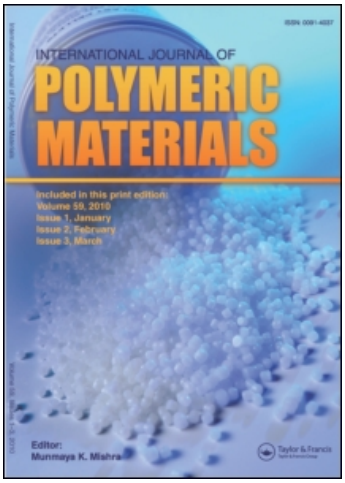

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New Thermoflameresistant Chlorinated Polymers for Rubber Bonding

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The use of new synthesized thermoflameresistant chlorinated polyolefines (64–67% Cl) with temperature of fluidity 130–340°C instead of commercial CPE, chlorinated NR and CPVC (also 64–67% Cl) with temperature of fluidity 105–120°C permits resolve the problem of the creation of heat resistant high temperature bondings for glues, adhesives for rubber bonding and other purposes.

Keywords: Chlorination; Polyolefines; Properties; Rubber bonding

INTRODUCTION

Highly Chlorinated Natural Rubbers (CNR), Chlorinated Polyethylenes (CPE), and also Chlorinated PVC (CPVC), containing 64–66% Cl, are widely used in industry for production of glues and adhesives for rubber bonding.

The main deficiency of these polymers is their low temperature of fluidity (T_F) – 105–120°C that provides long bonding of rubber to metal not higher 80°C.

At the same time the chlorination of polyolefines (PO) permits to obtain on their base new polymeric modifications with widely complex of valuable technical properties [1–6].

It was possible to suppose that heat resistant PO – polybutene-1 (PB), polypropylene (PP), poly-4-methylpentene-1 (PMP) and

polyvynylcyclohexane (PVCH) may be used as valuable raw material for production of high temperature bondings instead of CNR, CPE and CPVC.

EXPERIMENTAL

As raw material for production of chlorinated PO (CPO) were used Russian high quality PO-LDPE mark 15802-20 ($T_F = 121°C$), HDPE mark 20806-020 ($T_F = 148°C$), ethylenepropylene rubber – SKEP-40 (ML-100°C, 4′-41 units, $T_F = 57°C$), PP mark 04П000 ($T_F = 164°C$), atactic PP (APP) ($T_F = 36°C$), PB mark 21006 ($T_F = 115°C$), PMP mark 201-02 ($T_F = 239°C$) and PVCH ($T_F = 336°C$).

Chlorination of LDPE, SKEP-40 and PVCH were conducted in solution of CCl_4 in 2 litres reactor; HDPE, PB, PP and PMP – in solution of $C_2H_2Cl_4$. Concentration of polymers in solution was 3%; initiator of chlorination was –N, N′–azobisizobutironitryl. Chlorinated PO were stabilized by 3% of epoxy resin ED-20 on polymer, and dried in vacuum-drier up to volatile content 0,1 – 0,2%.

The method of conducted thermomechanical studies (TMC) was described earlier [6].

RESULTS AND DISCUSSION

The crystallinity of PO decreased with increase of degree of chlorination and full disappearance of crystallinity (amorphization) is reached when the concentration of Cl in polymers raises to 20 – 32%.

At the same time destruction of polymers and decreasing of characteristic viscosity take place (η – dl/g), see Figure 1.

At Cl content of 64 – 66% (η) for all CPO (0,11 – 0,20 dl/g) became equal to (η) for commercial analogues – CPE-5, CPE-20 (G^{t}Brit), CNR – R-10 (G^{t}Brit) or CPVC mark PSH-LS (Rus.), see Table I.

In comparison with the original PO, all CPO containing more than 62% Cl, became fully soluble in CCl_4 and other low-boiling solvents for glues, adhesives, varnishes, *i.e.*, xylene, toluene, ethylacetate, *etc.*, and formed transparent highly adhesive films.

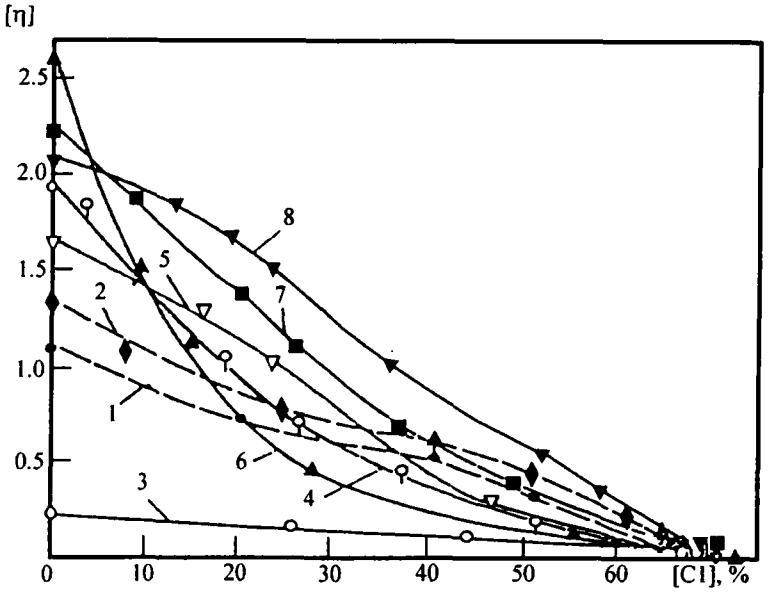

FIGURE 1 Characteristic viscosity of CPO in CCl_4 (for original PO in $C_2H_2Cl_4$) 1-CLDPE; 2-CHDPE; 3-CAPP; 4-CPP; 5-CSKEP-40; 6-CPB; 7-CPMP; 8-CPVCH.

TABLE I Properties of some highly chlorinated polymers

Polymer	*Cl, %*	*Density, g/cm³*	*Characteristic viscosity, dl/g*	T_F, °C	*Oxygen index, %*
CPE-5	64,1	1,571	0,14	119	56,1
CPE-20	65,2	1,523	0,14	114	57,3
R-10	63,8	1,511	0,19	116	55,8
CSKEP-40	64,2	1,496	0,12	115	59,6
CLDPE	64,8	1,569	0,14	123	62,1
CHDPE	63,4	1,629	0,15	135	61,9
CPVC-PSH-LS	63,9	1,534	0,20	106	61,6
CAPP	65,7	1,519	0,12	120	58,7
CPB	65,2	1,615	0,11	142	51,2
CPP	64,1	1,561	0,12	164	53,6
CPMP	64,5	1,498	0,15	243	58,8
CPVCH	65,1	1,479	0,14	341	57,5

Because of this no changes in the technology of production of adhesive compounds with the new CPO are needed.

All new CPO possess high flame resistance – oxygen index is on the level or higher (57,3 – 61,9%) present in the commercial analogues.

All the new CPO possess high char residue – 32–35% (original PO–2–7%), that is the thermal barrier, preventing spreading of flame.

T_F of the modifications increased with increasing of the rate of chlorination of APP, the by-product of production of isotactic PP (see Fig. 2). CAPP with 65,7% Cl has $T_F = 120°C$, *i.e.*, on the level of T_F for CPE-5.

The character of TMC for the new CPO is similar to those for commercial CPE-5, CPE-20, R-10 and CPVC, but they are displaced towards higher temperatures (130–340°C), see Figure 2.

From the TMC curves the CPO become glasslike at a level of chlorination higher than 61%; all CPO, containing more than 63% Cl, possess T_F of the original PO, and the character of TMC, without plateau of elasticity, is typical for glasslike resins such as R-10, CPE-20, CPVC (Fig. 2).

Changes of T_F for CPO with increasing of Cl content depend on several variables (Fig. 3).

The reduction of T_F for all CPO up to 27–32% Cl can be explained by that at this Cl content, large Cl atoms prevent the formation of crystalline phase in CPO and the CPO becomes fully amorphous.

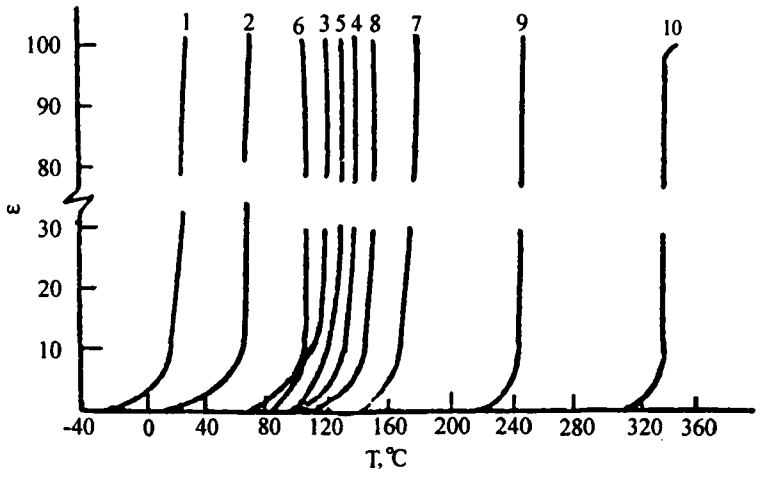

FIGURE 2 Thermomechanical curves (TMC) of CPO. APP with Cl content, %: 1–0,0; 2–46,5; 3–64,8; 4–67,5; 5–CPE-5, CPE-20, CLDPE, R-10; 6–CPVC-PSH-LS; 7–CPP (64,1% Cl); 8–CPB (65,2% Cl); 9–CPMP (64,5% Cl); 10–CPVCH (65,3% Cl).

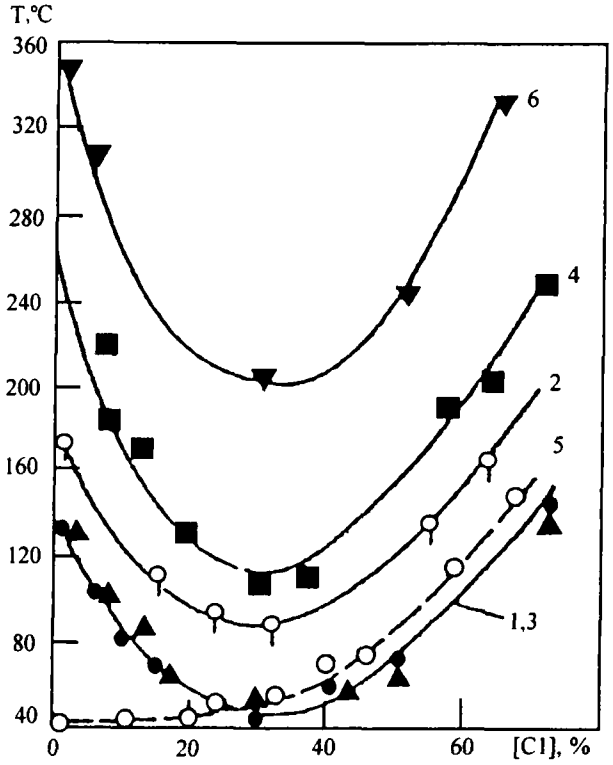

FIGURE 3 T_F of different CPO in dependence of level of chlorination 1-CLDPE; 2-CPP; 3-CPB; 4-CPMP; 5-CAPP; 6-CPVCH.

After, due to the interaction of Cl atoms in the chains of CPO, polymers become stiffer and more brittle, causing an increase in T_F.

The high melt PO maintain their high T_F over the whole range of Cl content (Fig. 3). Properties of commercial batches of CPO, obtained by chlorination in 680–3000 litres reactors, correspond to properties of laboratory specimens.

Adhesive strength of bonding of rubber composition with Steel-3 for adhesives with new CPO was equal to 5,7–6,6 MPa/cm^2, and for the same adhesive on base of chlorinated NR was equal to 4,9 MPa/cm^2. The improved adhesive strength of bonding with CPO can be explained by their tensile strength being higher than that of CPE or CNR and the presence in CPP, CPB and CPMP of considerable amounts of highly reactive functional groups, such as $-CH_2Cl$, $-CHCl_2$, $-CCl_3$.

CONCLUSION

The use of new highly chlorinated thermoflameresistent polyolefines (64–67% Cl)–chlorinated PP, PB, PMP and PVCH, with temperature of fluidity 130–340°C, instead of commercial CPE, chlorinated NR and CPVC (also 64–67% Cl) with temperature of fluidity 105–120°C, permits resolving the problem of the creation of heat resistant highly adhesive bondings for glues, adhesives and other purposes.

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