Adhesion between ethylene-propylene-diene monomer and thermoplastics in two-component injection molding: Effect of dicumylperoxide as curing agent

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ABSTRACT

Strong adhesion at the interface is an important aspect in two-component (2K) injection molding. It was therefore investigated whether dicumylperoxide (DCP) as curing agent in ethylene-propylene-diene monomer (EPDM) could stimulate interdiffusion and/or induce chemical bonding with thermoplastics. EPDM mixtures containing DCP concentrations between 2 to 8 parts per hundred rubber (phr) were combined with polar and non-polar thermoplastics. Changes in EPDM physico-mechanical bulk properties were analyzed, and the adhesion was evaluated by high temperature contact angle measurements and tensile testing. Results showed that DCP concentration did not influence EPDM-thermoplastic compatibility. However, EPDM adhesion with polyethylene (PE) did improve when using up to 6 phr DCP (57% adhesion) as crosslinking is promoted. While with polypropylene (PP), adhesion linearly decreased (from 55% to 35% adhesion) with higher DCP concentrations due to prevailing scission reactions. Adhesion through chemical bonding with acrylonitrile-butadiene-styrene (ABS) caused better adhesion at 4 phr (43% adhesion) compared to polycarbonate (PC) at 4 phr (13% adhesion) where only limited interdiffusion occurs. Thus, selecting the optimal DCP concentration is highly important to boost adhesion between EPDM and thermoplastics. Furthermore, at these optimal DCP concentrations, physico-mechanical properties require consideration as these properties were significantly affected.

INTRODUCTION

Ethylene-propylene-diene rubber (EPDM) as soft component offers excellent dynamic and heat aging properties together with resistance to polar solvents. Consequently, it is an ideal rubber for sealing applications. These seals are often incorporated and fitted mechanically or with an adhesive onto thermoplastics parts. However, a two-component (2K) process combining EPDM with thermoplastics would improve product reliability and offers perspectives for reducing material cost due to a re-design.[1] Unfortunately, 2K injection molding of EPDM combined with common thermoplastics like polyethylene (PE), polypropylene (PP), acrylonitrile-butadiene-styrene (ABS) and polycarbonate (PC) requires dealing with the low processing temperatures of the thermoplastic. Therefore, Bex et al. [1–3] developed a mold with thermally separated heat cavities and optimized the process to induce a thermoset rubber-thermoplastic adhesion. In 2K injection molding studies, the focus has mainly been on the influence of process parameters on the adhesion strength as already discussed by Bex et al.[1, 3].[4–6] Furthermore, material compatibility has been investigated to predict the adhesion in 2K injection molding.[7, 8] Additionally, Laing et al.[9] showed the importance of investigating the influence of EPDM composition on the adhesion with polar and non-polar thermoplastics. In that study, it was found that co-agent type and concentration at a fixed peroxide concentration significantly affect the adhesion strength and mechanism. To extend the scope of investigation, a study focusing on varying the peroxide concentration at a fixed co-agent concentration was deemed necessary and is presented here.

Organic peroxides, like dicumylperoxide (DCP), are widely used curing agents that can cure both saturated and unsaturated polymers.[10, 11] Other advantages that peroxides offer are the improved thermal resistance and lower compression set, ideal for sealing applications.[12] When exposed to heat, these peroxides will undergo homolytic cleavage by breaking the oxygen-oxygen bond yielding two radicals. These radicals can then initiate hydrogen abstraction from the polymer chain, or addition can take place to the double bond of unsaturated polymers creating a polymer radical. Finally, two radicals will recombine to form a carbon-carbon crosslink.[10, 11] Several studies have shown a significant influence of peroxide vulcanization on the crosslink density and general properties of vulcanized rubbers.[13–15] Consequently, an influence of the peroxide curing agent on the adhesion at the interface can be expected as well. Furthermore, peroxides could induce a co-vulcanization reaction, or crosslinks, between EPDM and thermoplastics as unsaturations are not required. Thust[16] studied the possibility of co-vulcanization between hydrogenated nitrile rubber (HNBR)-polyamide 6.6 (PA6.6) and found that direct contact was required between the peroxides and PA6.6 during 2K injection molding. However, interdiffusion was still deemed dominant but this was due to the better miscibility of peroxides in HNBR. Overall, Thust[16] indicated the occurrence of both interdiffusion and chemical bonding at a HNBR-PA6.6 interface. This combination of adhesion mechanisms was also presumed in a previous study by the authors.[9] For PE, it is known that DCP has a good efficiency to cure PE as the alkoxy radicals from DCP are prone to abstract hydrogen from PE and the extend of crosslinking is dependent on the peroxide amount.[17, 18] For PP, it is important to use a co-agent assisted peroxide curing system to minimize degradation as chain scission competes with crosslinking.[19, 20.] Studies of PP/EPDM thermoplastic vulcanizates (TPVs) have shown that DCP is less prone to degrade PP compared to other peroxides like di(2-tert butyl peroxy isopropyl)benzene or tert-butyl cumyl peroxide, but overall the peroxide concentration needs to be limited.[12, 21] Furthermore, peroxides can cure ABS which could lead to co-vulcanization with EPDM.[11] Peroxides may also migrate to the surface at higher concentrations causing a change in compatibility with polar and non-polar thermoplastics.[16] Overall, literature clearly shows the importance of peroxide concentration and its influence in blends, at interfaces and the general properties of polymers, but to the best of our knowledge an in-depth study on the effects on the EPDM-thermoplastic interface in 2K injection molding for the proposed material combinations is still lacking.

In this study, the influence of peroxide curing agent in EPDM on the adhesion with polar and non-polar thermoplastics is investigated. Therefore, concentrations of DCP are varied while maintaining a fixed concentration of co-agent trimethylolpropane trimetacrylate (TMPT). The adhesion between EPDM and thermoplastics PE, PP, ABS and PC is evaluated by contact angle measurements at high temperature and tensile tests. Possible co-vulcanization reactions and types of crosslinks between EPDM and the thermoplastics are discussed. Furthermore, cure characteristics and compound swelling are analyzed to determine the state of cure and crosslink densities as this may influence the adhesion mechanism. General properties of all EPDM compositions are determined as well, in particular tensile properties, thermal resistance, compressions set and hardness which are all important properties for sealing applications. Eventually, a final assessment is made of the optimal DCP concentration for each EPDM-thermoplastic combination while taking into account the possible changes in rubber bulk properties.

EXPERIMENTAL

Materials

The rubber compounds were mixed and provided by Hercorub, Belgium. The following raw materials were used: EPDM (Vistalon 2504N, Exxon Mobile, with Mooney Viscosity ML 1+4, 125°C = 25 Mooney units (MU); ethylene content = 56.0 wt%; ethylene norbornene (ENB) content = 3.8 wt%); paraffinic oil (Sunpar 2280, Petronas); silane treated calcined kaolin filler (Polarite 103A, Imerys); zinc oxide and stearic acid. TMPT (70% active ingredient) was used as co-agent and concentrations between 2 and 8 phr DCP with 40% active peroxide content were added. The chemical name and structure of components in the peroxide curing system components are listed in Table 1 and the EPDM compound compositions are listed in Table 2.

TABLE 1 Chemical names and structure of the peroxide curing system components.

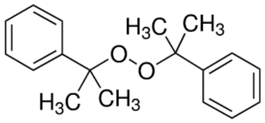
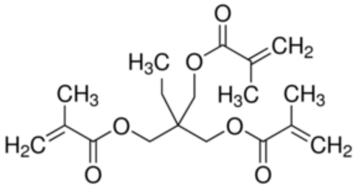
Chemical name	Abbreviation	Chemical structure
Dicumylperoxide	DCP	
Trimethylolpropane trimethacrylate	TMPT	

TABLE 2 EPDM compound compositions.

Component (phr)	DCP2	DCP4	DCP6	DCP8
EPDM	100	100	100	100
Zinc oxide	2.8	2.8	2.8	2.8
Stearic acid	1	1	1	1
Kaolin filler	110	110	110	110
Paraffinic oil	30	30	30	30
DCP[a]	2 (7.4)[b]	4 (14.8)	6 (22.2)	8 (29.6)
TMPT[a]	2	2	2	2

[a] Concentrations of DCP and TMPT are represented in phr of active amount.

[b] Values in parentheses correspond to milliequivalents of active DCP.

Each rubber compound was combined with two non-polar (a) and two polar (b) thermoplastics: (a) PP grade 400-GA05 (Ineos) (melting temperature = 164°C, yield stress = 25 MPa), and PE grade M80064 (Sabic) (melting temperature = 135°C, yield stress = 32 MPa); (b) PC grade Calibre 301-15 (Trinseo) (glass transition temperature = 150°C, yield stress = 60 MPa), and ABS grade Novodur P2H-AT (Ineos) (glass transition temperature = 110°C, yield stress = 44 MPa).

EPDM-thermoplastic sample preparation

Samples were made according to the process developed by Bex et al.[1–3] on an Engel ES330H/80V/80HL-F equipped with a vertical rubber unit and a horizontal thermoplastic injection unit. To combine EPDM with thermoplastics a versatile mold was employed with a rubber and thermoplastic cavity. In this mold, first, all thermoplastics parts were produced separately in the thermoplastic cavity while a metal insert was placed in the rubber cavity. Afterwards, the metal insert was removed from the rubber cavity. Then, a thermoplastic part was placed in the 2K mold and overmolded with rubber, resulting in 2K specimens with dimensions as shown in Figure 1 and a thickness of 2 mm.

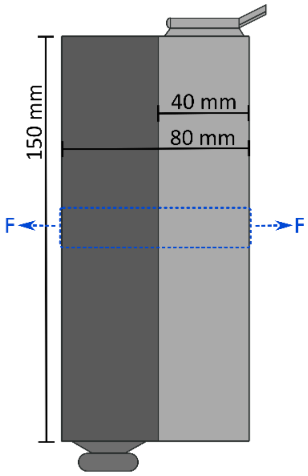


FIGURE 1 2K specimen dimensions. The thickness of both the rubber and thermoplastic part is 2 mm. The dotted line represents the sample location for tensile testing and how the force (F) will be applied to determine the adhesion strength.[9]

All injection molding parameters for the individual components are listed in Table 3. Recommendations by the suppliers were used for the injection and mold temperatures. The selected injection rate ensured constant viscosity and the high holding pressure caused a completely filled product without causing flash.

TABLE 3 Injection molding parameters.

Injection molding parameters	PP	PE	PC	ABS	EPDM
Injection temperature (°C)	230	230	300	260	80
Mold temperature (°C)	20	20	80	70	180
Injection rate (cm³/s)	38	38	87	96	59
Holding pressure (bar)	494	790	494	494	248

During production of 2K samples, the rubber cavity was set at 180°C to ensure vulcanization, while the thermoplastic cavity was set at a low temperature to achieve an optimal interface temperature for good adhesion as specified by Bex et al.[1, 2]. Table 4 contains the mold temperatures of each cavity and the accompanying interface temperatures. These interface temperatures were experimentally determined by Bex et al.[2] with an infrared camera (OPTRIS PI400). In addition, curing times are listed for all samples that ensured 90 % vulcanization. These 90 % vulcanization times were determined by the necessary times to vulcanize the rubber near the interface, as temperatures are much lower here than in the rubber bulk.

TABLE 4 Mold temperatures for thermoplastic and rubber cavity with the accompanying interface temperature and curing times.

	EPDM			
Mold temperature (°C)	PP	PE	PC	ABS
Thermoplastic cavity	140	80	155	90
Rubber cavity	180	180	180	180
Interface	161	139	166	143
Curing time (s)	1200	4000	800	4000

EPDM bulk properties

Cure characteristics

Cure characteristics of each rubber compound, i.e. cure time (t_{90}), scorch time (t_{s2}) and delta torque, (Δtorque), were determined with a moving die rheometer (MDR2000E, Monsanto). As the temperature during injection molding in the rubber bulk is set at 180°C, MDR measurements were taken at 180°C for 20 min. However, due to the lower temperatures at the EPDM-thermoplastic interfaces (Table 4), rubber near the interface will have different cure characteristics. Therefore, vulcanization degrees at 160°C were measured during 45 min and at 140°C during 160 min. Reversion resistance was determined for each compound at 180 °C after 60 min according to eq.(1), as the curing times for EPDM-PE and EPDM-ABS were set at 4000 s to ensure vulcanization of the rubber near the interface leading to a long exposure to 180 °C in the bulk.

$$Reversion\ index\ (\%) = \frac{S'_{max} - S'_{R}}{S'_{max}} \cdot 100 \qquad (1)$$

S'_{max} and S'_{R} are respectively maximum torque and torque after 60 min.

After injection molding, vulcanization degrees at the interface of all 2K samples were checked by Shore A hardness measurements as hardness relates linearly to the vulcanization degree.[22] Five hardness measurements were taken on each 2K combination according to ISO 7619 with a measuring time of 15 s and interfacial vulcanization degrees were calculated according to eq.(2).[2]

$$Interfacial\ vulcanisation\ degree = \frac{x - x_{min}}{x_{max} - x_{min}} \qquad (2)$$

where x is the hardness at a specific point 1 mm from, and parallel with the interface , x_{min} the hardness of unvulcanized rubber, and x_{max} the hardness of 100 % vulcanized rubber.

Crosslink density

Crosslink density ν was determined by equilibrium swelling measurements in cyclohexane. Three test pieces of each vulcanized compound were swollen for 72 h according to ISO 1817 at 23°C in 70 ml cyclohexane. Starting sample dimensions were 25 m x 25 mm x 2 mm. After reaching equilibrium swelling, excessive solvent was removed with filter paper, samples were weighed (m_{max}), dried in an oven at 60°C for 24 h to remove all the solvent and finally reweighed (m_0). Volume fraction of rubber in the equilibrium swollen vulcanized sample (V_r) was determined according to eq.(3), where ρ_s and ρ_e are the densities of solvent and elastomer samples. Density of the elastomer was determined with a METTLER Toledo density kit.

$$V_r = \frac{m_0 \rho_s}{m_0(\rho_s - \rho_e) + m_{max}\rho_e} \qquad (3)$$

Crosslink density ν (mol/cm^3) of each vulcanized compound was calculated according to eq.(4)[23] by applying the Flory-Rehner equation for tetrafunctional networks, where V_s is the molar volume of cyclohexane (108.105 cm^3/mol) and χ is the Huggins polymer-solvent interaction parameter ($\chi = 0.35$ for EPDM-cyclohexane[24]). An average crosslink density was taken of three samples and 95% confidence intervals are reported.

$$\nu = -\frac{1}{2\,V_s}\frac{\ln(1-V_r)+V_r+\chi V_r^2}{(V_r^{\frac{1}{3}}-0.5V_r)} \qquad (4)$$

Physico-mechanical properties

Physico-mechanical properties were evaluated on the rubber vulcanized bulk part of EPDM-PP samples (1200 s vulcanization at 180°C). Afterwards, samples were conditioned at 23°C for 3 days. Tests were selected based on important properties for the current material combinations, like good thermal resistance and mechanical strain, which are ideal for sealing applications. A Zwick Z050 equipped with a 1 kN load cell was used at room temperature, a crosshead speed of 200 mm/min and a gauge length of 13.5 mm to determine tensile properties. Shore A hardness was measured according to ISO 7619. Compression set tests were performed at 23°C for 24 h according to ISO 815. Heat aging was evaluated by exposing vulcanized samples to 100°C in an air circulated oven for 72 h according to ISO 188 and re-evaluating tensile strength and hardness. Significant differences between unaged and aged samples were compared by a paired t-test (for two dependent groups) with 0.050 as significance level. The null hypothesis corresponds to a zero mean difference between unaged and aged samples. When the p-value is smaller than 0.050, the null hypothesis can be rejected, indicating a significant difference between unaged and aged samples. The statistical analyses for heat aging were executed on Minitab 17. Average values of three samples of all compounds and the accompanying 95 % confidence intervals are reported.

Adhesion Characterization

Compatibility measurements

Similar to the previous study[9] on the influence of co-agents on EPDM-thermoplastics adhesion, contact angle measurements at high temperatures were executed to evaluate changes in material compatibility. Contact angles were assessed according to the method described by Bex et al.[8]. A Dataphysics OCA 15 plus, equipped with a Dataphysics TEC 350 temperature control unit was used and contact angles were calculated with Dataphysics SCA 202 analysis software.

Completely vulcanized EPDM rubber was selected as substrate (originating from the EPDM bulk of EPDM-PP samples) to prevent further vulcanization during compatibility measurements. A comparison was made between EPDM substrates containing increasing concentrations of DCP (DCP2, DCP4, DCP6 and DCP8) to analyze the influence of DCP concentration on wetting between thermoplastics and EPDM. The surface composition of each EPDM substrate was checked by acquiring infrared (IR) spectra with a Perkin Elmer Spectrum 65 FTIR coupled to an attenuated total reflection (ATR) unit. The average roughness values (R_a) of the rubber substrate, measured with a Diavite Compact VHF on the surface in the middle of the rubber part, were 0.47 ± 0.09 µm for DCP2, 0.45 ± 0.17 µm for DCP4, 0.49 ± 0.20 µm for DCP6 and 0.49 ± 0.10 µm for DCP8. These roughness values are low and comparable, limiting the effect of roughness on wetting, and therefore this is not taken into account. All samples were cleaned with isopropanol before measurements. A substrate with dimensions of 10 x 10 x 2 mm was placed in a heated chamber under N_2-environment and stabilized for five minutes. Then, a thermoplastic granule was placed on the rubber substrate with the spherical side facing down. Chamber temperatures for PE, PP and PC were respectively 180°C, 200°C and 230°C to enable the polymer to melt. ABS was not tested as degradation occurred too fast even under N_2-environment in the available heating chamber. After reaching a thermoplastic droplet with a contact angle of 110°, contact angles were registered every minute during 15 min. Overall, the methodology was kept similar to the previous study by the authors[9] to compare results as this is a follow-up study. Three measurements were performed for each combination of thermoplastic with EPDM rubber and average values with their 95 % confidence intervals are reported.

Adhesion measurements

EPDM-thermoplastic adhesion strength was evaluated by tensile testing.[2, 25] To be able to compare the adhesion strength to the EPDM strength a similar method was used: tensile testing on a Zwick Z050 equipped with a 1 kN load cell was used at room temperature with a speed of 200 mm/min and a gauge length of 13.5 mm. EPDM-thermoplastic samples were punched out the 2K specimens (Figure 1) perpendicular to the interface in the middle of the sample, resulting in samples dimensions of 80 x 10 x 2 mm for EPDM-PP and EPDM-PE. For EPDM-PC and EPDM-ABS samples, it was not possible with the available machine to punch out samples without damaging the interface due to the low adhesion and hardness of the thermoplastics. Thus, samples were cut out with a selected width of 30 mm, as this still fitted between the clamps of the tensile machine, resulting in sample dimensions of 80 x 30 x 2 mm. Adhesion strength (σ_a) was also compared to the EPDM strength (σ_t) by calculating a percentage of adhesion according to eq.(5). Five adhesion measurements were performed for each material combination and 95% confidence intervals are reported. A one-way ANOVA was used to verify differences in mean adhesion strength and adhesion percentage between the different samples. Significance level was set at $p < 0.050$ and Tukey's method was used to indicate which groups differed significantly. The statistical analysis was executed on Minitab 17.

$$Adhesion\,percentage\ (\%) = \frac{\sigma_a}{\sigma_t} \cdot 100 \tag{5}$$

A post-fracture visual analysis was done of the thermoplastic interface surface with a Keyence VHX-500F digital microscope and a 50x magnification.

RESULTS AND DISCUSSION

Effect of dicumylperoxide on EPDM bulk properties

Cure characteristics and crosslink density

Cure characteristics of all EPDM compounds are listed in Table 5. As DCP concentration increases, a clear increase in Δtorque can be seen, which is also shown in torque-time Figure S1. This is due to the improved crosslinking efficiency as peroxide decomposition follows first order reaction kinetics.[26, 27] Measurements of crosslink density (Figure 2) confirm Δtorque results indicating a linear correlation between crosslink density and DCP concentration. Furthermore, vulcanization times (t_{90}) at 180°C and 160°C do not differ much between different concentrations. However, at 140°C, higher concentrations do lead to better curing efficiency. Scorch time (t_{s2}) tends to decrease with higher concentrations at every temperature. These trends in t_{90} and t_{s2} are also illustrated in Figure S2. Furthermore, due to the high curing times for EPDM-PE and EPDM-ABS (Table 4) to ensure vulcanization at the interface, reversion index was examined as the vulcanization temperature in the EPDM bulk is 180°C during this time. Reversion in all compounds remains limited and reduces with higher peroxide concentration. However, it is recommended to use higher concentrations for EPDM-PE and EPDM-ABS to minimize reversion in the EPDM bulk. Furthermore, 90% vulcanization degrees was reached at the interface of all 2K samples, indicating that the curing times listed in Table 4 sufficed. The specific interfacial vulcanization degrees of all material combinations are listed in Table S1.

TABLE 5 Cure characteristics of the EPDM compounds.

Cure characteristics	DCP2	DCP4	DCP6	DCP8
Δtorque 180°C (dNm)	3.34	7.05	9.29	10.06
t_{90} (min) at 180°C	2.65	2.49	2.65	2.14
at 160°C	17.96	16.79	18.47	17.07
at 140°C	118.38	117.16	106.45	102.46
t_{s2} (min) at 180°C	1.23	0.63	0.54	0.50
at 160°C	6.93	2.64	1.82	1.80
at 140°C	53.69	24.88	16.40	13.16
Reversion index 180°C 60' (%)	14.39	15.34	10.18	1.38

Swelling measurements, followed by calculation of crosslink densities (Figure 2), indicate a linear relation between crosslink density and DCP concentration. This is due to an increasing amount of free radicals when adding higher concentrations of peroxides which cause an efficient formation of intermolecular bridges.[23] Even though these crosslink densities were determined in the EPDM bulk (cured at 180°C), a similar linear increase can be expected near the interface, which is cured at lower temperatures. Therefore, the increased crosslink densities have to be taken into account if both chemical bonding and/or interdiffusion occurs because higher crosslink densities may limit interdiffusion due to restriction of chain mobility, while interfacial bonding may be promoted due to increased reactivity at the interface.[9, 16]

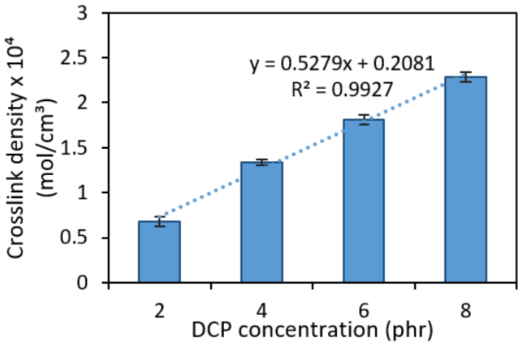


FIGURE 2 crosslink density, obtained from swelling measurements, in function of DCP concentration. The dotted line represent a linear fit, which is accompanied by the linear equation and the correlation coefficient R^2. Error bars represent 95% confidence intervals.

Physico-mechanical properties

In Figure 3 mechanical properties are represented in function of DCP concentration. Adding higher concentrations of DCP clearly increases tensile strength and hardness (Figure 3a,c) respectively by 70% and 22%, when going from 2 phr to 8 phr DCP. For compression set and elongation at break (Figure 3b,d), an opposite trend was established with respective decreases of 77% and 50%. These results confirm literature findings and can be ascribed to the general increase in crosslink density and dense network formation of carbon-carbon crosslinks.[11, 14] Thus, requirements in mechanical properties need to be taken into account when selecting the right peroxide concentration.

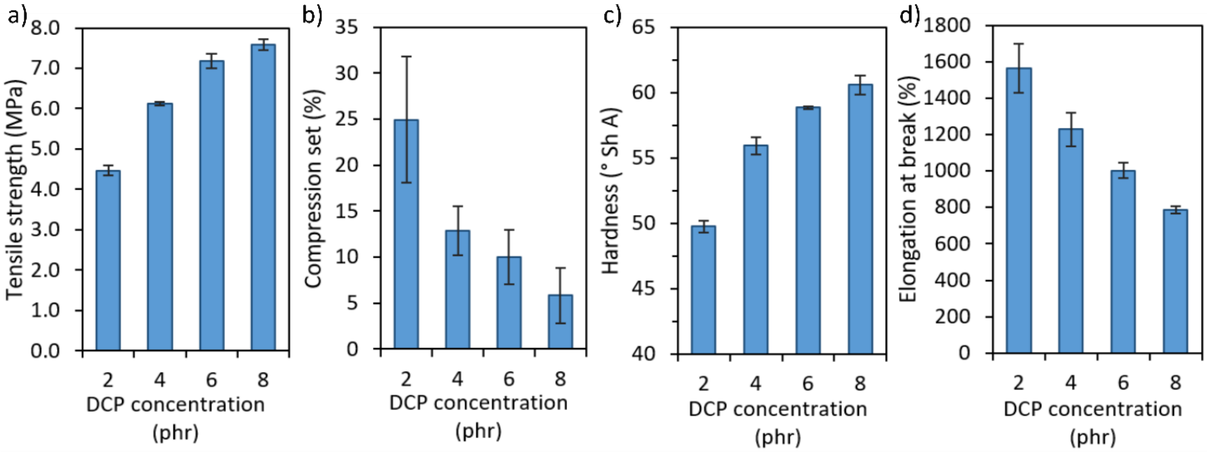


FIGURE 3 Mechanical properties of EPDM in function of DCP concentration: tensile strength (a), compression set (b), Shore A hardness (c), and elongation at break (d). Error bars represent 95% confidence interval.

Heat aging was assessed by tensile and hardness measurements before and after exposure to 100°C during 72 h. The effect of this thermo-oxidation process in relation to DCP concentration is important as thermal resistance is required for sealing applications at high temperature. Results are shown in Figure 4. Paired t-tests of tensile strengths did not show a significant difference between aged and unaged samples ($p<0.05$) and the tensile strength was retained for all samples with at least 97%. This high percentage of retention indicates good thermal stability. Thus, EPDM containing concentrations between 2 and 8 phr did not show any relative deteriorating in time in terms of tensile strength. However, hardness was significantly affected resulting in an average increase in hardness and p-value < 0.050 (2 phr DCP: by 2.4° Sh A, $p=0.000$; 4 phr DCP: by 1.3° Sh A, $p=0.001$; 6 phr: by 1.3° Sh A, $p=0.000$; 8 phr: by 1.44° Sh A, $p=0.001$). This change in hardness may be due to additional crosslinking or hardening caused by side reactions. For 2 phr DCP, hardness increased most from unaged to aged samples. The unsaturations of EPDM are probably affected by oxidation due to the lower peroxide crosslinking efficiency at this low concentration, but overall the change in hardness remains limited.[28, 29]

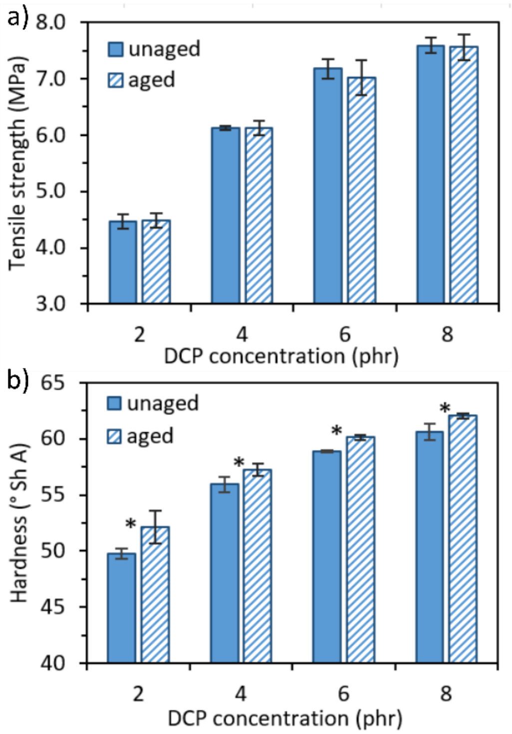


FIGURE 4 Tensile strength (a) and hardness (b) of unaged and aged samples. A significant difference ($p<0.05$) between mean values of aged and unaged samples of each compound is indicated with *. Error bars represent 95% confidence intervals.

Effect of dicumylperoxide on the adhesion

EPDM-thermoplastic compatibility

In the previous study by the authors[9], co-agents in the peroxide curing system significantly promoted wetting with the polar thermoplastic PC. Therefore, wetting behavior of molten PP, PE and PC was evaluated on EPDM substrates to analyze the influence of DCP concentration as well. Results of spreading of PE, PP and PC on each EPDM substrate (DCP2, DCP4, DCP6 and DCP8) are shown in Figure 5. Spreading dynamics cannot be compared directly between the different thermoplastics (PP, PE and PC) as viscosity values are not identical. This was, however, not the goal of these tests.

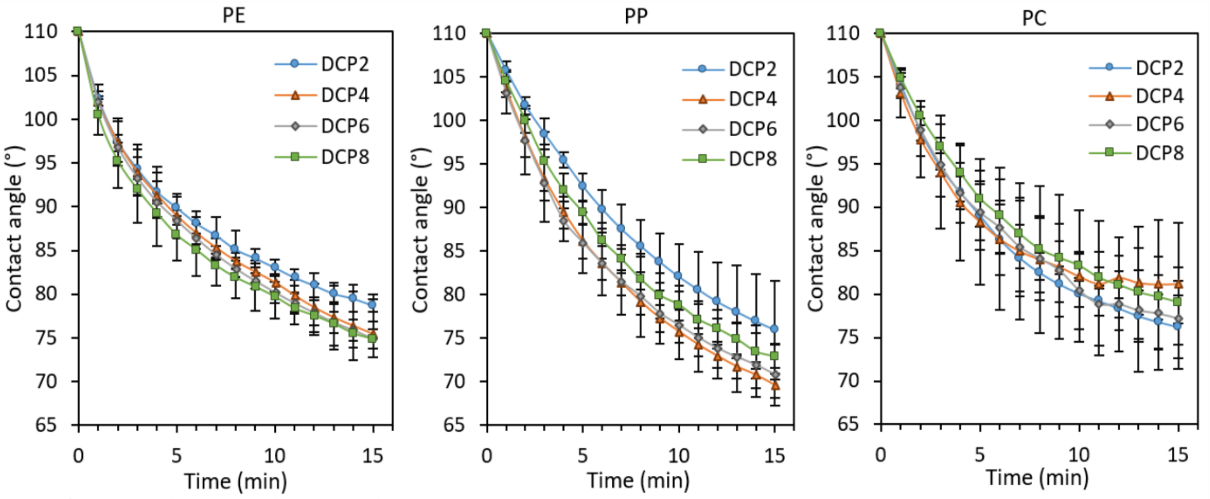


FIGURE 5 Contact angle measurements of thermoplastic melts of PE (180°C), PP (200°C) and PC (230°C) during spreading on EPDM with 2 phr DCP (DCP2), 4 phr DCP (DCP4), 6 phr DCP (DCP6) and 8 phr DCP (DCP8). Error bars represent 95% confidence interval.

In Figure 5, contact angles of PP and PE on vulcanized substrates indicate better wetting, after 15 min, on the substrates with 4, 6 and 8 phr DCP (respectively DCP4, DCP6 and DCP8) compared to 2 phr DCP (DCP2). The slightly higher contact angles of DCP2 may be caused by oxidation of the DCP2 surface. The ATR-FTIR spectra showed a broad band between 3100 and 3600 cm^{-1}, which was not observed for DCP4, 6 or 8 (Figure S3). Thus, polar hydroxyl groups were present on the surface of the DCP2 substrate. Similarly, for PC better wetting was reached on DCP2, which can be ascribed to the polar groups on the surface. Overall, between 4, 6 and 8 phr, no significant difference was found on polar or non-polar thermoplastics when increasing the DCP concentration. Furthermore, measurements were executed on fully vulcanized substrates, where DCP already participated in the vulcanization process leading to likely decomposition products methane, acetophenone and 2-phenylpropanol-2.[10] However, neither DCP, nor the decomposition products seem to significantly affect the surface composition of vulcanized EPDM with higher DCP concentrations which suggests that changes in surface free energies are limited. Thus, contrary to the previous study[9] showing a significant influence of co-agent concentration on EPDM-thermoplastic compatibility, no compatibility differences in function of peroxide concentration were found. However, it might still be possible that shear induced enrichment of peroxides occurs at the interface during the injection molding process as proposed by Thust[16].

EPDM-thermoplastic co-vulcanization reactions

The reaction mechanism during peroxide vulcanization of EPDM has already been extensively studied and reported.[30–32] During exposure to heat, DCP will decompose in cumyloxy radicals which in turn can rearrange to yield methyl radicals that are less sterically hindered.[10, 11] These radicals can then abstract hydrogen atoms from secondary and mainly tertiary carbons on the EPDM main chain, and the allylic hydrogen in the ENB unit, resulting in respectively alkyl and allyl macro-radicals.[32] Orza[32] provided a detailed description of peroxide crosslinking of EPDM with ENB as third monomer and based on this mechanism possible co-vulcanization reactions between EPDM and PE, PP or ABS are proposed in this study. For PC, crosslinking is unlikely due to the ester oxygen.

Crosslinking unsaturated polymers, like PE and PP, can only occur through hydrogen abstraction, followed by a recombination of macro-radicals.[10, 11] However, main chain scission reactions are prone to occur in the presence of tertiary radicals, which are abundant in PP. In contrast, primary and secondary radicals are more susceptible towards combinations reactions, indicating possible successful crosslinking in PE. In ABS, styrene, butadiene, and acrylonitrile structural units are present. Thus, both hydrogen abstracting reactions and addition reactions to the double bonds are possible. Specifically, for the double bonds, addition reactions are more amendable when they are located at the end of the polymer chain or in a side chain group, while in-chain double bonds are more sterically hindered. The presence of the electron withdrawing nitrile groups in ABS reduces the reactivity of the in-chain double bond, prevailing abstraction reactions.[10] In Figure 6, possible macro-radicals of EPDM, PE, PP and ABS are represented. The allyl and alkyl radicals in EPDM can form in a 1:1 ratio.[10] PE forms alkyl radicals on the CH_2 positions and for PP the alkyl radical on the CH position was selected because it has the lowest bond strength (tertiary: 380 kJ/mol; secondary: 405 kJ/mol [10]). Hydrogen abstraction reactions were presumed dominant in ABS forming stable benzyl and allyl macro-radicals due to possibility of resonance stabilization.

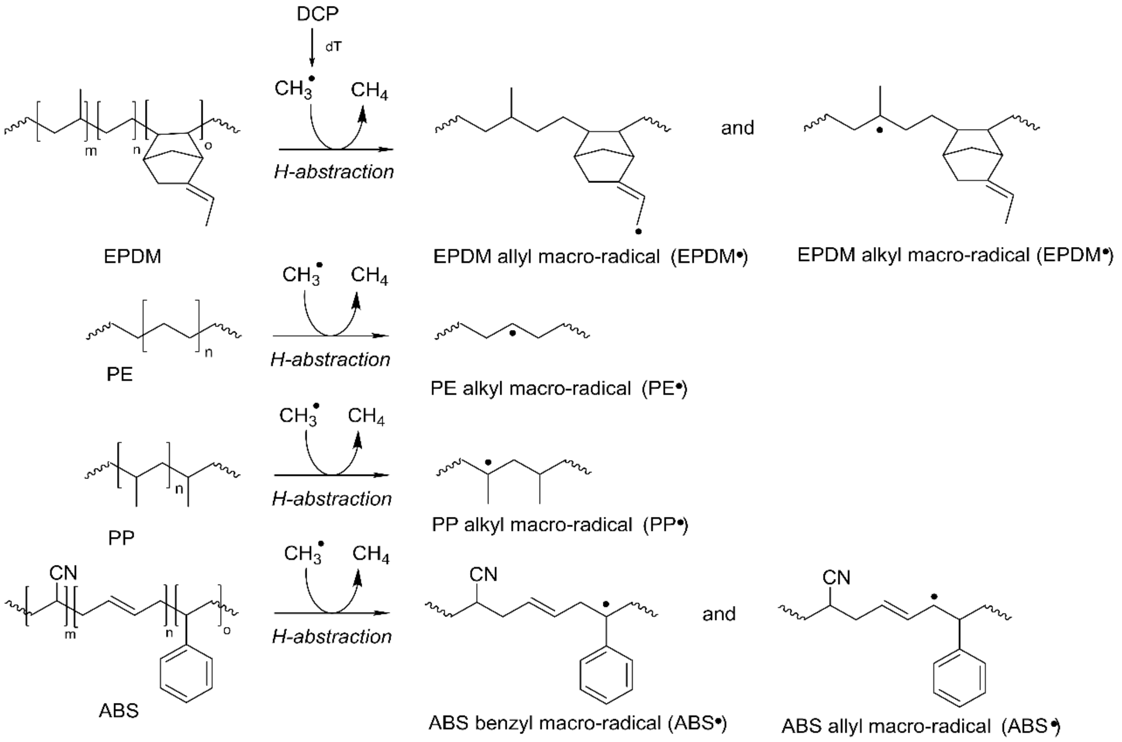
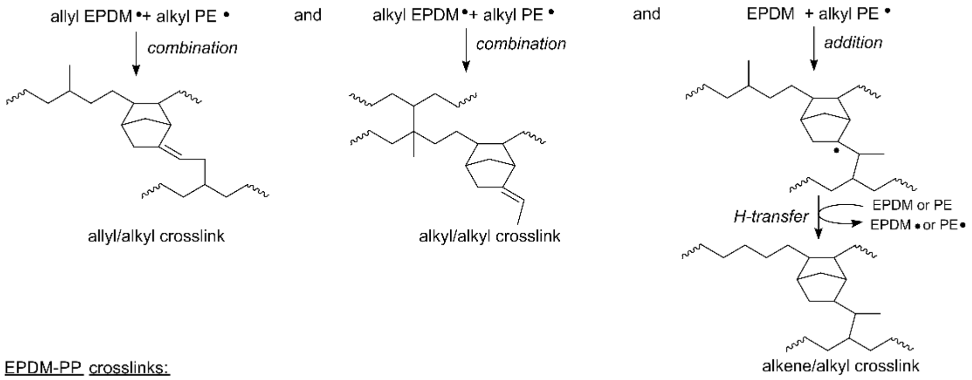


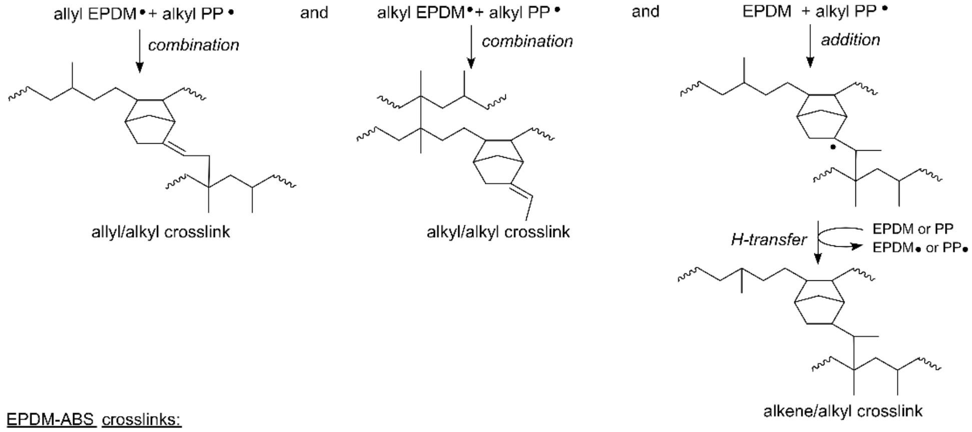
FIGURE 6 Hydrogen abstraction from EPDM, PE, PP and ABS chain by methyl radicals from DCP. The brackets indicate repeating units in each polymer, but these are removed in the reaction mechanism to give a clearer view.

In Figure 7 crosslinking reactions are represented that can occur between EPDM and PP, PE or ABS. Neither possible side reactions, nor the contribution of the co-agent are discussed. As Orza [32] states, EPDM yields ∼25 % alkyl/alkyl, ∼25 % allyl/allyl and ∼50 % allyl/alkyl combination crosslinks. Similarly, EPDM allyl and alkyl radicals might combine with an alkyl radical from PE resulting in allyl/alkyl and alkyl/alkyl crosslink, and through an addition to the double bonds of the ENB unsaturation an alkene/alkyl crosslink may occur. For PP, it has been suggested that between a PP radical and a neighbor chain with an allyl radical crosslinking is more probable.[20] In this case, EPDM can provide the allyl radical making the allyl/alkyl crosslink most likely. However, it is important that both radicals are in close vicinity.[20] Finally, several possible carbon-carbon bonds can form between ABS and EPDM as both polymers can donate hydrogens creating stable radicals. Besides combination reactions between ABS and EPDM radicals, addition reactions to the EPDM or ABS unsaturations, followed by H-transfer might occur as well. For the addition reaction of the allyl EPDM or alkyl EPDM radical to ABS, an alkyl radical forms, due to the addition to the butadiene unsaturation. The most stable location was selected for this radical, i.e. reduced influence of electron withdrawing nitrile group.

EPDM-PE crosslinks:



EPDM-PP crosslinks:



EPDM-ABS crosslinks:

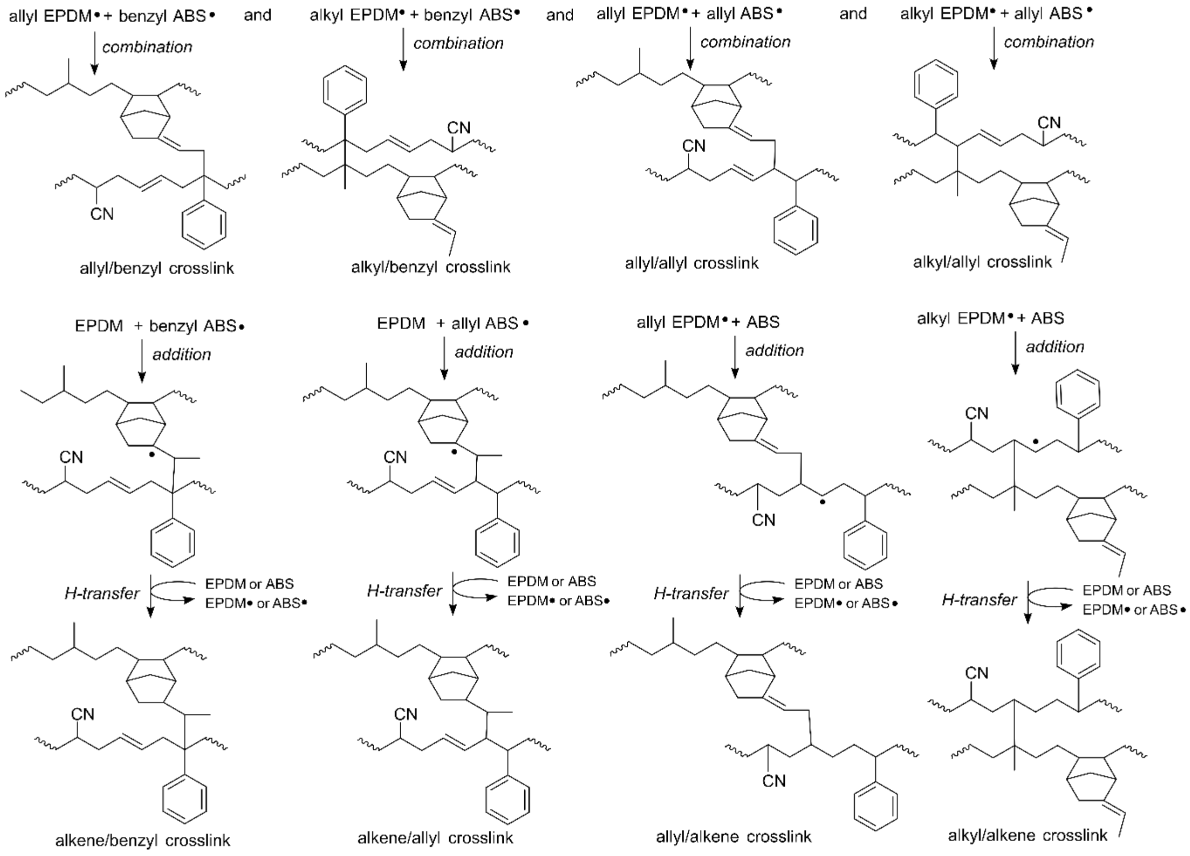


FIGURE 7 Co-vulcanization reactions between EPDM and PE, PP or ABS. For EPDM with PP or PE, two combination and one addition reaction result in three types of crosslinks. For EPDM with ABS four combination and four addition reactions result in a total of eight crosslink types.

EPDM-thermoplastic adhesion strength

The adhesion strength between EPDM and PE, PP, ABS or PC was determined by tensile testing. Results are represented in Figure 8. Besides the adhesion strength for the different material combinations, EPDM strength (σ_t) is shown as well per concentration.

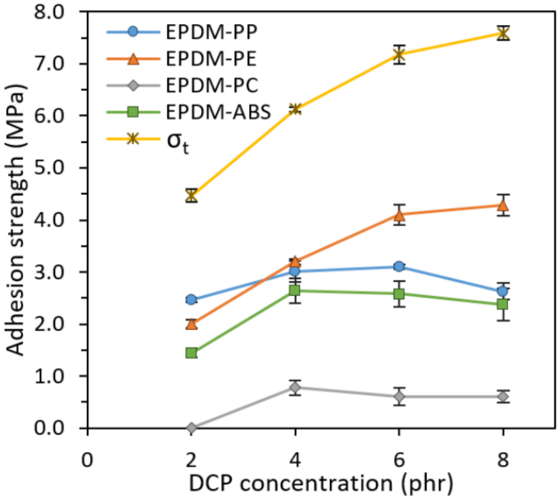


FIGURE 8 Adhesion strength in function of DCP concentration between EPDM and PE, PP, ABS and PC. EPDM strength (σ_t) is represented as comparison. Error bars indicate 95% confidence intervals.

As seen in Figure 8, only the adhesion with PE increases significantly from 2 to 8 phr DCP. For PP adhesion strength increases to an optimum at 6 phr DCP but afterwards decreases significantly again to 8 phr DCP. For ABS and PC, the adhesion strength improves significantly up to a 4 phr DCP but afterwards no significant differences are established between 4, 6 or 8 phr DCP. Furthermore, the EPDM strength also increases with higher DCP concentrations. Thus, to analyze whether the adhesion strength does not merely improve due to the increased EPDM strength, values of adhesion strength were compared to the EPDM strength at each concentration by calculating an adhesion percentage (eq.(5)), which is represented in Figure 9. An adhesion percentage of 100% is unlikely due to the different vulcanization temperatures in the bulk and at the interface. Consequently, crosslink densities will be higher in the bulk than near the interface due to the higher curing temperature, causing a higher tensile strength. In addition, the combination of hard-soft material causes a mismatch in Poisson ratio and stiffness leading to debonding near the edges.[1.] Thus, fracture mainly occurs near the edges cohesively or adhesively.

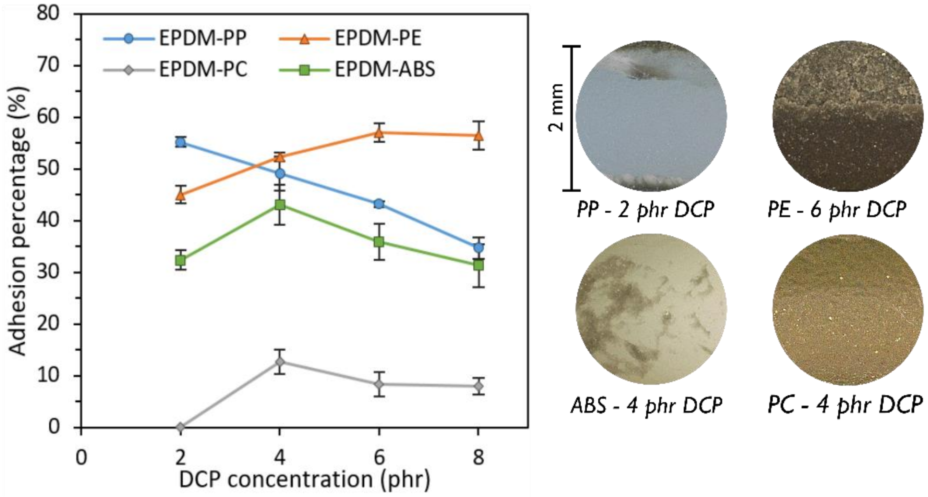


FIGURE 9 Adhesion percentage (adhesion strength divided by EPDM strength) in function of DCP concentration for PP, PE, PC and ABS. The error bars represent 95% confidence intervals. The microscopic images show a circular zone (2 mm radius) of the fracture surfaces at the thermoplastic side. Black indicates the rubber and white the thermoplastic. For PC - 4 phr DCP, no rubber is visible and for PE - 6 phr DCP only rubber is visible.

At the interface between EPDM and thermoplastics, adhesion mechanisms like chemical bonding or interdiffusion are expected. During injection molding, the crosslinking reaction in the EPDM part may influence these adhesion mechanisms at the interface. Specifically, when interdiffusion is dominant, formation of crosslinks will limit chain mobility. However, the radicals created during curing can increase reactivity near the interface and improve co-vulcanization which entails chemical bonding.[9] When both adhesion mechanisms are plausible, a combination of both is expected as also stated by Thust[16].

In case of PP, scission reactions compete with crosslinking. Results of adhesion percentage indicate that increasing the DCP concentration drastically decreases the adhesion percentage (from 55% at 2 phr to 35% at 8 phr) in a linear manner ($R^2 = 0.9921$). At the interface, both chemical bonding and interdiffusion could occur as adhesion mechanism, but it seems that both mechanisms are adversely affected by higher DCP concentrations. Interdiffusion is limited due to higher crosslink density in EPDM at the interface and probably degradation of PP prevails over crosslinking. This negative effect of higher peroxide concentrations was also seen in studies of EPDM/PP TPVs.12, 21 In addition, as peroxide concentration increases, more scission may occur which reduces molecular weight of PP near the interface, therefore, the adhesion caused by interdiffusion may be limited due to a lack of entanglements.[33] Thus, for EPDM-PP a low DCP concentration is recommended in combination with a higher co-agents concentration, as a previous study by the authors showed that 6 phr TMPT could reduce PP degradation at 3.2 phr DCP.

The adhesion percentage between EPDM and PE gradually increases with higher peroxide concentration (by 12% from 2 to 6 phr) up to a maximum at 6 phr DCP with a cohesive failure. At higher concentrations, i.e. 8 phr DCP, adhesion is not further improved, but merely adhesion strength increases due to an increase in EPDM strength (Figure 8). Literature also indicates the successful crosslinking of PE by DCP and confirms that increasing concentrations can lead to higher crosslink density of PE.[18, 34]

However, Cespedes et al.[18] highlighted that improved properties are only reached up to certain DCP concentration in TPVs containing EPDM, HDPE and ground tire rubber because the thermoplastic phase may be affected by a thermo-oxidation (degradation) process. Thus, similarly in this study EPDM-PE adhesion improves up to 6 phr DCP, which can be mainly attributed to an increase in chemical bonding or formation of more carbon-carbon bonds between EPDM and PE. Chemical bonding dominates over interdiffusion because the higher crosslink density would normally limit chain mobility. Additionally, to improve the adhesion even more, co-agent triallyl cyanurate (TAC) would be recommended as Laing et al.[9] indicated better adhesion at 1.5 phr TAC with 3.2 phr DCP, while TMPT did not enhance adhesion. The adhesion of ABS only improves up to 4 phr DCP after which the adhesion percentage decreases again to 6 phr. Mean values decrease further to 8 phr, but the difference with 6 phr DCP is not significant. PC shows a similar trend. In case of ABS, crosslinks between EPDM and ABS chains are possible. However, degradation may occur as well. Therefore, crosslinking reactions may be promoted up to 4 phr, but higher concentration may limit interdiffusion and cause chain scission of ABS near the interface instead of promoting crosslinking. At 4 phr, the ABS surface showed occasional partial cohesive failure. For PC, no adhesion was reached with EPDM containing 2 phr DCP during injection molding. In contrast, contact angle measurements indicated better wetting on 2 phr DCP, but FTIR measurements showed the presence of polar groups due to degradation. In unvulcanized EPDM with 2 phr DCP, these polar groups were not present yet at the interface and therefore did not affect adhesion during injection molding. Probably, this low concentration did not suffice to induce an adhesion through interdiffusion, but at higher DCP concentrations, a low adhesion was possible. Similarly as for ABS, 4 phr DCP is most optimal for adhesion with PC, but ABS reaches a higher adhesion percentage of 43% compared to 13% for PC as crosslinking may occur at the EPDM-ABS interface. Higher concentrations do not further improve adhesion with PC. This is in agreement with wetting measurements as compatibility was not affected by higher peroxide concentrations. The interdiffusion process will, however, be limited by higher crosslink density in EPDM causing a significant decrease in adhesion percentage from 4 phr to 6 phr. For polar thermoplastics, it would be recommended to implement a high TAC concentration to further improve adhesion as was shown in the previous study by the authors.[9]

The study by Thust[16] showed that adhesion between HNBR and PA6.6 was negatively affected by higher DCP concentration. In that study, co-vulcanization was not promoted due to the high miscibility of DCP in HNBR and the higher interaction parameter of DCP with HNBR compared to PA6.6. Thust ascribed the decrease in adhesion to a decrease in interdiffusion due to the higher crosslink densities with higher DCP concentrations. [16] This negative effect of DCP on the interdiffusion was also found in the present study by the authors. Overall, results from the current study together with results from Thust[16] show that selecting the optimal DCP concentration depends specifically on the 2K material combination and in particular on the dominant adhesion mechanism.

CONCLUSIONS

In this study, the influence of DCP in EPDM on the adhesion with polar and non-polar thermoplastics was investigated. Even though compatibility with polar or non-polar thermoplastics did not change with higher DCP concentrations, adding higher concentrations of the peroxide curing agent did significantly affect the adhesion percentage between EPDM and PE, PP, ABS or PC. Consequently, differences in adhesion percentage can be mainly attributed to changes in adhesion mechanisms occurring after contact between both polymers. Depending on the dominant adhesion mechanism and specific material combination, optimal DCP concentrations were found:

- For PE, higher DCP concentration improved the adhesion percentage up to 57 % at 6 phr showing a full cohesive failure. At this concentration, co-vulcanization between EPDM and PE may be promoted.
- PP tends to degrade when adding higher DCP concentrations inhibiting a proper adhesion. Therefore, a low DCP concentration is recommended with the addition of higher co-agent concentration to boost crosslinking which may also limit EPDM bulk degradation.
- For the polar ABS and PC, 4 phr DCP caused respectively adhesion percentages of 43% and 13%. In case of EPDM with ABS, a combination of crosslinking and interdiffusion is expected leading to higher adhesion strength percentages than for EPDM with PC were interdiffusion is deemed dominant.

Depending on the material combination, changes in EPDM bulk properties need to be taken into account because higher DCP concentrations signify higher tensile strength and hardness, as well as lower compression set and elongation at break. Current findings, together with results from the previous study on the effect of co-agents by Laing et al.[9], provide a guideline to define the optimal curing system to boost adhesion between rubbers and thermoplastics in 2K injection molding. Furthermore, to validate these findings, a more direct characterization of the adhesion mechanism is deemed necessary, e.g. by applying Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). In addition, a future study will focus on the effect of ENB, ethylene content and Mooney viscosity of peroxide cured EPDM to improve chemical bonding further and of sulfur cured EPDM to optimize the interdiffusion with thermoplastics.

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