



(86) Date de dépôt PCT/PCT Filing Date: 2012/02/29
(87) Date publication PCT/PCT Publication Date: 2013/09/06
(85) Entrée phase nationale/National Entry: 2014/08/14
(86) N° demande PCT/PCT Application No.: MY 2012/000039
(87) N° publication PCT/PCT Publication No.: 2013/129905

(51) Cl.Int./Int.Cl. *C09D 115/00* (2006.01),
C08C 19/22 (2006.01), *C08G 18/02* (2006.01),
C08J 3/21 (2006.01), *C08K 5/16* (2006.01),
C08L 15/00 (2006.01), *C09D 119/02* (2006.01)
(71) Demandeur/Applicant:
NOBEL SCIENTIFIC SDN. BHD., MY
(72) Inventeurs/Inventors:
CHIENG, DIING YAW, MY;
MAR, HUNG THAN, MY
(74) Agent: ROBIC

(54) Titre : PROCEDE DE FABRICATION D'UN ARTICLE EN POLYMERE, ET ARTICLE OBTENU
(54) Title: METHOD OF MAKING A POLYMER ARTICLE AND RESULTING ARTICLE

(57) **Abrégé/Abstract:**

A method of making a polymer article comprises the steps of making a polymer solution by mixing a first compound containing carbodiimide groups with a second compound containing carboxylated groups, applying the polymer solution to a former, wherein the step of applying occurs within 2 hours of the making of the polymer solution, and curing the polymer solution. The polymer solution can have a pH adjuster consisting of ammonium hydroxide.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)
(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 September 2013 (06.09.2013)

(10) International Publication Number
WO 2013/129905 A1

(51) International Patent Classification:

C09D 115/00 (2006.01) *C08J 3/21* (2006.01)
C08K 5/16 (2006.01) *C08C 19/22* (2006.01)
C09D 119/02 (2006.01) *C08L 15/00* (2006.01)
C08G 18/02 (2006.01)

(21) International Application Number:

PCT/MY2012/000039

(22) International Filing Date:

29 February 2012 (29.02.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): **NOBEL SCIENTIFIC SDN. BHD** [MY/MY]; 38D-2A, Jalan Rad-in Anum, Bandar Baru Seri Petaling, Kuala Lumpur, Wilayah Persekutuan (MY).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHIENG, Diing, Yaw** [MY/MY]; No 12 Jalan Puteri, 6/13 Bandar Puteri, 47100 Puchong, Selangor (MY). **MAR, Hung Than** [MY/MY]; No 26 Jin Jiran Satu, Happy Garden, Off Jin Kuchai Lama, 68200 Kuala Lumpur, W. Persekutuan (KL) (MY).

(74) Agent: **ROSHAYATI ABDUL GHANI, ZAHARIZAN AHMED MEAH & FOONG SEET FUN**; C/o Drew-marks Patents & Designs (Malaysia) Sdn. Bhd., 9th Floor, Bangunan Getah Asli (Menara), 148, Jalan Ampang, 50450 Kuala Lumpur (MY).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: METHOD OF MAKING A POLYMER ARTICLE AND RESULTING ARTICLE

(57) Abstract: A method of making a polymer article comprises the steps of making a polymer solution by mixing a first compound containing carbodiimide groups with a second compound containing carboxylated groups, applying the polymer solution to a former, wherein the step of applying occurs within 2 hours of the making of the polymer solution, and curing the polymer solution. The polymer solution can have a pH adjuster consisting of ammonium hydroxide.



WO 2013/129905 A1

METHOD OF MAKING A POLYMER ARTICLE AND RESULTING ARTICLE

FIELD OF THE INVENTION

5 [0001] This invention relates to methods of making polymer articles and the resulting articles, and more particularly to methods for reducing time and costs of making such articles.

BACKGROUND OF THE INVENTION

10

[0002] Polymer articles can be made from a number of materials and in a number of ways. Typically organic compounds in a liquid form are mixed together in a process where cross linking of the compounds occurs to form solid elastomeric polymer articles. Known processes are relatively energy and time consuming, and can
15 comprise dip coating and injection moulding, for example. In particular, known processes for making polymer articles have a maturation step after reacting compounds together which normally takes several days. Further cross linking through a vulcanizing step can be relatively slow. Moreover, many processes for making polymer articles comprise a leaching step where surface impurities are
20 removed which can also be relatively time consuming. All these steps increase costs required to make polymer articles.

[0003] It would be desirable to provide an improved method of making polymer articles which reduces costs by reducing time required for manufacture, including
25 reducing the amount of time for maturing, vulcanizing and leaching. It would also be

desirable to provide polymer articles which provide reduced susceptibility to chemical allergies.

SUMMARY OF THE INVENTION

5

[0004] In accordance with a first aspect, a method of making a polymer article comprises the steps of making a polymer solution by reacting a first compound containing carbodiimide groups with a second compound containing carboxylated groups, applying the polymer solution to a former, wherein the step of applying occurs within 2 hours of the making of the polymer solution, and curing the polymer solution. The polymer solution can have a pH adjuster consisting of ammonium hydroxide.

15

[0005] From the foregoing disclosure and the following more detailed description of various embodiments it will be apparent to those skilled in the art that the present invention provides a significant advance in the technology of making polymer articles. Particularly significant in this regard is the potential the invention affords for providing high quality polymer articles at much lower costs. Additional features and advantages of various embodiments will be better understood in view of the detailed description provided below.

20

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

25

[0006] It will be apparent to those skilled in the art, that is, to those who have knowledge or experience in this area of technology, that many uses and design

variations are possible for the making of polymer articles disclosed here. The following detailed discussion of various alternate features and embodiments will illustrate the general principles of the invention with reference to making thin wall polymer articles. Other embodiments suitable for other applications will be apparent to those skilled in the art given the benefit of this disclosure.

[0007] The present invention relates to methods of making polymer articles.

Representative examples of polymer articles which can be made using the process described herein comprise medical, surgical and/or laboratory gloves and condoms.

Other suitable polymeric articles will be readily apparent to those skilled in the art given the benefit of this disclosure. Advantageously, polymer articles made by the processes disclosed herein can be free of cross linking agents such as sulphur, zinc oxide, stearic acid and accelerators such as carbamates, thiazoles, thiurams, thioureas, sulphenamides, xanthates, guanidines and their derivatives.

[0008] In accordance with one embodiment, a method of making a polymer article comprises making a polymer solution by mixing a first compound containing carbodiimide groups with a second compound containing carboxylated groups. The polymer solution is applied to a former, and the polymer solution is cured. In accordance with a highly advantageous feature, the polymer solution can be applied to the former within 2 hours of the making of the polymer solution, greatly decreasing total manufacturing time.

[0009] As used herein, the term "polymer" is a large molecule comprising repeating structural units and can be an elastomeric polymer or latex which includes

homopolymers, copolymers, terpolymers and modifications thereof, including mixtures of polymers. The term polymer solution is a mixture of at least a first compound containing carbodiimide groups and a second compound containing carboxylated groups, along with any necessary solvents. A polymer article is an article formed as a result of the processes disclosed herein, such as a pair of gloves.

[0010] Suitable examples of first compounds with carbodiimide groups comprise, for example, mono-, di-, tri-, tetra-, oligo- or poly-carbodiimides, aliphatic or aromatic, and mixtures thereof, having a functional carbodiimide group $-N=C=N-$. Examples of suitable mono-carbodiimides include, but are not limited to dicyclohexylcarbodiimide, diisopropylcarbodiimide, dimethylcarbodiimide, diisobutylcarbodiimide, di-*t*-butylcarbodiimide, *t*-butylisopropylcarbodiimide, dioctylcarbodiimide, diphenylcarbodiimide, *N,N'*-Bis(2-methylphenyl)carbodiimide, 1,3-Di-*p*-tolylcarbodiimide, di- β -naphthylcarbodiimide, ethyl-3-(3-dimethylaminopropyl)carbodiimide, 1,3-Bis(Trimethylsilyl)carbodiimide, *N*-(*tert*-butyl)-*N'*-(2,6-dichlorophenyl)carbodiimide, *N*-(*tert*-butyl)-*N'*-(1-(2-chlorophenyl)-1-methylethyl)carbodiimide and *N*-butyl-*N'*-(1-(2-chlorophenyl)-1-methylethyl)carbodiimide. Examples of suitable poly-carbodiimides comprise, for example, polycarbodiimides terminated with aromatic, aliphatic or alicyclic diisocyanates and mixtures thereof, for example, tetramethylxylylene diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, 1,4-phenylene-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 3-isocyanatomethyl-3,3,5-trimethylcyclohexylisocyanate, 1,6-hexyldiisocyanate, 1,4-cyclohexyl-diisocyanate, norbonyldiisocyanate, 1,5-naphthylene diisocyanate, 4,4-

diphenyldimethylmethane diisocyanate, 1,3-phenylene diisocyanate, hexamethylene diisocyanate, xylylene diisocyanate, and methylcyclohexane diisocyanate. Other suitable carbodiimides will be readily apparent to those skilled in the art given the benefit of this disclosure.

5

[0011] Suitable examples of second compounds containing carboxylate groups comprise, for example, modified natural rubber latex, synthetic polymers such as acrylonitrile butadiene, isoprene, styrene, chloroprene, ethylene, vinyl chloride and copolymers, blends and mixtures thereof. The carboxylate groups in the polymer
10 comprise, for example, carboxylic acid such as prop-2-enoic acid, 2-methylpropenoic acid, 2-methylidenebutanedioic acid, (Z)-butenedioic acid, (E)-butenedioic acid and (E)-but-2-enoic acid, or an anhydride thereof with a prop-2-enoic ester such as methyl-, ethyl-, butyl-, 2ethylhexyl- and 2-hydroxyethyl propenoates, or an acrylic monomer other than prop-2-enoic acid
15 such as acrylamide and acrylonitrile, or a-methylstyrene, vinyl acetate or the like. In an example, the second compound can be an acrylonitrile with 2-methylpropenoic acid terpolymer, with an amount of 2-methylpropenoic acid equivalent of about 1 to 10% by dry weight of the base polymer, preferably 2 to 7% by dry weight of the base polymer. Other suitable polymers with carboxylate groups will be readily apparent to
20 those skilled in the art given the benefit of this disclosure.

[0012] The polymer solution comprises a mixture of the first compound having carbodiimide groups, a second compound having carboxylate groups and water, such as demineralised water. In accordance with a highly advantageous feature, a
25 weak alkali as a pH adjuster may also be present in the polymer solution. The weak

alkali can comprise, for example, ammonium hydroxide at about a 5-10% concentration by weight of a total weight of the solution. The polymer solution may also include additives such as anti-oxidants such as butylated reaction product of p-cresol and cyclopentadiene (BPC), anti-ozonants such as a paraffin wax, mineral fillers, lubricants, reodorants, colorants, biocides, thickeners, defoamers, wetting agents, pigments such as titanium dioxide.

[0013] In accordance with a highly advantageous feature, the polymer solution can be mixed under mild conditions, such as 30-40°C under slow agitation for less than two hours, or less than one hour, or even less than thirty minutes. Therefore the step of applying the polymer solution can occur within two hours, within one hour, or even within thirty minutes of the step of making the polymer solution. This short maturation step eliminates the need for large amounts of the polymer solution to be stored at the manufacturing site for multiple days.

[0014] Once the polymer solution is made and ready to be applied, it may be applied to a former. The term "former" is understood broadly to refer to a standard shape former, such as an element to which the polymer solution coats prior to curing and can comprise, for example, a former used in a dip coating process. Depending upon the desired polymer article, surfaces of a mould cavity used in an injection moulding process can also serve as the former.

[0015] For the dip coating process, prior to the step of dipping former into the polymer solution, a step of pretreating the former is desired. The step can comprise, for example, pretreating the former with a precoat which comprises at least a

surfactant, a release agent and an ionic solution. For example, a precoat can comprise a mixture of a precoat first solution 8-20% by weight of the first solution of calcium ions, a precoat second solution of 0.05-0.25% by weight of the second solution of a non-ionic silicone-free surfactant, and a precoat third solution of 0.5-2.5% by weight of the third solution of a pre-homogenized release agent. The former may have the precoat applied (by dipping, for example), and dried at 110-130°C for 60 seconds or longer. Preferably the former has a surface temperature of about 50-60°C when the polymer solution is applied to the former.

[0016] Once the former is prepared, the polymer solution may be applied to the former. This can be done in one of many different ways. For example, the (optionally precoated) former may be dipped into the polymer solution for a limited period of time (5-20 seconds) at generally ambient conditions, and then dried. Drying may occur in an oven at 110-130°C for 30-60 seconds. The result is that the former is coated with a wet gel. Optionally, this wet gel may be treated with a mild organic acid to help reduce the pH of the wet gel. Optionally a step of pre-leaching may also comprise dipping the wet gel coated former in warm water. A lubricant may also be applied to the wet gel. The edge of the semi-dried wet gel may be rolled down to form a bead. The bead can help with stripping the polymer article from the former.

[0017] In addition to reduced times for maturation, the step of curing the polymer solution can also be reduced. Curing the polymer solution creates an intermediate solid. For example, where first compound is a butadiene acrylonitrile elastomer latex, the curing step can be accelerated, can be performed at lower temperatures

and can occur in less than 20 minutes to form a cured carboxylated nitrile latex.

More preferably, the step of curing can occur in 8 to 20 minutes, or 12 to 16 minutes in an oven at a temperature of 80-130°, or even 80-90°C.

- 5 [0018] The intermediate solid or latex, can then be subjected to a step of leaching to remove surface impurities. In accordance with a highly advantageous feature, the time required for the step of leaching can also be reduced since there can be no accelerators, sulphur, zinc oxide or other cross-linking agents to be removed. The step of leaching can occur by dipping the latex into water having a temperature of
- 10 50-60°C for only 50-120 seconds, preferably only 50-70 seconds. Once the step of leaching is completed, the latex may be dried and a resulting polymer article (such as a thin wall article of thickness 0.03 to 0.33mm, forming a glove, finger cot, condom, balloon, bladder bag, catheter, tubing, rubber band, tourniquet, elastic band, diaphragm, dental dam, sheath, etc.,) may be removed from the former.
- 15 Optionally the resulting product formed by the above disclosed process may be allowed to set permanently for 12-24 hours in a humidity controlled room.

[0019] EXAMPLES 1-5. Polymer articles were made having the formulae set forth in Table 1 were mixed at a temperature of about 30°C for about 60 minutes.

- 20 Commercially available compounds containing carboxylate groups (ELx-A, ELx-B, ELx-C, ELx-E and ELx-F) are mixed with a carbodiimide compound (CDI), along with ammonium hydroxide, an antioxidant (butylated reaction product of p-cresol and cyclopentadiene (BPC)), and titanium dioxide (TiO₂). The amount of each component of the polymer solution is set forth based upon 100 dry parts by weight of
- 25 the compound containing the carboxylate groups. Demineralised water was added

to the compound to produce a formulation containing 15-20% solids. Clean formers were evenly coated with a precoat, and then with the various polymer solutions of Table 1. The wet gel on the formers was cured at 130°C for 15 minutes. The cured films were stripped from the formers and conditioned for 24 hrs.

TABLE 1

Formulation	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
ELx-A	100	-	-	-	-
ELx-B	-	100	-	-	-
ELx-C (5-6% MAA)	-	-	100	-	-
ELx-E	-	-	-	100	-
ELx-F	-	-	-	-	100
NH4OH	1	1	1	1	1
CDI eq. 430	2	2	2	2	2
BPC	1	1	1	1	1
TiO ₂	1	1	1	1	1

MAA = 2-methylpropenoic acid

[0020] The films made according to Examples 1-5 were each tested for tensile strength (TS), elongation, 300% modulus and 500% modulus per ASTM D-412, elongation break (Eb), solvent resistance in toluene (LS-t) and cyclohexanone (LS-c). The results of these tests are shown in Table 2. The results show that the

carboxylated compounds were effectively cross-linked using a carbodiimide compound producing polymer articles with high tensile strength and having good chemical resistance to non-polar toluene (<85% linear swell) and polar cyclohexanone (<123% linear swell).

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Physical Properties					
Thickness, mm	0.06-0.07	0.06-0.07	0.06-0.07	0.06-0.07	0.06-0.07
TS, MPa	21-23	32-37	29-35	29-37	30-37
M300, MPa	1.8-2.1	2.3-2.8	1.8-2.3	2.1-2.3	1.9-2.1
M500, MPa	4-5.2	5.9-8.8	4.4-5.9	4.5-6.3	4-4.6
Eb, %	700	650-700	650-700	700-750	700-750
LS-t, %	62-68	-	73-85	50-56	65-72
LS-c, %	100-112	100-112	104-108	115-123	108-123

Film linear swell in: toluene (LS-t); cyclohexanone (LS-c).

[0021] EXAMPLES 6-9. Thin wall polymer articles were made using the same method as in Example 1, but from formulations with various types of carbodiimide compounds (CDI) at 5 parts/100 of carboxylated compound as shown in Table 3.

The film characteristics are as shown in Table 4. The results show that the

carbodiimide compound crosslinks effectively with the compound containing carboxylate groups to produce thin wall polymer articles with high tensile strength. The polymer articles are chemically stronger towards both polar and non-polar solvents at a higher dosage of CDI as compared to that of Examples 1-5.

5

TABLE 3

Formulation	Ex. 6	Ex. 7	Ex. 8	Ex. 9
ELx-C 5.5% MAA	100	100	100	100
NH ₄ OH	1	1	1	1
CDI eq. 445	5	-	-	-
CDI eq. 590	-	5	-	-
CDI eq. 385	-	-	5	-
15 CDI eq. 430	-	-	-	5
BPC	1	1	1	1
TiO ₂	1	1	1	1

Eq = carbodiimide equivalent, chemical formula weight for 1 mole of carbodiimide group. For example, CDI eq. 430 means 1 mole of the carbodiimide group in the polycarbodiimide polymer chain has an average weight of 430 g.

20

TABLE 4

25

Ex. 6	Ex. 7	Ex. 8	Ex. 9
-------	-------	-------	-------

Physical Properties

	Thickness, mm	0.06-07	0.06-0.07	0.06-0.07	0.06-0.07
	TS, MPa	28-36	35-37	34-40	35-40
5	M300, MPa	3.6-4.7	1.9-2.6	4.1-5.4	5.5-7.5
	M500, MPa	12.7-25	4.1-5.6	32-38	28-36
	Eb, %	500-550	650-750	500-550	500-550
	LS-t, %	40-52	40-52	40-52	40-52
10	LS-c, %	81-85	96-108	73-77	77

Film linear swelling in: toluene (LS-t); cyclohexanone (LS-c).

[0022] EXAMPLES 10-15. Thin filmed polymer articles were made using the same
15 method as in Example 1, but from formulations with varying dosage of CDI with Eq.
430, as shown in Table 5. Polymer article characteristics are as shown in Table 6.
The results show that CDI could be used at about 1 to 15 parts per 100 of the
carboxylated compound to produce thin films with various levels of chemical
resistance. The data also show that the breakthrough leak time of the polar solvent
20 through the elastomeric film were more than 330 minutes.

TABLE 5

Formulation	Ex.10	Ex.11	Ex.12	Ex.13	Ex.14	Ex.15
-------------	-------	-------	-------	-------	-------	-------

	ELx-C 5.5% MAA	100	100	100	100	100	100
	NH ₄ OH	1	1	1	1	1	1
	CDI eq. 430	1	2	3	5	10	15
	BPC	1	1	1	1	1	1
5	TiO ₂	1	1	1	1	1	1

TABLE 6

10		Ex. 10	Ex. 11	Ex.12	Ex. 13
----	--	--------	--------	-------	--------

Physical Properties

	Thickness, mm	0.07-0.08	0.07-0.08	0.07-0.08	0.07-0.08
	TS, MPa	27-41	29-35	30-44	30-35
15	M300, MPa	1.5-2.1	1.8-2.3	2.6-4	4.8-5.1
	M500, MPa	2.7-5.1	4.4-5.9	9.5-16.5	19-20
	Eb, %	700-750	650-700	600-650	550-600

	LS-t, %	-	73-85	-	40-52
20	LS-c, %	123-135	100	85-88	77-88
	LS-h, %	0-4	0-4	0-4	0-4
	LS-a, %	42-50	35-48	35-42	27-35
	BT-c, min	-	-	-	> 360

Film linear swell in: toluene (LS-t); cyclohexanone (LS-c); hexane (LS-h); acetone (LS-a) BT-c = breakthrough time of cyclohexanone through the elastomeric film.

TABLE 6 - CONTINUED

5			
		Ex. 14	Ex.15
	Physical Properties		
	Thickness, mm	0.09-0.1	0.08-0.09
10	LS-t, %	40-44	40-44
	LS-c, %	68-72	64-68
	LS-h, %	0-4	0-4
	LS-a, %	30-38	30-38
	BT-c, min	> 334	> 330
15			

[0023] COMPARATIVE EXAMPLES.

EXAMPLE 16. Elastomeric films were made using accelerator-free and sulphur-free formulation adopted from the Example in US Patent Publication 2002/0114943 A1, as shown in Table 7. Zinc oxide (ZnO) was used to crosslink the carboxylated latex. Potassium hydroxide solution (KOH) was used to adjust the compound pH to about 9.5.

[0024] EXAMPLE 17. Elastomeric films were made using zinc-free formulation adopted from the Example in US Patent 6,451,893, as shown in Table 7.

Accelerators zincdi-n-butyldithiocarbamate (ZDBC) and zinc mercaptobenzothiazole (ZMBT) and sulphur were used to crosslink the carboxylated latex. Antioxidant 2,2'-methylene-bis-(4-methyl-6-butylphenol) (MBPC) was incorporated.

5 [0025] EXAMPLE 18. Elastomeric films were made using a conventional formulation comprising of accelerator, sulphur and zinc oxide as shown in Table 7.

[0026] EXAMPLE 19. Elastomeric films were made using a self-crosslinking carboxylated nitrile latex (X-NBR-SXL) adopted from WO 2011/068394, as shown in
10 Table 7.

[0027] The film characteristics are as shown in Table 8. The physical properties of the films were good, but the chemical resistance of the films was poorer than that of embodiments of polymer articles of the present invention. The breakthrough leak
15 times of cyclohexanone through the films were significantly shorter for the Comparative Examples.

TABLE 7

20	Formulation	Ex. 16	Ex. 17	Ex. 18	Ex. 19
	ELx-C 5.5% MAA	100	100	100	-
	X-NBR-SXL	-	-	-	100
	KOH	1	1	1	1.35
25	ZnO	1	-	1	1.2

	ZDBC	-	1	0.5	-
	ZMBT	-	1	-	-
	Sulphur	-	3	1	-
	BPC	1	-	1	1
5	MBPC	-	0.5	-	-
	TiO ₂	1.5	0.5	1	0.75
	Blue pigment	0.15	-	-	0.05

10

TABLE 8

		Ex. 16	Ex. 17	Ex. 18	Ex. 19
15	Physical Properties				
	Thickness, mm	0.09-0.1	0.08-0.09	0.08-0.1	0.1
	TS, MPa	45-46	36-43	31-47	24-25
	M300, MPa	3.8-4.5	8.9-9.3	2.1-3.6	3.1-7
	M500, MPa	10-13.4	4.4-6.6	4.1-8.3	6.9-8.2
20	Eb, %	650-700	700-750	650-750	650-750
	LS-t, %	84-88	80	70-74	68-72
	LS-c, %	112-168	148	120-128	120-124
	BT-c, min	8-12	15	7	10-13

25

Film linear swell in: toluene (LS-t); cyclohexanone (LS-c); BT-c = breakthrough time of cyclohexanone through the elastomeric film.

[0028] EXAMPLES 20-23. Elastomeric gloves were made using the same formulation as in Example 11, but cured at various temperatures from 80 to 130°C, for 15 minutes. The resulting characteristics are as shown in Table 9. The results show gloves with good physical and chemical resistance properties. The durability challenge shows the CDI crosslinked gloves could be worn for more than 3 hours without breaking down in human sweat under actual laboratory working conditions.

TABLE 9

	Ex. 20	Ex. 21	Ex. 22	Ex. 23
Cure temperature				
15	110°C	120°C	130°C	80°C
Physical Properties				
Thickness, mm	0.08-0.09	0.08-0.09	0.08-0.09	0.07-0.08
TS, MPa	36-41	34-41	35-41	36-44
20 M300, MPa	3.5-3.8	3.5-4	3.2-4.6	3.9-4.1
M500, MPa	10.6-12.9	8.2-14.8	9.2-13.3	10.2-11
Eb, %	600-650	600-650	600-650	650-700
LS-c, %	82-88	85-88	84-87	83-92
25 Durability, min	> 180	> 180	> 180	> 180

Film linear swelling in cyclohexanone (LS-c).

Durability = time taken for a glove to disintegrate, break up or tear (especially at crotches) after wearing under actual working conditions.

5

[0029] EXAMPLES 24-27. Thin filmed polymer articles were made using the same formulation as in Example 11, but dipped at various stages of its pot life from 1 to 168 hours after adding carbodiimides into the latex. The film characteristics are as shown in Table 10.

10

TABLE 10

	Ex. 24	Ex. 25	Ex. 26	Ex. 27
Pot life	1 hr	24 hr	48 hr	168 hr
Physical Properties				
Thickness, mm	0.08	0.08	0.08	0.08
TS, MPa	40-42	34-41	35-44	24-31
M300, MPa	3.8-4	2.6-3.2	2.6-3.3	2.3-2.5
M500, MPa	16.5	7.8-12.5	9.5-12.5	5.8-7.2
Eb, %	600	550-600	600-650	650-700
LS-c, %	89	89	85	100
Durability, min	> 180	> 180	> 180	> 120

15

20

5

Film linear swelling in cyclohexanone (LS-c);

Durability = time taken for a glove to disintegrate, break up or tear (especially at crotches) after wearing under actual working conditions.

- 5 [0030] From the foregoing disclosure and detailed description of certain embodiments, it will be apparent that various modifications, additions and other alternative embodiments are possible without departing from the true scope and spirit of the invention. For example, in certain embodiments zinc oxide can be used in combination with the first compound and second compound without significant
- 10 effect on the resulting polymer article. The embodiments discussed were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to use the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the
- 15 scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

CLAIMS

1. A method of making a polymer article comprising, in combination, the steps
5 of:

making a polymer solution by mixing a first compound containing
carbodiimide groups with a second compound containing carboxylated groups;
applying the polymer solution to a former, wherein the step of applying occurs
within 2 hours of the making of the polymer solution; and
10 curing the polymer solution.

2. The method according to claim 1, wherein the step of applying the polymer
solution to a former comprises dipping the former into the polymer solution.

15 3. The method according to claim 1, wherein the polymer solution further
comprises demineralised water.

4. The method according to claim 1 further comprising the step of pretreating the
former with a precoat, wherein the precoat comprises at least a surfactant, a release
20 agent and an ionic solution.

5. The method according to claim 1, wherein the step of making of the polymer
solution is done without use of sulphur, zinc oxide and/or an accelerator.

6. The method according to claim 1 further comprising the step of stripping the polymer article from the former.

7. The method according to claim 1, wherein the step of applying occurs within 1 hour of the step of making the polymer solution.

8. The method according to claim 7, wherein the step of applying occurs within 30 minutes of the step of making the polymer solution.

9. The method according to claim 1 wherein the step of curing lasts 8 to 20 minutes.

10. The method according to claim 9, wherein the step of curing lasts 12 to 16 minutes.

11. The method according to claim 1, wherein the step of curing cures the polymer solution to form a cured carboxylated nitrile latex, and further comprising the step of leaching the latex for 50-120 seconds after the step of curing.

12. The method according to claim 11, wherein the step of leaching the latex occurs 50-70 seconds after the step of curing.

13. The method of claim 1, wherein the step of curing is performed at a temperature of 80-90°C.

14. A product formed by the method of any of the preceding claims.

15. A polymer article formed from a cured carboxylated nitrile latex, comprising, in combination:

5 a first compound containing carbodiimide groups,

a second compound containing carboxylated groups, and

a pH adjuster consisting of ammonium hydroxide.

16. The polymer article according to claim 15, wherein the latex is free of any one
10 of a crosslinking agent containing sulphur, zinc oxide, stearic acid and an accelerator.

17. The polymer article according to claim 16, wherein the accelerator comprises carbamates, thiazoles, thiurams, thioureas, sulphenamides, xanthates, guanidines or
15 their derivatives.

18. The polymer article according to claim 15, wherein the latex further comprises at least one pigment.

20 19. The polymer article according to claim 15, wherein the latex further comprises an antioxidant and an antiozonant.

20. The polymer article according to claim 15, wherein the polymer article is a thin wall article having a thickness of 0.03 mm to 0.33 mm.