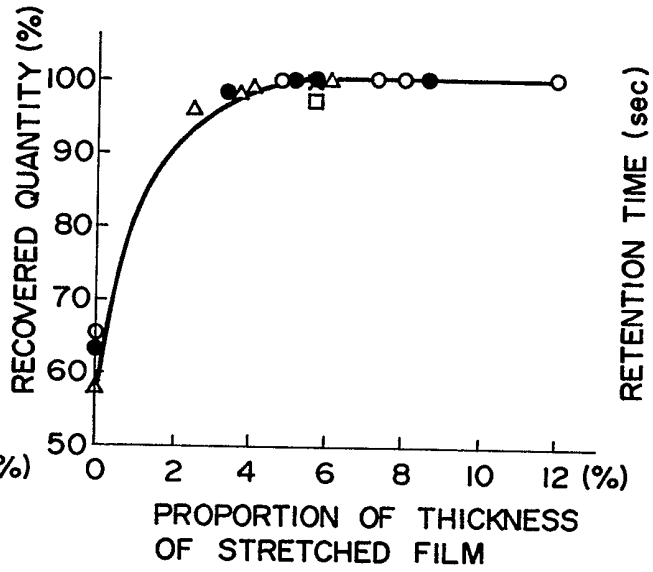


FIG. 1C

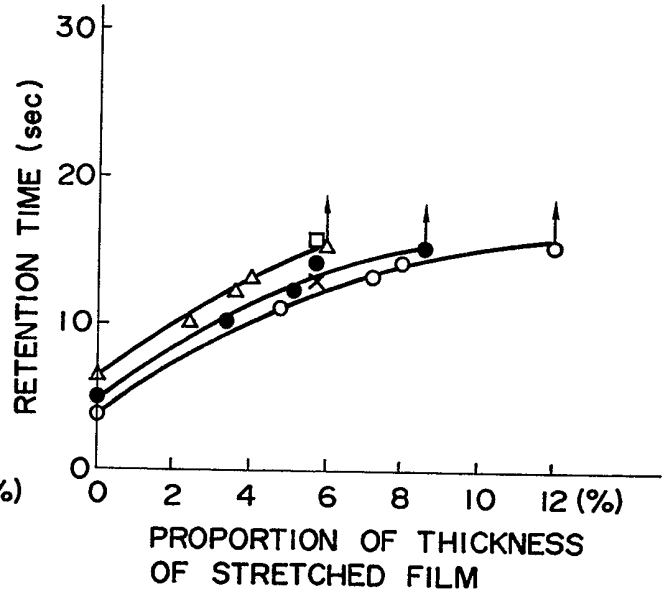


FIG. 2A

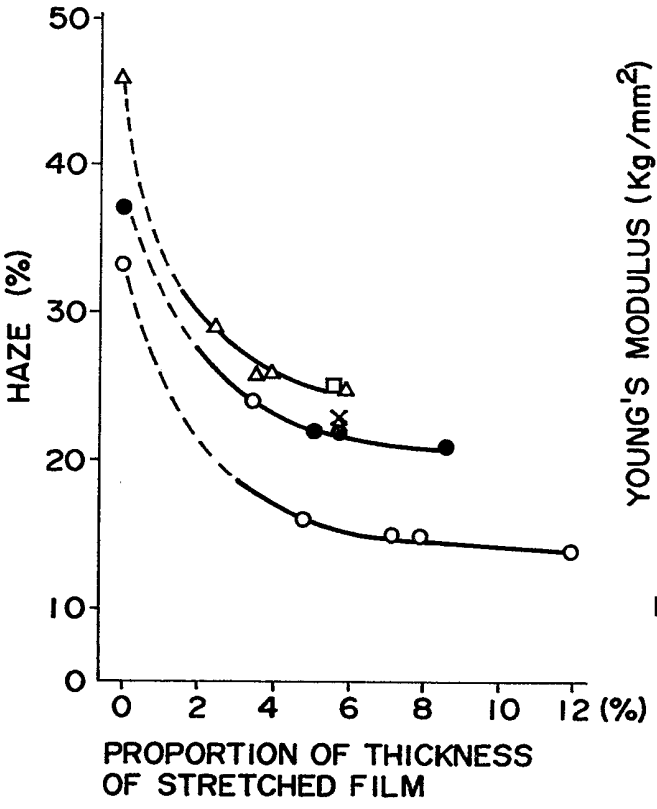


FIG. 2B

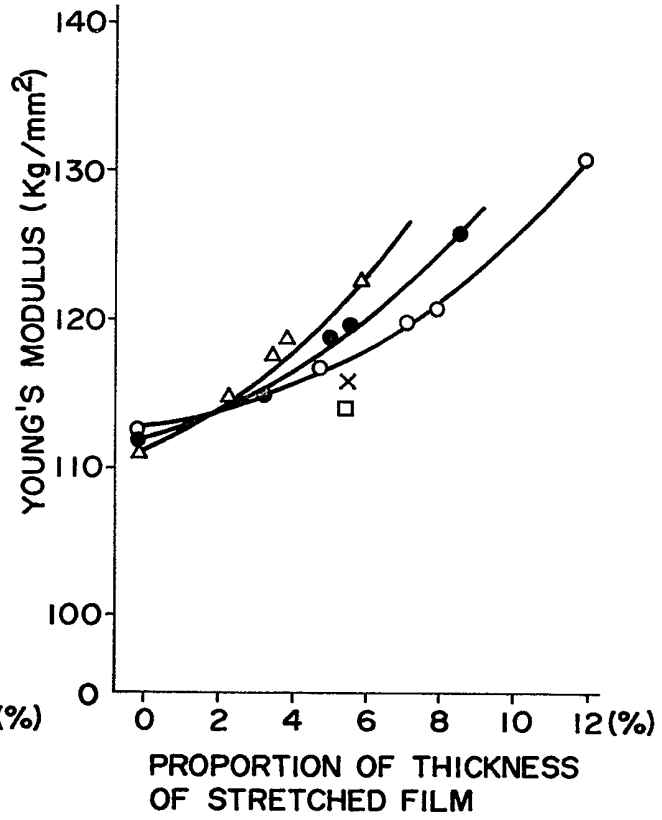
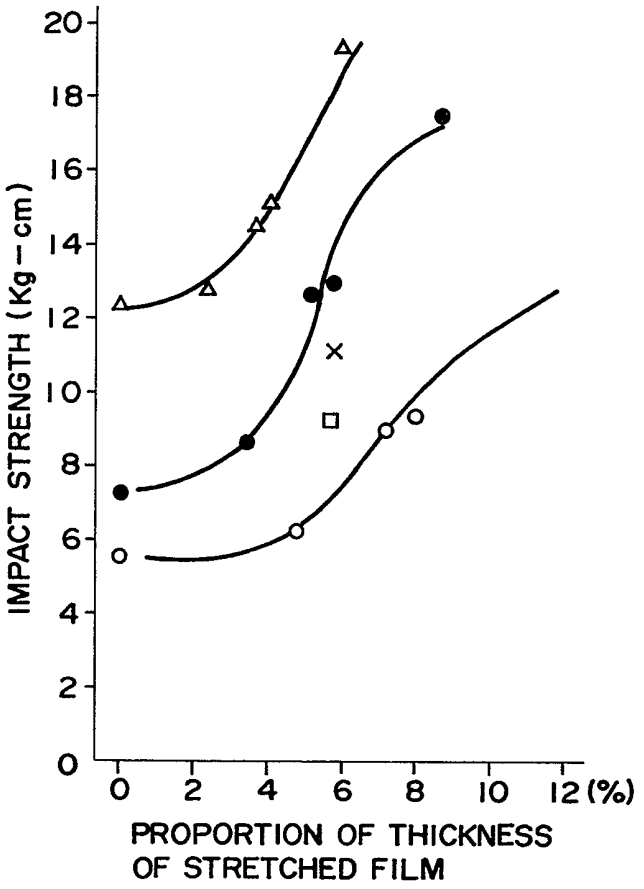


FIG. 2C



SPECIFICATION

Thermoplastic resin laminate for vacuum forming

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a thermoplastic resin laminate for vacuum forming. More particularly it relates to a thermoplastic resin laminate having an improved vacuum-formability, obtained by laminating a stretched thermoplastic resin film upon an unstretched thermoplastic resin sheet.

Description of the prior art

Thermoplastic resin sheets have been used as stocks for producing containers for foods, etc. or other molded products according to forming processes such as vacuum forming, air-pressure forming, etc. Among thermoplastic sheets, those comprising polyolefin resins, particularly polypropylene resins, are inferior to those comprising rigid vinyl chloride polymer resins or polystyrene in the point of processability for secondary processing such as vacuum forming or air-pressure forming (both the formings will hereinafter be collectively referred to as vacuum forming, etc.). As processes for overcoming such a drawback inherent to polypropylene resin (hereinafter abbreviated to polypropylene), the following improved processes are known: In the production of the sheets, polypropylene having a small MFR (melt flow rate) is used or a low density polyethylene (hereinafter abbreviated to LDPE) or a high density polyethylene (hereinafter abbreviated to HDPE) is blended to polypropylene. However, when such improvements are brought into practice, the processabilities in vacuum forming, etc. (hereinafter referred to as formability in vacuum forming, etc.) are improved to a certain extent, but on the other hand, other drawbacks such as lowering of transparency, rigidity and other physical properties of the resulting molded products are brought about.

On the other hand, lamination of thermoplastic resin films of the same or different properties upon one another has been widely carried out. Examples of such laminates practically used include mainly cellophane and LDPE film (designated also as "cellophane/LDPE film"; such designation being applied to the succeeding examples), biaxially stretched polypropylene film (hereinafter abbreviated to OPP)/LDPE film and OPP/unstretched polypropylene film (hereinafter abbreviated to CPP), and the object of such lamination is to improve characteristic properties of these films such as heat-sealability, moisture resistance, airtight property, etc. As seen from such object, the uses of these laminated films have been directed to packaging materials or the like. Further, the respective thickness of these laminated films are about 30 μ or less; hence such laminated films are different from the laminates of the present invention mentioned later in the thickness.

The present inventors have made earnest studies to overcome the above-mentioned drawbacks occurring when the thermoplastic resin sheets, particularly polyolefin resin sheets, above all polypropylene resin sheets are used in vacuum forming, etc., by way of processes different from the above-mentioned conventional ones. As a result, it has been found that the above-mentioned drawbacks (including new drawback accompanying the prior art) can be overcome by laminating a definite stretched thermoplastic resin film upon an unstretched thermoplastic resin sheet.

As apparent from the foregoing, the object of the present invention is to provide a thermoplastic resin laminated sheet having new uses. Another object is to provide molded products having superior physical properties and obtained by subjecting the above laminated sheet to secondary processing according to vacuum forming, etc. Other objects will be apparent from the following description.

Summary of the invention

The present invention resides in:

(1) A structure of a stretched thermoplastic resin film laminated upon an unstretched thermoplastic resin sheet, having a thickness proportion of said stretched thermoplastic resin film based on said structure of 1.0 to 20%, which structure is useful for vacuum forming (this structure will hereinafter be referred to as laminate);

(2) a laminate of the above-mentioned item (1) wherein said unstretched thermoplastic resin sheet comprises a polyolefin resin; and

(3) a laminate of the above-mentioned item (1) wherein said stretched thermoplastic resin film comprises a polyolefin resin and is prepared in a draw ratio of 4 times or greater.

Brief description of the drawings

Figure 1A, Figure 1B and *Figure 1C* show relationships between heating behaviors (sagging quantity, recovered quantity and retention time) of the laminates of the present invention and proportions of the thickness of stretched films.

Figure 2A, Figure 2B and *Figure 2C* show relationships between physical properties (haze, Young's modulus and impact strength) of the laminates of the present invention and proportions of the thickness of stretched films.

Detailed description of the invention

The constitutional elements and effectiveness of the present invention will be described below in detail.

(a) Unstretched thermoplastic resin sheet:

Thermoplastic resins used may be those which can be processed into sheets and further can be used for secondary processing, and examples of these are polyolefin resins such as LDPE, HDPE, polypropylene, polybutene-1, poly-4-methylpentene-1 and further, vinyl chloride polymer resins, polystyrene, polyester resins, etc. These resins include not only homopolymers, but also copolymers of monomers of the same or different kinds (random copolymers, block copolymers and graft copolymers). Further, not only polymers of one kind but also blends of polymers of two or more kinds can be used. Necessary stabilizers and besides, various fillers, pigments and additives can be, of course, added to these resins.

The sheets are prepared according to any one of processes, i.e. any of these such as calendering process, T-die process, roll uniaxial stretching process, etc. may be employed. The thickness of the sheets is in the range of 100 to 2,000 μ, preferably 200 to 1,000 μ. If the thickness is less than 100 μ, the sheets are unsuitable as materials for vacuum forming, etc. and if it exceeds 2,000 μ, other processing techniques such as press forming will be more suitable.

(b) Stretched thermoplastic film:

Thermoplastic resins used are the same as in the case of the thermoplastic resins described in the above item (a). The preparation of the film also is the same as in the above-mentioned sheet except for the thickness after stretching. Namely, the film has a thickness in the range of 5 to 50 μ, preferably 10 to 30μ and is prepred by stretching to 4 times or more (surface draw ratio). If the draw ratio is less than 4 times, the effectiveness of the present invention described later is very insufficient. Although the upper limit of the draw ratio is not limited, about 60 times are a limitative draw ratio in view of the current processing techniques, and even if a film obtained by stretching in a draw ratio exceeding the above value is used, the effectiveness of the present invention is not particularly enhanced. Any of known stretching processes may be employed such as tenter biaxial stretching process, inflation multi-axial stretching process, roll uniaxial stretching process, etc. Further, either of uniaxially stretched product or multi-axially stretched product can, of course, be used.

The sheet and the film prepared as described above are laminated according to any of known processes. As to such lamination processes, any of known extrusion lamination processes, dry lamination process and others may be employed. However, extrusion lamination process is preferred in view of the production efficiency and the quality of the resulting laminate of the present invention. If the respective thermoplastic resins of the sheet and the film of the present invention are of the same kind, the sheet and the film are generally easily melt-adhered together, but if they are of different kinds, they are not always melt-adhered together; hence in such a case, the sheet and the film are adhered together by an adhesive.

(d) Proportion of the thickness of the stretched thermoplastic resin film based on that of the resulting laminate:

The proportion of the thickness of the film constituting the laminate of the present invention based on that of the laminate must be in the range of 1.0 to 20%, preferably 3 to 15%. If it exceeds 20%, broken parts occur in the resulting laminate at the time of vacuum forming, etc. due to the loosening of orientation of the laminated stretched film, resulting in failure of vacuum forming, etc. Contrarily if the proportion is less than 1.0%, various effects brought about by the lamination of the stretched film (improvements in vacuum forming process, rigidity and impact strength) are notably decreased; hence the object of the present invention practically cannot be attained.

By carrying out vacuum forming, etc. by the use of the laminate of the present invention as described above in detail, it has now become possible to realize the following various effects:

(1) As to thermoplastic resins as raw material, it is unnecessary to use particularly those having a lower MFR.

(2) In the case of polypropylene resin, it is unnecessary to mix it with another kind of resin.

(3) Formability in vacuum forming, etc., expressed by heating behaviours (see Examples) is improved.

(4) Transparency of the resulting molded product is improved to a large extent.

(5) Rigidity (Young's modulus) and impact strength of the resulting molded product are improved.

Heating behaviours are measured as follows:

A laminate sample is fixed onto a frame having an opening part of 300 × 300 mm, and the thus fixed laminate is maintained horizontally for a definite period of time in a heating oven maintained at 180°C. By this heating, a central portion of the laminate first sags, thereafter the original state is partially recovered from such a sagging and such a recovered state continues for a definite period of time. The term "sagging quantity" referred to in the following Examples means the largest sagging quantity (mm) prior to initiating the above-mentioned partial recovery; the term "recovered quantity" means a percentage recover (%) in the state where the largest recovery occurred; and the term "retention time" means a period of time (sec.) for which the largest recovered quantity is maintained. The above-mentioned recovered state is lost by resagging which occurs after lapse of the retention time, and thereafter such a recovery phenomenon does not occur.

The present invention will be described by way of Examples.

Examples 1 - 14 and Comparative examples 1 and 2

A commercially available polypropylene resin having a MFR of 3.3 (Chissopolypro A5014, trade name of product manufactured by Chisso Corportion) was extruded through a T-die of 75 mmϕ established at a temperature of 250°C, and at that time, onto the resulting extruded sheet was laminated each of OPPs of 12, 18, 20 and 30 μ thick (draw ratio, 40 times; Examples 1 - 12), an inflation process, multi-axially stretched polypropylene film of 20 μ thick (hereinafter abbreviated to IOPP; draw ratio, 36 times; Example 13) and a uniaxially stretched polypropylene film of 20 μ thick (draw ratio, 8 times; Example 14), separately prepared, respectively, and the thickness of the unstretched part at the time of the extrusion was also adjusted to obtain laminates having respectively a thickness after the lamination of 250 μ (Examples 1 - 4), that of 350 μ (Examples 5 - 8, 13 and 14) and that of 500 μ (Examples 9 - 12). Further, as Comparative examples, laminates of CPP of 20 μ thick onto the extruded sheet (Comparative example 1) and a non-laminated sheet (Comparative example 2), each having a total thickness of 350 μ, were prepared. The constitutions and physical properties of these laminates and the sheet are shown in Table 1 and the respective relationships between various physical properties and the proportions of the thickness of the laminated stretched films are shown in Figure 1 and Figure 2. The relationships between heating behaviours (sagging quantity, recovered quantity and retention time) and vacuum-formability will be described below. Figure 1A, Figure 1B and Figure 1C show the relationships between sagging quantity, recovered quantity and retention time among the heat behaviours of the laminates of the present invention and proportions of the thickness of stretched films. The curves in these Figures are obtained by plotting the respective heating behaviours of each sample having the same thickness against the thickness proportions. In Figures 1A, 1B and 1C, symbols Δ, ● and ○ show measurement results of laminates of OPP having a thickness of 500 μ, 350 μ and 250 μ, of the present invention, respectively, and symbols × and □ show those of laminates of IOPP and monoaxially stretched polypropylene film, respectively. As apparent from Figure 1A, as to the sagging quantity, laminates having a larger total thickness are superior with regard to those having the same thickness proportions, but with regard to the same thicknesses of laminates, preferred results are obtained in thickness proportions of 2% or higher, particularly about 4% or higher. As apparent from Figure 1B, as to the recovered quantity, preferred results (close to 100%) are obtained in thickness proportions of 2% or higher, particularly 3% or higher, with regard to laminates having the same thickness proportions, indifferently from the total thickness of laminates. As apparent from Figure 1C, as to the retention time, laminates having a larger total thickness are superior with regard to those having the same thickness proportion, but with regard to the same thickness of laminates, preferred results are obtained in thickness proportions of 2% or higher, particularly 4% or higher. As apparent from the above description of the measurement items of heating behaviors, the laminates for vacuum forming, etc. are superior in the formability in vacuum forming, etc. with the decrease of the sagging quantity, with the increase of the recovered quantity and with the increase of the retention time. Three upward arrow marks at the right ends of the three curves in Figure 1C means "values indicated there or higher". Further, it goes without saying that the physical properties of the laminates, as they are, show processability or physical properties attained after forming.

Next, Figure 2A, Figure 2B and Figure 2C show curves obtained by plotting the transparency (haze, %), the rigidity (Young's modulus, Kg)mm^2) and the impact strength (Kg-cm) of the same samples as in Figure 1A, Figure 1B and Figure 1C, respectively against the thickness proportions of the stretched films in the laminates of the present invention. In Figures 2A, 2B and 2C, symbols Δ, ● and ○ show measurement results of laminates of OPP having a thickness of 500 μ, a thickness of 350 μ and a thickness of 250 μ, respectively, and symbols × and □ show measurement results of laminate of IOPP (an inflation process multi-axially stretched film) and a laminate of uniaxially stretched polypropylene film, respectively. As apparent from Figure 2A, as to haze, laminates having a smaller total thickness are superior with regard to the same thickness proportions, but with regard to the same thickness of laminats, preferred results are obtained in thickness proportions of 2% or higher, particularly 3% or higher. On the other hand, lamintes of uniaxially stretched polypropylene or IOPP in place of OPP, having a thickness proportion of 5.7%, also have almost the same haze values as those of laminates of OPP, and the values are improved as a whole, down to about 2/3 to 1/2 of those in the case of no lamination (0%). As apparent from Figure 2B, as to Young's modulus, laminates having a larger total thickness are superior with regard to the same thickness proportions, but with regard to the same thickness of laminates, preferred results are obtained in thickness proportions of 2% or higher, particularly about 5% or higher. On the other hand, laminates of uniaxially stretched polypropylene or IOPP in place of OPP, having a thickness proportion of 5.7% are considerably inferior to the corresponding laminates of OPP, differently from the case of haze (Figure 2A), but they are superior to a sheet of no lamination (0%) in the results. Further, as apparent from Figure 2C, as to impact strength, laminates having a larger total thickness are naturally superior with regard to the same thickness proportion, and preferred results are obtained in thickness proportions of 2% or higher, particularly about 4% or higher. On the other hand, laminates of uniaxially stretched polypropylene or IOPP in place of OPP, having a thickness proportion of 5.7%, are inferior to the corresponding laminates of OPP to a sheet of no lamination in the results. In addition, the laminates of CPP of Comparative example 1 exhibits no effectiveness except for improvement in transparency.

TABLE 1

		Unit	Example 1	2	3	4	5	6	7	8
Constitution of laminate	Total thickness of laminate	μ	250						350	
	Thickness of OPP	μ	12	18	20	30	12	18	20	30
	Thickness of IOPP	μ								
	Thickness of uniaxially stretched film	μ								
	Thickness of CPP	μ								
	Thickness of proportion of film based on laminate	%	4.8	7.2	8.0	12	3.4	5.1	5.7	8.6
Haze *		%	16	15	15	14	24	22	22	21
Young's modulus **		Kg/mm^2	117	120	121	131	115	119	120	126
Impact strength ***		KG-cm	6.2	9.0	9.4	13.1	8.6	12.7	13.0	17.5
Heating behavior	Sagging quantity	mm	30	26	27	23	29	27	27	24
	Recovered quantity	%	100	100	100	100	98	100	100	100
	Retention time	sec.	11	13	14	15 or longer	10	12	14	15 or longer

TABLE 1 (continued)

		Unit	Example						Comparative example	
			9	10	11	12	13	14	1	2****
Constitution of laminate	Total thickness of laminate	μ			500		350	350	350	350
	Thickness of OPP	μ	12	18	20	30				
	Thickness of IOPP	μ					20			
	Thickness of uniaxially stretched film	μ						20		
	Thickness of CPP	μ							20	
	Thickness proportion of film based on laminate	%	2.4	3.6	4.0	6.0	5.7	5.7	5.7	0
Haze *		%	29	26	26	25	23	25	28	37
Young's modulus **		kg/mm^2	115	118	119	123	116	114	108	112
Impact strength ***		Kg-cm	12.8	14.5	15.2	19.4	11.2	9.3	7.4	7.3
Heating behavior	Sagging quantity	mm	30	28	27	25	27	30	40	38
	Recovered quantity	%	96	98	99	100	100	98	61	63
	Retention time	Sec.	10	12	13	15 or longer	13	16	4	5

Notes: * ASTM D-1003, ** ASTM D-882, *** ASTM D-781 (These apply to Tables 2 and 3.)
**** non-laminated

Examples 15 and 16 and Comparative examples 3 - 6

Unstretched sheets were prepared as in Examples 1 - 14, using a commercially available polypropylene resin having a MFR of 0.5 (Chissopolypro K 4011, tradename of product manufactured by Chisso Corporation), a commercially available ethylene-propylene block copolymer resin having an ethylene content of 8% (Chissopolypro K7011, tradename of product manufactured by Chisso Corporation) and a commercially available ethylene-propylene random copolymer resin having a MFR of 0.5 and an ethylene content of 3% (Chissopolypro XK 0235, tradename of product manufactured by Chisso Corporation), respectively, and at that time, OPP of 12 μ was laminated upon the respective unstretched sheets to obtain laminates of 350 μ (Examples 15 and 16). For comparison, sheets of 350 μ having no OPP laminated were prepared (Comparative examples 3 - 5), and further, for comparison with the respective above Examples, a sheet of 350 μ having no OPP laminated was prepared using a blend of the polypropylene resin with 10% by weight of LDPE having a melt index (MI) of 2.0 and 5% by weight of an ethylene-propylene rubber (Comparative example 6). The constitutions and physical properties of the above laminates and sheets are shown in Table 2. When the Examples are compared with the Comparative examples corresponding thereto (Example 15 to Comparative ex. 3; Example 16 to Comparative ex. 5; and Examples 15 - 17 to Comparative ex. 6), it is apparent that the laminates of the above Examples are superior to the sheets of the above Comparative examples, in heating behaviors, transparency, rigidity and impact strength.

TABLE 2

Raw material	Type of polymer	Unit	Example 15 Homo	Example 16 Block	Example 17 Random	Comparative example 3 Homo	Comparative example 4 Block	Comparative example 5 Random	Comparative example 6 Homo
		g/10min.	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Thickness of OPP	μ	12	12	12	-	-	-	-
Constitution of laminate	Total thickness of laminate or sheet	μ	350	350	350	350	350	350	350
	Thickness proportion of OPP based on laminate	%	3.4	3.4	3.4	-	-	-	-
Haze		%	32	48	27	55	80	51	62
Young's modulus		Kg/mm^2	96	94	78	92	88	75	85
Impact strength		Kg-cm	12	30<	23	9	28	18	27
	Sagging quantity	mm	24	23	26	33	33	34	28
Heating Behaviors	Recovered quantity	%	100	100	100	80	82	81	98
	Retention time	sec.	13	14	14	7	8	7	20

Examples 18 and 19 and Comparative examples 7 and 8

Unstretched sheets were prepared as in Examples 1 - 14, using HDPE and LDPE having a MI of 1.0, and at that time, a uniaxially stretched HDPE film of 30 μ (draw ratio: 6 times) was laminated upon the respective unstretched sheets to obtain laminates of 350 μ (Examples 18 and 19). For comparison, sheets of 350 μ having no uniaxially stretched film laminated were prepared (Comparative examples 7 and 8). The constitution and physical properties of these laminates and sheets are shown in Table 3. When the above Examples are compared with Comparative examples corresponding thereto, it is apparent that the laminates of the Examples are superior to the sheets of the Comparative examples in heating behaviors, transparency and Young's modulus. Further, even when a stretched film of HDPE comprising a different resin is laminated onto a sheet of LDPE, as in Example 19, the effectiveness of the present invention is unchanged.

TABLE 3

		Unit	Example 18	Example 19	Comparative example 7	Comparative example 8
	Resin for laminate or sheet		HDPE	LDPE	HDPE	LDPE
Raw material	MI of resin for laminate or sheet	g/10min.	1.0	1.0	1.0	1.0
Constitution of laminate	Thickness of uniaxially stretched film of HDPE	μ	30	30	30	30
	Total thickness of laminate or sheet	μ	350	350	350	350
	Thickness proportion of film based on laminate	%	86	86	-	-
Haze		%	68	36	95	60
Young's modulus		Kg/mm^2	69	28	65	22
Impact strength		Kg-cm	30<	30<	30<	30<
Heating behaviors	Sagging quantity	mm	18	20	21	23
	Recovered quantity	%	100	100	95	98
	Retention time	sec.	35	32	32	27

CLAIMS

1. A laminate comprising a stretched thermoplastic resin film laminated to an unstretched thermoplastic resin sheet, the stretched film forming 1 to 20% of the thickness of the laminate.
2. A laminate according to claim 1, wherein the unstretched sheet is of polyolefin resin.
3. A laminate according to claim 1 or 2, wherein the stretched film is of a polyolefin resin.
4. A laminate according to claim 3, wherein the stretched film was stretched at a draw ratio of 4 or more.
5. A process for producing thermoplastics articles by vacuum forming of a thermoplastic substrate, wherein the substrate is a laminate according to any preceding claim.

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