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(54) TREATMENT OF POLYMERIC FILM LAMINATES

(71) We, KONINKLIJKE EMBALLAGE INDUSTRIE VAN LEER B.V., a Dutch body corporate, of Amsterdamseweg 206, Amstelveen, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention is concerned with the treatment of polymeric film laminates.

Thermoplastic polymeric film laminates are known, or have been described, which comprises two or more substantially monoaxially oriented layers, the directions of orientation of each layer being at an angle, preferably 45°, to the longitudinal dimension of the laminate and being at an angle, preferably 90°, to the direction of orientation of the adjacent layer(s). Such laminates are referred to herein, for convenience, as "cross-laminates". The layers of such cross-laminates may be bonded together in any suitable way, for example, by adhesive, spot-welding, diff-welding, puncturing, lub-welding, crystal-welding, or by extrusion lamination (that is the extrusion of a thin film of molten polymer between converging pre-formed films in the nip of a pair of nip rolls in which the laminate is formed). The production of cross-laminates is described, for example, in British Specification 1,414,785.

Cross-laminates have a number of advantageous properties, in particular they have much better tear resistance than a single-ply film of the same overall thickness and of the same polymer which has been biaxially oriented. We have now found that the impact strength and other properties of such cross-laminates can be improved by an annealing treatment.

According to the present invention, there is provided a method of treating a cross-laminate formed from two or more substantially monoaxially oriented thermoplastic polymeric films, which comprises annealing the cross-laminate by heating it at a temperature of from 35°C to below the melting or softening temperature of the lower (lowest) melting or softening of the films present in the laminate, excluding any adhesive or extruded bonding layer.

For best impact strength, the temperature should be as high as possible subject to the limitation with respect to the melting or softening temperature of the film having the lower (lowest) melting or softening temperature. In practice, the maximum temperature that can be used is about 1°C lower than said lower (lowest) melting or softening temperature. There may be some loss of strength as measured by standard puncture and propagation of tear tests as the annealing temperature approaches the upper limit specified.

The annealing step is carried out, for example, by passing the cross-laminate through an annealing oven or over a heated cylinder while substantially free of tension and pressure. The temperature used in preferably from 60 to 180°C, depending on the materials present in the laminate.

The plies of the laminate may be formed of the same or different polymers. Suitable thermoplastic polymers for the layers of the laminate are, for example, homo- and co-polymers of ethylene, polypropylene, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, and ethylene/vinyl acetate copolymers. The most preferred layer materials are polypropylene and high density polyethylene.

Cross-laminates which have been treated by the method according to the invention can be used to produce articles, such as sacks and tarpaulins, of improved strength. Alternatively a thinner cross-laminate can be treated to give the same strength properties as those of a thicker, untreated, cross-laminate.

In order that the invention may be more fully understood, the following examples and comparative experiments are given by way of illustration.

Example 1

Laminates were formed from two plies of high density polyethylene films having thicknesses of 50 microns and 37.5 microns, respectively, and mono-axially oriented at 45° to the longitudinal dimension of the film, using a two-component polyurethane adhesive (PU 12 which is commercially available from Bayer); that is two plies of the 50 micron material were used to form a first laminate having a nominal thickness of 100 microns, and two plies of the 37.5 micron material to form a second laminate having a nominal thickness of 75 microns. Application of the adhesive and the bonding conditions used were conventional and in accordance with the recommendations of the adhesive manufacturer.

Samples of each laminate were annealed by being passed over a roll maintained at a temperature of 120° - 130°C, the time of contact with the roll being 15 seconds.

The unannealed and annealed samples were then subjected to the following tests for packaging materials:

(1) PPT - a puncture and propagation of tear test, measured in Newtons, which is a modified version of ASTM D2582-67.

(2) Toyo - a test for impact strength, measured in joules, carried out essentially as described in ASTM D781 but with the pyramidal head replaced by a hemispherical head.

The results obtained were as follows:

Sample	Thickness microns	PPT (N)	Toyo (J)
unannealed	100	50.02	4.2
annealed	100	50.02	7.7
unannealed	75	36.7	7.1
annealed	75	38.97	9.8

Example 2

High density polyethylene tubular film (Unifos 2900) having a thickness of 45 microns was cold stretched lengthwise and cut open along a helical line according to U.S. Patent 2943356. The resulting film strip was oriented in a direction at 45° to the length direction of the strip and two such strips were extrusion laminated with low density polyethylene, such that the orientation of one layer of high density polyethylene was perpendicular to the orientation of the other layer. The resulting cross-laminate had a final thickness of about 100 microns.

Samples of this laminate were annealed using the same technique as described in Example 1, but at different annealing temperatures.

The following test results were obtained:

Sample	Annealing Temperature (°C)	PPT (N)	Toyo (J)
unannealed	-	50.0	10.6
annealed	110	60.3	12.1
annealed	124	71.3	13.6
annealed	130	22.7	17.2

The test results show increasing impact strength with increasing annealing temperature and increased PPT values for annealing at 110°C and 124°C. The drop in PPT value for annealing 130°C is probably due to the loss of orientation near this temperature.

Example 3

Example 1 was repeated except that a polypropylene film of 50 microns thickness was used (GPE 012 from I.C.I. Ltd., melting point 154°C). The annealing temperature was 141°C.

The following test results were obtained:

Sample	PPT (N)	Toyo (J)
unannealed	30.4	4.7
annealed	40.5	8.1

WHAT WE CLAIM IS:-

1. A method of treating a cross-laminate formed from two or more substantially monoaxially oriented thermoplastic polymeric films, which comprises annealing the cross-laminate by heating it at a temperature of from 35°C to below the melting or softening temperature of the lower (lowest) melting or softening of the films present in the laminate, excluding any adhesive or extruded bonding layer.
2. A method according to claim 1, in which the annealing temperature is approximately 1°C below said lower (lowest) melting or softening temperature.
3. A method according to claim 1, in which the annealing is effected by passing the cross-laminate through an annealing oven or over a heated cylinder while substantially free of tension and pressure.
4. A method according to any of claims 1 or 3, in which the annealing temperature is from 60 to 180°C.
5. A method according to claim 1, substantially as herein described in Example 1.
6. A method according to claim 1 substantially as herein described in Example 2 or 3.
7. A cross-laminate which has been treated by the method claimed in any of claims 1 and 3 to 5.
8. A cross-laminate which has been treated by the method claimed in claims 2 or 6.

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