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Maleated coupling agents for natural fibre composites

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Abstract

Maleated coupling agents are widely used to strengthen composites containing fillers and fibre reinforcements. The established role of MaPOs results from two main factors, economical manufacturing and the efficient interaction of maleic anhydride with the functional surface of fibre reinforcements. Peak performance was demonstrated in agrofibre polypropylene composites by selecting a maleated coupler that has the appropriate balance of molecular weight and maleic anhydride content. The flexural and tensile strengths of the 30% agrofibre composites increased by more than 60% with Epolene™ G-3015. Newly developed MaPE couplers for the wood-polyethylene market demonstrate superior performance compared against other potential polyolefin coupling agents. Results indicate that the new polyethylene couplers at 3% loading can double the tensile strength and triple the impact properties compared to non-coupled blend of wood and polyethylene.

Keywords: B. Fibre/matrix bond; B. Interface/interphase; D. Mechanical testing; A. Wood

1. Introduction

The use of MaPO coupling agents for glass-reinforced composites is well known and widely practiced. In natural fibre composites, weak adhesion may result from poor dispersion and incompatibility between the hydrophilic natural fibres and the hydrophobic polymer. Poor composite strength results from the lack of stress transfer from the polymer matrix to the load bearing natural fibres [1–4]. A direct measure of adhesion between natural fibres and thermoplastics is bonding strength. Interactions between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fibres can overcome the incompatibility problem to increase tensile and flexural strengths of natural fibre thermoplastic composites [3,5–7].

The initial discussion relates to the manufacture and acid number evaluation of MaPOs. Typical manufacturing methods for MaPOs and reasons for their success as couplers are provided.

The first investigation presented here was performed by Agrotechnological Research Institute (ATO-DLO) utilizing various maleated polypropylene (MaPP) coupling agents in agrofibre/polypropylene (PP) composites. Physical property data indicates a maleated coupling agent with the correct balance of maleic anhydride and molecular weight can achieve peak performance in natural fibre composites.

The second investigation compares the effectiveness of oxidized polyethylene, MaPP, and newly developed maleated polyethylene (MaPE) couplers in wood–fibre/high density polyethylene (PE) composites. The MaPE couplers were expected and shown to be superior in the PE composites based on physical property data.

2. MaPO—industry success and grafting mechanisms

The success of MaPO coupling agents may be attributed to two main reasons. First, MaPOs can be readily and economically produced. By the judicious choice of peroxide and reaction temperature, the grafting of maleic anhydride onto PP or PP copolymers can be controlled to give a polyolefin with the desired level of grafted maleic anhydride. The peroxide grafting of the maleic anhydride occurs at the tertiary carbons of the polymer chain or at the terminal unsaturation of the chain.

The exact mechanisms of the grafting reaction have been and continue to be debated in the literature [8,9]. Structural studies by Whitney et al. [10] suggest that the grafting utilizes the carbon–carbon unsaturation of the maleic anhydride group to form the bond to the polymer chain thus leaving the anhydride group free to react as an anhydride in the newly formed polymer. It is the presence of the relatively polar

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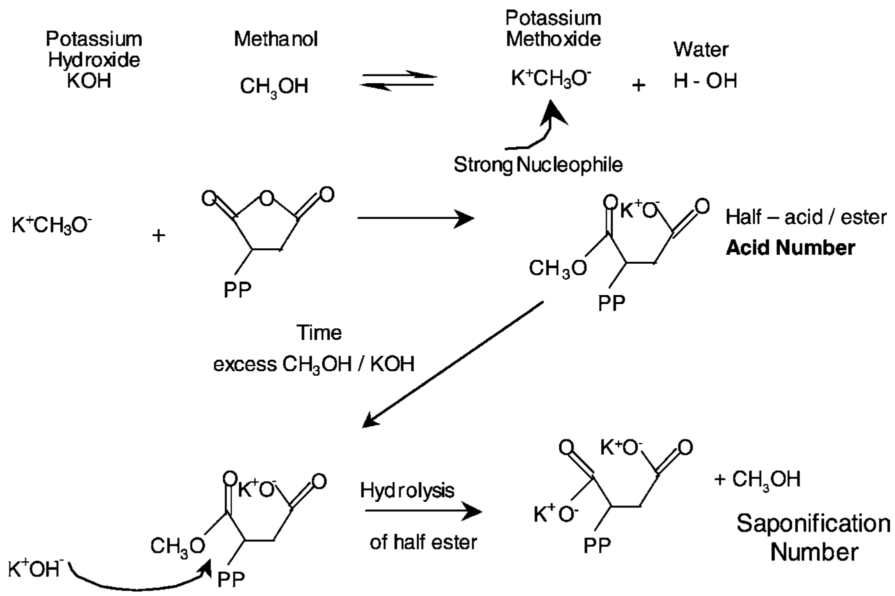

Fig. 1. Chemical reactions which occur in the acid number and saponification number tests.

anhydride group on the olefin which imparts the unique set of properties to the graft polymer that make these polymers good couplers for natural fibres in polyolefins.

Unlike acrylic or methacrylic acid, maleic anhydride does not readily react with itself under typical industrial grafting conditions. The decreased tendency to participate in side reactions and the versatility of the anhydride group over an acid group makes maleic anhydride the graft moiety of choice when grafting a reactive polar group onto PP. As the polymer is grafted with maleic anhydride, the viscosity and hence the molecular weight are lowered due to chain degradation via the beta-scission reaction.

The second reason for the success of MaPO couplers pertains to their excellent balance of properties to bridge the interface between polar and nonpolar species. A coupler holds dissimilar materials together. In the case of a MaPO, the coupler may co-crystallize with the continuous polyolefin while the maleic anhydride portion of the molecule can interact with the more polar wood surface.

Evidence suggests the interaction between the coupler and wood may be of a covalent nature per Qingxiu et al. [11]. Lu et al. suggest a broader interfacial bonding consisting of covalent bonds, secondary bonding (such as hydrogen bonding and van der Wales's forces) and mechanical interblocking [3]. The mechanical interblocking may occur between the wood and coupler and the polymer and coupler. All of these bonding forms may concurrently exist across the interface at varying degrees.

3. MaPO manufacturing, acid number measurement, and coupling description

Among the most efficient methods to produce MaPOs is reactive extrusion. The polyolefin, maleic anhydride, and peroxide are introduced into the extruder with inherent flexibility in the sequence of addition and operating conditions. The extruder process with its typically short residence time allows the acid number of the polymer to be controlled to a greater extent independently of the viscosity. In addition PE, which is very difficult to maleate in the melt except to very low acid number, can be readily and successfully maleated using reactive extrusion. Patented processes have been developed which greatly expand the availability of useful MaPOs.

A titration is used to measure the acid number of the maleic anhydride graft polymer. The acid number is a measure of the amount of maleic anhydride contained in the polymer. Acid number is defined in ASTM D 1386[1] as the milligrams of potassium hydroxide required to neutralize 1 g of sample. Alcoholic potassium hydroxide is used to titrate the MaPO, which has been dissolved in hot solvent (i.e. xylene). The basic potassium alcoxide solution neutralizes one carboxyl group of the maleic anhydride ring to create a half acid ester (Fig. 1). The saponification number reflects neutralization of both carboxyl groups of the maleic anhydride ring and is usually twice the acid number for maleic anhydride grafted polymers.

When the acid number test is run on a stored sample, a falsely high value may result due to the hydrolysis reaction that occurs at ambient conditions. The reaction opens the anhydride to the diacid resulting in both acid sites being neutralized. Heating the maleated coupler just enough to reach a molten state will drive off the water. After the sample cools it can be accurately tested for the acid number.

Traditional manufacturing methods require that the amount of peroxide and maleic anhydride be increased to

[1] ASTM D 1386 Test Method for Acid Number (Empirical) of Synthetic and Natural Waxes Vol. 15.04.

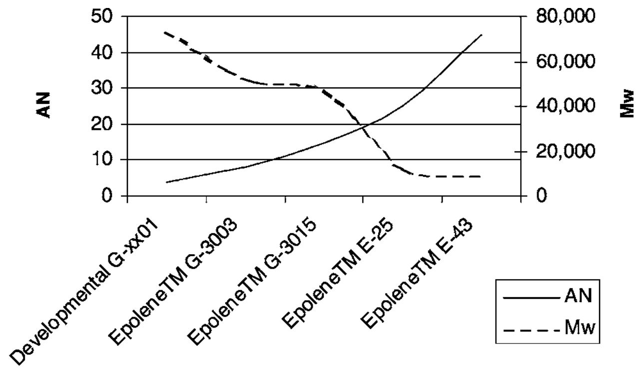

Fig. 2. Relationship between acid number and molecular weight of maleated polypropylenes produced in traditional processes.

increase the acid number which also increases chain degradation by beta scission. The challenge for manufacturers of MaPOs is to achieve the proper balance of molecular weight and number of grafts.

Low molecular weight will not allow the coupler to interact and entangle sufficiently with the polyolefin phase. Too high molecular weight may not allow the coupler to reside at the interface. A low acid number may not give the coupler enough sites for attachment to the polar filler. Too high of an acid number may hold the coupler too close to the polar surface and not allow sufficient interaction with the continuous nonpolar phase. Maleated couplers need enough acid functionality to attract the filler and enough molecular weight to entangle or crystallize into the base polymer. Fig. 2 depicts the acid number/molecular weight relationship for a number of commercial and developmental MaPP coupling agents.

4. Experimental—MaPP for agrofibre/PP composites

The demands required of a MaPP coupler can be application dependant. The optimum molecular weight/acid number balance for composites of fiberglass vs. natural fiber may differ [12]. The ATO-DLO [13] study was to assess performance of various MaPP coupling agents in PP composites containing natural fibres.

5. Materials—MaPP for agrofibre/PP composites

Agrofibre/PP composites were made from flax and jute agrofibres without sizing at a loading of 30 wt% fibre. The fibre chops were 6.25 mm before extrusion and 1–2 mm after extrusion. After processing the fibre diameter was 10–20 μ (i.e. basically the diameter of one fibre cell of flax or jute) and the aspect ratio was 50–100.

Tests specimens included 30 weight (wt)% fibre (jute or flax) in PP. The coupling agents were incorporated into the composites at 1, 3, and 5% levels. The physical properties of three Epolene™ G-series maleated coupling agents tested in agrofibre/PP composites at ATO-DLO are shown in Fig. 2. Their melting points were between 155 and 158 °C. The blank was 30 wt% fibre without coupler. The control was the 'best-to-date' maleated coupler that had been tested by ATO-DLO at the time.

6. Method—MaPP for agrofibre/PP composites

Sample preparation details were as follows: the twin screw extruder had a 38:1 L/D ratio, the extruder temperature was 200 °C, the extruder speed was 200 rpm, the PP and Ma-PP were pre-blended, and natural fibres were added using a proprietary technique with no pre-drying, but removal of volatiles from the melt.

All extrusion compounds were injection molded into specimens and conditioned at 23 °C and 50% relative humidity for 1 week before mechanical testing. Physical analysis included: flexural ISO 180[2], tensile ISO 527-2[3] specimen type 1BA, Charpy Impact ISO-179[4], and scanning electron microscopy (SEM).

7. Results—MaPP for agrofibre/PP composites

Physical property data are shown in Table 2 and SEMs are shown in Figs. 3(a) and (b) to indicate the benefits of utilizing a balanced maleated coupler. The % change values in Table 1 are based on the increase in performance using a maleated coupler compared to the blank that contained no coupler. Six main tests result areas are shown, three physical property tests for jute and three for flax. The highest % change in each of the six areas is highlighted with a box around the data. In four of the six areas, the highest performance resulted from Epolene™ G-3015, which is a medium molecular weight, medium acid number coupler. It should also be noted that the optimum concentration of the coupler appears to be 3%.

Epolene™ G-3015 has twice the acid number and 10% lower molecular weight than the Epolene™ G-3003. Comparing the Epolene™ G-3003 and Epolene™ E-43, the acid number is five times higher and the molecular weight is 80% lower for Epolene™ E-43. Epolene™ G-3015, with its intermediate acid number and molecular weight provides optimal performance in these natural fibre reinforced systems, illustrating the need for a versatile manufacturing process that can attain the required balance of properties in the coupling agent.

[2] Flexural ISO 180 Determination of Izod Impact Strength.

[3] Tensile ISO 527-2 Determination of Tensile Properties—Part 2: test conditions for moulding and extrusion plastics.

[4] Charpy Impact ISO Determination of Charpy Impact Properties.

(a)

(b)

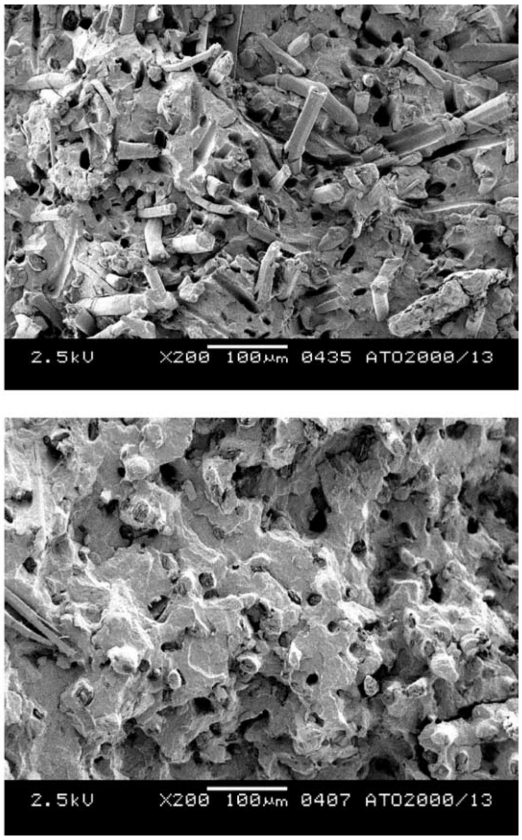

Fig. 3. (a) SEM ×200 of 30 wt% agrofibre/PP composite without coupler shows voids and pull outs (courtesy ATO-DLO). (b) SEM ×200 of 30 wt% agrofibre/PP composite with 3% Epolene™ G-3015 shows good fibre wetting and interblocking. (courtesy ATO-DLO).

8. Experimental—MaPE for wood/PE composites

The vast majority of the wood–polymer composites in North America are PE based. Newly developed MaPE couplers were shown to perform much better than other potential polyolefin couplers to improve the tensile and impact properties of wood/HDPE composites.

9. Materials—MaPE for wood/PE composites

The base polymer used was a 16 melt flow high density polyethylene (HDPE) supplied by Eastman Chemical Company. The wood fibre used was a 40 mesh oak supplied by American Wood Fibres. The coupled composites all contained 50% (±2%) wood and 3% coupler. The control was a 50/50 blend of wood and HDPE with no coupler. The physical properties of various couplers tested as potential couplers are shown in Table 2.

10. Method—MaPE for wood/PE composites

The HDPE/wood flour composites were produced on a Berstorff ZE25 25 mm 43L/D co-rotating twin screw extruder. The wood flour was dried at 100 °C in a forced draft oven for 24 h and was incorporated into the composite via a twin screw side feeder. The HDPE and coupler were dry-blended and added via the feed throat of the extruder. A nitrogen purge was maintained on the feed throat during compounding. The composites were extruded through a two hole die, cooled in a water bath, and strand cut into pellets. The pellets were then dried in a forced draft oven at 100 °C for 24 h before being injection molded into ASTM tensile bars for testing. Injection molding was done on an Arburg Allrounder 305. The injection pressure was 900 psi along with the following temperatures: zone 1 at 145 °C, zone 2 at 160 °C, zone 3 and zone 4 at 170 °C, and the mold at 140 °F. Details of the tensile test are as follows: test method ASTM D638[5], Instron Model 1122, Testworks Software Version 3.10, crosshead speed of two inches per minute, grip separation of 4.5 inches, conditioning for 2 weeks prior to testing at 23 °C (± 2 °C) and humidity of 50% (± 5%). Details of the un-notched Izod impact test are as follows: test method ASTM D256[6], TMI Model 43-02 Monitor/Impact Tester, and 10 foot-pound capacity.

JMP Statistical Discovery Software™, a product of SAS Institute, Inc was used for comparing datasets and outlier

Table 1
Performance tests results for maleated polypropylene couplers used in flax and jute polypropylene composites. Units: flex and tensile (MPa), charpy (KJ/m^2) (by courtesy of ATO-DLO)

	Flex	% Chg	Tensile	% Chg	Charpy	% Chg
30% FLAX						
Blank-no coupler	49.3		33.2		14.2	
1% Epolene™ G-3003	53.1	8	37.2	12	11.8	17
3% Epolene™ G-3003	70.3	43	49.7	50	19.8	39
5% Epolene™ G-3003	68.0	38	50.0	51	24.8	75
1% Epolene™ G-3015	67.0	36	46.8	41	16.2	14
3% Epolene™ G-3015	80.5	63	53.4	61	22.0	55
5% Epolene™ G-3015	74.9	52	52.6	58	24.6	73
1% Epolene™ E-43	65.4	33	46.4	40	16.2	14
3% Epolene™ E-43	65.3	32	45.9	38	19.9	40
5% Epolene™ E-43	69.1	40	46.6	40	18.2	28
1% MaPP-Control	52.7	7	36.0	8	13.0	8
3% MaPP-Control	57.0	16	39.6	19	13.0	8
5% MaPP-Control	61.5	25	41.9	26	13.6	4
30% JUTE						
Blank-no coupler	52.4		34.1		11.8	
1% Epolene™ G-3003	57.1	9	39.3	15	9.7	18
3% Epolene™ G-3003	80.7	54	55.5	63	20.7	75
5% Epolene™ G-3003	80.6	54	55.1	62	21.0	78
1% Epolene™ G-3015	73.0	39	50.5	48	16.9	43
3% Epolene™ G-3015	82.5	57	55.9	64	21.3	81
5% Epolene™ G-3015	84.3	61	54.4	60	20.7	75
1% Epolene™ E-43	68.9	31	48.1	41	16.0	36
3% Epolene™ E-43	63.3	21	46.3	36	15.3	30
5% Epolene™ E-4	68.1	30	44.3	30	15.1	28
1% MaPP-Control	55.2	5	36.3	6	10.3	13
3% MaPP-Control	63.2	21	42.8	26	11.0	7
5% MaPP-Control	70.2	34	47.6	40	12.9	9

[5] ASTM D 638 Test Method for Tensile Properties of Plastics Vol. 08.01.
[6] ASTM D 256 Test Method for Determining the Pendulum Impact Resistance.

Table 2
Physical properties of various materials tested as potential couplers for wood/PE composites

Coupler	Type	Acid No.	Viscosity cP at 190 °C
Control	50% HDPE + 50% Wood		
Epolene™ E-20	Oxidized PE	17	1,500
MaPE Wax	Maleated PE	2	450
Epolene™ C-16	Maleated PE	3	1,700
Epolene™ E-43	Maleated PP	45	300
Epolene™ G-3015	Maleated PP	15	20,000
Epolene™ G-3003	Maleated PP	8	60,000
Competitive MaPE	Maleated PE	5	5 Melt index
131-1	Maleated PE	6	6 Melt index
129-3	Maleated PE	9	139 Melt index

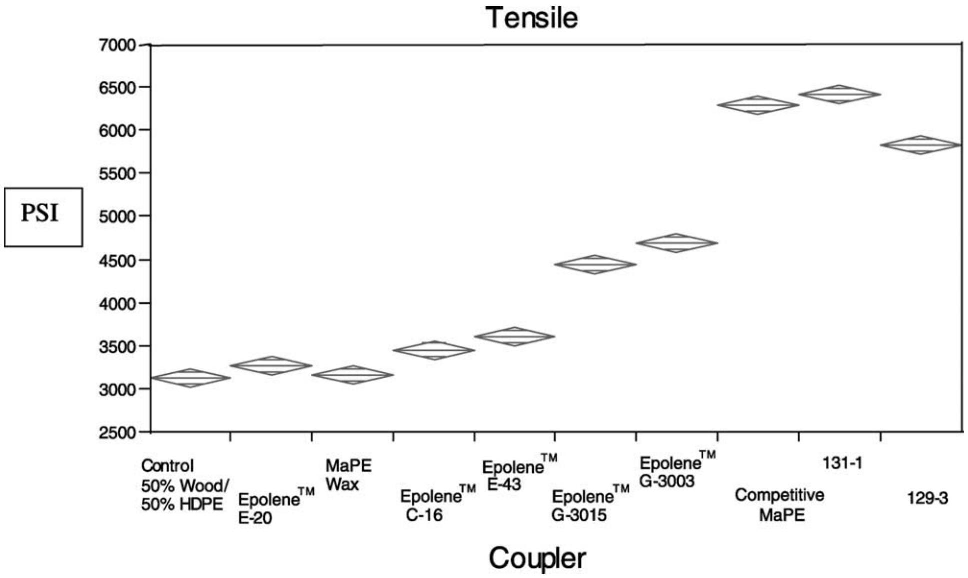

Fig. 4. Tensile results for wood/PE composites using various materials as potential couplers.

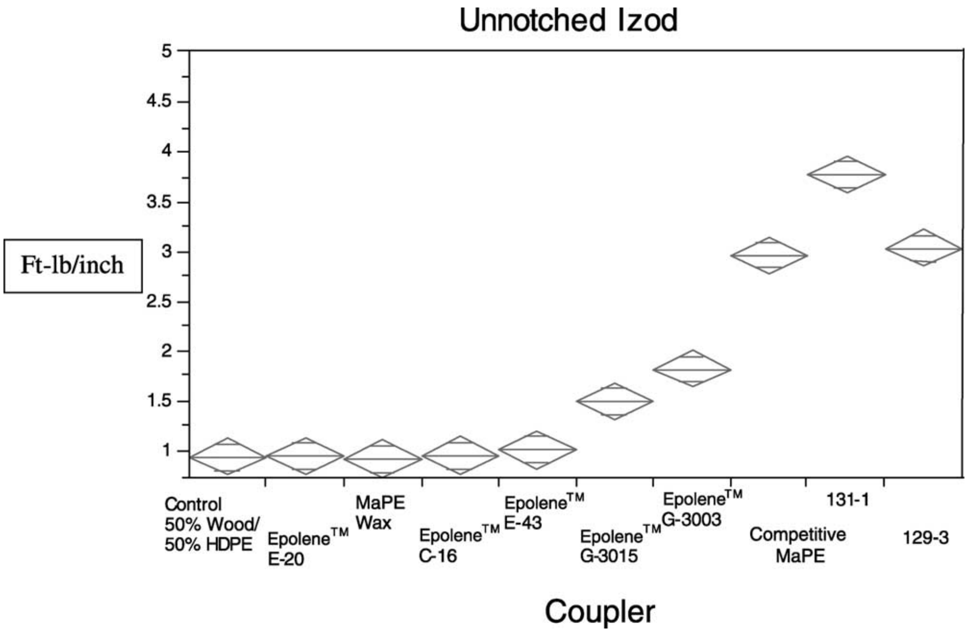

Fig. 5. Unnotched Izod results for wood/PE composites using various materials as potential couplers.

identification. Design Expert®, a product of Stat-Ease, Inc., was used for the experiment design and analysis.

11. Results—MaPE for wood/PE composites

The tests results for tensile and impact properties are shown in Figs. 4 and 5. The authors interpretations of the results are: the oxidized PE did not work well indicating that maleic functionality is required, the MaPE wax was much too low in molecular weight, Epolene™ C-16 was too low in maleic functionality, the maleated PP couplers were more effective than no coupler at all, and out of the three remaining higher molecular weight MaPEs, the newly developed MaPE labeled ‘131-1’ had the best balance of properties.

12. Conclusion

The physical properties of natural fiber/polyolefin composites can be greatly enhanced by MaPO coupling agents. Typical manufacturing processes necessitate that the molecular weight of a MaPO decrease as the acid number increases. Optimizing the balance of these two MaPO properties results in a coupler for natural fiber/polyolefin composites, which can yield 60% increases in flexural and tensile strengths. Epolene™ G-3015 was shown to be an optimized coupler by outperforming the ‘best to date’ MaPP control in ATO-DLO tests of 30% agrofibre in PP. Newly developed MaPE couplers for the wood-polyethylene market were shown to be superior to other potential polyolefin coupling agents. Results indicate that the new polyethylene couplers can double the tensile strength and triple the impact properties compared to non-coupled blend of wood and polyethylene. In all cases the optimum loading of the maleated polyolefin coupling agents was 3% based on the total composite weight.

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